Periodic Table of the Elements with the Gmelin System Numbers

1 H 2																1 H 2	2 He 1
3 Li 20	4 Be 26											5 B 13	6 C 14	7 N 4	8 O 3	9 F 5	10 Ne 1
11 Na 21	12 Mg 27											13 Al 35	14 Si 15	15 P 16	16 S 9	17 Cl 6	18 Ar 1
19 * K 22	20 Ca 28	21 Sc 39	22 Ti 41	23 V 48	24 Cr 52	25 Mn 56	26 Fe 59	27 Co 58	28 Ni 57	29 Cu 60	30 Zn 32	31 Ga 36	32 Ge 45	33 As 17	34 Se 10	35 Br 7	36 Kr 1
37 Rb 24	38 Sr 29	39 Y 39	40 Zr 42	41 Nb 49	42 Mo 53	43 Tc 69	44 Ru 63	45 Rh 64	46 Pd 65	47 Ag 61	48 Cd 33	49 In 37	50 Sn 46	51 Sb 18	52 Te 11	53 I 8	54 Xe 1
55 Cs 25	56 Ba 30	57** La 39	72 Hf 43	73 Ta 50	74 W 54	75 Re 70	76 Os 66	77 Ir 67	78 Pt 68	79 Au 62	80 Hg 34	81 Tl 38	82 Pb 47	83 Bi 19	84 Po 12	85 At	86 Rn 1
87 Fr	88 Ra 31	89*** Ac 40	104 71	105 71													* NH_4 23

**Lanthanides 39	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
***Actinides	90 Th 44	91 Pa 51	92 U 55	93 Np 71	94 Pu 71	95 Am 71	96 Cm 71	97 Bk 71	98 Cf 71	99 Es 71	100 Fm 71	101 Md 71	102 No 71	103 Lr 71

A Key to the Gmelin System is given on the Inside Back Cover

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8th Edition

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Fluorine

Supplement Volume 4

Compounds with Oxygen and Nitrogen

With 10 illustrations

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Preface

The present volume, "Fluorine" Suppl. Vol. 4, covers the oxygen compounds of fluorine and the binary fluorine-nitrogen compounds.

In the first part "Fluorine and Oxygen", oxygen fluorides O_nF_m are described in the order of decreasing F:O ratio. It finishes with a description of hyperfluorous acid HOF.

The second part "Fluorine and Nitrogen" deals with the binary fluorine-nitrogen compounds. They are subdivided on the basis of the number of nitrogen atoms per molecule. Thus, species such as NF_4^+, NF_3, NF_2, and NF are considered first followed by the dinitrogen and trinitrogen fluorides N_2F_4, N_2F_2, and N_3F and related ions.

The other compounds under the heading "Fluorine and Nitrogen", the fluorine-nitrogen-hydrogen and the fluorine-nitrogen-oxygen(-hydrogen) compounds, will be covered in "Fluorine" Suppl. Vol. 5.

Intense development in the field of inorganic fluorine-oxygen and fluorine-nitrogen chemistry began in the middle of the 1950s when in less than a decade numerous previously unknown compounds and a great deal of new information were produced. Research in this field was strongly stimulated by interest in these compounds as potential high-energy oxidizers for rocket fuels. That is also the reason why much of the pertinent chemical information is found in patent literature and U.S. Government contractor reports.

Volume 4 continues the series of supplement volumes on fluorine. The first supplement volume, "Fluor" Erg.-Bd. 1, 1959, to the main volume "Fluor" 1926, describes elemental fluorine and the compounds with hydrogen, oxygen, and nitrogen and covers the literature through 1950. The rapid progress in inorganic fluorine chemistry since the 1950s is documented in the more recent volumes "Fluorine" Suppl. Vol. 2, 1980, and "Fluorine" Suppl. Vol. 3, 1982, which deal with the element and the fluorine-hydrogen compounds, respectively.

Frankfurt am Main, August 1986 Peter Merlet

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Compounds of Fluorine

(continued)

3 Fluorine and Oxygen

Review

The following chapters focus on oxygen fluorides O_nF_2, n = 1 to 6, oxygen fluoride radicals O_xF, x = 1 to 4, and hypofluorous acid, HOF.

The oxygen compounds of fluorine constitute a group of compounds composed of the most electronegative elements. Substances of this kind are oxidants with a high energy store which are capable of releasing their chemical energy under certain conditions either instantaneously or at a controlled rate. Thus, in the late 1950s the oxygen fluorides attracted much attention as possible oxidizers in fuels for rocket propulsion systems.

Whereas the well-investigated oxygen difluoride is stable at room temperature, the higher oxygen fluorides (or polyoxygen fluorides) are thermally unstable and decompose far below room temperature, ultimately into fluorine and oxygen. Their synthesis has been accomplished by flow reactions of F_2 and O_2 in an electric discharge, sometimes also by photolytic and radiolytic reactions. The best known polyoxygen fluorides are O_2F_2 and O_4F_2, which are chemically and spectroscopically well characterized. A special case is trioxygen difluoride. The actual existence of "O_3F_2" as a discrete, isolable entity has been the subject of considerable controversy. O_3F_2 might not exist under the mild conditions reported for its preparation by electric discharges, since the energy is not sufficient to generate O atoms from O_2 which are required for the formation of O_3F_2. A possible explanation for O_3F_2 is that the fluoride is a mixture of O_2F_2 and O_4F_2. Compounds with the empirical formula O_5F_2 and O_6F_2 have been prepared, but their characterization relies only on the analysis of the oxygen and fluorine released on decomposition. No additional work to support these formulations has been carried out so far.

The OF radical was first postulated in the reactions of OF_2. Its existence was proved by application of the matrix-isolation technique. Of the polyoxygen fluoride radicals the O_2F radical has been definitely characterized by detailed matrix ESR and IR spectral techniques. This radical, which forms an equilibrium with O_4F_2, plays an important role in the formation processes of the oxygen fluorides from the elements and in their chemical reactions. IR peaks observed during the photolysis of fluorine in an oxygen matrix at 4 K were suggested to be due to the radicals O_3F and O_4F.

The simplest oxyacid of fluorine, hypofluorous acid, the synthesis of which had been unsuccessful until the beginning of the 1970s, is available by passing fluorine over water. Despite the strong tendency to decompose into HF and O_2 at room temperature, it may have a half-life of up to one hour. Only theoretically derived data are known for HO_2F, HO_3F, and HO_4F.

A list of general references follows. It comprises review articles on F–O and F–O–H compounds which have been published since 1960.

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3.1 The $(OF_6)^{7-}$ Cluster

CAS Registry Number: *[65629-42-7]*

An O^- center, substituting an F^- in CaF_2, and its six neighboring F^- ions may be considered an $(OF_6)^{7-}$ cluster. For this unit, multiple scattering Xα calculations were done. Energies ε_i of the outermost orbitals:

orbital	$5a_{2u}$	$6e_u$	$1a_{2g}$	$3b_{1g}$	$5e_u$	$1b_{2u}$	$2e_g$	$8a_{1g}$
$-\varepsilon_i$ in Ry	0.060	0.104	0.256	0.258	0.264	0.265	0.266	0.268

The ground state $^2A_{2u}$ is given as $\ldots 1a_{2g}^2 6e_u^4 5a_{2u}^1$. The total energy shows a minimum for a position of the axial ligands strongly distorted ($O–F_{axial} = 2.155$ Å) from the regular octahedral structure ($O–F_{equatorial} = 2.72$ Å). This strong, static Jahn-Teller effect thus favors an $(OF_2)^{3-}$ molecular ion [1]. The occurrence of a Jahn-Teller effect was earlier inferred from a super hyperfine splitting observed for the O^- center [2].

References:

[1] J. Weber, H. Bill (Chem. Phys. Letters **52** [1977] 562/6).
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3.2 Oxygen Tetrafluoride, OF_4

The existence of OF_4 was inferred on the basis of theoretical considerations of donor-acceptor interactions.

Reference:

H. A. Bent (Chem. Rev. **68** [1968] 587/648, 611).

3.3 Oxygen Trifluoride, OF_3

CAS Registry Number: OF_3^+ *[64710-09-4]*

For OF_3^+, the formation enthalpy $\Delta H_f^\circ = 304 (\pm 10)$ kcal/mol was estimated from core electron binding energies and formation enthalpies of several gaseous molecules [1]. The dissociation energy $D(F_2O^+{-}F) = 0$ eV follows from a method of isoelectronic similarity [2].

The ionization potential $E_i(OF_3) = 14.3$ eV and the dissociation energy $D(F_2O{-}F) = 0.7$ eV were estimated by a method of isoelectronic similarity [2].

References:

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3.4 Oxygen Difluoride, OF_2

CAS Registry Number: *[7783-41-7]*

Review

Oxygen difluoride is a colorless, foul-smelling gas at room temperature. It condenses near −145°C forming a pale-yellow liquid and freezes at about −224°C. It is thermally stable up to about 200°C. The compound is highly reactive. In many reactions it acts as a powerful fluorinating agent but is less reactive at low and moderate temperatures than elemental fluorine. In some cases photochemical reactions involving the addition of fluorine are known. Many investigations on OF_2 are based on its possible use as a component of space-storable, high-energy fuels for missiles and rockets.

The results of previous investigations are described in "Fluor" Erg.-Bd. 1, 1959, pp. 222/32.

3.4.1 Preparation

3.4.1.1 By Electrolysis of Aqueous Hydrogen Fluoride

The production of OF_2 by electrolysis of aqueous HF in the one-step reaction

$$2HF + 6H_2O \rightarrow OF_2 + O_2 + O_3 + 7H_2$$

is regarded as more efficient and less expensive than the conventional two-step synthesis in which F_2 is produced by electrolysis of HF followed by reacting with base (see p. 4) [1].

Investigations of the electrolysis of HF with variable water content (6 V, Ni anode, Fe cathode, 10 wt% NaF as the electrolyte) showed that the formation of OF_2 starts somewhat above 30 wt% H_2O. At 20 wt% H_2O the OF_2 yield reaches about 60%. This value remains constant down to 1 wt% H_2O. These results are interpreted as follows. At high H_2O concentrations ($\geq$40%) only O_2 and O_3 form because only OH^- is electrochemically efficient. At low H_2O concentrations the equilibrium $H_2O + HF \rightleftharpoons H_3O^+ + F^-$ is shifted toward the right side and the OH^- concentration decreases. The F^- ion is discharged at the anode and reacts with H_2O forming OF_2 and O_2 or is released as F_2 at very low H_2O concentrations [7], see also an alternative explanation of the mechanism [3].

The investigation on the OF_2 yield as a function of electrolysis time, H_2O concentration (between 0.2 and 7.8 mol%), current interruption, and anode surface (nickel-nickel fluoride anode) showed that the OF_2 yield decreases with time and decreases markedly, below 10 mol% OF_2, on raising the H_2O concentration above 0.5 mol%. Brief, periodic interruptions of the electric current gave constant yields of OF_2 at current efficiencies of at least 45% for several hours [1]. The decrease of the OF_2 yield with increasing time is explained by the formation of layers of nickel oxide fluorides which, however, are removed by current interruption [4], see also the investigations of pulsed electrolysis [5, 6]. These results are supported by the fact that the OF_2 formation depends on the formation of a black layer on the surface of the nickel anode, which is formed during an induction period [7]. OF_2 is formed in the range 0 to 20 wt% H_2O beginning at 4 V. The OF_2 yield decreases with increasing H_2O concentration and increasing voltage. The maximum yield, 45% by volume of OF_2 in the anode gas, is achieved with 2 wt% H_2O in the electrolyte and at 5 to 9 V. Below 2 wt% H_2O, fluorine is formed [7].

References:

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3.4.1.2 By Reaction of Fluorine with Water and with Aqueous Sodium Hydroxide

OF_2 is prepared by the introduction of fluorine into a mixture of H_2O and excess CsF, KF, or NaF in a glass vessel. Yields of OF_2>70% result using CsF or KF; with NaF, yields<60% are obtained. The yields are not sensitive to the reaction time (15 min to 3 h), or to the F_2:H_2O molar ratio (2:1 to 4:1), or to the fluoride:H_2O molar ratio (2:1 to 100:1). Very pure OF_2 can be obtained by this process since the by-products HF and SiF_4 (from attack of HF on the glass vessel) combine with the alkali metal fluoride, and the by-product O_2 and unreacted F_2 are removed by vacuum pumping at −196°C [2].

A very common preparation of OF_2 is the alkaline hydrolysis of F_2, see "Fluor" Erg.-Bd. 1, 1959, p. 223, and also [1]. Fluorine (2 to 6 L/h) is bubbled through a 3% aqueous NaOH solution (precooled in an ice bath). The base solution is continuously replaced at the rate of 1 to 2 L/h. Short contact time limits the formation of O_2. Purification by repeated distillation yields almost 100% OF_2 [3]. Variations of this method for large scale preparation of OF_2 are given [4, 5].

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3.4.1.3 By Other Reactions

Attempts to prepare OF_2 from the elements were not very successful, in contrast to the formation of the higher polyoxygen fluorides [1], see also "Fluorine" Suppl. Vol. 2, 1980, p. 139. Trace OF_2 formation was noted in a silent electric discharge [3] and in the synthesis of O_2F_2 in a glow discharge [2]. Extremely low rates (2 mmol/h) and a 27% yield (based on consumed F_2) are obtained for the formation of OF_2 by circulating an O_2–F_2 mixture through a silent electric discharge for five hours [4]. The photochemical reaction of F_2 and O_3 (1:2 mixture, at 120 K, $\lambda = 365$ nm) gives OF_2 with a 20% yield based on the amount of atomized fluorine [5].

OF_2 is obtained on reacting a mixture of F_2 (20 to 40%) and inert gas (Ar, He, or Ne) at 20 to 150°C with MO_2 (M = K, Na, Li) which is mixed with catalytic amounts of AgO and Ag_2O [6]. It is also prepared by fluorination of pure NaN_2O_5 and of NaN_2O_2 or NaN_2O_3 suspended in a perfluorohalocarbon (e.g. $CF_2ClCFClCF_2Cl$) with elemental fluorine (diluted with N_2) below −40°C (e.g., −70°C) [7]. OF_2 forms in the CsF-catalyzed reaction of F_2 with K_2CO_3 [8] and of F_2 with $KClO_3$ [9].

OF_2 is produced by electrochemical conversion of O_2 in the electrolysis of an essentially anhydrous HF electrolyte (<0.1 wt% H_2O) with added NH_4F or alkali metal fluorides at 60 to 105°C. The anode had pores through which O_2 was introduced [10]. Electrolysis of a melt consisting of ~60% KF, ~39% HF, and ~1% LiF, to which was added up to 1% H_2O, yields OF_2. The water may be replenished by a stream of moist air [11]. In almost all cases of fluorination of oxygen-containing inorganic compounds by electrolysis in liquid HF, the initially generated gas contains OF_2 (38 to 64 vol%). However, the OF_2 concentration drops to zero in the course of the electrolysis [12].

OF_2 forms in the electrolysis of FSO_3H in hydrofluoric acid [13] and of NO in anhydrous HF [14].

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3.4.1.4 Preparation of $^{17}OF_2$ and $^{18}OF_2$

The electrolysis of hydrogen fluoride to which was added up to 0.5 wt% water, containing 92.8% $D_2{}^{18}O$, gives oxygen difluoride with about 90% $^{18}OF_2$. The total yield of labeled OF_2, based on water used, was 34%. The electrolysis of labeled water containing 11.4% $D_2{}^{17}O$ and 41.2% $D_2{}^{18}O$, gave a 24% yield of labeled OF_2, containing 11.8% $^{17}OF_2$ and 42.5% $^{18}OF_2$. For details of the procedure, see the original paper.

Reference:

R. R. Reinhard, A. Arkell (Intern. J. Appl. Radiat. Isotop. **16** [1965] 498/9).

3.4.1.5 Analysis. Purification

OF_2 may be conveniently determined by quantitative application of spectroscopic methods. Wet-chemical analysis can be conducted either by digestion with excess NaOH, followed by measurement of the excess base and the fluoride ion, or by reaction with KI in an acidified solution, followed by measurement of the formed I_2 [1]. Amounts of OF_2 in the ppm-range can easily be detected when the gas is introduced into a glass tube packed with silica powder which is saturated with a fluorescein solution containing KBr and K_2CO_3. Displacement of Br from KBr by OF_2 forms eosin and the color changes to red [2].

Besides the purification of OF_2 by distillation (see e.g., [3]), gas chromatographic procedures are applied. For separation of gaseous inorganic fluorides, obtained in the electrofluorination of inorganic substances, a preheated (900°C) silica gel, coated with a halocarbon oil, seems to be appropriate [4]. Low-temperature, gas-solid chromatography on a silica gel column (−75 to −10°C) was applied to the separation of mixtures containing H_2, O_2, F_2, OF_2, and O_3 (produced by electrolysis of wet HF) [5] and (at −78°C) to the purification of OF_2 [6]. The use of alumina, silica, or magnesia as solid absorbents in the separation of OF_2 and O_3 is described [7]. A column of activated silica mixed with 10 wt% of a low molecular weight chlorotrifluoroethylene polymer was used for the gas-chromatographic separation of an O_2–OF_2 mixture [8].

Strongly oxidizing inorganic gases, including OF_2, can be identified by passing chromatographically separated gases over ^{85}Kr quinol clathrate. Reaction of OF_2 with the clathrate releases ^{85}Kr which is measured with a Geiger counter [9].

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3.4.1.6 Thermodynamic Data of Formation

ΔH_f is the enthalpy and ΔG_f the Gibbs free energy in kcal/mol for the formation of gaseous OF_2 from the gaseous elements.

There is considerable uncertainty in the enthalpy of formation of OF_2. It is not even clear whether the reaction is exothermic or endothermic. For discussions, see [1] and "Fluor" Erg.-Bd. 1, 1959, p. 225.

A positive value, $\Delta H^\circ_{f,298.15} = 5.86 \pm 0.38$, is obtained from the enthalpies of the reactions in the OF_2–H_2–H_2O system measured directly with a flame calorimeter [1]. This value is consistent with $\Delta H^\circ_{f,298.15} = 5.7 \pm 2$ and 4.7 ± 2 which are derived from earlier measurements [2] and [3], respectively, by the use of current, auxiliary data for the OF_2–H_2–H_2O reaction system [1]. $\Delta H^\circ_{f,298.15} = 5.86 \pm 0.38$ is cited and $\Delta H^\circ_{f,0} = 6.40 \pm 0.38$ is given in [4]. The selected value of $\Delta H^\circ_{f,298.15} = 7.6 \pm 2$ is cited in [5]. $\Delta H^\circ_{f,298} = 5.5$ was calculated [9] from thermochemical data [6, 7, 8].

A negative enthalpy, $\Delta H^\circ_{f,298.16} = -4.06 \pm 2.2$, results from measured enthalpies of the reaction of OF_2 with H_2 in a water-containing combustion bomb [10], for critical remarks, see [1]. $\Delta H^\circ_{f,298.16} = -5.2$ and $\Delta G^\circ_{f,298.16} = -1.1$ are reported (without references) [11]. Semiempirical calculations (MINDO) gave $\Delta H = -7.00$ [12].

Calculated values (selected) from the JANAF Tables [4]:

T in K	100	200	298	400	500	1000	2000	4000	6000
ΔH°_f	6.158	5.962	5.860	5.823	5.825	5.968	6.112	5.196	2.890
ΔG°_f	7.359	6.643	9.984	11.400	12.794	19.713	33.376	60.862	89.147

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3.4.2 Handling. Storage

OF_2 does not attack glass at low temperature. Gaseous and liquid OF_2 can be stored in dry glass vessels. It can also be handled easily and safely in common metals like stainless steel, copper, aluminium, Monel, and nickel from cryogenic temperatures to 200°C. At higher temperatures only nickel and Monel are recommended [1, 2, 3]. Due to the interest in OF_2 as a propellant, the resistivity of many materials has been tested (e.g., alloys (at −79°C) [4, 5], plastic material [5], cis-1,4-polybutadiene, Teflon, and other polymers [6]). The compatibility of OF_2 with process equipment depends largely on the cleanliness of the equipment; contaminants such as dirt, moisture, oil, and grease must be avoided. The apparatus should be passivated with F_2 or OF_2 before use [1, 3]. A review on the manipulation of volatile fluorides is given [7].

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3.4.3 Toxicity

OF_2 is extremely toxic. The colorless gas irritates the lungs and has a characteristic foul odor detectable to about 0.1 ppm. Concentrations of about 0.5 ppm are easy to detect. Because of the high toxicity of the compound and the rapid desensitization to its odor, inhalation should be absolutely avoided [1 to 4]. The maximum working-place concentration should be <0.005 ppm. The ceiling value 0.05 ppm together with short-term inhalation values have been reported [5].

Exposure of rats to OF_2 gave LD 50 less than 20 ppm after 5 min inhalation, 5 ppm after 20 min inhalation [1], and 2.6 ppm after 1 h inhalation [6]. Repeated inhalation of 0.5 ppm OF_2 killed all rats [1].

References:

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3.4.4 Use in Propellant Systems

OF_2 is a high-energy oxidizer suitable for rocket and missile propellants. It had received great attention as a space-storable oxidizer [1 to 5], also see the publications cited in the reviews [3, 4, 5]. The following bipropellants were examined in view of their efficiency and utilization: liquid OF_2 and H_2 [1 to 5], NH_3 [4], N_2H_4 [3, 4, 5], $(CH_3)_2NNH_2$ [4, 5], CH_3NHNH_2 [1, 4], LiH, MgH_2, BeH_2, AlH_3 [5], B_2H_6 [1, 4 to 10], B_5H_9 [4, 5], CH_4 [3], C_2H_2 [4], C_4N_2 [5], kerosene [4], or C_2H_5OH [3]. The efficiency of liquid OF_2-containing fuels was compared with those of fuels with liquid oxygen or liquid fluorine as oxidizer [4, 5].

References:

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3.4.5 Molecular Properties and Spectra

3.4.5.1 Point Group. Isomerism

The bent molecule (with two equivalent O–F bonds) has C_{2v} symmetry [1 to 3]. A nonlinear molecule with twenty valence electrons is in agreement with the qualitative MO scheme of Mulliken [4] and Walsh [5, 6]. The bent structure is also obtained by a calculation of approximate electronic energy surfaces [7], by a simple MO–LCAO calculation of the orbital energies for different valence angles [8], and by extended Hückel calculations [9]. For further MO calculations of the bond angle, see the section on the geometric structure, p. 25. The V shape of the molecule can also be derived from the qualitative theory of electron-pair repulsion (see [10]): two lone pairs and two bonding pairs arrange themselves symmetrically around the O atom [11, 12].

Both unsymmetrical species F---F$\underline{---}$O (bent) and F---O$\underline{---}$F (bent) were predicted [13] on the basis of the MO calculation for diatomic OF (see p. 67), which may form a weak σ bond by overlap of a p orbital of a highly electronegative atom with one lobe of its π^* orbital. However, this bonding model was criticized and replaced by a three-center model which does not support the unsymmetrical FFO species [16]. Heats of formation, calculated by the MNDO method [14] for (symmetrical) FOF (18.2 kcal/mol) and for FFO (125.8 kcal/mol), show the former to be the more stable species [15].

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3.4.5.2 Electronic Structure Calculations

3.4.5.2.1 MO Description

The present section contains some results from calculations of orbital energies ε_i, total energies E_T, and O–F overlap populations (o.p.). Theoretical results for molecular properties, such as dipole moment, ionization potential, and geometric structure, are mentioned in the respective sections.

Data have been taken mainly from ab initio self-consistent-field (SCF) calculations. The thermochemical stability of OF_2 can, however, only be accounted for by the inclusion of correlation effects [1].

The lowest ab initio SCF energy obtained so far, $E_T^{SCF} = -273.5594$ a.u., has apparently been calculated [2] at the optimized geometry with a polarized double or triple zeta basis of Slater-type orbitals (STO). The Hartree-Fock (HF) limit of the total energy has been estimated [10] to be $E_T^{HF} = -273.68$ a.u. A slightly higher estimate is due to Rothenberg and Schaefer [8].

Orbital energies ε_i from two calculations at the experimental geometry are collected in the following table. O–F Mulliken overlap populations are given for the ten valence orbitals, $3a_1$ through $2b_1$. They show $3a_1$, $2b_2$, $1b_1$, $5a_1$, and $3b_2$ to be bonding, $1a_2$ and $4b_2$ nonbonding, and $4a_1$, $6a_1$, and $2b_1$ antibonding (a_2, b_1 are out-of-plane orbitals [1]; for E_T^{SCF}, see the remarks). To make the meaning of b_1 and b_2 unambiguous, the molecular plane is chosen as yz.

orbital	$1a_1$	$1b_2$	$2a_1$	$3a_1$	$2b_2$	$4a_1$	remark	Ref.
$-\varepsilon_i$ in eV	718.4	718.4	566.6	47.71	44.49	35.96	a)	[3]
O–F o.p.	—	—	—	+0.202	+0.037	−0.205	c)	[4]

orbital	$1b_1$	$5a_1$	$3b_2$	$1a_2$	$4b_2$	$6a_1$	$2b_1$	remark	Ref.
$-\varepsilon_i$ in eV	22.34	21.85	21.77	19.70	18.53	17.85	15.88	a)	[3]
$-\varepsilon_i$ in eV	22.3	21.8	21.8	19.6	18.5	17.7	15.8	b)	[1]
O–F o.p.	+0.139	+0.084	+0.128	0.000	+0.015	−0.130	−0.234	c)	[4]

a) $E_T^{SCF} = -273.550743$ a.u. The Gaussian basis set with a polarization function was taken from [5]. – b) $E_T^{SCF} = -273.53655$ a.u. was calculated with a Gaussian basis set of double zeta quality from [6], but extended by d functions at each atom. For the ε_i, an even larger basis set was used (with additional polarization functions in the form of s and p bond functions). – c) $E_T^{SCF} = -273.4494$ a.u. A Gaussian basis set of double zeta quality [7] was used. The ε_i and the F–F overlap populations are given in the original paper [4].

Additional ab initio SCF energies are collected in the following table. The orbitals, for which ε_i were given in the original publications, are indicated as well as the geometry and the basis set (GTO = Gaussian-type orbital, DZ or TZ = double or triple zeta, P = polarization):

$-E_T^{SCF}$ in a.u.	orbitals	geometry	basis set	Ref.
273.5294	$1a_1$ through $2b_1$	experimental	GTO, DZ+P	[8]
273.5280	—	optimized	GTO, DZ(TZ)+P	[9]
273.5261	$1a_1$ through $2b_1$ ($3b_2 < 5a_1$)	experimental	STO, DZ	[10]
273.486881	$1a_2$ through $2b_1$	experimental	STO, DZ	[11]
273.4456	$1a_1$ through $2b_1$	a)	GTO	[12]
273.11712	—	b)	GTO, DZ	[13]
273.1004	—	optimized	GTO, P	[14]

a) Experimental internuclear distance r, optimized bond angle α. Graphs of ε_i vs. α and electron density contours, see original paper. – b) "Standard" geometry, r = 1.42 Å, α = 109.47°.

For ab initio SCF calculations with minimal basis sets, see also [15 to 17].

Semiempirical SCF calculations were done using the approximations NDDO (neglect of diatomic differential overlap) [18], MNDO (modified neglect of diatomic overlap) [19], INDO (intermediate neglect of differential overlap) [20], SINDO (symmetrically orthogonalized INDO [21]) [22], and CNDO (complete neglect of differential overlap) [20, 23]. Another type of approximation [24] to the ab initio method was also applied to OF_2 [16].

The σ (in-plane) and π (out-of-plane) contributions to the Mulliken O–F o.p. are +0.131 and −0.095, respectively, on the basis of the data [4] given in the table above. A DZ STO basis led to +0.2475 and −0.0721 [10]. The contributions from the O2s and O2p orbitals to the O–F o.p. are given as −0.19 and +0.26, respectively [25].

The total Mulliken O–F o.p. is +0.036 [26], in agreement with the data in [4]. Another indicator of the bond strength, the Roby [27] shared population, is calculated as +0.732 and found to be in better agreement with the conventional expectation for a single bond [26].

Configuration interaction (CI) methods have been applied [1, 28] to include correlation effects. The lowest value of the total energy obtained in [1] is $E_T^{CI} = -273.86787$ a.u.

Relativistic effects may contribute −0.2152 a.u. to the total energy (calculated for the separated atoms) [28].

Vertical excitation energies for a large number of low-lying states were calculated. The two different basis sets used (see original paper) allow some conclusions on the valence or Rydberg nature of the states. The 1^1B_1 valence state is calculated to lie 5.6 eV above the ground state and should be easily accessible by an electric dipole allowed transition (at 2215 Å) [1]. The states 1^3B_1, 1^1B_1 were considered by Herzberg [29].

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3.4.5.2.2 VB and Related Descriptions

The generally accepted valence-bond structure of the molecule is given by Pauling [1]. The bonding orbitals have a small amount of s character and are intermediate between p and sp^3 [1]. The profile and the size of the lone pair orbitals involved in this system were studied [2]. The ionic character of the O–F bonds was determined [3], using the definition of ionicity i in [4]:

i = 24%, if 23% double-bond character is taken into account. An ionic valence-bond structure was used in the calculation of the equilibrium bond angle [5].

The valence-shell electron-pair repulsion (VSEPR) theory of directed valency [6 to 8] was applied to OF_2, see [9 to 11].

The Linnett structure [12, 13] of OF_2 contains spatially paired electrons around the O atom. The unshared electrons around the F atoms are not spatially paired [12].

An increased valence formula [14] for OF_2 has been derived [15].

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3.4.5.3 **Ionization Potentials** E_i in eV. **Photoelectron Spectrum**

The first adiabatic ionization potential was measured by photoionization mass spectrometry as 13.11 ± 0.01 [1] and by photoelectron (PE) spectroscopy as 13.11 ± 0.05 [2, 3] and 13.13 [4]. The first vertical ionization potential was obtained from PE spectroscopy as 13.25 [2, 3] and 13.26 [4, 5] and from electron impact mass spectrometry as 13.7 ± 0.2 [6]. A more recent electron impact value is 13.12 ± 0.05 [28]. The tabulated $E_i = 13.7 \pm 0.2$ [7, 8] was used [9] for a discussion of the effect of F substituents on the ionization potentials of molecules. Another electron impact value $E_i = 13.54 \pm 0.03$ [7] was taken from [10]. The average $E_i = 13.6$ was used [11, 12] for a comparison of the electronic structures of the fluorides and hydrides of first-row elements. For calculated values, see the following discussion of the PE spectrum and Section 3.4.5.2.1, p. 10, on the orbital energies.

A vibrational structure was observed for the first peak in the PE spectrum. The wavenumber 1010 cm^{-1} of the vibrational progression was assigned to the totally symmetric O–F stretching vibration ν_1 of OF_2^+. The lower wavenumber 928 cm^{-1} of OF_2 (see p. 28) is in accordance with the antibonding character of the outermost $2b_1$ orbital [2]. $\nu_1 = 1032 \pm 40$ cm^{-1} was observed by others [4, 5].

Higher ionization potentials due to the above mentioned PE spectra follow:

type	ionization potentials					Ref.
adiabatic	15.74	—	~17.9	—	—	[2, 3]
vertical	16.10	16.44	18.50	19.55	20.7	[2, 3]
vertical	16.17	16.47	18.68	19.50	20.9 (?)	[4, 5]

The unequivocal assignment of the PE peaks to the MOs on the basis of theoretical ionization potentials is still not possible, as is shown in the following table. The experimental vertical ionization potentials (in eV) of Brundle et al. [2, 3] are listed in the heading. Calculated ionization potentials are reported in the remarks (in the order of the MOs listed in the respective row) together with the respective calculation procedures used:

13.25	16.10	16.44	18.50	19.55	20.7	remark	Ref.
$2b_1$	$6a_1$	$\overbrace{4b_2\ 1a_2}$	$1b_1$	$5a_1$	$3b_2$	a)	[13, 14]
$2b_1$	$4b_2$	$6a_1$	$1a_2$	$\overbrace{1b_1\ 5a_1}$	$3b_2$	b)	[15]
$2b_1$	$6a_1$	$4b_2$	$1a_2$	$1b_1$	$3b_2$	c)	[16]
$2b_1$	$6a_1$	$4b_2$	$1a_2$	$5a_1$	—	d)	[17]

a) In [13] the Green's function method of Cederbaum [18, 19] was used leading to 13.06, 16.37, 16.46, 16.95, 18.95, 19.49, and 20.57 eV. In [14] a perturbation correction to Koopmans' theorem, see [20], gives 13.29, 16.33, 16.54, 16.69, 18.55, 18.90, and 19.99 eV. Values for other basis sets are in the original paper [14] and in [21, 25]. In [14] the three orbitals $6a_1$, $4b_2$, and $1a_2$ were assigned to the two PE peaks at 16.10 and 16.44 eV. The assignment of $4b_2$ and $1a_2$ to the peak at 16.44 eV was previously suggested by Chadwick et al. [5] on the basis of an orbital correlation diagram for the difluoro molecules.

b) The OF_2^+ ground and excited states energies were calculated by configuration interaction (CI) methods: 13.43, 16.17, 16.36, 17.41, 19.52, 19.55, and 20.49 eV. In the authors' opinion [15], this treatment contains one serious discrepancy; the calculated value for $1a_2$ is 17.41 instead of 18.50 eV. Additionally, the assignment of the peak at 16.10 eV to $4b_2$ may be doubtful as another calculation yields 16.59 eV for this orbital [15]. Results from frozen-orbital and relaxed-orbital CI calculations were reported later [26].

c) Semiempirical MNDO (modified neglect of diatomic overlap [22]) calculations and application of Koopmans' theorem. No PE peak was assigned to another calculated value, 20.01 eV for $5a_1$ [16].

d) The differences of the total energies of the molecular and the ionic states were calculated using the INDO approximation and applying a first-order configuration-interaction treatment to OF_2^+: 16.8, 19.6, 20.0, 21.4, and 23.4 eV.

For previous attempts to interpret the PE spectrum on the basis of Koopmans' theorem, see [2 to 5].

The PE spectrum may also be interpreted in the context of localized-orbital ionization potentials defined by Jolly [27].

Calculations of the PE spectrum in the inner valence region (orbitals $3a_1$, $2b_2$, and $4a_1$, roughly corresponding to energies ≥ 20 eV) show that the single particle picture of ionization breaks down in this region. The intensities for these ionization events become distributed over several lines in a range of binding energies up to ~60 eV [13].

The O1s and F1s binding energies were measured by X-ray PE spectroscopy using MgKα radiation [23]. These data, 545.19 and 694.93 eV, respectively, have been slightly revised [24], probably because of a change in the binding energy of the reference compound used, to 545.33 eV for O1s and 695.07 eV for F1s. An ab initio calculation of the differences in the total energies of the neutral and the 1s ionized molecules (ΔSCF method) gives 545.43 and 694.46 eV, respectively [29]. Two O1s energies from the XαSW procedure are 551.7 (ΔSCF method) and 551.8 eV (transition state method) [30].

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3.4.5.4 Proton Affinity A_p

Ab initio SCF calculations for OF_2 and HOF_2^+ (see p. 136) yielded $A_p = 107.2$ kcal/mol (for protonation at the O atom).

Reference:

D. S. Marynick, D. A. Dixon (J. Phys. Chem. **87** [1983] 3430/3; Erratum: **89** [1985] 3946).

3.4.5.5 Electric Moments. Atomic Charges. Electric Field Gradient

Dipole Moment μ in D

An analysis of radio frequency transitions, occurring within individual rotational levels split by the Stark effect in external electric fields, yields $\mu = (\pm)0.30818$ with an uncertainty of $\pm 0.01\%$ [45].

The Stark effect in the microwave (MW) spectrum was used to obtain $\mu = (\pm)0.297 \pm 0.005$ [1], see also the tables of selected electric dipole moments [2] and of constants from the MW spectrum [3, 4]. The even lower moment $\mu = (\pm)0.1759 \pm 0.0010$ from similar measurements [6] has been criticized [1] on the grounds of an erroneous assignment of spectral lines. The moment $\mu = (\pm)0.4 \pm 0.1$ follows from the temperature dependence of the dielectric polarization, which was measured for OF_2 at atmospheric pressure between −78 and +80°C [7]. Compare also the tables [5] of experimental dipole moments.

Quantum mechanically calculated moments are generally negative, corresponding to negatively charged F (see below; for sign convention, see [8, 15]). Positive moments have been obtained by ab initio calculations with a minimal basis of Slater-type functions (STO) [9, 16], by the NDDO approximation (neglect of diatomic differential overlap) [10], and by another approximate calculation [11, 12]. Values from other ab initio and semiempirical calculations are reported in the following table. They are generally obtained for the calculated equilibrium geometries (internuclear distance r, bond angle α) except where noted:

$-\mu$ in D ..	0.19658	0.314	0.329	0.452	0.21	0.40	0.25	0.33
method ..	ab initio	ab initio	ab initio	ab initio	CNDO	INDO	SINDO	MNDO
remark ...	a)	b)	c)	d)	e)	f)	g)	h)
Ref.	[20]	[16]	[19]	[18]	[8, 15]	[8]	[14]	[17]

a) Minimal basis set of Gaussian functions (GTO). – b) Double zeta (DZ) STO basis set. Experimental geometry. – c) DZ (partly triple zeta) GTO basis set with d functions. – d) DZ GTO basis set with d functions. – e) Complete neglect of differential overlap. Experimental r, calculated α. – f) Intermediate neglect of differential overlap. Experimental geometry. – g) Symmetrically orthogonalized INDO, see [21]. – h) Modified neglect of diatomic overlap.

Additional moments have been calculated by ab initio [23], CNDO [13], CNDO-APSG (antisymmetrized product geminal) [24], and SINDO [22] methods.

The bond dipole moment $\mu_{OF} = 0.239$ D was obtained from a total measured dipole moment (0.297 D) by assuming μ to be the vector sum of the bond moments [25]. If, however, a lone-pair moment at O of 3.2 D is assumed (as in the case of H_2O), then a "true" value $\mu_{OF} = 2.9$ or 2.3 D results, depending upon the sign of the total moment (taken as (±)0.4 D) [7]. The derivative with respect to the internuclear distance, $\mu'_{OF} = 3.78$ D/Å, was determined from IR intensities [25].

Quadrupole Moment Q in 10^{-26} esu·cm^2

Components of the Q tensor along the principal inertial axes a, b, c (b bisects the bond angle, c $\perp$ molecular plane) from the first- and second-order Zeeman effect of several pure rotational transitions [26, 27, 32, 37] are $Q_{aa} = -1.6 \pm 1.4$, $Q_{bb} = +2.1 \pm 1.1$, and $Q_{cc} = -0.5 \pm 1.9$.

The components −0.41, +0.61, and −0.19 follow from ab initio SCF-MO calculations with a basis set of double zeta plus polarization quality [18]. Further values were calculated with a minimal [9] and a double zeta basis [16]. Two semiempirical methods [34, 35] were also employed [33].

Octupole Moment

For calculated values, see [18].

Atomic Charges

Most calculations agree on a positive charge at oxygen and a negative charge at fluorine. Charges of +0.52 and −0.26, respectively, were derived from the measured F1s binding energy (see p. 15) with a point-charge potential equation. These data are certainly too high and may be diminished by using longer distances from F to the effective centers of charge of the other two atoms. Adding 0.5 Å to the internuclear distances, one obtains +0.32 and −0.16, respectively [28]. The lower values +0.19 and −0.08 have been derived from calculated 1s orbital energies using a linear relation between the charges and the 1s energies of a specific atom (O, F) in several molecules. They are inconsistent with a vanishing molecular charge [29]. The charges used in obtaining these relations were determined by an integration procedure, see [30]. The atomic charge at F was calculated by a simple non-quantum-chemical approach and correlated with the ^{19}F chemical shift for a large number of binary fluorides including OF_2 [36]. Gross atomic charges at O from Mulliken population analyses, carried out with wave functions from ab initio calculations, were: +0.24 [38], +0.23 [18], +0.2295 [39], and +0.171 [16]. The net atomic charge was +0.03581 [20]. The charge at O from the Roby [40] method for population analyses was +0.17 [41]. A positive charge at O was also arrived at by the MNDO [42], SINDO [22], and CNDO [43] approximations, by the Xα SW method [44], and by a consideration of various valence-bond resonance structures [31].

Electric Field Gradient

For calculated components at the O and F nuclei, see [18].

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3.4.5.6 **Polarizability** α in Å^3

An estimate of $\alpha=8$ was made [1] from dielectric constant measurements [2] (see p. 16). $\alpha=2.54591$ was calculated by the δ-function potential model of chemical bonding [3]. The anisotropies $\alpha_{aa}-\alpha_{bb}=1.389\pm0.008$ and $\alpha_{aa}-\alpha_{cc}=1.883\pm0.010$ (a, b, c are principal inertial axes, see p. 22) were obtained from an analysis of radio frequency transitions occurring within individual rotational levels in the presence of external electric fields. Assuming $\alpha=8.0$, then $\alpha_{aa}=9.1$, $\alpha_{bb}=7.7$, and $\alpha_{cc}=7.2$ (original paper gave 9.4, 8.0, and 7.5) [1].

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3.4.5.7 Magnetic Constants

Susceptibility χ in 10^{-6} erg·G^{-2}·mol^{-1}

Inserting the components of χ in the principal inertial axis system (−16.2, −14.8, and −8.8) into the equation defining χ, $\chi=\frac{1}{3}(\chi_{aa}+\chi_{bb}+\chi_{cc})$, yields $\chi=-13.2$ (c ⊥ molecular plane, b bisecting the bond angle). Besides the two anisotropies given below, the third piece of information for determining χ was an assumed value of 3.0×10^{-16} cm^2 for the expectation value $\langle c^2\rangle$ of the electric (electronic + nuclear) charge distribution, the same value as that found in CO_2 and N_2O. This quantity is directly related to the anisotropy $2\chi_{cc}-\chi_{bb}-\chi_{aa}$. The diamagnetic and paramagnetic terms contributing to these components were derived from the estimated second moment of the electronic charge distribution and from the molecular g values (see below) [1]:

χ^d_{aa}	χ^d_{bb}	χ^d_{cc}	χ^p_{aa}	χ^p_{bb}	χ^p_{cc}
−42.0	−119.7	−136.2	25.8±0.5	104.9±0.5	127.4±0.5

$\chi=-16.82$, $\chi_{aa}=-20.91$, $\chi_{bb}=-17.50$, and $\chi_{cc}=-12.06$ were calculated [28] by solving the coupled Hartree-Fock equations in terms of localized MOs, each with an optimum gauge origin (see [29, 30]). The diamagnetic susceptibilities from an ab initio calculation with a contracted Gaussian basis set of double zeta quality plus polarization functions, $\chi^d_{aa}=-43.53$, $\chi^d_{bb}=-119.40$, $\chi^d_{cc}=-136.90$, agree quite well with the values tabulated above [2].

The magnetic susceptibility anisotropies $2\chi_{aa}-\chi_{bb}-\chi_{cc}=-8.8\pm1.4$ and $2\chi_{bb}-\chi_{aa}-\chi_{cc}=-4.4\pm0.7$ follow directly from the second-order Zeeman effect of several rotational transitions [1, 26, 27], see also the microwave spectral tables [3]. The theoretical anisotropies −12.26 and −2.03 have been derived from the respective components [28].

Molecular g Values

The components of the g tensor of the rotational magnetic moment $g_{aa}=-0.213\pm0.005$, $g_{bb}=-0.058\pm0.002$, $g_{cc}=-0.068\pm0.002$, in units of the nuclear magneton, were obtained from the first-order rotational Zeeman effect. The sign was chosen by consideration of the two resulting sets of molecular quadrupole moments ($g>0$ implies Q to be unreasonably large) [1, 3, 26, 27]; see also the tables of magnetic constants of asymmetric top molecules [4].

Spin-Rotation Interaction

The diagonal elements of the spin-rotation interaction tensor were derived from an analysis of hyperfine splittings due to the ^{19}F nuclei in radio frequency transitions occurring within individual rotational levels in the presence of external electric fields [34]: $M_{aa} = (\pm)59.60 \pm 0.07$, $M_{bb} = (\pm)25.05 \pm 0.11$, and $M_{cc} = (\pm)51.39 \pm 0.08$ kHz. A microwave study [5] yielded $M_{aa} = -42$, $M_{bb} = -22$, and $M_{cc} = -49$ kHz [3 to 5], if an estimated paramagnetic shielding constant was imposed as an additional constraint. The shift used [5] is, however, significantly in error; see remark b) of the table below. The difference $M_{bb} - M_{cc} = 27$ kHz agreed with a previous determination [6], giving 61 ± 4 kHz for the sum of the two ^{19}F nuclei.

Chemical Shifts δ, Nuclear Magnetic Shielding Constants σ, in ppm

^{19}F. The ^{19}F chemical shifts δ in the following table were measured against the commonly used reference compound $CFCl_3$ (liquid). The negative sign denotes a shift to lower field. Shifts from calculated shielding constants (see below) are generally compared with F_2. Therefore, a few data for F_2 and the shift δ′ of OF_2 relative to F_2 are included in the table:

state	vapor	vapor	vapor	solution	liquid
$\delta(O^{19}F_2)$	−248 ± 1	−249 ± 1	−250.0	−250	−249 ± 1
$\delta(^{19}F_2)$	−419 ± 1	—	—	—	−422 ± 1
$\delta'(O^{19}F_2)$	+171	—	—	—	+173
remark	a)	b)	c)	d)	e)
Ref.	[7]	[5]	[8]	[9]	[7, 10]

a) At room temperature and at an estimated pressure of 4 to 5 atm. See also the review [11] on ^{19}F chemical shifts. – b) The shift relative to F_2 is reported to be $\delta' = +205.2$. – c) Probably at room temperature. Pressure 5 atm. – d) Solutions of OF_2 together with O_2F_2 in CF_3Cl at 140 K. – e) At 77 K. See also [11]. The downfield shift on liquefaction is probably due to weak associative forces, which are absent in the gas phase, and due to the different temperatures and magnetic susceptibilities [7].

Two further shifts were internally referenced to F_2 or SF_6: With a 1:1 solution of OF_2 in F_2 at ∼ −193°C, $\delta' = +182.5 \pm 2.0$ was measured [13]. With a mixture of OF_2 and SF_6, a shift of −217.0 ppm relative to SF_6 (−8680 Hz at 40 MHz) was observed [14]. This shift is too large [7]. The corresponding $\delta' = +148.5$ (+149 in [16]) was obtained using an F_2 shift of −365.5 ppm versus SF_6 [14, 15]. This latter shift is in turn too low [7].

The shielding constant $\sigma = -59.3$ (negative sign implies antishielding) is derived [28] from $\delta = -248$ [7] using $\sigma(CFCl_3, \text{liquid}) = 188.7$. This latter constant (188.9 according to [31]) is based upon $\sigma(SiF_4, \text{gas}) = 363.2$ [32] and $\sigma(HF, \text{gas}) = 410.0$ [32]. Calculated constants from the coupled Hartree-Fock theory [29, 30] are $\sigma = 19.1$, $\sigma_{xx} = 368.3$, $\sigma_{yy} = 162.7$, and $\sigma_{zz} = -473.7$ (molecule in xy plane, $y \| C_2$) [28].

Theoretical shifts δ′ were derived from semiempirically calculated shielding constants of OF_2 and F_2 and are altogether too high. The methods used for calculating σ are included in the table; some σ data are given in the remarks:

$\delta'(O^{19}F_2)$	263.0	290.56	309	370.3	714.04
method	INDO	MINDO/3 + INDO/S	INDO, coupled HF	CNDO/S	MINDO/3
remark	a)	b)	c)	d)	e)
Ref.	[17]	[18]	[16]	[17]	[18]

a) $\sigma(OF_2) = +130.4$, the diamagnetic contribution was included. Components of the paramagnetic contribution (molecule in xz plane, $x \| C_2$): $\sigma^p_{xx} = -72.2$, $\sigma^p_{yy} = -552.0$, $\sigma^p_{zz} = -399.0$. See also [19]. – b) $\sigma(OF_2) = +55.07$, $\sigma^p(OF_2) = -415.95$. For MINDO/3 (a variant of modified INDO), see [20], for INDO/S (screened INDO), see [21]. – c) $\sigma^p(OF_2) = -366$. – d) $\sigma(OF_2) = +165.0$. Paramagnetic components (molecule in xz plane, $x \| C_2$): $\sigma^p_{xx} = -7.5$, $\sigma^p_{yy} = -483.6$, $\sigma^p_{zz} = -428.7$. – e) $\sigma(OF_2) = 108.56$. For the method used, see b).

The paramagnetic shielding $\sigma^p(OF_2) = -569$ was obtained from the shift $\delta' = 205$ (see the table of measured values) and from the F_2 paramagnetic shielding, $\sigma^p(F_2) = -774$, if differences in the diamagnetic contributions were neglected. $\sigma^p(F_2)$ was computed from the known spin-rotation constant in F_2 [5].

Diamagnetic shielding due to ab initio calculations: $\sigma^d = 561.8$ (the tensor components are also given) [2] and 560.3 (values for the NDDO (neglect of diatomic differential overlap) approximation, see original paper) [22].

^{17}O. The chemical shifts $\delta(^{17}OF_2) = -781 \pm 4$ and -799.1 ± 0.5 were measured for the gas (5 atm, 293 ± 2 K) and for the liquid (133 ± 2 K), respectively, both downfield from H_2O as an external standard [33]. $\delta = -830$ was measured for the liquid [23]. The shielding constant for gaseous OF_2 is given as $\sigma = -473.1$, based upon σ for gaseous CO [33]. $\sigma = -541$ for liquid OF_2 was derived [28] from the older measurement of δ [23] and from an assumed σ for gaseous H_2O. Calculated constants from the coupled Hartree-Fock theory [29, 30] are: $\sigma = -451.7$, $\sigma_{xx} = -401.8$, $\sigma_{yy} = -641.4$, and $\sigma_{zz} = -311.7$ (molecule in xy plane, $y \| C_2$) [28]. Ab initio calculations of the diamagnetic contribution to the shielding yielded $\sigma^d = 512.3$ (the tensor components are reported, too) [2] and 511.9 (for σ_d calculated by the NDDO approximation, see original paper) [22].

The spin-spin coupling constant $^1J(^{19}F\text{-}^{17}O) = (\pm)300 \pm 30$ Hz was derived from the three-line ^{17}O NMR spectrum of liquid OF_2 at 133 K [33]. The reduced constant $K = 2\pi J/\hbar\gamma_F\gamma_O$, γ = magnetogyric ratio, was semiempirically calculated [24]. It is expected to be positive [25].

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3.4.5.8 **Rotational Constants, Centrifugal Distortion Constants, and Rotation-Vibration Interaction Constants,** in MHz

For the notations used, see p. 146 and "Schwefel" Erg.-Bd. 3, 1980, p. 81. The principal axes are designated a, b (bisecting the bond angle), and c (⊥ molecular plane). OF_2 is nearly a prolate top: The asymmetry parameter $\varkappa=(2B-A-C)/(A-C)=-0.9303$ may be derived from the double-primed rotational constants given below.

For the electronic and vibrational ground state of $^{16}O^{19}F_2$, seven "determinable constants" were derived from a microwave spectrum [1], which was reanalyzed and extended by new unpublished measurements (the τ values are rounded) [2]:

A″	B″	C″
58782.6832 ± 0.0151	10896.3521 ± 0.0030	9167.37374 ± 0.00255

τ_{aaaa}	τ_{bbbb}	τ_{cccc}	τ_1	τ_2
−6.6515 ±0.0014	−0.0928 ±0.0001	−0.03670 ±0.00007	0.1748 ±0.0017	−0.0118 ±0.0003

Similar data were previously reported [3]. For the sextic centrifugal distortion constants H_J, H_{JK}, H_K, h_J, h_{JK}, and h_K [4], see the original papers [2, 3].

The following parameters were derived assuming planarity conditions (see [3]). τ_{aabb} and τ_{abab} were obtained from τ_1 and τ_{cccc}. They may also be obtained from τ_2 and τ_{cccc}, or from τ_1 and τ_2 (see the original paper) [2]:

A'	B'	C'
58782.655 ± 0.015	10896.418 ± 0.003	9167.422 ± 0.003

τ'_{aabb}	τ'_{bbcc}	τ'_{ccaa}	τ_{aabb}	τ_{abab}
0.0976 ±0.0012	−0.05568 ±0.00009	0.1329 ±0.0005	0.4044 ±0.0006	−0.14845 ±0.00041

Similar data were reported [1, 3]; see also the tables of constants of diamagnetic molecules [5] and the tables of molecular constants from microwave spectroscopy [6]. For preliminary data, see [8]; different values are given in [9]. The rotational constants [1] were expressed in cm^{-1} ($A'=1.96078$, $B'=0.363466$, $C'=0.305792$) and used for calculations of the rotational structure of the IR bands ν_1 and ν_2 (see p. 38) [7].

The centrifugal distortion constants τ_{aaaa}, τ_{bbbb}, τ_{aabb}, and τ_{abab} were also calculated from a molecular force field [10 to 12]. Also see [13] for τ_{abab}.

For the vibrationally excited states (100), (010), (001), and (020), the constants A′, B′, C′ were determined on the basis of the microwave spectra observed in these states. The Fermi resonance between (100) and (020) was taken into account and the corrected and uncorrected (in parentheses) constants for (100) are $A'=58744.08$ (59213.58), $B'=10830.66$ (10824.35), $C'=9160.23$ (9128.09) [2, 5, 14]. For the uncorrected constants (in cm^{-1}) of (100) and (020), see also [7]. Sets of constants including quartic centrifugal distortion constants (in kHz) for the two states (100) and (020) were determined from the IR-microwave double resonance [17]:

state	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$
(100)	59207.7 ± 0.3	10823.94 ± 0.05	9126.52 ± 0.04
(020)	59707 ± 1	10818.0 ± 0.2	9093.0 ± 0.2

state	Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
(100)	11.1*)	−40 ± 6	620 ± 30	4.59 ± 0.06	21 ± 6
(020)	24.9 ± 0.2	−83*)	1720*)	2.04 ± 0.06	424 6

*) Fixed to ground state value.

Equilibrium rotational constants [5, 14]:

A_e	B_e	C_e
58744.90	10985.28	9255.27

Rotation-vibration interaction constants [5, 14]:

i	α_i^A	α_i^B	α_i^C
1	38.55*)	65.77*)	7.18*)
2	−699.02	42.36	53.28
3	585.01	69.56	115.25

*) Corrected for the Fermi resonance with $2\nu_2$.

Somewhat different, corrected values (in cm^{-1}) for $i=1$ are reported elsewhere [15]. The interaction constants were also calculated from the molecular force field [15, 16].

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3.4.5.9 Moments of Inertia. Geometrical Structure

Moments of Inertia I in amu·Å^2

The effective [1] and the equilibrium [2] moments of inertia were derived from the respective rotational constants A′, B′, C′ and A_e, B_e, C_e. The average moments [1] were obtained by correcting the effective values for the harmonic part of the rotation-vibration interaction, see [3]:

type	I_a	I_b	I_c	remark	Ref.
effective	8.60006	46.3942	55.1444	a)	[4]
average	8.6744	46.5450	55.2191	b)	[1]
equilibrium	8.60553	46.0189	54.6209	c)	[2, 4]

a) With a different conversion factor, 8.60002, 46.3945, and 55.1436 were derived earlier from the same constants A′, B′, C′ [1]. For preliminary data, see [5]. – b) In 10^{-40}g·cm^2: 14.396, 77.255, 91.651 [7]. – c) Residual inertial defect is $\Delta^e = -0.0035$ amu·Å^2 [4].

Moments (in 10^{-40}g·cm^2), derived from older literature data for the molecular structure, are 14.24, 72.11, 86.35 [8] and 15.3, 73.6, 88.9 [9].

The inertial defect $\Delta = I_c - I_a - I_b$ (in amu·Å^2) in the molecular ground state was derived from four slightly different sets of effective moments of inertia, $\Delta = 0.14903 \pm 0.00012$ [10], 0.150 ± 0.005 [2], 0.1491 ± 0.0001 [1], and 0.1526 [5], and from a more divergent set, $\Delta = 0.217$ [6].

Inertial defects for vibrationally excited states ($v_1v_2v_3$) (all ± 0.005) [2]:

(100)	(100)	(010)	(001)	(020)
0.1414	−0.0940*)	0.3925	0.4677	0.3989

*) Corrected for the Fermi resonance with (020).

Theoretical Δ values were computed using the decomposition $\Delta = \Delta_{vib} + \Delta_{cent} + \Delta_{elec}$, where Δ_{vib} is the vibrational state dependent part and Δ_{cent} and Δ_{elec} are corrections due to the effects of centrifugal distortion and electronic interaction. The Δ_{vib} part is primarily related to the Coriolis coupling constants (ζ_{13}, ζ_{23}), Δ_{cent} to the distortion constant τ_{abab}, and Δ_{elec} to the diagonal elements of the g tensor [11]. Data for the vibrational ground state (for vibrationally excited states, see [2]) follow:

Δ	0.1597	0.1507	0.1500 ± 0.0039	0.1496	0.132
remark	—	—	—	a)	b)
Ref.	[12]	[2]	[10]	[1]	[11, 13]

a) Δ_{vib} only. – b) $\Delta_{vib} = 0.131$, $\Delta_{cent} = 0.001$, $\Delta_{elec} = 0$ (assumed). For the decomposition $\Delta_{vib} = \Sigma\Delta_i \cdot (v_i + ½)$ with v_i = vibrational quantum number (i = 1 to 3), the components $\Delta_1 = -0.411$, $\Delta_2 = +0.106$, and $\Delta_3 = +0.567$ are given [11].

Bond Length r in Å. **Bond Angle** α

Different types of geometric parameters were derived from the respective rotational constants, which in turn were based upon the microwave spectra in the ground state [1, 10] and vibrationally excited states [2]:

type	r(O–F)	α	remark	Ref.
effective (r_0)	1.4087	103°19′	a)	[1, 2, 4]
average ($\langle r \rangle$)	1.41246 ± 0.00011	103°9′ ± 1′	b)	[10]
average ($\langle r \rangle$)	1.4124	103°10′	c)	[1, 2, 4, 7]
equilibrium (r_e)	1.4053 ± 0.0004	103°4′ ± 3′	d)	[2, 4, 15, 16]

a) In the critical compilation [14] of molecular structures determined by spectroscopic methods, these data are reported as $r_0 = 1.409 \pm 0.002$, $\alpha_0 = 103.3° \pm 0.2°$. – b) From a renewed analysis and extension of the rotational spectrum [1]. – c) Rounded: $\langle r \rangle = 1.412 \pm 0.002$, $\langle \alpha \rangle = 103.2° \pm 0.2°$ [14]. – d) See also the Landolt-Börnstein tables [17] (with $\alpha_e = 103.067° \pm 0.050°$) and the compilations [14] (with $r_e = 1.405 \pm 0.002$, $\alpha_e = 103.1° \pm 0.2°$) and [18] (with $\alpha_e = 103.07°$).

Quantum mechanical calculations of r_e (in Å) and α_e. Ab initio SCF-MO methods yielded bond distances in the range 1.39 to 1.49 Å and bond angles in the range 101.7° to 103.3°: $r_e = 1.396$, $\alpha_e = 102.7°$ were calculated from a polarized double zeta STO basis set [62]. The experimental distance was also obtained [38, 58] with the double zeta Gaussian basis set of Dunning [59] and a Gaussian basis set of partly triple zeta character [63]. The Gaussian basis of Ditchfield et al. [60] yielded $r_e = 1.422$ [61]. $r_e = 1.36$ had previously been obtained with minimal basis sets [26, 27]. In order to understand the predictions of the VSEPR (valence-shell electron-pair repulsion) model of Gillespie [25], a study [19] was carried out for a series of tetrahedral and related molecules. An older study of α_e is in [28].

Configuration interaction (CI) methods were applied [38] to obtain a more reasonable bond distance $r_e=1.41$, with the Dunning basis [59] extended by d functions. Correlated wave functions were later applied [64].

Semiempirical SCF–MO methods often yielded r_e values that were too low (1.17 to 1.33 Å) and α_e values that were too high (105.3° to 109.1°), see [24] (CNDO/2), [23] (INDO), [66] (SINDO), [20] (SINDO 1 [29, 30]), and [21, 65] (MNDO [31]). A smaller bond angle was obtained by [36, 37] (99.2°, CNDO/2) and [35] (99.0°, INDO). Another version, MINDO/3 [32], of the MINDO [33] method suggested a 3-membered ring: $r_e=1.439$, $\alpha_e=55.2°$ [22, 34].

The qualitative behavior of the bond angle α, i.e., its proximity to, or deviation from, special values (such as 180°, 109.5°, or 90°) or its variation in a series of related molecules, has received much attention. The deviation from 180° was discussed in terms of qualitative MO theory [39 to 41], see also the extended Hückel calculations [42] and the calculations for a simple electrostatic model [43]. The deviation from 90° (pure p-electron valence in VB theory) was considered by Mulliken [44], see also Pauling [45]. The closeness to 109.5° (tetrahedral angle) was explained by the VSEPR theory [25, 46 to 49]. The decrease of α in going from H_2O to OF_2 may be rationalized in the VSEPR picture by the different electronegativities [46, 47, 50, 51]; this topic was further discussed [41, 52, 53]. The increase of α in going from NF_3 to OF_2 is not explained by the VSEPR model [54]. The group of molecules H_2O, OF_2, OCl_2, SH_2, SCl_2, SeH_2, and $TeBr_2$ was considered [55].

The angle α may also be estimated by a steric model, in which it is determined by the nonbonded contact between the two F atoms. A set of self-consistent, intramolecular van der Waals radii [56] (with 1.08 Å for F) yielded $\alpha=100.5°$ [57].

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3.4.5.10 Molecular Vibrations

Fundamental Frequencies

The symmetric stretching mode $\nu_1(a_1)$, the symmetric bending mode $\nu_2(a_1)$, and the antisymmetric stretching mode $\nu_3(b_1)$ are active both in IR absorption and in Raman scattering, see, e.g. [1, 2]. ν_1 and $2\nu_2$ are perturbed by Fermi resonance. The occurrence of this resonance was first detected by the microwave absorption in the corresponding vibrationally excited states [3]. In the following table, data for $2\nu_2$ are included. For further details pertaining to the Fermi resonance, see the remarks. The $\nu_1 > \nu_3$ ordering, unusual for bent XY_2-type molecules, was inferred from band profiles, see "Fluor" Erg.-Bd. 1, 1959, p. 226, and later found for the NF_2 radical, too [30]. Wavenumbers in cm^{-1}:

ν_1	$2\nu_2$	ν_2	ν_3	phase	spectrum	remark	Ref.
928	(917.8)	461	831	vapor	IR	a)	[6, 7]
925.6 ± 0.6	914.5 ± 0.8	459.8 ± 0.8	823.0 ± 0.5	solution (l)	IR	b)	[8]
915	925	461	821	matrix (s)	IR	c)	[9]
925.2	915.7	461.1	821.1	liquid	Raman	d)	[10]

a) At various pressures (up to 1 atm [6]) and probably at room temperature. $2\nu_2$ was not observed but was calculated [6] from the vibrational constants. Estimated uncertainties 1 to 3 cm^{-1} [2]. See also tables [11] of constants of diamagnetic molecules. $\nu_1 = 928.2$ and $2\nu_2 = 916.2$ cm^{-1}, combined with some other vibrational and rotational data, give the most satisfactory agreement between calculated and observed IR absorptions, which showed a partly smoothed-out rotational structure in the range 900 to 950 cm^{-1} [12]. $\nu_1 - 2\nu_2 = 10.5$ cm^{-1} was derived [12] from the difference 3.5 cm^{-1} of the unperturbed frequencies [3].

b) Solution of OF_2 in liquid N_2 at 80 K.

c) OF_2 in Ar at 4 K. The components of the "ν_1 doublet" were not definitely assigned to ν_1 or $2\nu_2$. However, it was shown that the observed splitting must arise from Fermi resonance (and not from multiple sites or from polymers). In some other matrices, essentially the same splittings (and intensity ratios) were obtained: 915 and 926 cm^{-1} in O_2 at 20 K, 911.5 and 921.5 cm^{-1} in CCl_4 at 48 K, and 910 and 920 cm^{-1} in Xe : Ar (1:30) at 4 K. For $^{18}OF_2$, $\nu_1 = 889$ or 898, $\nu_2 = 457$, and $\nu_3 = 794$ cm^{-1} were observed in Ar [9]. The ν_1 splitting with $^{16}OF_2$ in an N_2 matrix at 4 K was apparently first detected by Arkell et al. [13], but was not further discussed by them. With $^{18}OF_2$, only a singlet was observed [14].

d) At 77 to 128 K. Excitation by a He–Ne laser.

The band origins of the components ν_1 and $2\nu_2$ of the Fermi diad were determined from an IR-microwave double-resonance investigation using several lines of the CO_2 and the N_2O lasers: $\nu_1 = 928.067$ and $2\nu_2 = 916.040$, both ± 0.001 cm^{-1} [19].

The $^{16}OF_2$ IR bands at 15 K [4] and the Raman bands (in parentheses) at 16 K [5] in Ar matrices have been assigned [5] in the following way: 930 and 933 cm^{-1} (931) to $2\nu_2$, 920.0 (920) to ν_1, 466.0 (465) to ν_2, and 826.0 (825) to ν_3. This interpretation seems to be confirmed by ^{18}O substitution: ν_1 shifts to 893.0 (892), while $2\nu_2$, expected to be at 925, is no longer in Fermi resonance with ν_1 and thus unobservably weak. $\nu_2 = 462.5$ (461) and $\nu_3 = 799.0$ (799) [5]. $2\nu_2 > \nu_1$ were also observed [15] in the IR and Raman spectra of solid OF_2 (see pp. 38 and 39).

Unperturbed frequencies. Wavenumbers for the gas phase and for the solution in liquid N_2 are:

phase	vapor	vapor	solution (l)
ν_1 in cm^{-1}	924.13 ± 0.03	924.8	922.2 ± 0.8
$2\nu_2$ in cm^{-1} ...	919.97 ± 0.03	921.2	918.0 ± 0.8
Ref.	[19]	[6]	[8]

The difference $\nu_1 - 2\nu_2 = 3.65 \pm 0.10$ cm^{-1} was derived from the microwave spectrum [3, 16] and was used in [6].

For combination bands, see "Infrared Absorption" p. 37. Fermi resonance is possible between states (v_1, v_2, v_3) and ($v_1 - 1$, $v_2 + 2$, v_3). The unperturbed frequencies were reported [6, 8].

Harmonic Frequencies ω_i and Anharmonicity Constants x_{ij} in cm^{-1} (i,j = 1 to 3)

Values determined from the gas phase [6] and the liquid-N_2 [8] studies are as follows:

ω_1	ω_2	ω_3	x_{11}	x_{12}	x_{13}	x_{22}	x_{23}	x_{33}	Ref.
945.4	470.4	858.8	−4.5	−6.1	−19.2	−0.4	−11.0	−6.3	[6]
942.2 ±0.9	469.0 ±0.4	846.3 ±0.4	−3.6 ±0.3	−5.7 ±0.2	−20.2 ±0.2	−1.0 ±0.6	−8.8 ±0.9	−4.5 ±0.1	[8]

Very different constants ω_i (1167, 480, and 1227 cm^{-1}) were obtained from an ab initio calculation [32].

Vibrational Amplitudes

Root-mean-square amplitudes of vibration u at room temperature are calculated as u(O–F) = 0.0511 and u(F···F) = 0.0657 Å [31]. Similar amplitudes were previously derived [17, 18, 20, 21]. Mean-square amplitudes, including those with changes in the valence angle, and interaction terms were reported [17]. For mean-square amplitudes, see also [21, 22]; for the generalized mean-square amplitudes, see [23].

Coriolis Coupling Constants

ζ_{13}^{c} and ζ_{23}^{c} should obey the sum rule $(\zeta_{13}^{c})^2 + (\zeta_{23}^{c})^2 = 1$. The sign of ζ_{23}^{c} can be chosen to be negative, whereas ζ_{13}^{c} may have either sign [24]. $(\zeta_{13}^{c})^2 = 0.426 \pm 0.02$, corresponding to $\zeta_{13}^{c} = (-)0.653$, is an average of the constants in the vibrationally excited states (100), (010), and (001). These constants, as well as $(\zeta_{13}^{c})^2 = 0.438$ for the ground state, were derived from the respective inertial defects [3, 25]. $\zeta_{13}^{c} = -0.6568 \pm 0.0084$ and $\zeta_{23}^{c} = -0.7541 \pm 0.0073$ were calculated from the force constants and the centrifugal distortion constants [24]. Other values were also reported [18, 26 to 29].

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3.4.5.11 Force Constants

The general expression in internal coordinates (x_i, $i = 1$ to 3) of the intramolecular potential function is $V = {}^1/_{2!}\,\Sigma f_{ij}\,x_i\,x_j + {}^1/_{3!}\,\Sigma f_{ijk}\,x_i\,x_j\,x_k$ + (higher terms), with independent summation over each repeated index. The expression in (dimensionless) normal coordinates q_i is $V = \frac{1}{2}\Sigma\omega_i q_i^2 + \Sigma k_{ijk}\,q_i q_j q_k$ + (higher terms), with the constraint $i \le j \le k$ [2].

Quadratic Force Field

The quadratic part (valence force field) of the potential function written in internal coordinates (stretching coordinates $x_1 = \Delta r_1$, $x_2 = \Delta r_2$; bending coordinate $x_3 = r_e \cdot \Delta\alpha$, with r_e = equilibrium O–F distance = 1.4053 Å, see p. 25) is now given by $2V^{(2)} = f_r \cdot (\Delta r_1^2 + \Delta r_2^2) + f_\alpha r_e^2 \Delta\alpha^2 + 2f_{rr}\Delta r_1 \Delta r_2 + 2f_{r\alpha}(\Delta r_1 + \Delta r_2)\cdot r_e \Delta\alpha$, where $f_r = f_{11} = f_{22}$, $f_\alpha = f_{33}$, $f_{rr} = f_{12} = f_{21}$, $f_{r\alpha} = f_{13} = f_{31} = f_{23} = f_{32}$. The four constants cannot be determined from the harmonic or fundamental frequencies of one isotopic species alone. Thus, further experimental data have to be used as input parameters. The entries in the following table are all in mdyn/Å:

f_r	f_α	f_{rr}	$f_{r\alpha}$	input parameters	remark	Ref.
4.136	0.738	0.819	0.152	ω_i [5], ζ_{ij}^c [6], $\tau_{\alpha\beta\gamma\delta}$ [3]	a)	[2]
3.97	0.72	0.83	0.15	ν_i [5], ζ_{ij}^c [6]	b)	[1]
3.9499	0.7237	0.8059	0.1373	ν_i [9], Δ, $\tau_{\alpha\beta\gamma\delta}$	c)	[3]
4.1 ± 0.3	0.8 ± 0.1	1.0 ± 0.2	0.25 ± 0.1	ν_i; ν_1, ν_2 ($^{18}OF_2$)	d)	[4]

a) $r_e^2 \cdot f_\alpha = 1.457$ mdyn·Å, $r_e f_{r\alpha} = 0.214$ mdyn [2]. – b) Presumably, the ν_i from [5] were used together with $(\zeta_{13}^c)^2 = 0.426$ (see p. 29). $r_e^2 \cdot f_\alpha = 1.42$ mdyn·Å, $r_e f_{r\alpha} = 0.21$ mdyn. Constants also in [7]. – c) $f_r + f_{rr}$ (= F_{11}, see below) was fixed by the inertial defect Δ. Centrifugal distortion effects were used to discriminate between two possible sets of force constants [3]. $f_r = 4.05$, $f_\alpha = 0.707$, $f_{rr} = 0.906$, and $f_{r\alpha} = 0.200$ were derived earlier [8] by the same authors. – d) These values were regarded [4] as only approximate in view of complications due to Fermi resonance of ν_1 and $2\nu_2$ and the then existing uncertainty of the position of ν_1($^{18}OF_2$) (see p. 28).

The data in [11] were obtained by minimization of the main contribution to the average bending energy. For older data, see [12 to 14]. Three constants were determined by setting $f_{rr} = 0$ [15]. Only two constants, f_r and f_α, were derived in [16, 17], and from a different set of frequencies in [18].

Four constants were predicted from an electrostatic model [19]; for f_α, see also [20 to 22]. f_α was calculated semiempirically by the CNDO/2 method [23].

Urey-Bradley Force Field. With $F' = -0.1F$, the stretching, bending, and repulsion constants (in mdyn/Å) were $K = 3.262$, $H = 0.1886$, and $F = 1.3010$, respectively [24]; with $F' = 0$: $K = 3.15$, $H = -0.08$, and $F = 3.14$ [25]. The repulsion between the two F atoms was also discussed [26, 27].

Symmetry Force Constants F_{ij} in mdyn/Å

$F_{11}(a_1) = f_r + f_{rr}$	$F_{22}(a_1) = f_\alpha$	$F_{12}(a_1) = \sqrt{2}\,f_{r\alpha}$	$F_{33}(b_1) = f_r - f_{rr}$	remark	Ref.
4.65 ± 0.04	0.7051 ± 0.0009	0.202 ± 0.004	2.969 ± 0.016	a)	[28]
4.7557	0.7237	0.1941	3.1440	b)	[3]
4.8 ± 0.1	0.72 ± 0.01	0.21 ± 0.05	3.147 ± 0.005	c)	[6]

a) From centrifugal distortion constants, including τ_1 and τ_2. Similar data on the basis of τ_1 and τ_{cccc} or τ_2 and τ_{cccc}. – b) From fundamental vibrational frequencies in connection with the inertial defect and the centrifugal distortion [3]. From centrifugal distortion constants alone, $F_{11} = 4.6337$, $F_{22} = 0.7183$, $F_{12} = 0.1722$, and $F_{33} = 2.9335$ were obtained [6]. – c) From fundamental frequencies and Coriolis coupling constants.

Several methods for the determination of the three constants F_{11}, F_{12}, and F_{22} in the symmetry block A_1 from only two frequencies, ν_1 and ν_2, were discussed and applied to OF_2, see [10, 35 to 38]. The formalism of the Green's function analysis [29] and the L-matrix approximation method [30 to 33] were applied [34]. The constants were also derived on the basis of a "bond asymmetry parameter", η_b, which was used for the description of the spatial distribution of the binding forces in a molecule [48]. For η_b, see also [49]. Constants in terms of "Keating's coordinates" [55] were reported [56].

For an ab initio calculation of F_{11} and F_{22}, see [39]. F_{11} and F_{12} were used to establish a relationship between force constants and bond energies of bent XY_2 molecules [51].

The elements of the compliance matrix $C = F^{-1}$ were determined [40]. The compliance constants in turn were used to derive a set of "relaxed" force constants [50]. For these types of force constants, see [54].

Anharmonic Force Field

The cubic part of the potential function written in internal coordinates ($x_1 = \Delta r_1$, $x_2 = \Delta r_2$, $x_3 = \Delta\alpha$) is given by $6V^{(3)} = f_{rrr}(\Delta r_1^3 + \Delta r_2^3) + 3f_{rrr'}\Delta r_1 \Delta r_2(\Delta r_1 + \Delta r_2) + 3f_{rr\alpha}(\Delta r_1^2 + \Delta r_2^2)\Delta\alpha + 6f_{rr'\alpha}\Delta r_1 \Delta r_2 \Delta\alpha + 3f_{r\alpha\alpha}(\Delta r_1 + \Delta r_2)\Delta\alpha^2 + f_{\alpha\alpha\alpha}\Delta\alpha^3$. The following table shows two sets of these cubic force constants:

f_{rrr} mdyn/Å^2	$f_{rrr'}$ mdyn/Å^2	$f_{rr\alpha}$ mdyn/Å	$f_{rr'\alpha}$ mdyn/Å	$f_{r\alpha\alpha}$ mdyn	$f_{\alpha\alpha\alpha}$ mdyn·Å	remark	Ref.
−27.1	−1.6	−1.3	−0.4	−2.6	−3.3	a)	[1,7]
−27.86	−1.69	−0.65	−0.44	−1.35	−0.58	b)	[2]

a) Apparently derived [1] for a representation of the potential function in which products $x_i x_j x_k$ are constrained to $i \le j \le k$ and adapted [7] to the representation of the potential function given on p. 31. – b) Calculated from a model potential, containing three independent parameters for the anharmonic part, by a Monte-Carlo procedure.

f_{rrr} was also calculated using an electrostatic model [22]. The modified variables $(r - r_e)/r$ and $[\sin(\alpha/2) - \sin(\alpha_e/2)]/\sin(\alpha_e/2)$ were used in [43].

Constants k_{ijk} (in cm^{-1}) of the potential function written in (dimensionless) normal coordinates q_i (see above) were derived from the observed rotation-vibration interaction constants α_i, which were corrected for Fermi resonance [1, 6, 41, 42]:

k_{111}	k_{222}	k_{112}	k_{122}	k_{133}	k_{233}
−40.0	−16.0	−22.0	−9.8	−139.3*)	−31.8

*) −139.8 in [1, 42].

The constant k_{122}, giving rise to a Fermi resonance interaction between two vibrational levels (v_1, v_2, v_3) and ($v_1 - 1$, $v_2 + 2$, v_3) in OF_2 [1, 5, 6], was also determined from a treatment of the two resonating triads $(2,0,v_3) - (1,2,v_3) - (0,4,v_3)$ with $v_3 = 0,1$: $k_{122} = (\pm)9.7 \pm 0.1$, $(\pm)10.7 \pm 0.1$ cm^{-1} [52]. From the three resonating diads $(1,0,v_3) - (0,2,v_3)$ with $v_3 = 0$, 1, and 3, $k_{122} = (\pm)19.6 \pm 0.8$ cm^{-1} was obtained [44].

Constants k_{ijk} were also predicted from a van der Waals model and from a valence-force model [6, 41]. A complete set of constants k_{ijk} similar to those above and quartic constants were calculated from a model potential, containing three independent parameters for the anharmonic part, by a Monte-Carlo procedure [2].

Quartic constants were also derived in [1, 42] from the vibrational constants x_{ij} of Nebgen et al. [5] and in [44] from their own x_{ij}. For an approximate method, see [45]. A force field was also determined by an ab initio SCF-MO calculation [53].

Atomic Force Constants. For applications of this concept to OF_2, see [46, 47].

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3.4.5.12 Bond Dissociation Energy. Atomization Enthalpy

Dissociation Energy D(FO–F)

The dissociation energy (in kcal/mol, unless stated otherwise) is not very well known, as is shown by the large uncertainties in the data given in the table below. The three sources for D listed in the table are discussed separately. D = 39 (1.7 eV) has been estimated by a comparison with isoelectronic species [1], formerly D = 42 (1.8 eV) [2].

D(FO–F)	source	Ref.
38 ± 4	appearance potentials: OF^+ from OF and OF_2	[3]
39 ± 10	thermochemical data: ΔH_f of OF_2, OF, and F	[4]
40 ± 4	activation energies of thermal OF_2 decomposition	[5]

D(FO–F) from appearance potentials. $D_0 = 159 \pm 15$ kJ/mol has been derived from the measured difference $1.6_5 \pm 0.1_5$ eV of the OF^+ appearance potentials from OF and OF_2 [3]. $D_0 = 160.97 \pm 1.93$ kJ/mol was likewise obtained [18] from the difference between the OF^+ appearance potential from OF_2 (14.44 eV) [19] and the ionization potential of the OF radical (12.77 eV) [20]. Previously, too large a value D = 64.6 (2.8 eV) was derived from the measured appearance potential 1.2 eV of F^- from OF_2. An electron affinity of the F atom of 3.6 eV and an excess kinetic energy of 2.0 eV for the assumed products OF and F^- were taken into account. The latter was determined from the measured kinetic energy of the fluoride ion [6]. See also the tables of bond dissociation energies [7] ($D_0=64.6$) and [8] ($D_0=64.5$, $D_{298}=65.6$). The large D [6] was corrected on grounds of a revised electron affinity of F (3.45 eV; see, however, "Fluorine" Suppl. Vol. 2, 1980, p. 41): $D_0=61.1\pm4.6$ (2.65 ± 0.2 eV). This D_0 still implies a dissociation energy of only 1.25 eV for the OF radical, which is too low compared to 1.7 eV for F_2 (or 1.59 eV, see "Fluorine" Suppl. Vol. 2, 1980, p. 66), in view of the fact that F_2 contains one more antibonding electron than OF [5].

D(FO–F) from formation enthalpies. The relation $D=\Delta H_f(OF)+\Delta H_f(F)-\Delta H_f(OF_2)$ was used with the respective OF, F, and OF_2 formation enthalpies (26, 19, and 6 kcal/mol [9]) to give the second value in the table above [4]. The uncertainty ±10 was added [4] because of the poorly known [10] formation enthalpy of OF. $D_{298}=43$ is obtained from the formation enthalpies 29.7, 19, and 5.8 [11, 12]. $D_0=43.446$ ($D_{298}=44.508$) may be derived from the quantities 33.487 (33.502), 18.5 (19.003), and 8.541 (7.997) in [13]. These latter D values are cited as $D_0=43.4\pm10$ [8] and $D_{298}=44.5$ [7, 8]. $D_0=64$ was derived [7] from $\Delta H_{f,0}=41$, 18.5, and -4.7 (in [31]).

D(FO–F) from activation energies E; cf. p. 43; for the relation between D and E, see also [22]. $D=40\pm4$ was extracted [5] from measurements [12, 14 to 16] of activation energies for the thermal decomposition of OF_2. Two further measurements yielded $D_0=38.5\pm1.0$ [17] and 40 ± 1 [21].

Atomization Enthalpy ΔH_{at}. Average Bond Energy E_b

The atomization enthalpy ΔH_{at} and the average bond energy $E_b=\Delta H_{at}/2$ (both in kcal/mol, unless stated otherwise) may be computed from $\Delta H_{at}=\Delta H_f(O)+2\Delta H_f(F)-\Delta H_f(OF_2)$. At 0 K one obtains $\Delta H_{at,0}=89.4\pm0.5$ (374 ± 2 kJ/mol [3]), $E_b=44.7$, from $\Delta H_{f,0}=59.0$ for O and 18.4 for F (both from [31]), and 6.4 for OF_2 (on the basis of $\Delta H_{f,298}=5.86$, see below) [5]. At 298 K, $\Delta H_{at,298}=91.44$, $E_b=45.72$, from $\Delta H_{f,298}=59.553$(O), 37.75(2F), and 5.86 (own value for OF_2) [9]; $E_b=45.7$ [25]. The following atomization enthalpies were derived from various other OF_2 formation enthalpies (in parentheses): 90 (5.5 at 298 K) [26, 27], 89.4 (7.6 ± 2.0 at 298 K from [28]) [6, 29, 30], 87.446 (8.541 at 0 K) [13], 101.4 (-4.06, presumably at 298 K) [32, 33], 101.6 (-4.40 ± 0.82 at 298 K) [34], and 102 (-4.4 at 298 K) [35].

For a comparison of E_b in compounds of N, O, and F, see [36]. For a calculation from covalent and ionic contributions, see [37]. ΔH_{at} was derived from a Mulliken population analysis using Hückel theory [38] and from the Mulliken [23] magic formula [24].

For OF_2 dissociating into ionic fragments, the enthalpies were determined as follows: $\frac{1}{2}\Delta H_{at}(OF_2\rightarrow O^{2-}+2F^+)=2220$ kJ/mol and $\frac{1}{2}\Delta H_{at}(OF_2\rightarrow O^{2+}+2F^-)=2231$ kJ/mol [35].

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3.4.5.13 Microwave Spectrum

A table of the microwave spectra of triatomic molecules [1] contains 139 lines for OF_2 with frequencies ranging from 8299.51 to 59846.20 MHz, which were taken from the literature, and, in an appendix, 26 additional lines from 84401.810 to 95998.940 MHz and one line at 7803.49 MHz (transitions between rotational levels J_{K^-,K^+}, with J = total angular momentum quantum number excluding nuclear spin and K^-, K^+ = projections of J on the symmetry axis of the limiting prolate or oblate symmetric top). Eight of these known rotational transitions and seven new transitions, belonging to the $v_1 = 1$ and $v_2 = 2$ vibrationally excited states, were more recently observed by IR-microwave (MW) double resonance or IR–MW–MW triple resonance [12].

Most of the tabulated lines [1] are singlets belonging to the vibrational ground state of the molecule and were taken from the measurement of Pierce et al. [3]. Their data comprise 83 lines out of the regions 8 to 40 and 49 to 60 GHz and with $J'' \leq 39$. Their line at 13575.16 MHz ($13_{2,11} \leftarrow 14_{1,14}$), however, was erroneously described as a singlet, see [1, 4]. Their line at 29473.73 MHz ($36_{4,32} \leftarrow 37_{3,35}$) was not confirmed later. This frequency should possibly read 29443.73 MHz [5]. In the range 40 to 47 GHz, one singlet at 41064.05 MHz was observed [5] and two singlets at 45089.32 and 46795.92 MHz were derived [3] from older measurements [6]. From these studies [6], further lines at 63598.76 MHz (with the doubtful assignment $41_{10,32} \leftarrow 42_{9,33}$) and from 92195.43 MHz (confirmed in [1]) to 104837 MHz were evaluated [3]. The assignments in [6] were previously criticized by Pierce et al. [7, 8], who observed 17 singlets between 13 and 60 GHz and assigned 13 of them.

The eight reported triplets [1] in the vibrational ground state are due to spin-rotation interaction. Their middle components are at 10057.730 to 17257.96 [9], at 41298.01 [5], and at 95193.890 MHz [2].

Lines belonging to vibrationally excited states were measured by Morino and Saito [10]: eight lines were found for the $v_1 = 1$ state, twelve for $v_2 = 1$ and also for $v_3 = 1$, and six for $v_2 = 2$. Their frequencies range from 12 to 37 GHz and their J″ values from 2 to 13, and are collected in [1] as well. Additional transitions (four for $v_1 = 1$ and three for $v_2 = 2$) were found [12].

The Zeeman effect was observed for three transitions at 13804.03 ($3_{0,3} \leftarrow 2_{1,2}$), 33251.89 ($4_{2,3} \leftarrow 5_{1,4}$), and 36028.82 MHz ($4_{0,4} \leftarrow 3_{1,3}$) [11].

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3.4.5.14 Infrared Absorption

The IR spectrum was observed for gaseous OF_2 [1 to 4, 12], for OF_2 dissolved in liquid N_2 [5], in solid Ar [6, 7] (see also the comparison IR-Raman [8]), N_2 [9], O_2 [10], and for solid OF_2 [11].

The following table contains the band centers and intensities I from the gas-phase measurement [3] and the IR bands and intensities I from the liquid-N_2 measurement at 80 K [5]. Wavenumbers $\tilde{\nu}$ in cm^{-1}. Intensities in the gas phase are qualitative: s = strong, m = medium, w = weak, v = very. I in N_2 is relative to 1000 for ν_3.

$\bar{\nu}$ gas phase	461	831	928		1281	—	1648
I gas phase	s	vs	s		w	—	vw
$\bar{\nu}$ a) liquid N_2	459.8 b)	823.0	914.5 b)	925.6 c)	1274	1377	1636.1
I liquid N_2	18 ± 2	1000	210 ± 15		—	"weak"	4.7 ± 0.4 d)
vibration	ν_2	ν_3	$2\nu_2$	ν_1	$\nu_2+\nu_3$	$\nu_1+\nu_2$	$2\nu_3$
$\bar{\nu}$ gas phase	1728	1740		1840		2188	2455
I gas phase	m	m		w		vvw	w
$\bar{\nu}$ a) liquid N_2	1718.8	1730.0	1817.3	1832.3	1844.7	2175	2441.6
I liquid N_2	59.0 ± 3.5		3.2 ± 0.3			"weak"	2.5 ± 0.3
vibration	$2\nu_2+\nu_3$	$\nu_1+\nu_3$	$4\nu_2$	$2\nu_1$	$\nu_1+2\nu_2$	$\nu_1+\nu_2+\nu_3$	$3\nu_3$
$\bar{\nu}$ gas phase	—	—		2643		3324	
I gas phase	—	—		w		vw	
$\bar{\nu}$ a) liquid N_2	2531.1	2543.2	2599.4	2618.0	2629.3	3298.0	3310.6
I liquid N_2	0.1 ± 0.03		1.1 ± 0.1			0.23 ± 0.03	
vibration	$2\nu_2+2\nu_3$	$\nu_1+2\nu_3$	$4\nu_2+\nu_3$	$2\nu_1+\nu_3$	$\nu_1+2\nu_2+\nu_3$	$\nu_1+3\nu_3$	$2\nu_2+3\nu_3$

a) ± 0.5 cm^{-1} if not otherwise indicated. – b) ± 0.8. – c) ± 0.6. – d) Average value of the integrated absorption coefficient is $(0.2 \pm 0.15) \times 10^{-8} cm^2 \cdot mol^{-1} \cdot s^{-1}$ in the gas phase.

The spectrum in liquid N_2, especially in the range of the two triads $\{2\nu_1, \nu_1+2\nu_2, 4\nu_2\}$ and $\{2\nu_1+\nu_3, \nu_1+2\nu_2+\nu_3, 4\nu_2+\nu_3\}$, was further discussed and, in part, differently assigned [13].

The rotational structure in the region of the Fermi diad $\{\nu_1, 2\nu_2\}$ (900 to 955 cm^{-1}) was partly resolved. The comparison with a calculated curve led to the band origins [4]. Seven rotational -vibrational transitions in this range were observed and classified by IR-microwave double resonance using five CO_2 and two N_2O laser lines [14].

In solid matrices, only the fundamentals ν_1 (together with $2\nu_2$), ν_2, and ν_3 were observed, see pp. 28/9.

In the crystalline state at 10 K, the molecular vibrations ν_1, $2\nu_2$, and ν_2 are split: $\nu_1 = 914$ and 916, $2\nu_2 = 925$ and 927, and $\nu_2 = 456$ and 461 cm^{-1}. This must be due to a factor-group splitting since these vibrations are nondegenerate in the free molecule. A sharp peak at 812 cm^{-1} was assigned as ν_3. In an unannealed sample, a band at 823 cm^{-1} was observed. In addition, seven lattice vibrations were found at 48, 56(?), 59, 66, 71, 77, and 86 cm^{-1} [11].

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3.4.5.15 Raman Scattering

The Raman spectrum was obtained for liquid OF_2 [1], for OF_2 dissolved in solid Ar [2], and for solid OF_2 [3].

For the molecular vibrations, the following wavenumbers (in cm^{-1}) and depolarization ratios ϱ were observed with laser excitation:

state	T in K	laser	$\nu_1(a_1)$	ϱ	$2\nu_2(a_1)$	ϱ	$\nu_2(a_1)$	ϱ	$\nu_3(b_1)$	ϱ	Ref.
liquid	77 to 128	He–Ne	925.2	0.19	915.7	0.17	461.1	0.38	821.1	0.82	[1]
matrix	16	Ar^+	920	0.64	931	0.64	465	0.74	825	0.87	[2][a]
solid	~10	Ar^+	912	—	925	—	462	—	812 820 845	—	[3][b]

[a] The wavenumbers are accurate to ±1 cm^{-1}. For $^{18}OF_2$: $\nu_1=892$, $\nu_2=461$, $\nu_3=799$ cm^{-1}. ϱ ±15%. – [b] The components at 812 and 820 cm^{-1} of ν_3 are due to a factor-group splitting of the transverse component; the feature at 845 cm^{-1} belongs to the longitudinal component, see [4]. In addition, a shoulder was observed at 922 cm^{-1}.

Lattice vibrations were seen at 47, 54, 58, 73, 77 (shoulder), 82 (shoulder), and 85 cm^{-1} [3].

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3.4.5.16 Ultraviolet and Visible Absorption

Extinction coefficients ε were measured for the gaseous [1 to 3] and the liquid state [4].

In the vapor phase, an overall increase of ε (in 10^{-5} $Torr^{-1} \cdot cm^{-1}$ at 0°C) from 0.08 at 546 nm to 75.00 at 210.2 nm was observed. Flat maxima were superimposed at 421 nm ($\varepsilon = 0.35$), at 358 and at 294 nm. The maximum of the absorption beginning at 264 nm was not reached in the wavelength range covered [1]; see also "Fluor" Erg.-Bd. 1, 1959, p. 228. More recently, $\varepsilon = 0.76 \times 10^{-5}$ $Torr^{-1} \cdot cm^{-1}$ was measured at 365 nm and 20°C [2]. The temperature dependence of ε at 220 nm was studied in the range 600 to 1700 K [3].

In the liquid state, the molar extinction coefficient was measured [4] at 77 K:

λ in nm	350	400	450	500	550	600	650	700	750
ε in cm^2/mol	70	61	39	21	10	7	6	5	5

For an ab initio study of the electronic spectrum of OF_2, see [5] (and pp. 11/2).

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3.4.6 Crystallographic and Thermal Properties

Crystal Data

IR and Raman spectra of crystalline OF_2 indicate that OF_2 is not centrosymmetric. It contains at least two molecules per unit cell of C_s or C_1 symmetry [1].

Equation of State

The constants $a = 2.69 \times 10^6$ atm·cm^6·mol^{-2} and $b = 45.1$ cm^3/mol in the van der Waals equation $(p + a/V^2)(V - b) = RT$ were calculated from the critical constants $T_{cr} = 215.2$ K and $p_{cr} = 48.9$ atm [2, 3].

Density ϱ in g/cm^3

Pycnometric measurements of liquid OF_2 between −195.70 and −148.52°C resulted in the following (selected) values represented by $\varrho = 0.8225 - 0.004873\,t$ [4]:

t in °C	−195.70	−181.38	−174.14	−166.87	−157.72	−148.52
ϱ	1.776	1.706	1.672	1.635	1.592	1.546

Measurements of liquid OF_2 (by the flotation-temperature method) in a narrow range near its boiling point gave the following values [5]:

t in °C	−152.8	−152.0	−150.8	−148.7	−147.4	−145.8
ϱ	1.557	1.553	1.547	1.537	1.530	1.523

The values are represented by $\varrho = 2.190 - 0.00523T$. Extrapolation yielded $\varrho = 1.521$ for liquid OF_2 at the boiling point (−145.3°C) [5]. The density of gaseous OF_2 is 0.00241 at N.T.P. (undefined) [6].

Melting Point

OF_2 melts at −223.8°C, see "Fluor" Erg.-Bd. 1, 1959, p. 227. No new measurements have been reported.

Vapor Pressure p. **Boiling Point** t_b. **Heat of Vaporization** ΔH_v

Measured vapor pressures (selected values) for essentially 100% pure OF_2 [7] follow:

t in °C	−195.4	−181.3	−178.1	−169.6	−163.2	−157.0
p in Torr	1.4	15.4	24.1	72.2	142.8	279.0

t in °C	−152.0	−151.2	−147.9	−146.0	−145.3
p in Torr	424.4	471.3	618.8	735.0	740.0

The values fit the equation log $p = 7.2242 - 555.42/T$ (T in K) from which extrapolation gives $t_b = -145.3$°C [7]. In about the same temperature range the following pressures for 99.6% pure OF_2 are obtained [4] (selected values):

t in °C	−182.88	−176.86	−169.61	−158.65	−154.97	−152.22	−149.45	−146.68	−145.30
p in Torr	10.8	25.0	65.0	243.3	321.7	414.5	526.3	662.1	735.9

The values are represented by log $p = 7.4199 - 581.19/T$ (T in K). From this equation, $t_b = -145.2$°C and $\Delta H_v = 2.66$ kcal/mol are obtained [4]. $\Delta H_v = 2400$ cal/mol is computed by means of correlation increments [3]. A critical comparison of the measurements in [4, 7] and [8] (see "Fluor" Erg.-Bd. 1, 1959, p. 227) is given in [9].

Critical Constants

The following constants were obtained: $t_{cr} = -58 \pm 1$°C (method of disappearing meniscus) [5], -59.7 ± 0.3°C (from vapor pressure measurements) [4], −58.0°C (215.2 K) (calculated using the theorem of corresponding states) [3].

$p_{cr} = 48.9$ atm (calculated using the Dieterici equation of state) [5], 49.5 atm (from vapor pressure measurements) [4].

$\varrho_{cr} = 0.553$ g/cm^3, $V_{cr} = 97.6$ cm^3/mol (from density measurements) [5], $\varrho_{cr} = 0.570$ g/cm^3, $V_{cr} = 93.5$ cm^3/mol (calculated values) [3], $V_{cr} = 126.9$ cm^3/mol (from vapor pressure measurements) [4].

Heat Capacity. Thermodynamic Functions

Enthalpy H and Gibbs free energy G are given in kcal/mol, molar heat capacity C_p and entropy S in cal·mol^{-1}·K^{-1}.

Experimentally determined C_p values [10] are:

T in K	82.1	100.0	117.1	125.7	139.2	159.2	197.9
C_p	17.820	18.090	18.198	18.414	18.846	19.062	20.142

It is stated [9] that there is a wide variance between these measured and the calculated [11] capacities; see also the values given below.

Calculated (selected) values for the ideal gas [12]:

T in K	100	298	400	500	1000	1500	2000	2500	3000	4000	5000	6000
$H^\circ - H^\circ_{298}$	−1.807	0	1.109	2.283	8.723	15.486	22.343	29.239	36.154	50.014	63.894	77.784
$-(G^\circ - H^\circ_{298})/T$	67.457	59.118	59.538	60.361	65.082	68.961	72.058	74.612	76.777	80.312	83.134	85.481
S°	49.383	59.118	62.311	64.928	73.805	79.286	83.230	86.307	88.829	92.816	95.913	98.445
C°_p	8.066	10.349	11.373	12.061	13.348	13.650	13.762	13.815	13.844	13.873	13.886	13.893

$S^\circ = 59.11$; $C^\circ_p = 10.35$ and $H^\circ_{298} - H^\circ = 2.604$ are given for T = 298 K in [13]. $S^\circ = 59.0 \pm 0.2$ in [14]. $H_T - H_{298.15} = 12.48\,T + 0.49 \times 10^{-3} T^2 + 2.16 \times 10^5\,T^{-1}$ up to 1500 K is given in [15].

Viscosity. Thermal Conductivity

Measurements of liquid OF_2 between −145.8 and −152.8°C result in the following (selected) values of the viscosity η [5]:

t in °C	−145.8	−147.4	−148.7	−150.6	−151.5	−152.8
η in cP	0.2852	0.2933	0.3014	0.3140	0.3188	0.3259

The values fit the equation $\log \eta = -1.5768 + 131.5/T$ (η in cP, T in K); $\eta = 0.2826$ cP at −145.3°C (boiling point) [5]. $\eta = 168\,\mu P$ at 300 K is given in [6].

Measurements at lower temperatures gave the following viscosities which fit the equation $\log \eta = -1.4508 + 112.4/T$ (η in cP, T in K) [4]:

t in °C	−195.7	−180.2	−174.1	−169.6	−160.5	−155.8
η in cP	1.004	0.572	0.470	0.422	0.344	0.323

The thermal conductivity of liquid OF_2 was measured to be 0.00058 (±6%) and 0.00061(±2%) $cal \cdot s^{-1} \cdot cm^{-1} \cdot K^{-1}$ at −195.8°C and −183°C, respectively [4].

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3.4.7 Chemical Behavior

The following chapter includes information on the miscibility and the compatibility of liquified OF_2 with elements and compounds at cryogenic temperatures. As pointed out by A. G. Streng (J. Chem. Eng. Data **16** [1971] 357/9), the data were based on comparatively short observation times and on the use of pure substances. At other conditions (e.g., catalytic amounts of impurities or higher temperatures) some of the mixtures may react slowly or violently.

3.4.7.1 Thermolysis

Activation energy E_a in the Arrhenius equation $k = A\ \exp(-E_a/RT)$ is given in kcal/mol.

The first kinetic investigation [1], see "Fluor" Erg.-Bd. 1, 1959, p. 229, showed that OF_2 decomposes in a homogeneous monomolecular reaction between 523 and 543 K at some hundred Torr. The measured rate constant k was assumed to correspond to the activation process in reaction (1), see below (formation of $OF_2{}^*$, followed by decomposition). The constant $A = 10^{14.43}\ L \cdot mol^{-1} \cdot s^{-1}$ found, is regarded to be a factor of six too high for a monomolecular reaction. On this basis it was supposed that the activation energy $E_a = 39$ was too high (this was not confirmed later, see below) or that chain reactions were involved [2]. The reaction is discussed in light of the theory of monomolecular reactions (see, e.g. [3, 4]).

To clarify the mechanism, flow- and static-reactor experiments as well as shock-tube investigations at much higher pressures and temperatures were performed with sometimes disagreeing results, even within the same group of experiments.

The decomposition was investigated under static conditions [2, 5] by pressure measurements between 503 and 583 K in vessels of vitreous silica, magnesium, or aluminium. The total pressure was between 10 and 750 Torr; added gases were O_2, N_2, F_2, He, or SiF_4. The homogeneous reaction is of second order at OF_2 pressures above some hundred Torr. All added gases have a specific accelerating influence on the reaction which is proportional to the partial pressure of the gas. This is interpreted as an activation process of OF_2 forming $OF_2{}^*$ in reaction (1) [2].

(1) $OF_2 + M = OF + F + M$ (3) $OF + OF = 2F + O_2$ ($M = OF_2$ or
(2) $OF_2 + F = OF + F_2$ (4) $F + F + M = F_2 + M$ added gases)

The observed increase of the overall second-order rate constant with decreasing pressure is interpreted by the consumption of F atoms in reaction (2) rather than by the three-body collision (4) at low pressures and by the generation of F atoms according to reaction (3), by which the reaction assumes the character of a chain reaction. The chain length decreases with increasing OF_2 pressure and with increasing temperature. For undiluted OF_2 the rate equation is $-d[OF_2]/dt = k_1\ [OF_2]^2 + k^*\ [OF_2]^{3/2}$, with $k^* = k_2 \cdot k_1{}^{1/2} \cdot k_4{}^{-1/2}$. The experiments yielded $k_1 = 10^{13.89 \pm 0.04} \times 10^{-(38.4 \pm 0.5)/4.57T}\ L \cdot mol^{-1} \cdot s^{-1}$ and $k^* = 10^{10.36 \pm 0.04} \times 10^{-(33.6 \pm 0.9)/4.57T}\ L^{1/2} \cdot mol^{-1/2} \cdot s^{-1}$. Estimations gave $E_2 \approx 13.9 \pm 1.5$ and $A_2 \approx 10^{7.8}\ L \cdot mol^{-1} \cdot s^{-1}$.

The proposed mechanism is supported by investigations of the OF_2 photolysis (see p. 45) [2, 5]. The evidence that the decomposition of OF_2 includes a step involving the formation of OF radicals is confirmed by mass spectrometry of OF_2 in the range 520 to 770 K [6]. No OF radicals were detected in a mass spectrometric study of the pyrolysis of OF_2 on metallic filaments [7].

A mass spectrometric study between 773 and 973 K at low OF_2 pressure (0.1 to 1.0% OF_2, He as carrier; total pressure 60 to 100 Torr) using a nickel flow reactor results in $k = 10^{15.2 \pm 0.2}$ $\exp(-32.200/RT) cm^3 \cdot mol^{-1} \cdot s^{-1}$. No details on the mechanism are provided [8, 9] (values of [8] were corrected in [9]). The mass spectrometric investigation of the decomposition of OF_2 pure and diluted by N_2 and Ar, in a static system (passivated Al reactor) at 563 to 634 K showed a temperature-dependent induction period followed by an apparent first-order reaction for which $k = 10^{9.0 \pm 0.4}\ \exp(-30.1 \pm 1.0/RT) s^{-1}$ was found. The reaction is inhibited by fluorine. The data are discussed in terms of decomposition by means of a chain reaction [10]. In another mass spectrometric study between 603 and 704 K [11] (Monel stirred-flow reactor, 1 to 10% OF_2 in He, 1 atm total pressure) no induction period was observed. The reaction was found to be slightly less than first order with respect to the reactant concentrations. The initial data could be represented by the equation $-d[OF_2]_0/dt = k_1[OF_2]_0[M] + k'[OF_2]_0^{1/2}\ [M]$ with

$k_1 = 10^{16.9 \pm 0.6} \exp(-39.2 \pm 1.7/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$. The results are interpreted by a chain mechanism in which the step $OF + M = O + F + M$ (see p. 76) is of special importance; for details, see [11].

Shock-tube experiments on the decomposition of OF_2 (0.2 to 1% in He, $[Ar] = 6 \times 10^{-5}$ to $3 \times 10^{-4}\ mol/cm^3$) between 820 and 1240 K yielded (by UV spectrometric measurements) $k = 10^{15.1} \exp(-34.2/RT)$ [12] in reasonable agreement with $k = 10^{14.2} \exp(-31.5/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$, obtained in shock-tube investigations at temperatures between 860 and 1300 K. The discussed chain mechanism consists of the reactions (1) to (4) [13]. Another (mass spectrometric) study of the shock-tube decomposition of OF_2 (Ar as carrier) [14] between 770 and 1390 K yielded for $T < 1000$ K (all k and A in $cm^3 \cdot mol^{-1} \cdot s^{-1}$) $k = 10^{15.8} \exp(-37.8/RT)$. The data are accounted for by the scheme

$$(1, -1)\ OF_2 + Ar \rightleftharpoons OF + F + Ar \qquad (3, -3)\ OF + OF \rightleftharpoons 2F + O_2$$
$$(4, -4)\ F + F + Ar \rightleftharpoons F_2 + Ar$$

with $k_1 = 10^{17.3 \pm 1.0} \exp(-42.5 \pm 4.1/RT)$, $k_3 = 10^{12.10 \pm 0.12}$, and $k_4 = 10^{11.3} \exp(+9.9/RT)$. It is shown that the reverse reaction (−1), with $A_{-1} = 10^{15.6}$, $E_{-1} = 0$, and reaction (−4), with $A_{-4} = 10^{12.5}$, $E_{-4} = 27.3 \pm 2.5$, cannot be neglected, even in the early stages of the reaction. Thus, the overall second-order constant k should not be taken as the constant k_1 of the initiation reaction (1). The accelerating effect of F_2 on the rate of OF_2 decomposition is confirmed [10], which is in contrast to results showing an inhibition [1]. The inhibition was explained by reactions (−4) and $OF + F_2 \rightleftharpoons OF_2 + F$. The decrease in the O_2 yield at $T > 1000$ K is explained by the reactions

$$OF + M \rightleftharpoons F + O + M,\ OF_2 + O \rightleftharpoons 2OF, \text{ and } O + F_2 \rightleftharpoons OF + F$$

A plot of the observed rate constants k obtained by analysis of static- and flow-system data [1, 8, 9, 10] and of shock-tube data [12, 13, 14] with the assumption $k = k_1$ shows that the former investigations yielded higher k values than the latter one, probably due to surface effects in the static and flow systems. Above about 1000 K the k values level off because the rate-controlling step (1) is near equilibrium. For further discussion, see [14].

$k_1 = 10^{16.7} \exp(-40.5 \pm 0.3/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ for $T = 770$ to 1230 K results from k_1 values in [12, 14] combined with data from the OF_2–CO reaction in shock tubes [15].

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3.4.7.2 Photolysis

In the **gas-phase** decomposition of OF_2 (150 to 750 Torr) by 365 nm radiation between 15 and 45°C the quantum yield $\Phi = 1.0$ was observed. This means that after the primary process (1a) no further steps seem to follow. Addition of F_2 had no influence on the reaction [1]. Above 200°C, where OF_2 thermolysis begins the quantum yield became greater than one. This is shown by the photolysis ($\lambda = 365$ nm) of OF_2 (7 to 150 Torr, added gases of up to 50 Torr F_2 and up to 80 Torr N_2) in quartz vessels. It was found that $(\Phi - 1)$ is independent of the OF_2 pressure and increases strongly with an increase of temperature, whereas an increase of light intensity and of total pressure have an opposite influence. The results are explained by a mechanism analogous to that of the OF_2 thermolysis [2]:

(1a) $OF_2 + h\nu = OF + F$
(1b) $OF_2 + M = OF + F + M$
(2) $OF_2 + F = OF + F_2$
(3) $OF + OF = 2F + O_2$
(4) $F + F + M = F_2 + M$

The primary steps (1a) and (1b) are followed by additional decomposition of OF_2 in reaction (2), which is of importance only above 200°C because of its high activation energy, $E_2 = 14 \pm 2$ kcal/mol. The OF radicals disappear presumably according to (3) forming additional F atoms [2].

Photolysis of OF_2 in **matrices** at low temperatures is covered in the section on OF formation, see p. 64.

UV irradiation of **liquid** OF_2 at −196°C and of OF_2 in a $CFCl_3$ matrix at −134 to −184°C gave an ESR signal which was assigned to the OF radical [3]. The ESR spectrum in similar experiments (photolysis of liquid OF_2 by sunlight or UV light) is assigned to the O_2F radical; for discussion of the mechanism, see [4].

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3.4.7.3 Radiolysis. Dissociative Ionization Processes

Following radiolysis of OF_2 at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 219$ K) showed the formation of O_2, F_2, O_2F_2, and O_3F_2 [1].

In the mass spectrum (70 eV electrons) of OF_2 were observed the ions OF_2^+ (relative intensity in %, 100) at 13.7 eV, OF^+ (91) at 15.8 eV, O^+ (4.3), F^+ (<0.5), and F^- (63) at 1.2 eV [2]. In another study of the mass spectrum (corresponding to 800 Å photoionization), the ions OF_2^+ (100) at 13.13 eV and OF^+ (43.6) at 14.44 eV were found [3], for discussions, see the original papers. In a third study [4], the appearance potentials and the kinetic energies of all ions detected in the mass spectrum were measured as a function of the admission conditions and the temperature of the gas. With 18 eV (a) and 70 eV electrons (b), the observed ions (relative intensity in parentheses) at 77 K are OF_2^+ (a 100, b 100) at 13.12 eV, OF^+ (48, 153) at 14.52 eV, O_2^+ (15, 12), HF^+ (~0, 7), F^+ (~0, 78), O^+ (~ 0, 51), F_2^- (5, –) at 0.04 eV, OF^- (30, –) at 0.02 eV, and F^- (100, –) at 0.02 eV. The temperature dependence of the intensities and appearance potentials of the positive ions (350 to 770 K) and the differences with earlier results [2], especially concerning F^-, are discussed [4].

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3.4.7.4 Reactions with Noble Gases

F_2 mixes homogeneously with equimolar amounts of Ar at 85 K or Kr at 120 K without reaction. It dissolves about 30 mol% of Kr at 77 K and forms two separate layers with Xe at 90 K [1].

No reaction is observed in equimolar mixtures of OF_2 and Kr [3] or Xe [2] in the dark at 25°C. Irradiation of the mixtures with sunlight gives the noble gas difluorides [2, 3].

Pressure measurements show that heating an equimolar mixture of OF_2 and Xe above 560 K initiates a reaction (no further details) [4]. The reaction of OF_2 with Xe in an electric discharge (195 K, 3 to 62 Torr) or in a nickel tube at about 400°C at a starting pressure of about 3.5 atm yields XeF_4 and xenon oxide fluorides [5]. Thus, xenon oxide fluorides are obtained from equal volumes of OF_2 and Xe at 195 K and a maximum pressure of 60 Torr applying 1.2 to 3.6 keV and 12 to 32 mA. Heating a 1:1 molar OF_2–Xe mixture for 4.75 h at 300°C in a nickel tube gives crystals of the empirical formula $Xe_{1.2}O_{1.1}F_{3.0}$ [6].

The radiolysis of a mixture of OF_2 and Xe at 77 K (3 MeV bremsstrahlung up to 200 Mrad/h, mass spectrometric analysis at $T \leq 293$ K) yields O_2F_2, O_3F_2, O_4F_2, XeO_2 (?), O_2, and F_2 (tentative assignment) [7]; for critical remarks concerning the O_3F_2 and O_4F_2 peaks, see [13].

Collision-quenching reactions of metastable noble gas atoms $Z(^3P_2)$ (Z = Ar, Kr, Xe) with small halogen-containing molecules, among them OF_2, were investigated by the flowing-afterglow technique. The most important reaction was the formation of noble gas fluoride excimers ZF* which subsequently underwent radiative decay to the dissociative ground state:

$$Z^* + OF_2 \rightarrow ZF^* + OF \qquad ZF^* \rightarrow Z + F + h\nu$$

The following total quenching rate constants k (in 10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) and the branching fractions Γ (ratio of the rate constant for the formation of an individual species to the total quenching rate constant) were obtained [8, 11]:

Ar	Kr	Xe
k = 57, Γ = 0.62	k = 53, Γ = 1.0	k = 57, Γ = 0.92

For the discussion of the mechanism, see [12].

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3.4.7.5 Reactions with Hydrogen

At room temperature no reaction occurs between OF_2 and H_2, see "Fluor" Erg.-Bd. 1, 1959, p. 230.

The kinetics of the OF_2–H_2 reaction at 110 to 220°C at 1 atm total pressure in a Monel stirred-flow reactor was studied by mass spectrometry. The reaction time was 0.5 to 20 s, the initial reactant concentration ranges were 0.5 to 2.0 mol% OF_2 and 0.5 to 5.0 mol% H_2. The concentration of added O_2 was 0 to 5 mol%. Helium was used as the carrier gas. The approximate stoichiometry is shown by

$$4\,OF_2 + 6\,H_2 \rightarrow 8\,HF + 2\,H_2O + O_2$$

The reaction is strongly inhibited by oxygen but not affected by the other products. Limiting inhibition was achieved by initially adding 5 mol% O_2; at these conditions the reaction was first order with respect to OF_2 and had a weak H_2-concentration dependence (on the order of about 0.3). The reaction showed a substantial heterogeneous component; for details, see [1, 2, 3]. The investigation of the reaction in a magnesium stirred-flow reactor at 160 to 310°C showed that magnesium has an insignificant influence on the reaction. The contact time was 2 to 12 s, the initial concentration ranges were ⅛ to ½ mol% OF_2, 3/16 to 5 mol% H_2, and ¼ to 5.0 mol% O_2; helium was used as a diluent. The rate of disappearance of OF_2 was strongly influenced by OF_2 concentration, weakly influenced by H_2 concentration, and inhibited by oxygen formed in the reaction. A ten-step mechanism was proposed [4]:

(1) $OF_2 + M \rightarrow OF + F + M$
(2) $F + H_2 \rightarrow HF + H$
(3) $H + OF_2 \rightarrow HF + OF$
(4) $OF + H_2 \rightarrow HOF + H$
(5) $HOF + H \rightarrow HF + OH$
(6) $OH + H_2 \rightarrow H_2O + H$
(7) $OH + OF_2 \rightarrow O_2 + HF + F$
(8) $H + O_2 + M \rightarrow HO_2 + M$
(9) $HO_2 + OF_2 \rightarrow HF + O_2 + OF$
(10) $HO_2 + H \rightarrow H_2 + O_2$

The steady-state treatment of this sequence yielded

$$d[OF]/dt = k_0[OF_2]^2[O_2]^{-1/2}\,(1 + \alpha[OF_2]/(\alpha[OF_2] + \beta[H_2]))$$

with $k_0 = k_1k_9/k_8k_{10}$, $\alpha = k_7$, and $\beta = k_6$. An Arrhenius treatment resulted in $k_0 = 10^{8.41 \pm 0.24}$ exp $(-17.3 \pm 0.5\ \text{kcal}\cdot\text{mol}^{-1}/RT)$ $L^{1/2}\cdot \text{mol}^{-1/2}\cdot s^{-1}$. The probability of contributions from heterogeneous reactions is discussed [4]. The enthalpy of the reaction

$$OF_2(g) + 2\,H_2(g) + n\,H_2O(l) \rightarrow [2\,HF\cdot(n+1)H_2O](l),\ n = \infty$$

is $\Delta H^\circ_{298.16} = -223.3 \pm 0.4$ kcal/mol, by calorimetric measurements of the combustion of an H_2–OF_2 mixture in a bomb containing excess H_2O [5]. The value was recalculated as -222.93 kcal/mol [6]. By flame calorimetry $\Delta H_{303.4} = -227.5 \pm 0.2$ was obtained [6] for the reaction

$$OF_2(g) + 2\,H_2(g) + 99\,H_2O(l) \rightarrow 2\,[HF\cdot 50\,H_2O](l)$$

Atomic hydrogen reacts with OF_2 even at 77 K and 0.4 to 1.0 Torr to form HF, H_2O, H_2O_2 (and N_2O_4) [7]. Estimations from flow experiments gave $k \leq 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at room temperature. However, the reaction path could not be evaluated [18]. Vibrationally excited HF molecules, as shown by IR emission, are formed in a flow system [8] according to the reaction

$$OF_2 + H \rightarrow HF^{\dagger} + OF$$

The stimulated emission from $HF^{\dagger}$ ($DF^{\dagger}$) molecules generated behind overdriven detonation waves [9] and by flash photolysis in H_2–OF_2 mixtures [10, 11] has been investigated. Studies of the above reaction in the microwave cavity of an ESR spectrometer suggest the formation of OH radicals according to $H + OF \rightarrow OH + F$ [12].

The measurement of the burning velocity v of premixed OF_2–H_2 flames, as a function of the OF_2 content, gave v = 3250 cm/s for mixtures of 14 vol% OF_2 and 86 vol% H_2 (v is defined as the ratio of gas flow (in cm^3/s) to the surface area of the cone (in cm^2) produced by the incoming unburnt gas). Flashbacks occur at higher OF_2 concentrations. With N_2 as diluent the amount of OF_2 that can be used without flashback is 80% of stoichiometric when the hydrogen contained 55.2% N_2. This flame has the velocity v = 1750 cm/s [13, 14, 15]. These properties make these flames unsuitable for systems with high light output. Diffusion flames burning in mixtures of OF_2 and H_2 with added BF_3 or B_2H_6, are more appropriate. BO_2 and BO are shown to be the visible-light emitting species [14, 15]. For the use of OF_2–H_2 as a bipropellant system, see [7, 16, 17].

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3.4.7.6 Reactions with Oxygen, Ozone, and Nitrogen

OF_2 mixes homogeneously with equimolar amounts of O_2 at 90 K or O_3 at 77 K without reaction [1]. Mixtures of liquefied O_3 and O_2, which are not completely miscible at −183°C or below, are stabilized by addition of OF_2 to form a single liquid phase at −183°C. From the O_3–O_2–OF_2 phase diagram the minimum amount of OF_2 required is about 8% when there is about 45% O_3 in the O_3–O_2–OF_2 solution [2].

OF_2 and O_2 react in a high-voltage electric discharge to yield O_2F_2, O_3F_2, and O_4F_2 [3]. In the radiolysis of an OF_2–O_2 mixture at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 192$ K) mass peaks were tentatively assigned to O_2, O_3, F_2, O_2F_2, and O_3F_2 [4], for critical remarks concerning O_3F_2, see [9].

Earlier results on the UV photolysis of OF_2–O_2 mixtures indicating the formation of O_2F_2 and O_3F_2 are reported in "Fluor" Erg.-Bd. 1, 1959, p. 230. The UV photolysis of an OF_2–O_2 mixture at 95 K for 10 min yielded a deep orange solution which became red after removal of oxygen. The ESR spectrum of the liquid showed a signal at g = 2.004 which decayed over several hours. It was assigned to the O_2F radical. The following mechanism was postulated [5]:

(1) $OF_2 + h\nu \rightarrow F + OF$ (3) $OF + OF_2 \rightarrow F_2 + O_2F$

(2) $F + O_2 \rightarrow O_2F$ (4) $2O_2F \rightarrow (O_4F_2) \rightarrow O_2F_2 + O_2$

The photolysis of OF_2–O_2 mixtures in an inert matrix at 4 K yielding O_2F is described [6]. The production of $^{16}OF_2$ during the photolysis of $^{18}OF_2$ in $^{16}O_2$ suggests an exchange mechanism involving O_2F_2 [6] according to

$$^{18}OF_2 + {}^{16}O_2 \rightleftharpoons F^{18}O^{16}O^{16}OF \rightarrow {}^{16}OF_2 + {}^{16}O^{18}O$$

Investigations of the thermolysis of OF_2 between 770 and 1390 K by shock waves yielded for the equilibrium reaction $OF_2 + O \rightleftharpoons 2OF$ the Arrhenius parameters $A = 10^{11.0}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$, $E_a = 10.0$ kcal/mol (forward reaction) and $A = 10^{10.6}$, $E_a = 16.0$ (reverse reaction) [7]. From flow experiments $k \leq 10^9$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (forward reaction) was estimated [10].

OF_2 mixes with equimolar amounts of nitrogen homogeneously at 77 K without reaction [1]. OF_2 reacts with N_2 at −180°C in an electrical discharge to give O_2, some N_2O, FNO_2, and FNO_3 [8]. The radiolysis (see above) of mixtures of OF_2 and N_2 ($T \leq 191$ K) gave O_2, F_2, N_2O, N_2O_4, NF_3, N_2F_2, and FNO_2 [4]. From flow experiments a rate constant $k \leq 10^9$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ for the reaction of OF_2 with N atoms was estimated [10].

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3.4.7.7 Reactions with Halogens

OF_2 mixes homogeneously with fluorine in a 1:1 molar ratio at 77 K [1].

Data from the thermolysis of OF_2 between 503 and 583 K give for the reaction of OF_2 with F atoms according to

$$OF_2 + F = OF + F_2$$

the rate constant $k = 10^{7.8} \exp(-13.9 \pm 1.5\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ [2], for similar results, see also [3]. From flow experiments $k \leq 10^9\ \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ was estimated [13]. From OF_2-photolysis experiments, activation energies $E_a = 14.3 \pm 1.5$ [4] and $E_a > 15$ kcal/mol [5] were estimated.

Mixtures of OF_2 and Cl_2, Br_2, or I_2 explode on warming [6].

No reaction occurs between OF_2 and chlorine (liquid or gas) on heating to 100°C [7]. When a mixture of OF_2 and Cl_2 was passed through a copper tube warmed to 300°C, the reaction proceeded with little or more violent explosions forming ClF, Cl_2O, and ClOF [6]. In another investigation (flow system, 250 to 800°C) no formation of ClOF or Cl_2O was observed [8]. A Cl_2–OF_2 mixture (1:1 by volume) explodes upon spark ignition to give ClF and O_2 [9]. In an electric discharge through a mixture of OF_2 and Cl_2 at −196 to −90°C, ClF, ClO_2, ClO_2F, but no ClOF were formed [8].

No reaction occurs between OF_2 and bromine (liquid or gas) on UV irradiation or on heating to 100°C [7, 10]; the reaction starts at ~130°C. BrF was obtained from a 1:1 ratio of OF_2 to Br_2 [12]. When a mixture of three volumes of OF_2 with one of Br_2 vapor was ignited by heat or spark, oxygen and BrF_3 were formed. Exploding a 5:1 mixture of OF_2 and Br_2 generated BrF_5 and O_2 [9, 12].

At room temperature OF_2 reacts slowly with solid iodine to give IF_5 and a yellow solid. The reaction of gaseous OF_2 with I_2 vapor yields yellow solids of the empirical formula IO_xF_y ($x = 0.96$ to 1.98 and $y = 0.35$ to 1.61). The reaction of OF_2 with iodine in CCl_4 gives IO_xF_y ($x = 0.78$ to 1.31 and $y = 1.31$ to 1.68). Iodine at elevated temperature burns in OF_2 to give IF_5 and O_2 [9].

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3.4.7.8 Reactions with Other Elements

On testing the shock sensitivity of materials for liquid-propellant systems, explosive reactions of graphite in OF_2 were observed under shock loading at intensities corresponding to about 8200 atm [1].

Many common metals react with OF_2, but the reaction stops after a passive metal fluoride coating is formed, see "Fluor" Erg.-Bd. 1, 1959, p. 230, and [2].

On depositing simultaneously OF_2 diluted in Ar and a beam of Li, Na, K, or Mg atoms onto a salt window at 15 K, absorption bands due to the appropriate metal fluorides and weakly bonded MF···OF dimers were observed. In the case of Li the formation of LiOF is also assumed [3].

Mass spectrometry studies on OF_2 indicate the formation of HgOF by reaction between OF_2 and Hg at temperatures above 520 K [4].

Heating a platinum sponge in an atmosphere of OF_2 leads to the formation of O_2PtF_6 [5, 6]. The introduction of OF_2 into a uranium(IV) solution induces chemiluminescence by forming the UO_2^{2+} ion in an excited state [7].

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3.4.7.9 Reactions with Water and Hydrogen Peroxide. Alkaline Hydrolysis

OF_2 does not behave like the anhydride of an acid. It has only a low solubility in water, see "Fluor" Erg.-Bd. 1, 1959, p. 230. Even on shaking a solution of OF_2 in 40% KOH for five minutes at room temperature, approximately half of the OF_2 reacted [1, 2]; none of its reactions produced HOF [3].

The alkaline hydrolysis of OF_2 according to

$$OF_2 + 2OH^- \rightarrow O_2 + 2F^- + H_2O$$

has been studied [4] (see "Fluor" Erg.-Bd. 1, 1959, p. 232) under such conditions that the rate-controlling step was the rate of dissolving the gas rather than the rate of hydrolysis when in solution. In a further study [5] the rate of disappearance of dissolved OF_2 was measured. Investigations at 20°C and pH = 9.6 to 11.8 gave the rate equation

$$-d[OF_2]/dt = k[OF_2]\cdot([OH]^{1/3} - 0.0105)$$

with $k = 4.1 \times 10^{-3}$ when t in s and concentration in mol/L. From runs using buffered solutions at pH = 10.0 at 25 and 30°C an activation energy of 8.5 kcal/mol was calculated [5]. The reaction rate of OF_2 with a 40% KOH solution is

$$-d[OF_2]/dt = k[OF_2]$$

with $k = 2.8 \times 10^{-4}\ s^{-1}$ at 248 K, $9.5 \times 10^{-4}\ s^{-1}$ at 273 K, and $2.2 \times 10^{-3}\ s^{-1}$ at 293 K [1]. The alkaline hydrolysis is interpreted by a water-catalyzed reaction mechanism involving O–F bond polarization [6].

Concentric streams of OF_2 and steam, preheated to about 100°C and fed with a linear velocity of 107 cm/s are not hypergolic under these conditions. They can be readily ignited by a flame or a glowing wire, or by introducing a few milligrams of cotton, glycerin, or hydrazine into the OF_2–steam stream. Twenty-seven other materials caused no ignition of the stream. The OF_2–steam diffusion flame was stable and weakly luminous. Burning proceeded smoothly [7].

H_2O_2 is immiscible with OF_2 below 25°C [8].

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3.4.7.10 Reactions with Nitrogen Compounds

Ammonia. Amines. Pyridine. Ammonium Nitrate

A mixture of NH_3 and OF_2 does not ignite at room temperature [7]. The mixture reacts at room temperature to give N_2O and NH_4F, if the reaction is run slowly to avoid combustion [1, 2]. N_2O, H_2O, N_2, and unidentified products are obtained from NH_3 and OF_2 between −196 and +25°C [3]. With aqueous and nonaqueous NH_3 the reaction yields N_2O, H_2O, and $NH_4F \cdot HF$ [4].

OF_2 reacts with NHF_2 between −80 and +25°C, with or without UV irradiation, to give FNO_3 and degraded products (some explosions) [13] and on standing at 25°C for one hour to yield N_2F_4, NF_3, FNO, and FNO_2 [3]. The reaction in acetic acid or in $C_2Cl_3F_3$ and by an electric discharge gave unspecified N–O–F compounds [13]. The UV photolysis of an OF_2–$ClNF_2$ mixture at −23 or +25°C gave NO_2, FNO, and other products [13].

NF_3 mixes homogeneously with equimolar amounts of OF_2 at 77 K [5] or 82 K [7]. A 1:2 OF_2–NF_3 mixture exploded violently on warming from −183°C to room temperature [1]. An electric discharge through a diluted mixture of NF_3 and OF_2 forms F_3NO. The radiolysis of an OF_2–NF_3 mixture at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 253$ K) showed the formation of N_2, O_2, F_2, N_2O, N_2O_4, O_2F_2, and cis- and trans-N_2F_2 (tentative assignment) [8].

Primary amines RNH_2 ($R = C(CH_3)_3$, C_2H_5, $C(CH_3)_2CH_2C(CH_3)_3$, cyclopropyl, cyclohexyl) are oxidized by OF_2, dissolved in Freon 11, below −42°C in a rapid and controllable reaction to give the nitroso R–N=O or oxime R=NOH derivatives. The latter being formed if a hydrogen atom is geminal to the amino group [9]; for the mechanism, see [9, 10]. Gaseous $(CH_3)_3N$ and OF_2 ignite instantly on contact. Slowly adding OF_2 to excess $(CH_3)_3N$, both components being mixed with an eightfold amount of N_2, yields CO_2, N_2O, and $(CH_3)_3N \cdot HF$ [1, 2].

The reaction with pyridine yielded CO_2, N_2O, and $C_5H_5N \cdot HF$ [1, 2].

NH_4NO_3 reacts with OF_2 at 100°C (30 min) to give traces of NO_2 [3].

Fluorine Azide. Dinitrogen Difluoride

UV photolysis of an OF_2–N_3F mixture at 25°C gave NF_3 [11].

An electric discharge through an OF_2–N_2F_2 mixture yielded N_2O, NO_2, and FNO_2 [12]. NO, NO_2, and NF_3 form on heating OF_2 with cis- and trans-N_2F_2 at 100 and 135°C. No reaction occurred between 25 and 40°C with or without UV irradiation [13].

Hydrazines

At 150°C, OF_2 reacts with N_2H_4 to yield N_2, N_2O, H_2, and NH_4F (?) [4]. Liquid N_2H_4 and OF_2 ignite on contact. Shaking an aqueous solution of $N_2H_4 \cdot H_2SO_4$ for several hours with OF_2 yielded N_2 and F^-. Similarly, the reaction of OF_2 with a solution of $NH_2OH \cdot H_2SO_4$ gave N_2O and F^- [1, 2].

N_2F_4 is miscible with OF_2 between −188 and −120°C [14]. It mixes homogeneously with equimolar amounts of OF_2 at 110 K [5]. The UV photolysis of an OF_2–N_2F_4 mixture at −63 or at −83°C led to the formation of NO_2, N_2F_2, FNO, and FNO_2 [13].

On exposing the mixture to an electric discharge at −196°C, NF_3, FNO, and FNO_2 are formed [3]. Mass spectrometric analysis of an OF_2–N_2F_4 mixture warmed from 77 to 223 K led to the formation of N_2, N_2O, NO, N_2O_4, NF_3, FNO, and NF_2NO(?). Radiolysis of the mixture at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 240$ K) yielded N_2, F_2, O_2, N_2O, N_2O_4, cis- and trans-N_2F_2, NF_3, FNO, and FNO_2 (tentative assignment) [8].

At 25°C and 3 atm, as well as at 150°C, no reaction between N_2F_4 and OF_2 was observed [3, 15]. Further investigations showed that OF_2 reacts with N_2F_4 at 125°C over a 12-hour period to give NF_3 and NO_2 [1]. OF_2 reacts with N_2F_4 at 120 to 170°C in a homogeneous gas-phase reaction forming FNO and NF_3. According to the equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ (see p. 326) the reaction follows the overall equations

$$2N_2F_4 + OF_2 \rightarrow FNO + 3NF_3 \quad \text{and} \quad 4NF_2 + OF_2 \rightarrow FNO + 3NF_3$$

The primary step is the abstraction of an F atom from OF_2 according to $NF_2 + OF_2 \rightarrow NF_3 + OF$ with an activation energy of 22.1 kcal/mol [16].

Nitrogen Oxides

No reaction occurs between N_2O and OF_2 at 270 atm on exposing the mixture to a spark [15]. Radiolysis of an OF_2–N_2O mixture at 77 K (3 MeV bremsstrahlung up to 200 Mrad/h, mass spectrometric analysis at $T \leq 199$ K) yielded N_2, O_2, F_2, FNO, FNO_2(?), and N_2O_4 (tentative assignment) [8]. The UV photolysis of an OF_2–N_2O mixture in an N_2 matrix at 4 K gave a higher concentration of OF radical than for pure OF_2 [17].

No reaction occurs on mixing OF_2 and NO at room temperature. With a doubled flow rate (60 mL/min) a blue flame is observed. A blue liquid forms on passing NO over liquid OF_2 at −191°C. No visible interaction or solubility is found on warming the mixture to −145°C [7]. A mixture of OF_2 and NO slowly turns brown and forms FNO and F_2NO. A gaseous mixture may explode from a spark [18]. The reaction at 25°C or at −160 to −70°C yielded NO_2, FNO_3, FNO, and NO_2 [4] and at 650 to 750°C in a flow system NO_2, N_2O, FNO, and FNO_2 [12]. An OF_2–NO diffusion flame (total pressure 70 Torr) burns orange. Spectroscopic measurement shows the formation of FNO [19].

No reaction between OF_2 and N_2O_3 is observed at temperatures below 0°C [7].

No reaction occurs on mixing streams of OF_2 and NO_2 (60 mL/h) at 25°C. A small CH_4 flame ignited the mixture. Mixing OF_2 (60 mL/min) with a large excess of NO_2 in a preheated tube results in spontaneous combustion [7]. The thermal reaction of OF_2 with NO_2 was investigated between 60 and 80°C. The reaction takes place with a decrease in pressure: one molecule of OF_2 being consumed for every two molecules of NO_2. The reaction products are FNO_2 and O_2 at low pressures and FNO_2 and FNO_3 at high pressures. The rate-determining step of the reaction is

$$OF_2 + NO_2 \rightarrow FNO_2 + OF$$

with $k = 1.28 \times 10^8 \cdot \exp(-14.5 \pm 0.6\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. The OF radical adds to NO_2 yielding the intermediate $FO \cdots NO_2$ that forms FNO_3 or decomposes to give an F atom and NO_3. The NO_3 radicals form O_2 and NO_2. The latter reacts with F atoms to give FNO_2 [20].

OF_2 reacts with N_2O_4 at low temperatures to form a mixture of FNO, FNO_2, and FNO_3 [22]. An electric discharge through a mixture of OF_2 and N_2O_4 yields N_2O, FNO_2, FNO_3, and some F_3NO [3]. The radiolysis of an OF_2–N_2O_4 mixture at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 193$ K) gave O_2, F_2, O_2F_2, FNO, and FNO_2 (tentative assignment) [8].

Nitrogen Oxide Fluorides. Chlorine Nitrate

FNO is not miscible with OF_2 at −145°C and 1 atm [7]. A mixture of pure OF_2 and pure FNO (gas or liquid) is not explosive, if pure [14]. The explosion of an equimolar, liquefied mixture on warming [18] was presumably caused by nitric oxide impurities in FNO. This is indicated by the self-ignition of FNO, NO, and OF_2 mixtures [7]. In contrast to earlier results, see "Fluor" Erg.-Bd. 1, 1959, p. 231, no remarkable reaction occurs in a mixture of OF_2 (up to 200 Torr) and FNO (up to 200 Torr) at ≤170°C [16].

The 365-nm photolysis of an OF_2–FNO mixture yields FNO_2 and F_2. The quantum yield is less than one and depends on the concentration of FNO_2, which acts as an inhibitor [22].

Radiolysis of an OF_2–FNO mixture at 77 K (3 MeV bremsstrahlung up to 200 Mrad/h, mass spectrometric analysis at $T \leq 249$ K) yielded N_2, O_2, F_2, N_2O, N_2O_4, and NF_3 (tentative assignment) [8].

FNO_2 is not miscible with OF_2 at −145°C and 1 atm. No reaction between OF_2 and FNO_2 is observed at 25°C or in a preheated tube. The mixture is ignited by a CH_4 flame [7]. No products were given for the reaction of OF_2 with FNO_2 initiated by an electric discharge [3].

The photolysis of OF_2 in the presence of FNO_3 yields FNO_2 via a mechanism involving the formation and reaction of OF radicals [22]. No reaction occurs at 28°C with or without UV irradiation [9]. Both compounds are miscible without reaction from −160 to −78°C [14].

$ClNO_3$ and OF_2 are slightly miscible at −78°C [7, 14].

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3.4.7.11 Reactions with Halogen Compounds

OF_2 dissolves only traces of O_2F_2 at 135 K. Two separate layers form on mixing OF_2 and O_2F_2 at 135 K [1].

With O_3F_2, OF_2 mixes homogeneously in all proportions at 116 K [2].

There was no noticeable reaction in equimolar mixtures of OF_2 and anhydrous HCl at 25°C and 1 atm. Solid HCl does not react with liquid or gaseous OF_2 between 90 and 140 K [2].

No reaction is observed between Cl_2O and OF_2 at room temperature [11]. The compounds are slightly miscible at −78°C under pressure [13].

ClF mixes with equimolar amounts of OF_2 homogeneously at 125 K without reaction [1]. On standing at 25°C or in UV light at −80°C, the mixture reacts to give Cl_2, Cl_2O, and unidentified products [3].

OF_2 dissolves 0.05% by weight of ClF_3 at 140 K [1, 2], see also [6]. It forms two separate layers with ClF_3 on mixing at 140 K [1]. OF_2 and ClF + ClF_3 are compatible and miscible between −78 and +25°C [4]. No reaction between OF_2 and ClF_3 is observed in the gas phase at room temperature, in the liquid phase [2], or on UV irradiation at −80 or +25°C [3]. The photolysis of a mixture of OF_2 (213 Torr) and ClF_3 (177 Torr) with light of 250 to 400 nm for 45 h yields $ClOF_3$ [5].

In a liquid solution of ≤16% ClF_5 in OF_2, hypergolicity of OF_2 is enhanced while its vapor pressure is lowered. The solubility is complete between −78.5°C and the critical temperature of OF_2 (~−58°C, see p. 41). Below −78.5°C miscibility is incomplete [6].

UV photolysis of an equimolar OF_2–ClO_2F mixture for 4.1 h at −60°C yields $ClOF_3$ (20 mol%), ClF_3 (17), and ClF (57) [7]. The ternary system OF_2–ClO_3F–ClF_3 under pressure at −78°C shows complete miscibility [8, 13].

OF_2 and BrF_5 are compatible and miscible between −78 and +25°C [4]. No reaction occurs between OF_2 and BrF_5 below 200°C. The reactions with BrF_3 at ≤200°C and with IF_5 at ≤150°C give BrF_5 and IF_7, respectively [9]. Slow addition of OF_2 to ICl generates an orange solid of variable composition $IO_xF_yCl_z$. If OF_2 was added too rapidly, the ICl ignited [10, 11].

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3.4.7.12 Reactions with Sulfur Compounds

H_2S. A strong explosion occurred on mixing gaseous OF_2 and H_2S at room temperature [1], see "Fluor" Erg.-Bd. 1, 1959, p. 231. A mixture of OF_2 (100 Torr) and H_2S (40 Torr) in a glass bulb reacts overnight to form a sulfur deposit, SO_2, SOF_2, and SiF_4 [2]. Between 90 and 150 K gaseous and liquid OF_2 do not react with solidified H_2S. At 195 K and 400 Torr, a 1:1 gaseous mixture of OF_2 and H_2S reacts slowly forming a white solid. During one hour the pressure decreased to about 100 Torr. When the reaction vessel was taken out of dry ice, a violent explosion occurred [1].

SO_2. Between 300 and 500°C (10 min) OF_2 reacts with SO_2 forming SO_2F_2, SOF_2, SO_3, and O_2 [3]. On heating OF_2 and SO_2 a gas mixture was obtained which yielded after condensation at −185°C SO_2F_2, $FSOOSO_2F$, and a small amount of a compound, apparently FSO_2OOSO_2F [2]. FSO_2F and FSO_2OSO_2F are also reported as products [4]. The photolysis ($\lambda = 365$ nm) of OF_2 and SO_2 at room temperature gave FSO_2OSO_2F and SO_2F_2 [5]. The radiolysis of an OF_2–SO_2 mixture at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 110$ K) showed the formation of O_2F, F_2, SF_2(?), SF_4, SF_6, SOF_4, and SO_2F_2 (tentative assignment) [13].

SO_3. In an OF_2–SO_3 mixture no reaction is observed at room temperature within a week as shown by IR spectroscopy [2]. On irradiation with monochromatic UV light at a wavelength of 365 nm at room temperature, FSO_2OOF [6] is formed quantitatively with traces of FSO_2OSO_2F [7]; for kinetics, see [6].

Pure FSO_2OOF is also obtained on irradiating excess OF_2 and SO_3, with filtered UV light (window glass $\lambda > 350$ nm) [5, 7]. If radiation includes quanta with sufficient energy for the excitation of SO_3, then FSO_2OOF is formed in trace amounts and the main products are FSO_2OSO_2F and FSO_2F [5]. By a tracer-atom method and by ^{17}O NMR analysis it was shown that the OF group in FSO_2OOF originates from OF_2 [8].

SF_4. The reaction of OF_2 with SF_4 (2:1) at 450°C (10 min) gives SO_2F_2, SF_6, F_2SOF_2, and O_2 [3]. At 150°C, the formation of SF_6 and O_2 is reported [4].

The photochemical reaction between OF_2 and SF_4 at 365 nm between 40 and 65°C is a chain reaction with a relatively short chain length. The main products are SF_6 and O_2; furthermore, small amounts of SF_5OF, very small amounts of SF_5OSF_5 and $SF_5O_2SF_5$, and traces of S_2F_{10} are formed. The concentration of SF_4 has no influence on the reaction rate which is given by

$$+d[SF_6]/dt = k' I_a^{2/3} p^{2/3} \quad (p = OF_2 \text{ pressure, } I_a = \text{intensity of absorbed light})$$

with $k' = (4.74 \pm 0.4) \times 10^3 \cdot \exp(-6.8 \pm 1.0\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ L^{1/3} \cdot \text{mol}^{-1/3} \cdot s^{-1/3}$. Addition of O_2 changes the course of the reaction. The experimental results with or without the addition of small amounts of oxygen can be represented by the following reactions [9]

(1) $OF_2 + h\nu\ (365\ \text{nm}) = OF + F$
(2) $SF_4 + F + M = SF_5 + M$
(3) $SF_5 + OF_2 = SF_6 + OF$
(4) $OF + OF = O_2 + 2F$
(5) $SF_5 + OF = SF_5OF$

SF_5OSF_5 and $SF_5O_2SF_5$ are formed partly by the reaction of SF_5 radicals with SF_5OF and partly by the reactions of SF_5O_2 which results from the addition of O_2 to SF_5. When $k_4 = 2 \times 10^{10}\ L \cdot \text{mol}^{-1} \cdot s^{-1}$ and $E_4 \approx E_5 \approx 0$, $k_3 = (1.63 \pm 0.15) \times 10^9 \exp(10.2 \pm 1.5\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ L \cdot \text{mol}^{-1} \cdot s^{-1}$ results [9]. The photochemical reaction at high O_2 pressures (~300 Torr) at 23 to 50°C produced SF_6 and $SF_5O_2SF_5$ as the only F-containing products; for details of the reaction mechanism which involves in addition to the reactions (1), (2), and (4), reactions of F atoms and SF_5 radicals with O_2, see the paper [10].

SF_5OF is formed in the photolysis of an OF_2–SF_4 solution in $CFCl_3$ at −80°C. The intermediates SF_5, SF_5O, and SF_5OSF_4 were detected by ESR spectroscopy [11]. UV photolysis of a 1:2 OF_2–SF_4 mixture at −78°C yields SF_5OSF_5 [12].

SF_6. The radiolysis of an OF_2–SF_6 mixture at 77 K (3 MeV bremsstrahlung, up to 200 Mrad/h, mass spectrometric analysis at $T \leq 161$ K) led to the formation of O_2, F_2, O_2F_2, OF_2, and SOF_4 (tentative assignment) [13].

SOF_2. No reaction of OF_2 with SOF_2 occurs between 20 and 50°C [14]. At 200°C (nickel reactor), SOF_4 and small amounts of SO_2F_2 are formed [2]. The reaction between 350 and 500°C yields SO_2F_2, SOF_4, SF_6, and O_2 [3]. In the photochemical reaction with light of 365 nm at 20 to 50°C, SOF_4 and SO_2F_2 are formed in equal amounts, two moles of SOF_2 being consumed per mol of OF_2. The rate of reaction is proportional to the intensity of absorbed light and is independent of the temperature and of the concentration of the reactants. Oxygen does not influence the reaction. The proposed reaction mechanism is

$OF_2 + h\nu \rightarrow OF + F$; $F + SOF_2 \rightarrow SOF_3$; $SOF_2 + OF \rightarrow SO_2F_2 + F$; $2SOF_3 \rightarrow SOF_4 + SOF_2$ [14]

FSO_2OOSO_2F. Irradiation of a mixture of OF_2 and FSO_2OOSO_2F with unfiltered 365 nm UV light yields FSO_2OOF and FSO_2OF [5]. Examination of this reaction at 18 and 38°C with light of 365 nm showed that both compounds form in equal amounts and equal quantum yields of 1.0. The proposed reaction mechanism is

$OF_2 + h\nu \rightarrow OF + F$; $FSO_2OOSO_2F + F = FSO_2OF + FSO_3$; $FSO_3 + OF = FSO_2OOF$ [15]

$RN{=}SF_2$, $R = CF_3$, C_2F_5, $(CF_3)_2CF$, $ClCF_2CF_2$, and $BrCF_2CF_2$. The photochemical reaction of OF_2 and $RN{=}SF_2$ proceeds according to

$$2\,RN{=}SF_2 + OF_2 \xrightarrow{UV} RN{=}SOF_2 + RN{=}SF_4$$

followed by the decomposition of $RN{=}SF_4$ into $RN{=}SF_2{=}NR + SF_4$. The yields of $RN{=}SOF_2$ are between 31 and 70% based on $RN{=}SF_2$ [16].

$FC(O)N{=}SF_2$. UV irradiation of mixtures of OF_2 and $FC(O)N{=}SF_2$ gives $FC(O)N{=}SOF_2$, $(FC(O)N)_2SF_2$, SF_5NCO, and $SF_5OC(O)F$. Small amounts of $SF_5OOC(O)F$ and traces of COF_2, SO_2F, SOF_4, and SF_6 are also formed [17]. One of the reaction paths suggested accounts for the presence of SF_5NCO and the absence of $FC(O)N{=}SF_4$ among the reaction products [17]:

$$2\,FC(O)N{=}SF_2 + OF_2 \xrightarrow{UV} FC(O)N{=}SOF_2 + FC(O)N{=}SF_4;\ FC(O)N{=}SF_4 \rightarrow SF_5NCO$$

For this reaction, see also [16].

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3.4.7.13 Reactions with BF_3 and B_2H_6

No reaction was observed between OF_2 and BF_3 below 320°C [1].

The reactions in the system OF_2–B_2H_6 are of special interest because the mixture can be used as a space-storable bipropellant, see p. 9. Mixtures of OF_2 and B_2H_6 can explode on warming from −195°C to ambient temperature. Between 120 and 170°C and below 20 Torr, OF_2 and B_2H_6 react slowly [2] according to

$$3\,OF_2 + 3\,B_2H_6 \rightarrow B_2O_3 + 2\,B + 2\,BF_3 + 9\,H_2$$

The initial rates of consumption of OF_2 and B_2H_6 and the initial rate of formation of BF_3 were determined for the reaction between OF_2 and B_2H_6 at 300 K. The initial partial pressures were 5 to 40 Torr for OF_2 and 1 to 30 Torr for B_2H_6. In addition, the initial consumption rates of OF_2 and B_2H_6 were determined between 300 and 330 K. These initial rates were correlated to initial reactant concentrations and to reactor temperature (p in Torr, t in min, T in K) [3]:

$$[d(p_{BF_3})/dt]_0 = 2.16\times10^{-3}\,(p_{OF_2})_0^{1.699}\cdot(p_{B_2H_6})_0^{-0.432} \text{ at } 300\text{ K}$$

$$-[d(p_{B_2H_6})/dt]_0 = 2.82\times10^{6}\,(p_{OF_2})_0^{2.200}\cdot(p_{B_2H_6})_0^{-0.562}\cdot\exp(-11466\text{ cal}\cdot\text{mol}^{-1}/RT)$$

$$-[d(p_{OF_2})/dt]_0 = 0.294\,(p_{OF_2})_0^{1.624}\cdot(p_{B_2H_6})_0^{-0.024}\cdot\exp(-2822.5\text{ cal}\cdot\text{mol}^{-1}/RT)$$

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3.4.7.14 Reactions with CO, CO_2, COF_2, and COS

CO and **CO_2**. At 77 K OF_2 mixes with CO or CO_2 homogeneously in a 1:1 molar ratio [1]. The reaction of OF_2 with CO yields COF_2 as the main product. The reaction path and the formation of other products (CO_2, O_2, F_2, FCOOF, and $[FCO]_2O_2$) depend on the experimental conditions. The kinetic results of the thermal reaction in a static system (323 to 353 K) [2] and in shock waves (76 to 1400 K) [3] as well as of the photochemical reaction (283 to 308 K, $\lambda = 365$ nm) [4] are presented in "Kohlenstoff" D 3, 1976, p. 13. The increase in yield of OF radicals in the photolysis of OF_2–CO_2 mixtures in a nitrogen matrix compared with its yield without added CO_2 is reported [5].

COF_2. At 25°C OF_2 reacts with COF_2 in the presence of alkali fluorides MF (M = K, Rb, Cs) as catalysts yielding CF_3OOOCF_3. The proposed mechanism [6]

(1) $COF_2 + MF \rightarrow M^+(OCF_3)^-$
(2) $OF_2 + CF_3O^- \rightarrow CF_3OOF + F^-$
(3) $CF_3OOF + CF_3O^- \rightarrow CF_3OOOCF_3 + F^-$
(4) $CF_3OOF + COF_2 \rightarrow CF_3OOOCF_3$

is confirmed [7].

COS. The thermal reaction between 323 and 363 K and the photochemical reaction with light of 366 nm at 273 K give the primary products SOF_2 and CO plus SOF_4, SO_2F_2, and COF_2 [8, 9]; for details, see "Kohlenstoff" D 5, 1977, p. 134.

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3.4.7.15 Reactions with SiO_2 and SiF_4

A mixture of OF_2 on silica gel (60/80 mesh) and liquid OF_2 at 254 Torr in 3- or 4-mm internal diameter tubes exploded spontaneously when the temperature exceeded 77 K. With a 5-mm tube there was no explosion [1, 2], see [3] for an explanation. Mixtures of liquid OF_2 with pyrogenic silica (Cab-O-Sil) in 10- to 12-mm tubes are shock sensitive but are chemically stable at −78°C. Explosions of silica gel and liquid OF_2 mixtures might be due to traces of water [4, 5].

No reaction occurs between SiF_4 and OF_2 below 150°C [6].

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3.4.7.16 Reactions with AsF_5, SbF_5, and PF_5

OF_2 reacts with AsF_5 (2:1 molar ratio) at 200°C and at 200 atm forming the dioxygenyl salt O_2AsF_6 in yields up to 80%. Similar results were obtained using SbF_5 as the Lewis acid. With PF_5 the reaction at $\leq$200°C yields small amounts of a white solid (no details) [1]. The photochemical reactions in the systems OF_2–AsF_5 and OF_2–O_2–AsF_5 (at 200 Torr) also yielded O_2AsF_6 [2]. Regarding O_2^+ salt formation, the intermediate $O_2F_3^+$ was assumed to form by F^- abstraction from OF_2 [3] according to

$$OF_2 \rightarrow F^- + OF^+ \text{ and } OF^+ + OF_2 \rightarrow O_2F_3^+$$

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3.4.7.17 Reactions with $(CN)_2$, NaSCN, and $M_4Fe(CN)_6$

OF_2 and $(CN)_2$ exploded violently when heated above 140°C but reacted very slowly at 135°C to form CF_4, CO_2, COF_2, $CF_3N{=}NCF_3$, and $CF_3NFNFCF_3$ [1]. No reaction was observed in the UV photolysis of an OF_2–$(CN)_2$ mixture at 25°C [2].

A stream of OF_2 reacts with NaSCN powder at room temperature to form parathiocyanogen $(SCN)_x$, NaF, SO_2, SOF_2, CO_2, and some HCN [1].

The reaction of OF_2 with an aqueous solution of $M_4Fe(CN)_6$ (M = Na, K), giving a deep-purple solution (see "Fluor" Erg.-Bd. 1, 1959, p. 232), presumably yields the compound $M_6Fe(CN)_5O_2(CN)_5Fe \cdot 6H_2O$ [3].

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3.4.7.18 Reactions with Hydrocarbons, Halogenated Hydrocarbons, and Adamantane

CH_4 mixes homogeneously at 90 K with OF_2 in a 1:1 molar ratio without reaction. However, the mixture explodes at slight provocation and at higher temperatures [1, 2]. No spontaneous reaction at room temperature is observed for mixtures with $CH_4:OF_2$ ratios from 1:4 to 1:10 and at pressures of 6 to 60 Torr. The exposure of the mixtures to sparks results in explosions, which occur as low as 6 Torr with 1:4 mixtures. Products are CF_3OF, CO_2, HF, SiF_4 (from the vessel), and small amounts of COF_2 [3]. The burning velocity of premixed OF_2–CH_4 flames (see p. 48) increases with the OF_2 content. The sharp increase between 27 and 30 vol% OF_2 is presumably due to the formation of H_2 (by decomposition of CH_4), which burns rapidly with OF_2 causing flashbacks [4, 5]. The velocity for flames burning in mixtures with 96 to 98 vol% OF_2 increases with decreasing OF_2 concentration [5].

A suspension of solid C_2H_4 in concentrated liquid OF_2 exploded violently slightly above 77 K. However, a 10 mol% solution of OF_2 in CF_4 reacted with a 10 mol% solution of C_2H_4 at 77 K without violence. The main product was CF_3OF [1]. Mixtures of OF_2 and C_2H_4 at a total pressure of 100 Torr exploded after standing for 10 min. Mixtures at 60 Torr reacted slowly without explosions to form C_2H_5F and FCH_2CH_2F [6].

The reaction of OF_2 with cyclopentene or 2-pentene is extremely hypergolic yielding only CO_2 and COF_2 [7].

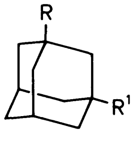
Oxidative fluorination of olefins, allenes, and acetylenes are reported [11, 12]. The reaction of OF_2 with olefinic fluorocarbons is used for the synthesis of fluoropolymers [13].

CHF_3 reacts with OF_2 in an equimolar mixture (20 to 100 Torr) at room temperature only on strong UV irradiation forming HF, CF_4, COF_2, CO_2 (and SiF_4 from the glass vessel) in a slow reaction. Initiation of the reaction by sparking a mixture at >25 Torr leads to explosions; below 25 Torr the explosion does not propagate. At 50 Torr CF_3OF is also obtained [3].

CF_4 or CF_3Cl mixes homogeneously with equimolar amounts of OF_2 at 90 K without reaction [1]. Slowly warming a 2:1:8 mixture of OF_2, C_2F_4, and N_2 from −183 to +20°C produces C_2F_6 and COF_2 [6, 7]. At −50°C the reaction proceeds smoothly, at higher temperature vigorously [7]. At 38°C the rapid reaction gives an equimolar mixture of CF_4 and COF_2 as well as traces of C_2F_6 [8]. At 250°C CF_4 and COF_2 are obtained [9, 10]. Perfluoropropene is completely unreactive toward OF_2 at room temperature in the absence of light. After 12 h of UV irradiation at 35°C both reactants were totally consumed producing C_3F_7 and $CF_3\overline{CFCF_2O}$ as main products, plus CF_4, CF_3COF, COF_2, and C_2F_6. With perfluorocyclobutene (after 6 h of irradiation) the main product is C_3F_7COF; CF_4, COF_2, and C_2F_5COF are also formed. With perfluoro-2-butene the reaction is completed after 8 h to give (in decreasing yield) CF_4, C_2F_5COF, CF_3COF, C_2F_6, COF_2, and C_4F_{10} [8].

In the presence of CsF as catalyst, OF_2 oxidizes CF_3COF in a slow reaction to give $C_2F_5OOOC_2F_5$ [14]. UV irradiation of a mixture consisting of OF_2 and $(CF_2Cl)_2CO$ gives $CFCl_2OF$ and CF_2ClOF [15].

Fluorinating adamantanes A(R = H, R^1 = H, OH, Br, COOH, CN) with OF_2 without a HF trap gave varying amounts of fluoroadamantanes (R = F) and adamantanols (R = OH). Increased yields of A (R = F) were obtained with a Na_2CO_3 trap for HF; oxahomoadamantanes B (R^1 = OH, CN) also form [16].



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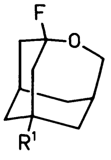

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3.4.8 The OF_2–F_2 System

The OF_2–F_2 system exhibits typical eutectic formation with a probable break in the fluorine-rich liquidus curve due to a solid-phase transition at 45 ± 0.5 K at about 82 mol% F_2. The eutectic point was determined to be at 59 ± 2 mol% fluorine; the eutectic temperature is 43 ± 0.5 K.

Reference:

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3.5 The OF_2^+ Ion

CAS Registry Number: *[39432-25-2]*

The enthalpy of formation $\Delta H^\circ_{f,298} = 307$ kcal/mol was derived from $\Delta H^\circ_{f,298}(OF_2) = -5.2$ kcal/mol and the OF_2 ionization potential $E_i = 13.54$ eV [1]. Using $\Delta H^\circ_{f,298}(OF_2) = +5.86$ kcal/mol (see p. 7) and the more recent $E_i = 13.11$ eV (see p. 13), one obtains $\Delta H^\circ_{f,298} = 308.4$ kcal/mol. Other formation enthalpies [1, 2] were based upon the even larger $E_i = 13.7$ eV and the negative OF_2 formation enthalpy.

The electronic configuration of the ground state $^2B_1$ is...$1a_2^2\,4b_2^2\,6a_1^2\,2b_1$ on the basis of the MO description of OF_2 (see p. 10). The total energy $E_T = -273.37440$ a.u. from an ab initio calculation with configuration interaction corresponds to a difference of 13.43 eV between the OF_2 and OF_2^+ ground states [3]. E_T was also calculated by an ab initio SCF-MO method with a minimal basis of Slater-type orbitals [10]. Electronically excited states for which energies were calculated follow: $^2A_1(6a_1^{-1})$, $^2A_1(5a_1^{-1})$, $^2B_2(4b_2^{-1})$, $^2B_2(3b_2^{-1})$, $^2A_2(1a_2^{-1})$, $^2B_1(1b_1^{-1})$; the superscript -1 denotes an electron removed from the respective orbital of OF_2 [3]. For further discussion, see p. 14.

The internuclear distance $r = 1.151$ Å and the bond angle $\alpha = 110.4°$ were semiempirically calculated using the CNDO/2 approximation [4].

The symmetric stretching frequency $\nu_1 = 1010$ cm^{-1} [5] or 1032 ± 40 cm^{-1} [6] is taken from the observed vibrational structure in the OF_2 photoelectron spectrum (see p. 13).

The bond dissociation energy $D(FO^+{-}F) = 2.1 \pm 0.4$ eV was derived from the appearance potential 15.8 eV of OF^+ (from OF_2) and from $E_i(OF_2) = 13.7$ eV [7]. $D(FO^+{-}F) \approx 0.3$ eV was interpolated from isoelectronic species [8], previously 0.7 eV [9].

The hydrogen affinity A_H (ΔH for $OF_2^+ + H \rightarrow HOF_2^+$) was derived as 96.4 kcal/mol from $A_H = A_p + E_i(OF_2) - E_i(H)$, where A_p is the proton affinity of OF_2, see p. 16, and E_i are ionization energies; $E_i(OF_2) = 13.13$ eV was used [11].

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3.6 The F_2OOF^+ and OOF_3^+ Ions

CAS Registry Numbers: F_2OOF^+ *[62611-02-3]*, OOF_3^+ *[64710-08-3]*

The formation of $O_2F_3^+$ has been suggested to explain the reaction of OF_2 with Lewis acids (SbF_5, AsF_5) giving dioxygenyl salts. The reaction was observed [1], and it has been proposed [2] that the ion is formed initially by the abstraction of F^- from OF_2 and by the simultaneous attack of a second OF_2 molecule. On the basis of O–F bond polarization [3], the ion has the structure $(F_2O\text{–}OF)^+$ with a relatively weak O–O bond [2].

For OOF_3^+, the formation enthalpy $\Delta H_f^\circ = 374 \pm 10$ kcal/mol has been estimated from core electron binding energies and the formation enthalpy of isoelectronic F_3NO [4].

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3.7 The OF Radical

CAS Registry Numbers: OF *[12061-70-0], [77318-95-7]*, ^{18}OF *[38536-87-7]*

3.7.1 Formation and Detection

Matrix-Isolated Radicals

The radical was first detected [1] by its IR absorption during the UV photolysis (high pressure Hg arc) of OF_2 isolated in an N_2 or an Ar matrix at 4 K. Recombination of OF and F limited the production of OF in matrices containing only OF_2 [1]. Recombination may be suppressed, however, by additives such as N_2O or CO_2 which react with atomic fluorine forming OF [1, 3]: $F + N_2O \rightarrow OF + N_2$, or $CO_2 + O \rightarrow CO_3$ (O coming from the photolysis of OF), followed by $CO_3 + F \rightarrow OF + CO_2$. Also, the photolytic equilibrium $CO_3 \rightleftharpoons CO_2 + O$ may increase the range of migration of O atoms in the matrix and thereby the probability of an $O + F \rightarrow OF$ reaction [3]. The light from an Ar^+ laser with wavelengths of 488.0 and 457.9 nm was also photolytically active for OF_2 in an Ar matrix at 16 K [2]. UV irradiation (Hg lamp) of liquid OF_2 at −196°C or OF_2 in a $CFCl_3$ matrix at −180°C produced a species which gave detectable ESR signals, but its identification as OF was uncertain [19].

Formation of OF was also observed [3], when F_2–N_2O mixtures were photolyzed in an N_2 or an Ar matrix at 4 K. The OF radical had not been detected previously under these conditions (Ar matrix) [4]. This was attributed to the reactions $OF + F \rightarrow OF_2$ and $OF + F_2 \rightarrow OF_2 + F$, favored by a large excess of fluorine. The IR detection of OF [4] may also have been prevented by the presence of SiF_4 which shows strong absorption in the region of the OF fundamental band [3].

OF radicals were also produced and were detected by IR spectroscopy, when OF_2 diluted in Ar was co-deposited with a beam of alkali metal atoms (Li, Na, K) or Mg atoms on a CsI window at 15 K [5].

The production of the radical through direct combination of O and F atoms was observed during Hg-arc photolysis of N_2 matrices containing F_2 and NO_2 molecules at 8 K. The OF radical was detected by its IR absorption band [6], see also [7].

Free Radicals

The radical was first detected mass spectrometrically as the product of O abstraction by atomic F from O_3 [8 to 10], see also [11, 12]:

$$(1) \quad O_3 + F \rightarrow OF + O_2$$

Reaction (1) and mass spectrometric radical detection were later also used [13, 14] for kinetic studies of OF reactions. Radicals produced by reaction (1) were also detected by photoelectron spectroscopy [15]. Reaction (1) was assumed to occur in the photochemical reaction of F_2 with O_3 at 273 and 293 K, giving O_2 and F_2 [16]. The subsequent formation of O_2F_2 after reaction (1), studied at 120 K, is taken as an affirmation of radical production [17]. The rate constant $k_1 = (8 \pm 2) \times 10^{12}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 298 K was measured mass spectrometrically in a flow system [12] and was practically independent of temperature between 253 and 365 K: $k_1 = 1.7 \times 10^{13} \cdot \exp(-450 \pm 400\ cal \cdot mol^{-1}/RT) cm^3 \cdot mol^{-1} \cdot s^{-1}$ in the above range [12]. The k_1 values seem to be reasonable in view of the reactivity of atomic Cl with O_3 [18]. A preliminary value for k_1 of $\sim 5 \times 10^{12}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 298 K was reported [8, 9]. An activation energy $E_1 \approx 3$ kcal/mol had previously been estimated from studies of reactions occurring in the $F_2 + O_3$ photochemical system [16].

The abstraction of H from HOF by atomic F in a discharge-flow apparatus at 296 to 298 K was measured mass spectrometrically by determining F concentrations. In about 1 Torr of He carrier gas with an initial F atom concentration of $\sim 1.5 \times 10^{12}\ cm^{-3}$, the reaction

$$(2) \quad HOF + F \rightarrow OF + HF$$

was at least 50% complete in 2 ms. Thus, a lower limit for the rate constant was established as $k_2 \geq 2 \times 10^{-10}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 298 K [21] ($1.2 \times 10^{14}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [20]). See also the review [22] on elementary reaction kinetics of F atoms, OF, and NF free radicals.

The first spectroscopic observation of the radical in the gas phase employed the CO_2 laser magnetic resonance (LMR) technique. The Zeeman splitting of rotational transitions within the fundamental vibration band was tuned to selected lines of a CO_2 laser containing a microwave discharge in CF_4 at about 0.2 Torr flowing through a fused quartz tube. The radical was probably formed by O atoms from an erosion of the walls of the discharge tube. Addition of about 20 mTorr O_2 increased the OF signal by about 50%. The radical was also formed from pure SF_6 or from an F_2–He (1:9) mixture [23], see also the review [24] on mid-IR LMR spectroscopy. Later LMR studies employed a diode laser and a mixture of 200 mTorr CF_4 and 30 mTorr O_2 or CF_4 in an SiO_2 or Al_2O_3 tube [28].

The radical is assumed to be formed by the reaction of F_2 with O:

$$(3) \quad F_2 + O \rightarrow OF + F$$

A rate constant $k_3 = 10^{12.99 \pm 0.68} \cdot \exp(-10.36 \pm 1.51\ kcal \cdot mol^{-1}/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ was calculated from the O atom concentration determined in a flow system by ESR between 461 and 523 K. The OF radical was not detected by ESR. Thus, for the OF consuming reaction $OF + O \rightarrow O_2 + F$, a rate constant $\gg k_3$ was assumed [25]. See also the report [26] on the dynamics of O atom reactions. Reaction (3) was also studied in a static reactor at room temperature, and heterogeneous contributions (from the surface of the reaction vessel) to the rate were found [29]. The failure to detect the OF radical by rotational ESR [27] may be caused by too small a value of its dipole moment [23]. From the $F_2 + O_3$ photochemical system, studied at 0 and 20°C, it was concluded that reaction (3) was slower than $O_3 + O \rightarrow 2O_2$ by four orders of magnitude [16].

The radical is further supposed to be produced by F elimination or abstraction from gaseous OF_2 and to be an important intermediate in the reaction chemistry of this compound (see pp. 42/62).

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3.7.2 Enthalpy of Formation ΔH°_f (in kcal/mol unless stated otherwise)

$\Delta H^\circ_{f,0} = 26.1 \pm 2.3$ was derived [1] from the dissociation energy $D^\circ_0(OF) = 51.4$ kcal/mol [2]. The error limits obviously correspond to an error of ±0.1 eV [2] in the measured appearance potentials. This enthalpy of formation was cited by Baulch et al. [3, 4]. $\Delta H^\circ_{f,300} = 26 \pm 1$ was given in a data compilation by Benson [5]. An older estimate $D_0(OF) = 51.4 \pm 10$ kcal/mol led to $\Delta H^\circ_f = 26 \pm 10$ [6]. The OF enthalpy of formation was also discussed in [7]: $\Delta H^\circ_f = 106$ kJ/mol was derived from a lower limit $D(OF) \geq 2.2$ eV from ab initio calculations [8].

The smaller value $\Delta H^\circ_{f;298} = 22(\pm 10)$ corresponds to an older estimate $D^\circ_{298}(OF) = 56 \pm 10$ kcal/mol [9]. Higher values are: $\Delta H^\circ_{f,0} \approx 30.2 \pm 4.1$, derived [10] from D(FO–F), which was determined from the kinetics of thermal decomposition of OF_2, and from $\Delta H^\circ_f(OF_2)$ [11]; and

$\Delta H^\circ_{f,0} = 33.487 \pm 10$ (sic), based upon $D_0(OF) = 44.000 \pm 10$ kcal/mol [12]. $\Delta H^\circ_f = 39 \pm 3$ [13] and 41 [14, 15] seem to be out of date.

Formation enthalpies were also calculated by semiempirical MO procedures [16, 17].

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3.7.3 Molecular Properties

3.7.3.1 Electronic Structure

The configuration of the 17 electrons in the inverted $^2\Pi_i$ ground state of the radical is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^3$ [1, 4] or $KK(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4(v\pi)^3$ in the Mulliken [3] notation. The lower component $^2\Pi_{3/2}$ of the ground state was observed [2]: Several rotational-vibrational transitions were detected in the fundamental IR absorption band by tuning the Zeeman splitting of rotational transitions in the fundamental band to selected lines of a CO_2 laser (laser magnetic resonance, LMR) and had the appearance of Q branch transitions of a diatomic molecule in a $^2\Pi_{3/2}$ state. Furthermore, the fine structure constant A proved to be negative, see below, [2]. The ground term $^2\Pi_i$ is expected for OF [4] by analogy with the other halogen monoxides [5]. A $^2\Pi$ ground state resulting from three (antibonding) π electrons was calculated [6]. The configuration... $\sigma^2\pi^4\pi^{*3}$(π^* = antibonding π-MO) follows from a simple MO description of the first row diatomics and predicts a bond order of $3/2$ (the 2s electrons are considered to be nonbonding) [7], see also [8].

The total energy $E_T = -174.19502$ a.u. was calculated [4], $E_T = -173.91011$ and -171.80257 a.u. come from ab initio SCF–MO calculations with a double zeta and a minimal basis set, respectively [6]. Hückel MO calculations yielded a simple empirical relation between overlap populations and the atomization energy [11].

The Linnett [12, 13] treatment of the Lewis-Langmuir octet as a double quartet of electrons leads to an OF structure with three bonding electrons, see also [14] and the preliminary considerations in [15, 16].

A radical structure with a single bond plus a (weaker) three-electron bond in the Pauling sense [17] was suggested [18]. The three-electron bond in OF has also been discussed [19].

The dipole moment μ (in D) was measured directly for the $^2\Pi_{3/2}$ ground state from the saturated absorption signals of the LMR spectrum (see above) in the presence of an electric field: $\mu = (\pm)0.0043 \pm 0.0004$ for $v = 0$, $\mu = (\pm)0.0267 \pm 0.0009$ for $v = 1$, with the same sign in both vibrational states [29, 30]. Similarly low values were theoretically calculated (up to $v = 6$): $\mu = -0.0089$ ($v = 0$), -0.0318 ($v = 1$). The negative sign implies the polarity O^+F^-. The effect of rotation was rather small. A theoretical dipole moment function adjusted so as to exactly reproduce the experimental dipole moments for $v = 0$ and $v = 1$ yielded the polarity O^-F^+ for the equilibrium internuclear distance [31]. $\mu = -0.361$ was calculated by an ab initio SCF–MO method [4], $\mu = (\pm)0.29$ [9] by the semiempirical SINDO method [10].

The quadrupole moment $Q = 0.134 \times 10^{-26}$ esu · cm^2 was calculated by an ab initio SCF–MO method [4].

The atomic charges (in units of e) −0.06 at F and +0.05 at O were calculated [20] using SCF wave functions [4] and a procedure developed in [21]. Formal charges of +0.5 at F and −0.5 at O are involved in the Linnett structure. Due to this unusual charge distribution, OF was believed nonexistent [12, 13], see also [22] and the discussion in [8].

The fine structure constant A was determined indirectly from the perturbations by the $^2\Pi_{1/2}$ state of the observed Zeeman shifts in the $^2\Pi_{3/2}$ state, $A = -177.3 \pm 5.6$ cm^{-1} [2]. A splitting of 160 ± 30 cm^{-1} was derived from an asymmetry of the vibrational components of three photoelectron bands [1]. $A = (\pm)188$ cm^{-1} was calculated from the atomic spin-orbit coupling constants and from the ^{19}F hyperfine coupling constant [2]. The method used was described in [23]. A splitting of 404 cm^{-1} was roughly estimated from that of atomic F in its ground state [24].

The axial component of the ^{19}F hyperfine coupling constant in the vibrational ground state was derived from LMR measurements (see above), $h_0 = a + \frac{1}{2}(b + c) = 0.02322 \pm 0.00059$ cm^{-1} [2].

The first excited state, $A^2\Pi$, is expected to result from the electron configuration $\ldots 1\pi^3 2\pi^4$ [5]. By analogy with the states of the isoelectronic O_2^- ion, an energy of 29000 cm^{-1} was estimated for $A^2\Pi$ [25]. No banded absorption attributable to the transition $A \leftarrow X$ was observed in flash-photolyzed O_3–F_2 mixtures [26] or in a flow system with continuum sources between 150 and 300 nm [27]. Presumably then, the band system A–X is diffuse due to predissociation [2], see also [27, 28].

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3.7.3.2 Ionization Potentials E_i, Electron Affinity A, Proton Affinity A_p, in eV

Ionization Potentials

The first adiabatic ionization potential $E_i = 12.77 \pm 0.01$ was observed in a He I photoelectron (PE) spectrum [1]. An appearance potential 12.82 ± 0.09 was measured for OF^+ from the mass spectrum of OF_2 at 770 K [25]. A similar value $12.7_9 \pm 0.1_0$ had been indirectly obtained as the difference between the independently determined formation enthalpies of the OF^+ ion, 13.92 eV (see p. 78), and the OF radical, 1.13 eV (see p. 66) [2]. The electron configuration $\ldots 2\pi^2$ of the cation gives rise to three states, $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$ with statistical weights of 3, 2, and 1, respectively. Three bands in the PE spectrum of OF have relative intensities very nearly corresponding to these statistical weights, the strongest band being at lowest energy on a binding energy scale. Consequently, the first ionization potential of OF is assigned to the $^3\Sigma^-$ $(2\pi^2)$ cationic state, in agreement with SCF open-shell calculations [1].

The vertical value from the PE spectrum is $E_i = 13.08 \pm 0.01$ [1]. $E_i = 13.1 \pm 0.3$ was derived [3] from the mass spectrometric investigations of O_2F_2 [4]: The appearance potential of OF^+, AP = 17.5 eV, was ascribed, contrary to [4], to the process $O_2F_2 \rightarrow OF^+ + O + F + e^-$ [3]. A similar value $E_i = 13.0$ had previously been derived [5], see also [6]. However, the measured OF^+ appearance potential from OF_2 (15.8 eV) was combined with too high a value (2.8 eV) of D(FO–F), see also the discussion in [3].

$E_i = 12.7 \pm 0.4$ was deduced by assuming the first ionization potential of OF to be equal to the difference between the energy of the $^3\Pi(2p\pi^3)$ state of K shell excited O_2 and the average energy of the states $^4\Sigma^-(2p\pi^2)$ and $^2\Sigma^-(2p\pi^2)$ of K shell excited O_2^+ ("equivalent cores model"). The energy of the K shell excited state of O_2 was measured by electron loss spectra and those of O_2^+ were taken from the literature [7]. A method of isoelectronic similarity had previously been used to estimate E_i values of 12.5 [8] and 12.2 [9].

Vertical ΔSCF values with respect to the $^3\Sigma^-(2\pi^2)$ state of OF^+ were calculated by two ab initio methods, $E_i = 12.46$ [1] and 13.1 ± 0.5 [3], or semiempirically by the MNDO method, $E_i = 14.11$ [10]. $E_i = 13.73$ [12] follows from the SINDO method [11].

For higher ionization potentials, two vertical values, 14.48 and 15.16 eV, were observed in the PE spectrum and ascribed to the ionic states $\ldots 2\pi^2\ ^1\Delta$ and $\ldots 2\pi^2\ ^1\Sigma^+$, respectively [1]. For ionic states due to the ionization from a 1π or a 5σ orbital, the following vertical values were obtained by the ΔSCF procedure [1]:

electron configuration of cation	$5\sigma^2\ 1\pi^3\ 2\pi^3$						$5\sigma\ 1\pi^4\ 2\pi^3$	
cationic state	$^1\Sigma^-$	$^3\Sigma^-$	$^3\Delta$	$^3\Sigma^+$	$^1\Delta$	$^1\Sigma^+$	$^3\Pi$	$^1\Pi$
E_i in eV	15.50	15.56	15.59	15.67	15.68	15.79	17.68	18.82

Electron Affinity

OF^- ions were observed mass spectrometrically as products of electron bombardment of CF_3OF [13], ClO_3F [24], and OF_2 [25]. From the energetics of the process $OF_2 + e^- \rightarrow OF^- + F$ (appearance potential and kinetic energy of OF^- fragments, dissociation energy D(F–OF), and an estimated excess energy), $A = 2.05 \pm 0.08$ for OF was obtained [25]. Weaker estimates are $A \geq 2.15 \pm 0.12$ from the occurrence of OF^- in the process $ClO_3F + e^- \rightarrow OF^- + ClO_2$ [24, 25] and $A \geq 1.4 \pm 0.5$ from the mere existence of the OF^- ion apparently showing it to be stable against dissociation into F^- and O [13]. $A = 1.3$ was obtained by a combination of the F_2 ionization potential with energy differences between (isoelectronic) OF and F_2^+ and between OF^- and F_2. These energy differences were derived from electrostatic potentials at the nuclei, computed from near Hartree-Fock wave functions [26]. The vertical ΔSCF value $A = 1.4 \pm 0.5$ was calculated by an ab initio method, and the adiabatic value $A \approx 1.2$ was estimated therefrom [3], see also [15]. $A = 1.63$ (vertical, eigenvalue of the highest occupied MO of OF^-) and $A = 1.48$ (adiabatic, ΔSCF value) were calculated by the MNDO method [16].

The ionization potential $E_i = 18.91 \pm 0.5$ and the electron affinity $A = 8.18 \pm 1.0$ were calculated by a transition operator method (see [17]) and combined to give the (Mulliken) orbital electronegativity $\chi_M = 13.55$. The corresponding Pauling value is $\chi_P = 4.32 = 0.334 \cdot (\chi_M - 0.615)$ [18]. The method of Hinze et al. [19] was modified and used to calculate the group electronegativity $\chi_M = 12.95$ [20]. $\chi = 3.70$ was derived by the method of Clifford [21] as an average of atomic values. For preliminary data, see [22].

Proton Affinity

$A_p = 5.8_2$ (134.2 kcal/mol) was deduced [23] from $\Delta H^\circ_{f,0}$ (HOF^+) = 270.3 kcal/mol, see p. 158, and $\Delta H^\circ_{f,0}$ (OF) = 26.1 kcal/mol, see p. 66. (The value of $\Delta H^\circ_f(H^+)$ implied by these figures differs by ~10 kcal/mol from that adopted in the JANAF Tables [27].)

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3.7.3.3 **Rotational Constants** in cm^{-1}. **Internuclear Distance** r in Å

Constants of the ground state and the v = 1 vibrational state were measured using a tunable IR diode laser in the range of the fundamental vibration band and the Zeeman modulation of the absorption lines. The true values depend on the unobserved $^2\Pi_{1/2}$ state. From line positions, only effective B_v values, defined as $B_v^{eff}(^2\Pi_{3/2}) = B_v(1+B_v/A)$ (A = fine structure constant, see p. 68) can be deduced [1, 4], from which the following constants were derived [4] taking $A = -177.3\ cm^{-1}$ [1]:

B_0	D_0	B_1	D_1
1.052850 ± 0.000092	$(4.42 \pm 0.41) \times 10^{-6}$	1.039328 ± 0.000079	$(4.39 \pm 0.31) \times 10^{-6}$

$B_0=1.05282\pm0.00019$, $B_1-B_0=-0.013475\pm0.000035$, and $D_0=D_1=(39\pm33)\times10^{-7}\approx0.12$ ±0.10 MHz were previously measured by CO_2 laser magnetic resonance in the same spectral region. $B_e=1.05955\pm0.00019$ was obtained by setting the rotation-vibration constant α_e equal to B_0-B_1. $D_e\approx4B_e^3/\omega_e^2\approx4B_0^3/\nu_0^2=0.13$ MHz [1]. $\alpha_e=0.0097$ was calculated by an ab initio SCF-MO method [2]. $\alpha_e=0.020$ had been estimated for the calculation of thermodynamic functions [3].

The equilibrium distance $r_e=1.35789\pm0.00025$ follows from the experimental B_e value [1]. $r=1.35$ was estimated [5] from a comparison of r(M-F) for first row elements M; $r=1.36\pm0.03$ comes from a plot of force constants versus r(M-F) [6]. For thermodynamic calculations, r_e was set equal to 1.30 Å, the bond length of the isoelectronic O_2^- ion [3]. Ab initio SCF-MO methods yield values of $r_e=1.321$ [2] and 1.337 [7], whereas semiempirical methods give $r_e=1.310$ (SINDO1, see [8]), [9] and 1.223 (MINDO) [10].

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3.7.3.4 Molecular Vibrations. Force Constants

The band origin of the fundamental vibration was measured as $\nu_0=1033.4829$ ±0.0005 cm^{-1} using a tunable diode laser with Zeeman modulation of the absorption lines [1]. A previous measurement by CO_2 laser magnetic resonance gave $\nu_0=1033.4812\pm0.0002$ cm^{-1} or $\nu_0=1033.4947\pm0.0002$ cm^{-1}, depending on the choice of the matrix representation of the Hamiltonian for a molecule in a multiplet electronic state, which is to some extent arbitrary. The band origin in the gas phase is about 4.7 cm^{-1} larger than that obtained for a solid Ar matrix (see below), and such a matrix shift is considered to be quite reasonable [2]. Fourteen ro-vibrational transitions in the fundamental band, ranging from $P(\frac{23}{2})=1007.8441$ to $R(\frac{29}{2})=1062.4751$ cm^{-1}, were observed by IR diode laser spectroscopy [1].

The following table lists wavenumbers ν of the fundamental vibrations of isotopic molecules isolated in Ar matrices at different temperatures T. The radicals were produced by F abstraction from OF_2, and IR or Raman spectra were observed:

T in K	4		15		16	
F abstraction by	photolysis		$OF_2+M\rightarrow OF+MF$		laser photodetachment	
spectrum	IR		IR		Raman	
molecule	^{16}OF	^{18}OF	^{16}OF	^{18}OF	^{16}OF	^{18}OF
ν in cm^{-1}	1028.5	997.4	1028.6±0.3	997.7±0.3	1028.9±0.5	998.4±0.5
Ref.	[3]		[4]		[5]	
remark	a)		b)		c)	

a) Values for an N_2 matrix with probably two different sites: 1025.5 and 1030.5 cm^{-1} for ^{16}OF, 994.5 and 999.5 cm^{-1} for ^{18}OF [3], see also [6]. – b) M = Li, Na, K, Mg. – c) Depolarization ratio $\varrho = 0.47$ [5].

The constant $\omega_e = 1044\ cm^{-1}$ was estimated [7] from the approximate relation for the rotational distortion constant $D \approx 4B_e^3/\omega_e^2 \approx 4B_0^3/\nu_0^2$ with B_e, B_0, and ν_0 taken from [2]. $\omega_e = 1056\ cm^{-1}$ was obtained from the lower of the two ν values reported [3] for an N_2 matrix, and from $\omega_e x_e = 15\ cm^{-1}$ as derived from a Morse potential function with an assumed dissociation energy of 2.23 eV [8]. $\omega_e = 1211\ cm^{-1}$ and $\omega_e x_e = 5.15\ cm^{-1}$ were calculated by an ab initio SCF–MO method [9].

Vibrational energies and lifetimes for the levels v = 0 through v = 6 were derived from a potential for the $^2\Pi$ state calculated by ab initio SCF–MO methods. The calculated fundamental frequency is 1023.55 cm^{-1} [10].

The force constant f = 5.416 mdyn/Å is reported for the radical isolated in an Ar maxtrix [4]. $f_e = 7.5$ mdyn/Å follows from the calculated ω_e value [9].

An analytical expression for the potential function ("extended-Rydberg function" [11]) was based upon available data for r_e, ω_e, $\omega_e x_e$, and D_e [12].

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3.7.3.5 **Dissociation Energy** D (in kcal/mol unless stated otherwise)

$D_0^\circ = 51.4 \pm 4.1$ (215 ± 17 kJ/mol, 2.23 eV) was obtained from the appearance potentials of OF^+ from OF and OF_2. The measured difference of $1.6_5 \pm 0.1_5$ eV corresponds to D_0°(FO–F) and was combined with the OF_2 atomization enthalpy $\Delta H^\circ_{at,0}(OF_2) = 374 \pm 2$ kJ/mol (see p. 35) [1]. This D_0° and $\omega_e = 1044\ cm^{-1}$ imply $D_e = 2.31 \pm 0.15$ eV [3]. $D_0^\circ = 51 \pm 2$ was estimated from the bond dissociation energy D(FO–OF) = 46 ± 4 kcal/mol. This latter value was predicted from a comparison of the central bond energies of FNNF, HNNH, and HOOH. $D_0^\circ = 51.4 \pm 10$ was then adopted as an average of this and other estimates [2].

D was also derived from the atomization and bond dissociation energy of OF_2 taken from various kinetic studies of its thermal decomposition, see p. 35. D so obtained is between 48 and 62 kcal/mol [5 to 11].

$D^\circ_0 = 58.1 \pm 4.2$ (2.52 ± 0.18 eV) was obtained from a study of the OH production in the reaction of OF_2 with H: OF from $OF_2 + H \rightarrow OF + HF$ was assumed to be in the vibrational ground state and the observation of OH from $OF + H \rightarrow OH + F$ in vibrational states up to $v = 4$ then led to $2.34\ \text{eV} < D^\circ_0 < 2.70\ \text{eV}$ [12].

Since the fundamental frequency of OF is higher than the O–F stretching frequency of OF_2, D may be higher than the average bond energy in OF_2 [14] and close to the estimated value $D \approx 56$ (2.45 eV) [13]. $D = 55 \pm 5$ was derived from a plot of force constants versus bond dissociation energies for species such as NO, O_2, ClF, and F_2 [15].

$D = 52$ (2.25 eV) was estimated by a method of isoelectronic similarity [16], see also [17].

Values favored in several review articles are $D^\circ_0 = 55 \pm 10$ [18], $D^\circ_0 = 55 \pm 9$ (2.4 ± 0.4 eV) [19, 20], and $D^\circ_{298} = 56 \pm 10$ [18].

A lower limit $D \geq 40$ may be derived from the energy requirements of the reaction $N_2O + F \rightarrow OF + N_2$ which was supposed to occur during the low-temperature photolysis of fluorine trapped with N_2O in an Ar matrix [21], see also [22, 23]. The formation of OF in this reaction was proved [24].

Thus, these combined findings rule out the low value $D = 25$ (1.1 eV), which had been based on the bond dissociation energy $D(FO{-}F) = 2.8$ eV [25] (see p. 34).

$D = 69$ ($3.0^{+0.3}_{-0.8}$ eV) was calculated by an ab initio SCF–MO method [6]. A relation between D and the Mulliken overlap populations was considered [26]. D(OF) and D(OCl) were compared on the basis of the electronic structure of the radicals [4]. D_e was also calculated by a semiempirical SCF–MO method (SINDO1) [27].

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3.7.4 Thermodynamic Functions

The values in the following table for the molar heat capacity C_p°, entropy S°, Gibbs free energy function $(G^\circ - H^\circ_{298})/T$, in cal·mol^{-1}K^{-1}, and for the enthalpy $H^\circ - H^\circ_{298}$ in kcal/mol are taken from the JANAF Tables [1], where they were calculated in intervals of 100 K up to T = 6000 K for the ideal gas at 1 atm on the basis of estimated rotational and vibrational constants (see pp. 71/3) and of a $^2\Pi$ electronic ground state:

T	0	100	298	500	1000	2000	4000	6000
C_p°	0	6.958	7.319	8.007	8.750	9.144	9.512	9.904
S°	0	44.076	51.765	55.720	61.554	67.767	74.224	78.152
$-(G^\circ - H^\circ_{298})/T$.	∞	58.080	51.765	52.619	55.774	60.384	65.865	69.345
$H^\circ - H^\circ_{298}$	−2.095	−1.400	0	1.550	5.780	14.765	33.439	52.837

Older data are given for $-(G^\circ - H^\circ_{298})/T$ between 298 and 3000 K in 100 K intervals and for $H^\circ - H^\circ_0$ at 298 and 2000 K [2], for C_p° at five temperatures (300 to 1500 K) and for S°_{298} [3], and for S° and $H^\circ - H^\circ_0$ between 293.15 and 6000 K in 100 K intervals [4].

A polynomial expression for the partition function was given for the range 1000 to 9000 K [5].

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3.7.5 Chemical Behavior

There are only a few observations of specific reactions of the OF radical and even fewer direct measurements of rate constants. This lack of data is partly due to the difficulties associated with radical detection. Several radical reactions were assumed in reaction mechanisms, particularly in those involving OF_2 chemistry. Based on these mechanisms some rate constants were indirectly determined. Mass spectrometric detection enabled direct determination of some rate constants. The rapid exothermic reaction of OF with NO to give NO_2 and F (reaction enthalpy $\Delta H^\circ_{298} = -239$ kJ/mol [26]) was used to obtain absolute radical concentrations [1 to 3].

The dissociation reaction

$$(1)\quad OF \xrightarrow{M} O + F$$

was assumed to occur in the OF_2 thermal decomposition in shock waves at 770 to 1390 K with M = Ar [4] and in a stirred-flow reactor at 330 to 431°C with M = He [5]. The rate constant $k_1(Ar) = 10^{13.0} \cdot \exp(-37.3\ kcal \cdot mol^{-1}/RT) cm^3 \cdot mol^{-1} \cdot s^{-1}$ was given [4].

The equilibrium constant for the thermal dissociation equilibrium $OF \rightleftharpoons O + F$ was given by a polynomial expression between 1000 and 9000 K [25].

The bimolecular decomposition reaction

$$(2a)\quad 2OF \rightarrow O_2 + 2F$$

was assumed to occur during the reaction of O_3 with atomic F between 253 and 365 K [6], in the OF_2 thermal decomposition in shock waves (see above) [4] and in static reactors between 503 and 583 K [7, 8], in the OF_2 photolysis at temperatures up to 272°C [9], and in the thermal reaction of OF_2 with CO in shock waves between 800 and 1400 K [10]. Possibly, reaction (2a) takes place by way of the intermediate step

$$(2b)\quad 2OF \rightarrow O_2F + F$$

followed by $O_2F \rightarrow O_2 + F$ [4, 6]. For (2b) as a separate reaction channel, see also the reviews [11, 26, 27] on kinetic data for atmospheric chemistry.

The reaction

$$(2c)\quad 2OF \rightarrow O_2 + F_2$$

was assumed to occur in the photochemical reactions of OF_2 with SO_3 [12] and of F_2 with CO_2 [13] and in the OF_2 photolysis [14]. This channel is also listed in [11, 26, 27].

The reaction

$$(2d)\quad 2OF \rightarrow O_2F_2$$

was suggested [15] since the formation of O_2F_2 was observed during the photochemical reaction between F_2 and O_3 at 120 K. The reaction

$$(2e)\quad 2OF \rightarrow OF_2 + O$$

and its reverse (−2e) were supposed to be involved in the OF_2 decomposition in shock waves (see above) [4].

For the bimolecular decomposition, $k_2 = (8.5 \pm 2.5) \times 10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 298 K was directly measured by mass spectrometric detection of OF on the basis of the NO titration method [1], see also [2, 11]. The concentration profiles of F, OF, O_2, and O_3, which were observed in the reaction of O_3 with atomic F, were used to calculate $k_{2a} \approx 2 \times 10^{13}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 298 K [6] ($3.3 \times 10^{-11}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [11]). The limits $2 \times 10^{-12} < k_2 < 2 \times 10^{-11}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 298 K had been estimated earlier [16]. A constant k_2 was also derived from the OF_2 decomposition in shock waves on the basis of an assumed mechanism [4, 10]. For critical remarks, see [17].

The termolecular decomposition reaction

$$2OF \xrightarrow{M} O_2 + 2F$$

was assumed to be part of the chain mechanism of the OF_2 thermal decomposition in incident shock waves between 860 and 1300 K and from 17 to 20 atm [18, 19].

Reactions with the atomic species H, N, O, and F and with H_2, O_3, and F_2 are mentioned in the chapters dealing with the chemical behavior of F_2, see "Fluorine" Suppl. Vol. 2, 1980, p. 140, and of OF_2, see pp. 47/9 of the present volume.

For the reaction

$$(3) \quad OF + NO \rightarrow NO_2 + F$$

$k_3 = (2.60 \pm 0.50) \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 298 K was measured mass spectrometrically in a discharge-flow system [3]. Estimated rate constants at 298 K are $k_3 > 5 \times 10^{-12}$ [2] and $k_3 = 2 \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [11]. The temperature dependence is expected to be small [11].

The rate constant for

$$(4) \quad OF + NO_2 \xrightarrow{M} FONO_2$$

is taken from the analogous ClO reaction [11]. The ClO data [11] have been changed meanwhile, and thus, the following constants are given [26, 27]: for the limit $[M] \rightarrow 0$ where $M = N_2$ or O_2, $k_{4,0} = 1.6 \times 10^{-31} \cdot (T/300)^{-3.4}$ $cm^6 \cdot molecule^{-2} \cdot s^{-1}$ from 200 to 400 K (error in $\log k_{4,0}$ at 298 K is ± 0.7); for the limit $[M] \rightarrow \infty$, $k_{4,\infty} = 2 \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ over the same temperature range (error in $\log k_{4,\infty}$ is ± 0.5). Reaction (4) was previously considered in a kinetic study of the thermal reaction between OF_2 and NO_2 [20].

Further reactions together with the pertaining systems are listed in the following table:

reaction	system	Ref.
$OF + NF_2 \rightarrow ONF_2 + F$	$OF_2 + N_2F_4$ thermal reaction	[21]
$OF + FSO_3 \rightarrow F_2SO_4$	$OF_2 + SO_3$ photochemical reaction	[12, 22]
	$OF_2 + F_2S_2O_6$ photochemical reaction	[23]
$OF + F_2SO \rightarrow F_2SO_2 + F$	$OF_2 + F_2SO$ photochemical reaction	[24]
$OF + CO \rightarrow CO_2 + F$*)	$OF_2 + CO$ thermal reaction (cf. p. 59)	[10]

*) $k = 7.5 \times 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$, independent of temperature, was derived from shock wave studies [10].

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3.8 The OF$^+$ Ion

CAS Registry Number: *[12763-67-6]*

The ion was formed by electron impact (EI) or photoionization (PI) methods applied to the OF radical or to compounds containing the OF group. The measured appearance potentials (AP) are listed in the following table and are briefly discussed in the remarks:

compound	OF	OF	OF_2	OF_2	O_2F_2	CF_3OF
method	PI	EI	PI	EI	EI	EI
AP of OF$^+$ in eV	12.77 ± 0.01	—	14.43_8	14.52 ± 0.06	17.5 ± 0.2	38 ± 1
Ref.	[1]	[2]	[3]	[5]	[6]	[7]
remark	a)	b)	c)	d)	e)	f)

a) Adiabatic value; for the vertical process, AP = 13.08 eV (see p. 69). – b) The appearance potential was smaller by 1.65 eV than that for OF$^+$ from OF_2. – c) The value is for 0 K and was derived from the measured value (upper limit) 14.38_9 eV at ca. 298 K. – d) According to [5], the AP value 15.8 ± 0.2 [4] (see also the tabulation [8]) is in error probably due to the low sensitivity of the detection system. Other data for D(FO–F) and E_i(OF) [9] lead to AP = 14.8, see [3]. – e) The appearance potential was measured at 130 K [6], see also [8], and was originally ascribed to the reaction $O_2F_2 \rightarrow OF^+ + OF + e^-$ [6]. The only thermodynamically plausible process is $O_2F_2 \rightarrow OF^+ + O + F + e^-$ [9]. – f) AP ≥ 34 eV for the process $CF_3OF \rightarrow OF^+ + C + 3F + e^-$ was estimated from thermochemical data. This process may thus be responsible for OF$^+$ formation at the observed AP, if an excitation of the C atom to its ^1D state is taken into account [7].

The formation enthalpy $\Delta H^\circ_{f,0} = 321.0$ kcal/mol (13.92 eV) was derived from the OF$^+$ appearance potential from OF_2, 14.43_8 eV (see above), together with the formation enthalpies of OF_2 and F [3]. This is not at variance with $\Delta H^\circ_{f,0} = 330$ kcal/mol which may be obtained from AP of OF$^+$ from O_2F_2 when this AP is referred to the process $O_2F_2 \rightarrow OF^+ + F + O + e^-$, see above, and using the well-established enthalpies of formation of atomic F and O, and $\Delta H_f(O_2F_2)$ as given on p. 85. $\Delta H_f^\circ(OF^+) = 367$ kcal/mol [8] is obviously based on the process $O_2F_2 \rightarrow OF^+ + OF + e^-$ [6]. $\Delta H_f^\circ(OF^+) = 340$ kcal/mol [8] is based on $AP(OF^+) = 15.8$ eV for OF^+ from OF_2, a value now known to be invalid. Moreover, some of the auxiliary thermochemical data used in [8] appear to be out-of-date.

The Hartree-Fock total energy $E_T = -173.74250$ a.u. and the orbital energies ε_i given below were calculated for the ion in its $^3\Sigma^-(2\pi^2)$ ground state by an ab initio SCF-MO method. The equilibrium internuclear distance calculated for OF (1.32 Å) was used [9]:

orbital	1σ	2σ	3σ	4σ	5σ	1π	2π
$-\varepsilon_i$ in a.u.	26.8503	21.3313	2.1750	1.7210	1.1990	1.1705	1.2213

E_T for the $^3\Sigma^-(2\pi^2)$ ground state was also calculated [10] with an extended Gaussian basis set [11] and with a smaller basis set [12]. For Linnett structures of the ion, see [13].

The dipole moment $\mu = -1.574$ D (from the geometric midpoint between the two nuclei; negative end at F) and the quadrupole moment $Q = 2.564 \times 10^{-26}$ esu·cm² (referred to the center of mass) were calculated [9]. The atomic charges +0.80 at O and +0.32 at F were determined [14] using the wave functions [9] and a procedure developed by Politzer and Harris [15].

The singlets belonging to the electronic ground state configuration are expected to be $^1\Delta$ and $^1\Sigma^+$. Excitation energies E may be derived from the OF photoelectron (PE) spectrum [1] or from ab initio SCF-MO calculations of total energies (ΔSCF) [10]. For $^1\Delta$, a value was also estimated by interpolating between the corresponding level energies of isoelectronic O_2 and NF [16]:

state	$^1\Delta$	$^1\Delta$	$^1\Delta$	$^1\Delta$	$^1\Sigma^+$	$^1\Sigma^+$
E in eV	1.39 ± 0.02	~1.3	2.26	3.94	2.24 ± 0.02	4.23
method	PE	isoelectronic comparison	ΔSCF	ΔSCF	PE	ΔSCF
Ref.	[1]	[16]	[1]	[10]	[1]	[1]
remark	a)	b)	c)	d)	a)	c)

a) Differences between the three lowest adiabatic ionization energies of OF. – b) E ≈ 130 kJ/mol from interpolation between E = 92.0 kJ/mol for O_2 (22 kcal/mol, see [17]) and 173.4 kJ/mol for NF (1.8 eV, see [18]). – c) Calculated at the experimental equilibrium bond length of OF. – d) From the difference 0.14482 a.u. of the respective total energies at the optimized OF^+ bond lengths. The value has been criticized [19].

Calculated energies of states arising from the configurations $5\sigma^2 1\pi^3 2\pi^3$ and $5\sigma 1\pi^4 2\pi^3$ are given in the section on the OF ionization potential, p. 70.

The internuclear distances r_e and the vibrational constants ω_e of the three lowest electronic states were derived by an analysis of the vibrational structure of the corresponding PE bands (error in r_e equals ± 0.01 Å). An anharmonicity constant $\omega_e x_e = 10 \pm 20$ cm⁻¹ was estimated for all three states [1]. r_e was also calculated by an ab initio SCF-MO method [10]:

state	$X^3\Sigma^-$	$^1\Delta$	$^1\Sigma^+$
r_e in Å [1]	1.23_4	1.23_9	1.24_6
r_e in Å [10]	1.414	1.280	—
ω_e in cm⁻¹ [1]	1300	1280	1230

The dissociation energy $D(F\text{–}O^+) = 2.7$ eV was derived as $D = D(OF) + E_i(O) - E_i(OF)$ using the vertical ionization potential of OF [9]. $D(F\text{–}O^+) = 2.5$ eV ($D_0 = 58 \pm 15$, $D_{298} = 59$ kcal/mol) [20] is based on D(OF) = 44 kcal/mol, and D(F–O^+) = 1.7 eV [4] on D(OF) = 1.1 eV (25 kcal/mol). These two latter D(OF) values are now known to be invalid, see p. 73. D(F–O^+) = 3.7 eV [21 to 23] and D(F–O^+) = 3.3 eV [24] were estimated by a method of isoelectronic similarity.

$D_e(O–F^+) = 6.96 \pm 0.16$ eV (for the $X^3\Sigma^-$ state) was derived as $D_e = D_e(OF) + E_i(F) - E_i(OF)$ using the adiabatic first ionization potential of OF. The higher adiabatic ionization potentials of OF led to $D_e = 5.57$ and 4.72 eV (both ±0.16 eV) for $OF^+(^1\Delta)$ and $OF^+(^1\Sigma^+)$ [1].

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3.9 The OF^- Ion

CAS Registry Number: *[12763-66-5]*

The ion was produced by electron impact on CF_3OF, appearance potential AP = 3.9 ± 0.1 eV [1], on ClO_3F, AP = 0.31 ± 0.06 eV [11], and on OF_2, AP = 0.02 ± 0.05 eV [12]. The other reaction products were CF_3 [1], ClO_2 [11], and F [12].

The formation enthalpy $-\Delta H_f^\circ \geq 6$ kcal/mol follows from the lower limit for the electron affinity of OF, A(OF) ≥1.4 eV (see p. 70) and ΔH_f°(OF) = 26 kcal/mol (see p. 66). $\Delta H_{f,0}^\circ = -8$ kcal/mol was given by O'Hare and Wahl [2] according to their value for the dissociation energy $D_0(O\text{–}F^-)$ = 3.5 kcal/mol, see below. $\Delta H_{f,298}^\circ = -9$ kcal/mol was then estimated by making use of enthalpy functions of the isoelectronic F_2 molecule [2]. $\Delta H_f^\circ = -12.4$ kcal/mol follows from a semiempirical SCF–MO calculation [3].

The total Hartree-Fock energy $E_T = -174.20482$ a.u. and the orbital energies ε_i as given below were calculated for the ion in its $^1\Sigma$ state by an ab initio SCF–MO method. The internuclear distance (1.32 Å) was taken from OF [2]:

orbital	1σ	2σ	3σ	4σ	1π	5σ	2π
$-\varepsilon_i$ in a.u.	25.9792	20.2154	1.3280	0.8275	0.3867	0.3347	0.0991

$E_T = -173.94136$ a.u. was calculated [6] with an extended Gaussian-type basis [4] at the optimized OF^- distance (1.56 Å). For E_T values from a simpler basis [5] and at a shorter distance, see the original paper [6]. $\varepsilon(2\pi) = -1.63$ eV (−0.06 a.u.) was calculated semiempirically [3]. The energy difference between OF^- and the isoelectronic F_2 molecule was derived from the electrostatic potentials at the nuclei [13].

The calculated dipole moment is 1.477 D (from the geometric midpoint between the two nuclei; negative end at O) and the quadrupole moment -2.339×10^{-26} esu·cm^2 (referred to the center of mass) [2]. The atomic charges −0.61 at O and −0.39 at F were determined [8] using the wave functions of [2] and a procedure developed by Politzer and Harris [9]. For effective charges of the atoms and orbital populations, see [7].

The internuclear distance of 1.561 Å follows from an ab initio SCF–MO calculation with an extended Gaussian basis [6]. Calculations with a minimal basis gave r = 1.48 Å (2.8 a.u.), that is, 0.3 a.u. higher than the calculated $r_e = 2.4958$ a.u. for OF [2]. Still smaller values are 1.400 Å (minimal basis) [6] and 1.268 Å (semiempirical) [3].

The $O\text{–}F^-$ dissociation energies $D_0 = 3.5$ kcal/mol (0.15 eV) and $D_{298} = 3.9$ kcal/mol were derived from experimental values for the dissociation energy of OF and the electron affinity of atomic fluorine, but using an electron affinity of OF calculated by ab initio methods [2]. For the decomposition reaction $OF^- \rightarrow O + F^-$, $\Delta G_{298}^\circ = -2.2$ kcal/mol was then obtained with an estimated $\Delta S_{298}^\circ = 20.6$ cal·mol^{-1}·K^{-1}. It thus was concluded that OF^- would be thermodynamically only marginally stable at room temperature [2]. However, this is only valid for the spin-forbidden reaction path $OF^-(^1\Sigma) \rightarrow O(^3P) + F^-(^1S)$, which is unlikely to occur since spin conservation is well obeyed for dissociation reactions in which light atoms are involved [10]. From thermochemical and spectroscopic data $\Delta G_{298}^\circ = 179.5$ kJ/mol (42.9 kcal/mol) and $\Delta G_{298}^\circ = 181.7$ kJ/mol (43.4 kcal/mol) were calculated for the spin-allowed dissociation pathways $OF^-(^1\Sigma) \rightarrow O(^1D) + F^-(^1S)$ and $OF^-(^1\Sigma) \rightarrow O^-(^2P) + F(^2P)$, respectively. Thus, spin conservation suggests OF^- to be kinetically highly stable [10].

Solvent effects, that is, the macroscopic electrostatic interaction between OF^- and a surrounding dielectric, were calculated by an ab initio self-consistent reaction field (SCRF) method [14].

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3.10 The OF^{2-} Ion

CAS Registry Number: *[51429-71-1]*

A paramagnetic center OF^{2-} was generated in MgO single crystals which contained fluorine impurities and were irradiated by fast neutrons at 27 and 77 K. The center was identified by its ESR spectrum observed at both irradiation temperatures. Appreciably higher center concentrations were found in single crystals obtained from a PbF_2 flux melt [1]. Subsequent studies with ^{17}O enriched MgO [2] confirmed these observations and showed that the ion is probably formed by trapping an interstitial oxygen at a substitutional fluorine. The possibility was not ruled out, however, that a fluorine is displaced and combines with a (substitutional) oxygen. The center occupies an anion site [2]. It is oriented along $\langle 111 \rangle$ directions at a position with local symmetry C_{3v} [1, 2]. A more loosely bound OF^{2-} paramagnetic center was produced by X irradiation of a hydrolyzed CaF_2 crystal and was also identified by its ESR spectrum at 78 K [3, 4]. These observations were also confirmed by ^{17}O studies [5]. The hydrolysis reaction $CaF_2 + H_2O \rightarrow CaF^+ + OH^- + HF(g) \rightarrow CaO + 2HF(g)$ introduces O^{2-} at anion sites. An O^- ion, formed by X irradiation, will move toward one of its six neighboring F^- ions, probably because of a Jahn-Teller instability. Thus, the center becomes oriented parallel to a fourfold crystal axis [4], see also [3, 5]. The local symmetry is C_{2v} [3, 5]. The OF^{2-} center in CaF_2 is stable at room temperature [10], whereas in MgO the center anneals within a few minutes at room temperature [2]. The center in CaF_2, however, could be only observed in the purest crystals, either self made or commercially available [3, 11]. The very low spin density at fluorine, as inferred from hyperfine structure constants, suggested the center in CaF_2 as the limiting case of an O^- strongly perturbed by an adjacent F^- [6 to 8].

The configuration $\ldots\sigma^2\pi^4\pi^{*4}\sigma^*$ with the unpaired electron in an antibonding σ^* orbital is supposed to be analogous to that of the isoelectronic molecular ions FX^-, X = F through I. The ground term is then $^2\Sigma^+$ [2]. The spin densities (= fraction of unpaired spin localized at O or F) 0.79 at O^- and 0.21 at F^- were derived for the center in MgO from the ^{19}F and ^{17}O hyperfine (hf) coupling parameters on the basis of theoretical relations which were originally developed [9] for homonuclear molecules and involve calculated hyperfine coupling constants for the free ions O^- and F^-. Spin densities for various choices of the signs of the hf tensor components were considered. The greater spin density at O^- is in agreement with the antibonding nature of the outermost σ orbital [2]. For the center in CaF_2, the most probable values derived by the same procedure appeared to be 0.97 at O^- and 0.03 at F^- [2]. Similar figures were also derived by others [3, 5 to 8].

An electronically excited state for the center in MgO corresponding to the transition $\pi^* \rightarrow \sigma^*$ is assumed to be in the region 35000 to 50000 cm^{-1} on the basis of g-tensor components and individual spin densities [2]. For the center in CaF_2 an absorption in the visible region was not observed [11].

The internuclear distance for the center in CaF_2 will be ~2.4 Å (i.e., smaller than the normal spacing of 2.72 Å between two nearest F^- ions in CaF_2) on the basis of the observed ^{19}F hf structure in the ESR spectrum [3]. The spin density values, then, indicate that the O^-–F^- distance of the center in MgO will be smaller than that in CaF_2 [2].

Axially symmetric ESR spectra were observed for the centers in MgO single crystals at 27 K [1] and at 77 K [1, 2] and even in CaF_2 at 78 K despite a local C_{2v} symmetry [3, 5]. The axis of symmetry coincides with ⟨111⟩ of MgO [1], and is parallel to a fourfold axis of CaF_2 [3 to 5]. For MgO not aligned along special crystal axes, eight lines arise from the four equivalent sites and splitting by the ^{19}F hf structure [1]. For CaF_2 six lines are generally observed [10]. An additional hyperfine structure due to the interaction of the unpaired electron with the five residual F^- nearest neighbors was observed in [10] and apparently also in [3], with splittings of 2.4 G [10] or 3.28 ± 1 G [3]. The ^{17}O hf structure was fully resolved in ^{17}O enriched MgO [2] and in CaF_2 hydrolyzed by H_2O enriched in ^{17}O [5]. The spectra do not give the signs of the hf coupling constants a; it is only known that the $a_{\parallel}$ tensor components must have the signs of the nuclear g factors (+ for ^{19}F, − for ^{17}O) [2]. Among the four possible sets of signs for $a_{\perp}(F)$ and $a_{\perp}(O)$, the set [2] which gave the most plausible values of spin densities at F and O is given in the following table. The unit of the hf coupling constants is G.

crystal	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}(F)$	$a_{\perp}(F)$	$a_{\parallel}(O)$	$a_{\perp}(O)$	Ref.	remark
MgO	2.0022 ±0.0002	2.0085 ±0.0002	+455 ±1	+172 ±1	−118 ±1	−15 ±1	[1, 2]	a)
CaF_2	2.0016 ±0.0008	2.0458 ±0.0008	+53.7 ±0.4	+15.0 ±0.4	−104.5 ±2.1	+20.0 ±1.5	[2 to 5]	b)
CaF_2	2.0016	2.0415	(±)49	(±)14	—	—	[10]	

a) $a_{\parallel}(F) = +1273$ MHz, $a_{\perp}(F) = +482$ MHz [1]. $a_{\parallel}(O) = -(110 \pm 4) \times 10^{-4}$ cm^{-1}, $a_{\perp}(O) = -(14 \pm 3) \times 10^{-4}$ cm^{-1}. $a_{\perp}(F) < 0$ cannot be ruled out [2]. – b) g and a from [3 to 5]; signs of hf coupling constants from [2], see text. $a_{\perp}(F) < 0$ cannot be ruled out.

The g-tensor components in MgO are in qualitative agreement with the theory, which predicts $g_{\parallel} = g_e = 2.0023$ and $g_{\perp} > g_e$ [2]. The differences between the two sets of constants for the center in CaF_2 as presented above may be ascribed to different levels of purity of the crystals used [10]. The dynamic polarization of the ^{19}F nuclei was studied [10].

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3.11 Dioxygen Difluoride, O_2F_2

CAS Registry Numbers: O_2F_2 *[7783-44-0]*, $^{17}O_2F_2$ *[12178-94-8]*

Review

O_2F_2 is a pale yellow solid which melts at about 120 K to give a yellow liquid. Another melting point of ~110 K was presumably caused by admixtures of other oxygen fluorides leading to an orange-red color of both the solid and the liquid. The compound decomposes at temperatures below its (extrapolated) boiling point of about 216 K. It reacts readily at 120 K and below. The mechanism of its reactions is explained primarily by cleavage of the O–F bond leading to the formation of F atoms and OOF radicals; the formation of two OF radicals by cleavage of the O–O bond is energetically disfavored. If O_2F_2 is allowed to react quickly with other compounds, simple fluorination usually results, for example, the fluorination of SO_2 gives SO_2F_2. The controlled reactions of O_2F_2, however, yield products that appear to be formed by way of an OOF intermediate, for example, the reaction with BF_3 yields the dioxygenyl salt O_2BF_4.

3.11.1 Preparation

Methods

The **radiolysis** of a 3:1 F_2–O_2 mixture with 3 MeV bremsstrahlung at 77 K yielded a reddish-brown solid which melts giving a red liquid consisting of O_2F_2 and $(O_2F)_n$ with possibly small amounts of higher oxygen fluorides. Warming the red liquid to 195 K for 3 h gave O_2 and a yellow product which is pure O_2F_2 as shown by IR spectroscopy [1, 2].

O_2F_2 can be prepared in a glow **discharge** through an equimolar F_2–O_2 mixture or one containing a slight excess of fluorine, at liquid-oxygen temperatures, see "Fluor" Erg.-Bd. 1, 1959, p. 233. A detailed description of the procedure is given in [3, 4]. Conditions for preparation are: 1:1 F_2:O_2 molar ratio, 90 K, 12 ± 5 Torr, 25 to 30 mA, and 2.1 to 2.4 kV [4, 6].

The amount of O_2F_2 obtained from a stoichiometric F_2–O_2 mixture (~1 Torr) at 77 or 90 K in a glow discharge (10 to 40 mA) depends on the specific energy U/v (electrical power U in W, gas flow rate v = 0.4 to 11.0 L/h). The degree of conversion depends on the current strength at U/v below about 30 $W \cdot h \cdot L^{-1}$ and is constant (at ~85%) at higher U/v values up to 100 $W \cdot h \cdot L^{-1}$ [5]. Dilution of the F_2–O_2 mixture with argon insignificantly alters the degree of conversion to O_2F_2 [7]. O_2F_2 is also formed at conditions appropriate for the preparation of O_3F_2 (F_2:O_2 ratio of 2:3) [8] (see p. 104), as shown by cryogenic mass spectrometry at 77 to 150 K [9]; above about 110 K, O_2F_2 forms by decomposition of O_3F_2 [8].

Relatively pure O_2F_2 was prepared by an electrical discharge (4 to 5 kV, 2 mA) through an O_2–F_2 (1:2) mixture at 77 K followed by removal of unreacted O_2 and F_2 by pumping to 10^{-5} Torr and distilling O_2F_2. All surfaces of the apparatus must be kept at liquid-nitrogen or dry-ice temperature to avoid decomposition of O_2F_2. The pale yellow product is pure O_2F_2 with a trace of $(O_2F)_n$ as impurity as shown by Raman spectra [10]. It forms with a rate of production of 2.5 g/h by quantitative conversion of an $OF_2 + 0.5\ O_2$ mixture (pressures 1 to 10 Torr) at 77 K in an electric discharge (power 44 to 65 W) [11].

Circulation of an F_2–O_2 mixture (100 to 400 Torr) through a silent discharge resulted in the formation of a mixture of oxygen fluorides with O:F ratios of ~1.1 to ~2.04:1, probably O_2F_2 and O_4F_2 [12], but the synthesis of O_2F_2 by this route does not seem to be appropriate [13].

O_2F_2 (>1 mol in 100 mL) is prepared by 365-nm **photolysis** of mixtures of F_2 and (up to 50 mol%) O_2 at 77 K [14] and by photolysis of an equimolar O_2–F_2 mixture with the unfiltered light of a 1000-W Xe–Hg arc lamp at 77 K [15].

It forms in the photolysis ($\lambda = 313.0$ nm) of an F_2–O_2 mixture at 231 K (for decomposition of O_2F_2, see p. 97), presumably by $F + O_2 + M \rightarrow O_2F + M$ followed by $O_2F + F + M \rightarrow O_2F_2 + M$ (M = third body) [16]. The photochemical conversion of O_2F into O_2F_2 according to $O_2F + h\nu \rightarrow O_2 + F$ followed by $O_2F + F + M \rightarrow O_2F_2 + M$ is reported in [17]. O_2F_2 forms in the photolysis of OF_2–O_2 and of F_2–O_2 mixtures at 4 K [18] and of OF_2–O_2 mixtures at 20 K in N_2, Ar, or O_2 matrices [19] as well as by codeposition of a stream of F atoms in Ar together with oxygen at 14 K [20]. The 365-nm photolysis of an ~1:2 molar mixture of F_2 and O_3 at 120 K gives along with OF_2 the dioxygen difluoride in 36% yield, based on the amount of fluorine atomized [21], for the mechanism of the reaction, see "Fluorine" Suppl. Vol. 2, 1980, p. 140.

Purification. Storage

O_2F_2 is purified by distilling the product, obtained in the electric discharge, into a 77 K trap followed by pumping at 113 K (isopentane-slush bath), warming the sample to 143 K (n-pentane-slush bath), cooling the middle fraction to 77 K, and repeating this procedure several times [22]. Similar purifications have been reported [1, 10, 13].

O_2F_2 should be kept in a dry atmosphere and below 116 K to avoid thermal decomposition [23]. It can be stored for a long time in Pyrex cooled to 93 K [2] or for days at 195 K in vacuum in stainless steel [20].

Enthalpy of Formation

The enthalpy of formation $\Delta H^{\circ}_{f,298} = +4.73 \pm 0.30$ kcal/mol was obtained from the heat of decomposition of liquid O_2F_2 into the elements [23]. Similar values have been reported, $\Delta H^{\circ}_{f,298.15} = +4.3$ [24] and $+4.7 \pm 9.3$ kcal/mol [6]. Semiempirical SCF–MO calculations (MINDO approximation) gave $\Delta H = -90.84$ kJ/mol (-21.7 kcal/mol) [25].

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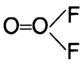
3.11.2 Molecular Properties and Spectra

3.11.2.1 Point Group. Electronic Structure

The molecule has C_2 symmetry [1, 2]. The rotational spectrum in the microwave region shows that O_2F_2 has a zigzag F–O–O–F chain structure (see Fig. 2, p. 91) rather than the  $O{=}O\genfrac{}{}{0pt}{}{\diagup F}{\diagdown F}$ type of structure. The latter had been expected [3] based on the decomposition (see p. 97) into O_2 and F_2. The chain has a C_2 axis of symmetry; the molecular structure is at least formally analogous to that of H_2O_2 with a dihedral angel Φ (see p. 90) of about 90° [4]. The zigzag, skewed chain structure has also been confirmed by several ab initio [5, 6] and semiempirical (CNDO/2 [7], MINDO [8], extended Hückel [33]) SCF–MO calculations.

The bond lengths (see p. 90), however, are unusual. The O–O distance is exceptionally short; it is much shorter than that in H_2O_2 and practically the same as in O_2. The O–F distance is much longer than that in OF_2 [4], see also [9]. The strong O–O bond also manifests itself in a high-frequency absorption of the corresponding stretching vibration (see p. 92), compared, for example, to that of H_2O_2 [10]. Nevertheless, the frequency seems to be lower than that in O_2F, for which a similar type of bonding would be expected [11]. A significantly greater bond order than in H_2O_2 is further indicated by the much higher barrier to internal rotation (see p. 93) [12].

To account for these results, several interpretations have been tried. A valence bond approach considers the ionic structure $F^-O{=}O^+{-}F$ and its mirror image besides the F–O–O–F structure. The ionic structures are favored by the electronegative character of F and lead to a shortening of the O–O and to a lengthening of the O–F distances [4], see also the reviews on oxygen fluorides [13] and on the geometric and dynamic structures of fluorocarbons and related compounds [14].

The modification of the valence bond description using the "double-quartet" instead of the "octet" rule [15], gives ten possible structures for O_2F_2 (see the papers [15, 16]). Two of these, with small formal charges on the atoms and reduced interelectron repulsion, account for the observed peculiar bond lengths as they place only one electron between O and F but four electrons between the two O atoms [15, 16], see also [17]. This "one-electron bond model" [18, 19] was used in an interpretation of the ^{19}F NMR spectrum [18]. The molecule could be described as a donor-acceptor complex between O_2 as the donor and two acceptor F atoms [20]. The "increased valence" formula (see original paper [21]) is obtained from the octet formula by delocalizing F electrons into antibonding O_2 orbitals, or with the Linnett formula for O_2 by spin pairing [21], or with the simple valence bond structure by delocalizing O electrons into bonding O_2 orbitals [22].

Qualitative MO descriptions consider the interaction of the F2p orbital with one of the antibonding π^* orbitals of O_2, see [23 to 25]. Because of the high electronegativity of the F atom, very little electron density is released into π^* resulting in a weak O–F bond (a $(p\text{–}\pi^*)\sigma$ bond) and only a small reduction of the O–O bond order [26]. This model, however, was criticized and replaced by another three-center bonding model [34].

Quantitative MO calculations [27], see also [28], take into account the interaction of F2p with both π and π^* and show that extensive delocalization of the O2pπ electrons explains the weak O–F and the strong O–O bonds. Coulson bond orders were derived for the experimental bond lengths, $\Phi = 90°$, and an OOF bond angle of 120° (values for 90° in parentheses): 2.34 (2.09) for O–O, 0.66 (0.95) for O–F [27]. MO calculations [11] using the extended Hückel method also indicate a large delocalization. A Mulliken population analysis results in an "overlap" O–O bond order of 0.40, compared to 0.18 for H_2O_2 [11]. However, the significant differences of the O–O and O–F bond lengths versus H_2O_2 and OF_2, respectively, are reproduced by neither the ab initio calculations [29] nor the INDO calculations [30]. Ab initio SCF and CI calculations with different basis sets [6] show that the shortening of O–O can be achieved by the addition of O polarization functions and the lengthening of O–F by the inclusion of correlations; see also [29].

Orbital energies were calculated by the extended Hückel method [11]. The total energy was calculated by ab initio SCF [5, 6, 31] and CI [6] methods for several basis sets. The lowest values are $E_T^{SCF} = -347.77591$ a.u. and $E_T^{CI} = -348.65416$ a.u. [6]. Values from the CNDO/2 method [7, 32] and the MINDO method [8] have been reported.

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3.11.2.2 Dipole Moment μ. Ionization Potential E_i. Polarizability α

$\mu = 1.44 \pm 0.04$ D has been derived from the Stark effect of four rotational transitions in the microwave region. The dipole moment vector points along the intermediate axis of inertia b (= C_2 axis of symmetry). For vibrationally excited states, presumably belonging to the torsional vibration, a small variation of μ was observed: $\mu = 1.43$ (v = 1), 1.47 (v = 2), 1.48 D (v = 3) [1]. For μ (v = 0), see also the table [2] of selected dipole moments. Theoretical moments from ab initio [3, 4] and CNDO/2 [5, 6] calculations lie between 0.26 and 0.80 D. For the atomic charges involved, see the original papers [3 to 6].

$E_i \leq 13.4$ eV was based upon the measured appearance potential of O_2F^+ in the mass spectrum of O_2F_2, $AP(O_2F^+) = 14.0$ eV, upon the assumption $D(F\text{–}O_2F^+) \geq 0$, and upon an excess kinetic energy of 0.6 eV for $O_2F_2 + e^- \rightarrow O_2F^+ + F + 2e^-$. $D(F\text{–}O_2F^+) = 0$ seems reasonable, since $O_2F_2^+$ was not observed in the mass spectrum. The kinetic energy was derived from $AP(O_2F^+)$, from the directly measured $E_i(O_2F) = 12.6$ eV (see p. 116), and from an estimated bond dissociation energy $D(F\text{–}O_2F) = 0.8$ eV (see p. 94) [7]. A previous estimate was $E_i \approx 13.0$ eV [8]. $E_i = 14.9$ [9] and 16.11 eV [4] were predicted from extended Hückel and ab initio calculations, respectively.

$\alpha = 3.738$ Å^3 was derived [10] from the δ-function potential model of chemical binding [11].

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3.11.2.3 ^{19}F and ^{17}O NMR Chemical Shifts

The ^{19}F NMR spectrum has been studied in liquid solutions of O_2F_2 in CF_3Cl [1, 2], in CF_3Cl with added OF_2 [2], in $CFCl_3$ [2], and in OF_2 [3], and also in the pure liquid [4, 5], see also [3]. The very large (negative) shift to the low-field side of the $CFCl_3$ reference signal points to considerable antishielding, probably due to the long O–F bond [4], see also [6]. The chemical shifts in the following table are referenced to $CFCl_3$:

solvent	CF_3Cl	CF_3Cl	CF_3Cl	$CFCl_3$	—	—
mol% O_2F_2 ...	20	30	45	50	100	—
temperature in K	190	190	190	200	145	130(?)
^{19}F shift in ppm .	−830	−844	−852	−850	-865 ± 1	∼−868
Ref.	[2]	[2]	[2]	[2]	[4]	[5]
remark	a)	a)	a)		b)	c)

a) The extrapolation to infinitely dilute solution yields ∼−825 ppm; for this value, see also [7]. The extrapolation to high concentrations gives a liquid value which is approximately the same as that in [4]. The shifts of the samples with OF_2 added at 140 K are −830, −837, −841, and −852 ppm for 8, 10, 40, and 50 mol% OF_2, respectively [2]. – b) Shift also in [7]. – c) Shift measured in systems containing O_2F_2 and probably O_4F_2 in equilibrium with O_2F (see p. 109).

The shift of a dilute solution of O_2F_2 in CF_3Cl, (-865 ± 10) ppm relative to CF_3Cl, does not change between 143 and 193 K [1]. See also the review [8] on ^{19}F chemical shifts.

The ^{17}O NMR spectrum consists of one line. The shift −647 ppm with respect to $H_2{}^{17}O$ has been measured at 108 K with a liquid sample containing probably O_4F_2 and O_2F in addition to O_2F_2 [3, 5]. A triplet splitting of the line due to ^{17}O-^{19}F spin-spin coupling was resolved yielding $^1J(^{17}O\text{-}^{19}F) = 424$ Hz [5].

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3.11.2.4 Rotational Constants. Moments of Inertia. Geometric Structure

For three isotopic species in their vibrational ground states, the following rotational constants (in MHz) were derived from the microwave spectrum [1], see also the tables [2] of molecular constants from microwave spectroscopy (for axis system, see **Fig. 1** [1]).

species	A	B	C
$^{16}O_2F_2$	20266.18	5011.09	4360.14
$^{16}O^{18}OF_2$	19531.98	4975.78	4318.68
$^{18}O_2F_2$	18859.19	4938.34	4279.31

Constants for vibrationally excited states of $^{16}O_2F_2$ are also reported [1, 2].

The above rotational constants correspond to the following effective moments of inertia (in amu·Å²) [1]:

species	I_a	I_b	I_c
$^{16}O_2F_2$	24.94456	100.8824	115.9438
$^{16}O^{18}OF_2$	25.88222	101.5981	117.0570
$^{18}O_2F_2$	26.80555	102.3686	118.1338

The following values of the bond distances r (in Å), the bond angle α(OOF), and the dihedral angle Φ (see **Fig. 2**) were derived from the above rotational constants [1], see also [3]. The type of the respective geometric parameter ("substitution" or "effective") has been added according to the tables [4] of molecular structures; see also tables [5] of structural data.

r(O–O)	r(O–F)	α(OOF)	Φ
1.217 ± 0.003	1.575 ± 0.003	109°30′ ± 30′	87°30′ ± 30′
substitution (r_s)	effective (r_0)	effective (α_0)	effective (Φ_0)

The remarkably short O–O distance has been discussed by many authors (see Section 3.11.2.1, the quantum chemical calculations cited below, and the review [6] correlating the O–O bond distances and the charges of the O–O group in a variety of molecules, including O_2F_2 and O_2).

α(OOF) = 108.1° was estimated from a steric model, in which this angle was determined by the nonbonded contact between the outer O and F atoms. The set of self-consistent intramolecular van der Waals radii [7] with 1.13 Å for O and 1.08 Å for F was used [8].

Ab initio SCF–MO calculations [9 to 12] yield O–O distances in the range 1.29 to 1.40 Å, O–F distances 1.358 to 1.49 Å, bond angles 104.2° to 105.48°, and dihedral angles 83.6° to 88.42°. An enlarged (compared to [12]) double zeta basis improved the calculated geometry [19]. Distances (O–O 1.22, O–F 1.63 Å) in essential agreement with the experimental ones were obtained from correlated wave functions [20]. Semiempirical calculations (CNDO/2 [13], INDO [14], and MINDO [15]) of all four parameters yield 1.22 to 1.253 Å for O–O, 1.18 to 1.492 Å [15] for O–F, 108.0° to 113.3° for α, and 85.8° to 89.73° for Φ. The dihedral angle has also been calculated at the experimental values of the other parameters: 85° to 88° by the CNDO/2 method [13, 16, 17] and 87.5° by the extended Hückel method [18].

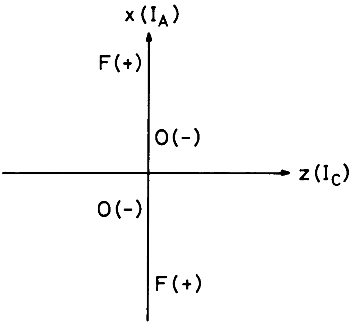

Fig. 1. Distribution of the atoms of O_2F_2 with respect to the a- and c-inertial axes (O atoms lie in a plane below the (xz) plane, F atoms lie above). The C_2 axis is perpendicular to the xz plane.

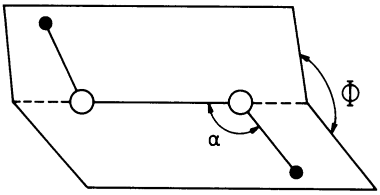

Fig. 2. Structural model of O_2F_2.

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3.11.2.5 Molecular Vibrations. Force Constants. Rotational Barriers

Due to the C_2 symmetry of the molecule, all normal vibrations ν_i (i = 1 to 6) are both IR and Raman active, see [1].The wavenumbers (in cm^{-1}) in the following table have been obtained from the IR spectrum of O_2F_2 in the gas phase [19], of O_2F_2 isolated in solid Ar [1, 5], and from the Raman spectrum of O_2F_2 dissolved in liquid CF_3Cl [2]. The assignments (ν = stretching, δ = bending vibration) and the symmetry species (a, b) are taken from [1]:

ν_1(a) ν(O–O)	ν_2(a) ν(O–F)	ν_3(a) δ(OOF)	ν_4(a) torsion	ν_5(b) ν(O–F)	ν_6(b) δ(OOF)	phase	T in K	spectrum	Ref.	remark
1210	630	—	—	614	—	gas	173	IR	[19]	a)
(1257)	611	366	—	624	459	Ar	20	IR	[1]	b)
(1250)	612	366	195	627	466	Ar	14	IR	[5]	c)
—	610.6	366.1	195.6	624.3	—	CF_3Cl	190	Raman	[2]	d)

a) ν_2 and ν_5 assignments in accord with a solid state study [9], see p. 95, but differing from matrix [1, 5], solution [2], and other solid state studies [1, 8]. Combination bands observed: $\nu_1+\nu_2=1835$, $\nu_1+\nu_3=1570$, $\nu_2+\nu_3=980$, $\nu_2+\nu_4=832$, $\nu_5+\nu_6=1085$ cm^{-1}. – b) For ν_1, see discussion below. Older data for ν_2 and ν_5, see [3]. – c) The entries are for $^{16}O_2F_2$ (ν_1 was assumed). For $^{16}O^{18}OF_2$ and $^{18}O_2F_2$: $\nu_2=595$ and 584, $\nu_5=618$ and 601, $\nu_6=459$ and 452 cm^{-1}. For $^{16}O_2F_2$ in a second type of site: $\nu_2=612$, $\nu_5=636$, $\nu_6=483$ cm^{-1}. – d) ν_6 obscured by a CF_3Cl band.

Two peaks of ν_5 were observed in an O_2 matrix (12 K) at 626.5 and 628.5 cm^{-1} [18]. For older data of ν_2, ν_3, ν_5, and ν_6, see [4].

IR and Raman data for ν_2 to ν_6 of solid O_2F_2 will be found on p. 95. The data for ν_1 have been included in the following section.

As to the O–O stretching fundamental ν_1, there has been and is still some discussion, see [5]. The above matrix value seems to be unusual since it is of lower frequency than the bands assigned to polymers (see p. 95) [1]. Moreover, it is somewhat surprising in view of the corresponding values 1555 cm^{-1} for O_2 and 1500 cm^{-1} for O_2F [2], see also [6], and it could not be found in the Raman spectrum of O_2F_2 dissolved in CF_3Cl [2]. A ν_1 wavenumber in the range 1250 to 1300 cm^{-1}, however, is supported by the behavior of the O–F stretching overtones observed in the matrix IR spectrum. There will be Fermi resonance interaction between ν_1 and these overtones [5]. A ν_1 value around 1300 cm^{-1} is suggested by the Raman studies of liquid and solid O_2F_2 and the IR studies of the solid. Raman shifts assigned to ν_1 are: ~1300 (liquid) [7], 1300 [8], 1305 and ~1270 (shoulder) [1] (all solid); IR absorptions: 1308 and ~1270 (shoulder) [1], 1306 [6, 9], and 1239 ($^{18}O_2F_2$) [6].

For the torsional vibration ν_4, a wavenumber of ~160 cm^{-1} was estimated from the microwave spectrum [10].

Wavenumbers (in cm^{-1}) of combination and overtone vibrations due to Ar matrix IR absorption studies are:

$\nu_2+\nu_3$	$\nu_5+\nu_6$	$2\nu_2$	$2\nu_5$	T in K	Ref.	remark
980	1070	1214	1228	20	[1]	
—	—	1210	1233	14	[5]	a)

a) Entries for $^{16}O_2F_2$. Values for a second type of site (1204 and 1229 cm^{-1}) and ^{18}O substituted molecules were also given [5].

The following set of generalized valence force constants was derived from the fundamental vibrations ν_2 through ν_6 observed in an Ar matrix at 14 K and from an assumed value $\nu_1=1250$ cm^{-1} [5]. The indices R, r, α, and τ pertain to the O-O bond, the O-F bond, the OOF bond angle, and the torsion, respectively:

f_R	f_r	f_α	f_τ	$f_{r\alpha}$	$f_{\alpha\tau}$
7.00±0.03 mdyn/Å	1.85±0.12 mdyn/Å	1.05±0.06 mdyn·Å	0.24±0.01 mdyn·Å	0.18±0.05 mdyn	0.11±0.01 mdyn·Å

A similar set, but with $f_{\alpha\tau}=0.014$, was derived [2] from the older IR data for five normal vibrations [1] and the Raman value for ν_4 [2]. If $f_{R\alpha}$ is included instead of $f_{\alpha\tau}$, virtually identical results are obtained. The high value of f_r, compared to 1.3 for O_2F, may be due to the neglect of f_{Rr}. For an assumed value $\nu_1=1500$ cm^{-1} the following constants were determined: $f_R=10.36$, $f_r=1.69$, $f_\alpha=1.12$, $f_\tau=0.24$, $f_{R\alpha}=0.077$, and $f_{r\alpha}=0.12$ [2].

A somewhat different set of seven constants, including f_{Rr} but not $f_{\alpha\tau}$, was determined from the solid state wavenumbers of $^{16}O_2F_2$ and $^{18}O_2F_2$. With $\nu_1(^{16}O_2F_2)=1306$ cm^{-1}, a remarkably high value of f_R (10.25 mdyn/Å) was obtained [9], see also the critical remarks [2]. For older stretching force constants, see [11].

A rotational barrier $\Delta V=V_0\approx30$ kcal/mol was derived from the observed torsional wavenumber, $\nu_4=195$ cm^{-1}, assuming a symmetric potential well $V=\frac{1}{2}V_0[1-\cos(2\Phi-\pi)]$, Φ = dihedral angle [2]. $\Delta V\approx30$ kcal/mol was previously estimated on the basis of $\nu_4=160$ cm^{-1} [10]. The observed variation of the dipole moment with the vibrational state might be interpreted in terms of a lower cis barrier (ΔV(cis), $\Phi=0°$) than a trans barrier (ΔV(trans), $\Phi=180°$) [10]. From a normal coordinate analysis it was concluded, however, that ν_4 cannot be identified as a pure torsional mode and thus cannot be used for the calculation of ΔV [9].

The quantum chemical calculations differ as to the relative magnitude of ΔV(cis) and ΔV(trans). ΔV(cis) < ΔV(trans) was obtained by semiempirical methods using the experimentally determined geometry. ΔV(cis) > ΔV(trans) follows from ab initio calculations and also from the CNDO/2 and the MINDO methods if the energy is minimized with respect to the residual geometric parameters (EH = extended Hückel calculation):

ΔV(cis) in kcal/mol ...	16.62	17.1	~25	37	11.8	17.7	6.05	21.1
ΔV(trans) in kcal/mol .	20.83	21.3	~30	44	8.1	12.7	4.50	15.3
method	CNDO/2	CNDO/2	EH	EH	ab initio	ab initio	CNDO/2	MINDO
Ref.	[12]	[13]	[2]	[14]	[15]	[16]	[13]	[17]

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3.11.2.6 **Bond Dissociation Energies** D, **Atomization Enthalpy** ΔH_{at}, in kcal/mol

D(FO–OF) = 47.5 (2.06 eV) may be derived at 298 K from the now generally accepted formation enthalpies $\Delta H_f(O_2F_2)$ = 4.7 kcal/mol (4.73 ± 0.30 measured [1], see p. 85) and ΔH_f(OF) = 26.1 kcal/mol (see p. 66). Higher D values given in the literature were obtained either from higher OF formation enthalpies (or dissociation energies) or a lower O_2F_2 formation enthalpy, thus, D(FO–OF) = 62.1 [1] using D(OF) = 44.7 (assumed, implying ΔH_f(OF) = 33 kcal/mol), D(FO–OF) = 78 [2] using ΔH_f(OF) = 41 kcal/mol [3], and D(FO–OF) = 72.5 [4] using $\Delta H_f(O_2F_2)$ = −21.7 kcal/mol (MINDO calculation). A value almost as high as the O_2 dissociation energy, D(FO–OF) = 103.8 ± 5 (4.5 ± 0.2 eV), was derived via the relation AP(OF^+) = D(FO–OF) + E_i(OF) from the measured appearance potential of OF^+ from O_2F_2, AP(OF^+) = 17.5 eV, and from the ionization potential E_i(OF) = 13.0 eV (see p. 70) [5]. This high value was apparently favored by Turner [6]. The above relation for AP is, however, not valid, since the process involved will be $O_2F_2 \rightarrow OF^+ + O + F + e^-$ [8].

D(FO_2–F) ≈ 16.5 (0.72 eV) may be derived at 298 K from $\Delta H_{at}(O_2F_2)$ = D(FO_2–F) + D(O_2–F) + D(O_2) using $\Delta H_{at}(O_2F_2)$ = 152.2 (see below) and D(O_2) = 119.1 under the reasonable assumption D(FO_2–F) ≈ D(O_2–F). Both relations were used [5] to get D(FO_2–F) = 0.8 eV (18.4 kcal/mol) at 0 K from $\Delta H_{at}(O_2F_2)$ = 6.7 eV and D(O_2) = 5.1 eV.

ΔH_{at} = 152.2 may be derived at 298 K from $\Delta H_f(O_2F_2)$ = 4.7 kcal/mol using D(O_2) = 119.1 and D(F_2) = 37.8. The early value ΔH_{at} = 151.5 [1] was derived using D(O_2) = 118.4. The similar ΔH_{at} = 6.7 eV (154.6 kcal/mol) resulted from the partial cancellation of too high a value for D(FO–OF) (4.5 eV, see above) and too low a value for D(OF) (1.1 eV [7]) [5].

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3.11.2.7 Spectra

Microwave Absorption

For $^{16}O_2F_2$ in its vibrational ground state, 16 lines from 13406.8 ($2_{1,2} \leftarrow 3_{0,3}$) to 49860.8 MHz ($4_{1,4} \leftarrow 3_{0,3}$) were recorded. Nine of them were assigned to transitions $J''=J'=1$ to 9; for the remaining seven transitions, $\Delta J=\pm1$, $J''=0$ to 4. For the isotopic species $^{16}O^{18}OF_2$ seven lines and for $^{18}O_2F_2$ six lines were recorded and assigned. "Satellite" lines were observed for five vibrationally excited states. Four of these states probably correspond to the torsional oscillation ν_4 ($\nu_4=1$ to 4). The fifth state ($v=1$) has not been identified. Numbers of assigned lines for $^{16}O_2F_2$: 11 for both $\nu_4=1$ and 2, 8 for $\nu_4=3$, 2 for $\nu_4=4$, and 7 for $v=1$; for $^{16}O^{18}OF_2$: 2 for $\nu_4=1$ [1].

Infrared Absorption

Relative intensities (peak heights) of fundamentals and combinations in the gas phase at 173 K (wavenumbers see p. 92) [17]:

ν_1	ν_2, ν_5	$\nu_1+\nu_2$	$\nu_1+\nu_3$	$\nu_2+\nu_3$	$\nu_2+\nu_4$	$\nu_5+\nu_6$
1.0	0.9	0.12	0.21	0.21	0.21	0.24

Integrated molar absorption coefficient $A=17\pm3$ km/mol for ν_1 (integration from 1150 to 1270 cm^{-1}, including $2\nu_2$ and $2\nu_5$) [17]. For wavenumbers of fundamentals, overtones, and combinations from Ar-matrix studies [2 to 5], see p. 92. Additional features (in cm^{-1}) and assignments: 1274 (ν(O–O) of the dimer), 1290 (ν(O–O) of the trimer and of higher polymers), 1340 (possibly ν(O–O) + lattice vibration) [3]. The absorbance of ν_5 was followed in an O_2 matrix to obtain the laser excitation spectrum of the O_2+F_2 reaction in the low-energy range 14500 to 16600 cm^{-1} [18]. Wavenumbers (and assignments) of the spectrum of solid O_2F_2 at 77 K (the transmittance between 300 and 1600 cm^{-1} is reproduced in [3]): 370 (ν_3), 456 with two shoulders at 450 and 466 (ν_6), 612 (ν_2), 618 (ν_5), 975 ($\nu_2+\nu_3$), 1070 ($\nu_5+\nu_6$), 1212 ($2\nu_5$), 1220 ($2\nu_2$), 1308 with a shoulder at 1270 (ν_1), and 1338 (possibly ν_1 + lattice vibration) [3]. Spectra of $^{16}O_2F_2$, of O_2F_2 enriched with ^{18}O, and of $^{18}O_2F_2$ in the solid state have been observed [6, 7]. A doublet found in the far IR at 202 and 209 cm^{-1} was believed to be the low-lying fundamental ν_4 split by intermolecular coupling. The weak absorption at 1270 cm^{-1} could be the difference band of ν_1 and the above lattice vibration. Other wavenumbers for $^{16}O_2F_2$ (in parentheses for $^{18}O_2F_2$) are: $\nu_3=369$ (362), $\nu_6=457$ (444), $\nu_5=615$ (586), $\nu_2=621$ (595), $\nu_1=1300$ (1232) (shoulder) and 1306 (1239) [6].

Raman Scattering

Raman spectra have been observed for O_2F_2 dissolved in liquid CF_3Cl at ~190 K [8] and in the solid state at 77 K [3, 9]. For the fundamentals ν_2 to ν_5 from the solution study, see p. 92. The corresponding depolarization ratios are 0.36, 0.31, 0.69, and 0.83 [8]. Wavenumbers (and assignments) from the solid state spectrum are: 1300 (ν_1), 606 and 611 (ν_2), 363 and 371 (ν_3), 198 and 205 (ν_4), 623 (ν_5), 460 (ν_6). The a modes ν_2 to ν_4 are split, presumably due to solid state effects [9]. Similar data and the additional wavenumbers ~1339 (possibly ν_1 + lattice vibration), 1060 ($\nu_5+\nu_6$), 982 ($\nu_2+\nu_3$), and 173 (possibly lattice vibration) were reported [3].

Ultraviolet and Visible Absorption

Spectra have been measured for gaseous O_2F_2 below 213 K in the range 522.5 to 220 nm [10] and at 193 K from 260 to 190 nm [11, 12], for O_2F_2 dissolved in liquid Ar at 87 K [13], and in a mixture of Freons at 77 K [14], see also a graphic reproduction [15], and at 140 and 175 K [14].

The older data [10] have been converted into molar extinction coefficients ε [13, 16]. For critical remarks regarding the spectrum [10], see [13]. In the range 260 to 190 nm, increasing absorption for decreasing wavelength was measured [11].

For O_2F_2 isolated in Ar at 14 K, no discrete electronic absorption was found between 870 and 220 nm [2].

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3.11.3 Thermal Properties

The density of liquid O_2F_2 between 117 and 186 K is given by $\varrho = 2.074 - 0.00291\,T$ (ϱ in g/cm^3, T in K) and the vapor pressure between 141 and 173 K by $p = 7.515 - 1000/T$ (p in Torr) in "Fluor" Erg.-Bd. 1, 1959, p. 234. The values p = 1 Torr at 130 K and p = 0.05 Torr at 110 to 115 K were reported [5].

The boiling point $T_b = 216.2$ K, the enthalpy of vaporization $\Delta H_v = 4583 \pm 100$ cal/mol (by Trouton rule, $\Delta H_v/T_b = 21.2\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), the estimated heat capacity of gaseous O_2F_2 $C_v = 10.0 \pm 1$, and the measured heat capacity of liquid O_2F_2 between 121 and 186 K $C_v = 24.5 \pm 0.7\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ were reported [1].

The melting point was reported as 119 K [2]. A lower melting point 109.7 K (which is cited e.g. in [3]) is thought to be caused by contamination of O_2F_2 by other oxygen fluorides [2].

The following values were estimated by means of correlation increments: $\Delta H_v = 3950$ cal/mol, the critical constants $T_{cr} = 359.2$ K, $p_{cr} = 43.5$ atm, $\varrho_{cr} = 0.590$ g/cm^3, $V_{cr} = 119.2$ cm^3/mol, and the van der Waals constants $a = 8.42 \times 10^6\ \text{atm}\cdot\text{cm}^6\cdot\text{mol}^{-2}$ and $b = 84.6$ cm^3/mol [4].

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3.11.4 Chemical Behavior

O_2F_2 has a remarkable oxidizing power. With most of the substances tested, it reacted at cryogenic temperatures. Inadequate cooling or rapid combination of reagents can cause explosions [1].

3.11.4.1 Thermolysis. Photolysis. Reactions with Electrons

Thermolysis

O_2F_2 is sufficiently stable at temperatures below its melting point of about 110 K (see above) but decomposes at temperatures below its boiling point (216 K) to give O_2 and F_2 [1, 2]. A decomposition temperature of 195 K was cited [3, p. 152]. O_2F_2 is considerably less stable than previously reported [4, 5]; a 4% per day rate of decomposition at 113 K was found [6] in contrast to a 4.3% per day rate at 195 K [4, 5].

The rate constant of the monomolecular, homogeneous decomposition reaction of O_2F_2 is given by $k = 10^{12.4}\exp(-17.0\ \text{kcal}\cdot\text{mol}^{-1}/4.57\ T)\text{s}^{-1}$ (213 to 248 K) [4, 5], see "Fluor" Erg.-Bd. 1, 1959, p. 235. The equation $k = 7.6\times10^{12}\exp(-17.5\ \text{kcal}\cdot\text{mol}^{-1}/RT)\text{s}^{-1}$ (263 to 363 K) was obtained from the rate of decrease of the optical density of O_2F_2 that was formed during the flash photolysis of an OF_2–F_2 mixture [7]. The most probable reaction mechanism [8], which involves the formation of O_2F radicals in the primary step, is

(1) $O_2F_2 + M \rightarrow O_2F + F + M$ (3) $O_2F_2 + F \rightarrow O_2F + F_2$
(2) $O_2F + M \rightarrow F + O_2 + M$ (4) $F + F + M \rightarrow F_2 + M$

The formation of OF radicals in the first step of the reaction is unlikely, since it requires a considerably higher activation energy [8].

No explosions or inflammation of O_2F_2 occur on subjecting samples of liquid O_2F_2 at dry ice temperatures to the flame of a safety fuse, a 1.25-Joule electric spark, or the impact of a 22-caliber bullet [2].

Photolysis

Studies of the photodecomposition of O_2F_2 in liquid Ar into O_2F radicals and F atoms gave a threshold near 500 nm and increasing absorption of O_2F_2 at $\lambda < 500$ nm, both in the gas phase and dissolved in liquid Ar [10]. Similarly, rapid decomposition of O_2F_2 in an Ar matrix near 300 nm was reported [11]. The observation of O_2F in the vibrational spectra of O_2F_2 in matrices at low temperatures support the decomposition mechanism starting with $O_2F_2 \rightarrow O_2F + F$ [12] in contrast to the suggestion [13] that the first step does not involve the formation of the O_2F radical.

Reactions with Electrons

In the mass spectrum of O_2F_2 between 77 and 150 K, the parent ion $O_2F_2^+$ was not observed. The appearance of the ions O_2F^+ at 14.0 ± 0.1, OF^+ at 14.0 ± 0.1, and OF^+ at 17.5 ± 0.2 eV at 130 K was interpreted [14] by the reactions

$$O_2F_2 + e^- \rightarrow O_2F^+ + F + 2e^-$$
$$O_2F_2 + e^- \rightarrow OF^+ + OF + 2e^-$$

For a mass spectrometric investigation of O_2F_2–O_3F_2 mixtures, see [15].

For references, see p. 102.

3.11.4.2 Reactions with Elements

The reaction of xenon with a large excess of O_2F_2 at 155 K gives XeF_2 almost quantitatively. No reaction occurs with krypton up to 195 K [16]. Radon or xenon di- and tetrafluorides were obtained from O_2F_2 and xenon or radon, respectively, below 173 K [17].

There was no reaction between O_2F_2 and molecular hydrogen when H_2 (1.25 L/h, 1 Torr) was pumped through a U tube, cooled to 77 K, containing condensed O_2F_2 on the walls. Atomic hydrogen, however, reacted with O_2F_2 at 77 K to yield a white solid that decomposed on warming to the melting point of O_2F_2 to give HF, H_2O_2, and H_2O. The amounts of the products indicated that the overall reaction is represented [1, 2] by

$$O_2F_2 + 5H \rightarrow 2HF + \tfrac{1}{2}H_2O_2 + H_2O$$

O_2F_2 is immiscible with oxygen at 90 K and with nitrogen or fluorine at 77 K [2, 18]. It mixes homogeneously with equimolar amounts of ozone at 116 [2] or 120 K [18]; above ~120 K explosions occurred [2, 18]. No reaction occurs on mixing O_2F_2 with gaseous O_2 (760 Torr) at 195 K followed by rapid freezing to 90 K then allowing the mixture to stand for 13 h, or on mixing liquid O_2 with O_2F_2 at 90 K [19].

A rapid addition of chlorine to O_2F_2 cooled to 140 K caused a violent explosion. On adding small portions to O_2F_2 cooled to 130 K, a violet intermediate forms together with ClF_3. In the first step of the reaction ClF forms which reacts further with O_2F_2 (see p. 99) [1, 2, 20]; for remarks on the violet compound, see [45]. Near its melting point liquid O_2F_2 reacts vigorously when added to solid bromine cooled to 90 K. A spontaneous reaction occurred on rapid addition of liquid O_2F_2 cooled to 110 K to iodine crystals cooled to 90 K. No visible reaction is observed between I_2 and an 8 to 50% solution of O_2F_2 in CF_3Cl below 195 K [1, 2].

When rapidly added to sulfur cooled to 90 K, liquid O_2F_2 reacted instantaneously with a flash [1, 2]. The reaction with sulfur gave S_2F_2, SOF_2, SOF_4, SF_6, and SO_2 [21].

Liquid O_2F_2, close to its melting point, reacts vigorously when added to charcoal cooled to 90 K. It does not appear to react with beryllium powder even upon warming to room temperature [1, 2]. O_2F_2 reacted vigorously when added rapidly to red phosphorus at ~110 K [1, 2].

The reactions with lithium, sodium, and potassium are surprisingly mild. The products of these reactions were not identified. Calcium showed no sign of reaction with O_2F_2 [22].

In contact with a platinum sheet covered with PtF_4, O_2F_2 exploded at 160 K [1, 2].

For references, see p. 102.

3.11.4.3 Reactions with Compounds

Water

O_2F_2 caused explosions when added to ice at 130 to 140 K. It also reacted with traces of water at 195 K if dissolved in HF containing H_2O; the brown color of the solution disappeared and O_2 escaped [1, 2].

Oxygen Fluorides

O_2F_2 is immiscible with OF_2 at 135 K [18]. It dissolves about 40% by weight of OF_2 and mixes homogeneously with O_3F_2 at 116 K [2].

Nitrogen Compounds

Liquid O_2F_2 reacted vigorously when added to solid anhydrous NH_3 at temperatures close to 110 K [1, 2]. NO_2, FNO_3 (and $(NO_2)_2SiF_6$) are obtained from the reaction of NO with OF_2 between 113 and 203 K. No reaction occurred with N_2O at 133 K [23]. The reaction with N_2O_4 at 143 K gave FNO_2 [24]. The reaction of O_2F_2 with a NO_2–N_2O_4 mixture between 113 and 298 K gave an unstable white solid [23].

O_2F_2 mixes homogeneously with equimolar amounts of N_2F_2 at 120 K [2, 18]. N_2F_2 dissolves some O_2F_2 at 140 K [2]. O_2F_2 is immiscible with NF_3 and with N_2F_4 at 130 K [18]. There was no visible reaction between NF_3 and O_2F_2 at 130 to 140 K. N_2F_4 reacted with O_2F_2 at 170 K forming NF_3 and O_2 [1, 2]. Some explosions occurred in the reaction between O_2F_2 and N_2F_4 at 77 K or at 193 K [26]. An unstable violet solid forms from O_2F_2 and $ClNF_2$ at 113 K [27].

O_2F_2 is soluble in FNO_2 at 195 K forming a very fluid orange solution. A slow decomposition of O_2F_2 takes place at this temperature, but no reaction with O_2F_2 is observed [1, 2, 18].

Halogen Compounds

O_2F_2 dissolves ~10% of anhydrous HF at 186 K [2, 18]. The solubility of O_2F_2 in anhydrous HF is ~5.8% by weight at 176 K and ~11.6% at 186 K [2].

Liquid O_2F_2 reacts with solid HCl at 130 to 140 K to give a violet compound of the formula O_2ClF_3 according to $2O_2F_2 + HCl \rightarrow O_2ClF_3 + HF + O_2$. The reaction actually takes place between gaseous HCl and liquid or gaseous O_2F_2 by the formation of Cl_2 and then of ClF which reacts with O_2F_2 [1, 2]. ClO_3F, O_2, and F_2 are formed in the reaction of O_2F_2 with Cl_2O_7 at 195 K [27].

At temperatures above 140 K, O_2F_2 and ClF react violently with heat evolution, forming O_2 and ClF_3. At moderate temperatures (119 to 130 K) and with slow addition of ClF an additional reaction occurs giving a violet compound of the formula O_2ClF_3 [1, 2, 20]. The reaction of O_2F_2 with excess ClF at 119 K yields a blue compound [28], the formation of which may be described by

$$O_2F_2 + 2ClF \rightarrow F_2ClO_2ClF_2$$

For remarks on the blue and violet compounds, see [45]. No reaction was observed between O_2F_2 and ClF_3, neither in the solid state at 90 K nor in the liquid state below 190 K [1, 2]. The compounds mix homogeneously at 180 K [1, 18]; only a slight decomposition of O_2F_2 was found [18]. On raising the temperature of a mixture of excess O_2F_2 and ClF_3 from 110 to 190 K, the formation of a violet intermediate (see [45]) was observed that decomposed to give ClF_5 as well as uncharacterized products [29]. Warming a mixture of O_2F_2 and ClF_3 from 77 to 195 K quantitatively gives ClF_5 after 16 h [30]. O_2F_2 and ClO_3F are completely miscible at 127 K [18].

Small amounts of O_2F_2 react with excess HBr at ~130 K according to

$$O_2F_2 + 2HBr \rightarrow 2HF + Br_2 + O_2$$

After condensing HBr at 90 K onto solid O_2F_2 and warming the mixture to 130 K, a reaction in the gas phase occurs, giving O_2 and Br_2. On condensing HBr at <90 K and bringing it into contact with an excess of liquid O_2F_2 at 130 K, a violet compound is formed, presumably O_2BrF_5 [1, 2].

On dropping liquid BrF_3 near its melting point (282 K) onto solid O_2F_2 cooled to 90 K, an exothermic reaction occurs according to

$$O_2F_2 + BrF_3 \rightarrow BrF_5 + O_2$$

Under milder conditions (i.e., addition of small amounts of BrF_3 and slow warming to 130 K) an intermediate, brown-violet compound is obtained, presumably O_2BrF_5, which decomposes into BrF_5 and O_2. The colored intermediate is also formed in the reaction of O_2F_2 with a mixture of BrF_3, BrF, and Br_2 [1, 2]; for remarks on the colored compounds, see [45]. No reaction was observed between O_2F_2 and BrF_5 at 195 K [27].

IF_5 did not react with O_2F_2 between 90 and 195 K; only a slow decomposition of O_2F_2 took place [1, 2].

Sulfur Compounds

O_2F_2 reacts with H_2S according to

$$4O_2F_2 + H_2S \rightarrow 2HF + 4O_2 + SF_6$$

The reaction starts very slowly at 130 K in the gas phase [1, 2].

The reaction of O_2F_2 with SO_2 at 113 K or below produced mainly SO_2F_2, smaller amounts of FSO_2OOF and FSO_2OSO_2F as well as traces of FSO_2OF [6, 24, 31]. From ^{17}O tracer and ^{17}O NMR measurements it was concluded that FSO_2OSO_2F is formed by way of an FSO_3 intermediate and FSO_2OOF by way of an OOF intermediate [31]. The reaction of O_2F_2 with SO_3 is very vigorous, and explosions occur if the reaction is carried out in the absence of a solvent. The reaction at 193 K in SO_2F_2 or $C_2F_4Cl_2$ as solvent gave FSO_2OOSO_2F and FSO_2OF in equal amounts after 56 h. Essentially all of the oxygen and half of the fluorine from the original O_2F_2 were released in the form of O_2 and F_2. Large amounts of F-, S-, and O-containing polymers were also formed [6].

When H_2SO_4 was allowed to react with O_2F_2 at 143 K (6 h), only small amounts of a product were obtained. It consisted of FSO_2OF, FSO_2OOSO_2F, FSO_2OSO_2F, and (up to 50%) SiF_4. The primary reaction is apparently the fluorination of the O–H bond to form HF which subsequently reacts with the glass of the vessel [6]. The reaction with H_2SO_5 proceeds at a faster rate. It yields at 173 K (1 h) large amounts of HF and small amounts of FSO_2OF, FSO_2OOF, $F_2S_3O_8$, and higher polymers similar to the reaction with H_2SO_4 [6].

O_2F_2 and SF_4 react violently at 130 K producing SF_6 and O_2. In the presence of ClO_3F as solvent it is possible to obtain a violet, extremely unstable product, presumably O_2SF_6 [1, 2]; for remarks on the violet compound, see [45].

The reaction of O_2F_2 with SOF_2 produced SOF_4 as the only product which did not react further with O_2F_2 [6]. With SO_2F_2 at 193 K only decomposition of O_2F_2 is observed. O_2F_2 is miscible with FSO_2F without reaction (no temperature was given) [21].

Carbon Compounds

O_2F_2 reacts with CO at 113 K to give COF_2 and O_2. No reaction occurs with CO_2 between 77 and 298 K. O_2F_2 reacts with $(CN)_2$ diluted with He at 131 K to produce COF_2, CF_4, and NO_2, and with $(CN)_2$ in CF_3Cl at 113 K to yield NO, NO_2, and C_4F_{10} (explosive without solvent) [23].

On adding a drop of liquid O_2F_2 to liquid CH_4 cooled to 90 K, a white flame was instantaneously produced which turned green upon further burning. Adding 0.2 cm^3 of liquid O_2F_2 to 0.5 cm^3 of liquid CH_4 at 90 K resulted in a violent explosion. O_2F_2 reacts instantaneously with solid C_2H_5OH producing a blue flame and an explosion. Addition of acetone to a mixture of O_2F_2 and dry ice resulted in sparking accompanied by an explosion. A 2% solution of O_2F_2 in HF reacts violently with a flash with C_6H_6 at 195 K [2].

O_2F_2 mixes homogeneously at 116 K with equimolar amounts of CF_2Cl_2 or of CF_3Cl. It is immiscible with CF_4 at 90 K and with C_3F_8 at 140 K [2, 18]. Less than 1% of O_2F_2 is soluble in CF_4 at 116 K. C_3F_8 dissolves some O_2F_2 at 130 K [2]. No reaction occurs between O_2F_2 and CF_4 at 195 K [1]. A mixture of O_2F_2 and CF_3CN is explosive at 77 K [23]. COF_2 reacts with O_2F_2 to give CF_3OOOF [32, 33].

C_2F_4 reacts on condensing onto solid O_2F_2 at 77 K with flashes forming COF_2, CF_4, and smaller amounts of C_2F_6, CF_3OOCF_3, and SiF_4. With Ar as diluent, the reaction also produces CF_3OF, C_4F_{10}, and OF_2. When C_2F_4 was highly diluted with He and passed at 2 to 3 Torr through the reaction vessel cooled to 77 K few flashes occur on warming the mixture. The reaction products included all compounds (except OF_2) obtained previously plus CO_2, $C_2F_5OCF_3$, and $\overline{CF_2CF_2CF_2CF_2O}$ [34]. The reaction of O_2F_2 with $CF_3CF{=}CF_2$ takes place smoothly in CF_3Cl at 70 K to give a 75:25 mixture of $CF_3CF(OOF)CF_3$ and $CF_3CF_2CF_2OOF$ plus smaller amounts of COF_2, C_2F_6, C_3F_8, CF_3OOF, SiF_4, and a thermally unstable mixture of perfluoroalkyl compounds [35], see also [25, 32, 33]. Little reaction or sometimes explosions occurred in the reaction of O_2F_2 with cyclo-C_3F_8. Explosive reactions were observed on reacting O_2F_2 with tetrafluoroethylene oxide [32, 33]. In recording the IR spectrum of O_2F_2 at 80 to 90 K, polyethylene was used as the window for the cell [36]. O_2F_2 attacks Teflon if used in an absorption cell [37].

Other Compounds

BF_3 reacts with O_2F_2 at low temperatures to give the dioxygenyl salt O_2BF_4 [29, 36, 38, 39]. The reaction is complete within 10 min at 147 K [36].

O_2F_2 does not attack quartz. Solid SiF_4 does not react with liquid O_2F_2 [1, 2]. About 20% of SiF_4 is soluble in liquid O_2F_2 without noticeable reaction [1, 2, 18]. At about 195 K the reaction of an O_2F_2–SiF_4 mixture is caused only by decomposition of O_2F_2 [1, 2].

PF_3 reacted with O_2F_2 at 125 K forming PF_5 and O_2. Some of the formed oxygen reacted with PF_3 giving a white solid which was fairly stable at 273 K. The solid, which decomposes at >273 K, is presumably polymeric POF_3. On warming the PF_3–O_2F_2 mixture quickly, it ignited [1, 2]. The reaction of O_2F_2 with POF_3 at 113 K gave a solid which decomposed at 195 K forming POF_3 and O_2 [27].

At temperatures near its melting point, O_2F_2 reacts with the pentafluorides MF_5, $M = P$ [27, 38, 40, 41], As [27, 40, 41], Sb [27, 29, 40, 41], or Bi [41], to give the dioxyenyl salts O_2MF_6.

A mixture of O_2F_2 and $ClO \cdot AsF_5$ yielded ClO_3F, O_2, F_2, Cl_2, and unidentified products at 113 K [27]. The reaction of SbF_3 with O_2F_2 gave a solid, but no dioxygenyl salt [27]. O_2F_2 reacted with polymeric VF_5 between 154 and 195 K forming the intermediate $F{-}O\cdots O\overset{\delta+}{\underline{\cdots}}F\overset{\delta-}{\cdots}V_2F_{10}$ or $O_2F^+ + F^- + V_2F_{10}$. The intermediate decomposed rapidly at 298 K to give the salt $O_2V_2F_{11}$ [42]. Very unstable white solids, presumably O_2WF_7 and O_2MoF_7, were formed from O_2F_2 and WF_6 and MoF_6, respectively, between 110 and 120 K [29].

The reaction with CsCl gave CsF, O_2, and Cl_2 (no details) [27]. No fluorination reaction, but only decomposition of the components, was observed in the reaction between O_2F_2 and NaOC(O)OC(O)ONa [44]. No reaction occurred with $CsClF_4$ or $CsBrF_6$ at 195 K. With $CsBrF_4$ possibly $CsBrF_6$ forms. No O_2PtF_6 was obtained from O_2F_2 and PtF_4 at 113 K [27]. O_2F_2 did not attack AgCl windows of an IR cell [36]. O_2F_2 reacts with oxides, fluorides, or oxide fluorides of plutonium at room temperature and below to give volatile PuF_6. This process is used in the nuclear industry to remove plutonium compounds formed in nuclear processes [43].

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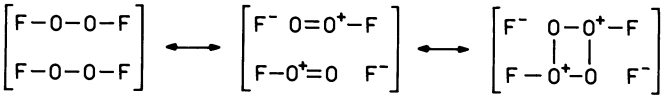
3.12 Ionic and Polymeric O_2F_2 Species

Since $O_2F_2^+$ has not been observed in the O_2F_2 mass spectrum, the bond dissociation energy $D(F–O_2F^+)$ may be zero [1], see also [2].

Several features of the IR absorption spectrum around 1280 cm^{-1} were assigned to the O–O stretching vibration of di- and polymeric species, see p. 95. Assuming ν(O–O) of the monomer to be at ~1500 cm^{-1}, the above assignment would be in accordance with the valence bond models for $(O_2F_2)_2$ [3]:



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3.13 Trioxygen Difluoride, O_3F_2

CAS Registry Number: *[16829-28-0]*

Review

The first reports of the synthesis of trioxygen difluoride by electric discharge through an F_2–O_2 mixture in 1938 [1] and by UV photolysis of a liquid F_2–O_2 mixture in 1941 [2] were regarded with scepticism, since no quantitative analysis of the product was given. Furthermore, the formation of a mixture with the composition O_3F_2, formed by dissolving O_2 in O_2F_2 during the preparation, could not be excluded. It was later shown [3] that the product, which is a dark red, viscous liquid at 90 K, should be regarded as a definite compound. But, investigations of its physical properties fueled doubts on the existence of the O_3F_2 molecular entity.

O_3F_2 is a very strong oxidizer, similar to O_2F_2. Solutions of O_3F_2 in liquid O_2 were investigated as rocket propulsion systems. It is an endothermic compound and decomposes at ~115 K to give O_2F_2 and O_2 and at ~200 K to give O_2 and F_2, with heat evolution. It melts at about 83 K. The extrapolated boiling point is 213 K.

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3.13.1 Preparation

The compound was prepared by quantitative conversion of an O_2–F_2 mixture (3:2 by volume) in a glow discharge (20 to 25 mA, 2.0 to 2.2 kV) at a total pressure of 12 ± 1 Torr. O_3F_2 condensed on the reactor walls which were kept at 77 or 90 K. The yield reached 3 to 4 g O_3F_2/h [1]. It was noted [2] that the desired product can be by no means always synthesized by this method. As a rule, O_2F_2 is formed in the synthesis of O_3F_2, and the oxygen present in excess of the amount required for the synthesis of O_2F_2 either does not react at all or is converted into O_3 [2]. Objections have been given on energetic grounds [16]. This method of preparing O_3F_2 is also described with some variations [3 to 7]. An apparatus for continuous production has been claimed [8].

O_3F_2 is obtained (production rate 1.75 g/h) by passing a gaseous OF_2–O_2 mixture (feed rate 900 cm^3/h) through an electric discharge (maximum electric power 60 W) at 90 K and ≤ 10 Torr total pressure [9].

A continuous production of O_3F_2 in liquid oxygen (see p. 107) by photolysis of O_2–F_2 mixtures was described [10]. O_3F_2 may be distilled between 96 and 114 K at 0.1 to 1.5 Torr with only slight decomposition [1, 4]. It can be stored for a long time at 77 K in darkness in Pyrex. The rate of decomposition, given as the fraction decomposed per hour, is about 3.6×10^{-5} at this temperature [4]. In view of the use of O_3F_2 as an oxidizer in propellant fuels, acceptance criteria for "good" O_3F_2 based on its melting point were reported [11].

The matrix isolation of O_3F_2 as an intermediate in the formation of $^{16}OF_2$ from $^{18}OF_2$ in an $^{16}O_2$ matrix according to

$$^{18}OF_2 + {}^{16}O_2 \rightarrow F^{18}O^{16}O^{16}OF \rightarrow {}^{16}OF_2 + {}^{16}O^{18}O$$

was briefly mentioned [17].

The **standard enthalpy of formation** of O_3F_2 from the elements was determined to be $\Delta H^\circ_{f,298} = 6.24 \pm 0.75$ kcal/mol, obtained from the heat of decomposition of liquid O_3F_2 into O_2 and F_2 [12]. Other reported values are $\Delta H^\circ_{f,298.15} = 3.8$ kcal/mol [13] and $\Delta H^\circ_{f,298} = 6.42 \pm 1.10$ kcal/mol [14]. $\Delta H_f = -11.23$ kJ/mol was obtained by a semiempirical SCF–MO calculation (MINDO) [15].

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3.13.2 Physical Properties

Structure

O_3F_2 was investigated spectroscopically in order to elucidate its molecular structure, but no definite conclusion could be drawn about the molecular entity, as shown in the following short summary.

The appearance of only one ^{19}F NMR signal for O_3F_2 was interpreted by a model consisting of O_2F_2 and interstitial oxygen [1]. This model was dismissed since in a further study the singlet was resolved into a doublet. Moreover, the expected release of the interstitial oxygen, during the reaction of O_3F_2 with BF_3 yielding O_2BF_4, was not observed [2]. ^{17}O and ^{19}F NMR spectra of an O_3F_2 specimen were interpreted by a model consisting of an O_2F_2–O_4F_2 mixture in equilibrium with O_2F radicals that decompose irreversibly on raising the temperature [3] according to

$$[O_2F_2, O_4F_2] \rightleftharpoons 2OOF \rightarrow O_2F_2 + O_2$$

For critical remarks, see [4]. Cryogenic mass spectrometry of O_3F_2 led to the assumption that O_3F_2 consists of loosely bound O_2F and OF radicals [5], see [4]. Studies of the ESR spectrum that is identical with that of O_2F_2 and caused by O_2F radicals also did not lead to a reasonable model of the O_3F_2 molecule [6, 7].

Energetic and structural parameters have been calculated by an ab initio [8] and a semiempirical [9] SCF–MO method. A zig-zag, skew chain structure (point group C_2) was found [8, 9]. A tetrahedral form with a central O atom, OF_2O_2, was suggested [10], since O_3F_2 is isoelectronic with CF_4. The electronic structure has previously been considered in [11] (special case n = 1 of the series $F(O_2)_nOF$) and in [5] (single-electron bond between the radicals OF and O_2F). The dipole moment $\mu = 0.22097$ D has been calculated [8]. Internuclear distances r in Å, bond angles α and dihedral angles Φ from the two SCF–MO calculations [8, 9] are:

r(O–F)	r(O–O)	α(OOF)	α(OOO)	Φ(OOOF)	Φ(FO···OF)	Ref.
1.3564	1.4069	103.77°	102.76°	—	88.37°	[8]
1.481	1.331	112.7°	120.2°	71.1°	—	[9]

Thermal Properties

The van der Waals constants $a = 9.03 \times 10^6$ atm·cm^6·mol^{-2} and $b = 9.29$ cm^3/mol were calculated by means of correlation increments [12].

Measured densities ϱ (in g/cm^3) of liquid O_3F_2 are represented by $\varrho = 2.357 - 0.00676\,T$ for $T = 82$ to 90 K [13], for critical remarks, see [14].

O_3F_2 solidifies at 83 K and melts at 84 K. It is always a liquid at 90 K but may be supercooled to 77 K [13]. The melting point 82.3 K is quoted in [15]. Measured vapor pressures (p in Torr) fit the equation $\log p = 6.1343 - 675.57/T$ for $T = 79$ to 114 K. Thus, the equation given in [13] and quoted in other publications (e.g. [15, 16]) is in error [14]. Single values are $p = 0.010$ at 83.052 K, 0.100 at 94.693 K, 1.00 at 110.130 K, and 10.00 Torr at 131.580 K. The extrapolated boiling point is 213 K (decomposition). Estimations gave the vaporization enthalpy $\Delta H_v = 4.581 \pm 0.200$ kcal/mol at 121 K, entropy $\Delta S_v = 21.51$ cal·mol^{-1}·K^{-1} [14], and the molar heat capacity of gaseous O_3F_2 $C_v = 16.0 \pm 1.5$ cal·mol^{-1}·K^{-1} [17]. Calculations by means of correlation increments gave $\Delta H_v = 3.805$ kcal/mol and the critical constants $T_{cr} = 350.9$ K, $p_{cr} = 38.7$ atm, $V_{cr} = 144.9$ cm^3/mol, and $\varrho_{cr} = 0.601$ g/cm^3 [12].

Optical Properties

The molar extinction coefficient between 350 and 750 nm is claimed to have been measured with a solution of "O_3F_2" in a $CClF_3$–CCl_2F_2 mixture at 77 K [18], see also a comparison with the data of other oxygen fluorides [19].

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3.13.3 Chemical Behavior

Thermolysis. Photolysis

O_3F_2 is stable at liquid-nitrogen temperatures [1 to 3].The decomposition half-life at 77 K is about two years [1]. At higher temperatures, O_3F_2 decomposes exothermally to give O_2F_2 and O_2. The rate of decomposition, given as fraction decomposed/h, is 3.6×10^{-5} at 77.3 K, 8.3×10^{-5} at 79.4 K, $\sim1.4\times10^{-3}$ at 89.5 K, 7.2×10^{-2} at 113.8 K, and 6.12×10^{-2} at 116.0 K. The activation energy of decomposition is 3.7 kcal/mol. At higher temperatures (~200 K), the decomposition of O_2F_2 leads to O_2 and F_2, as the final products of the O_3F_2 decomposition [1, 2]; for determination of the heats of decomposition, see [3].

An electric spark did not cause O_3F_2 to explode [1, 2]. An approximate detonation velocity of pure O_3F_2 was calculated to be 550 m/s for the reaction $2O_3F_2(l) \rightarrow 3O_2(g) + 2F_2(g)$, $\Delta H_{90} = -6.94$ kcal, assuming the products to be ideal gases [5].

Light causes a slow decomposition of O_3F_2 into O_2F_2 and O_2 [4].

Saturated solutions of O_3F_2 in liquid O_2 are relatively stable when stored at 90 K in darkness [5].

Reactions with Elements

No noticeable reaction occurs between O_3F_2 and H_2 at 77 K. The reaction with H atoms gave HF, H_2O, and H_2O_2 [2].

O_3F_2 is insoluble in liquid O_2 at 77 K and slightly soluble at 90 K forming a pale yellow solution [1]. The solubility is 0.046% and 0.11% by weight at 77 and 90 K, respectively [2, 6]. O_3F_2 mixes homogeneously with O_3 at 90 K, this mixture readily explodes [2]. The solutions of O_3F_2 in liquid O_2 have been investigated as rocket propulsion systems. The solutions are hypergolic when combined with most of the fuels used for propellant systems [2]. O_3F_2 as ignition additive was first proposed in 1965 [7]. Reviews cover preparation, handling, and storage of O_3F_2–O_2 solutions and materials resistant to this system [6, 8, 9]. Environmental limits for reliable hypergolic ignition of the O_3F_2–O_2 solutions with gaseous and liquid hydrogen were investigated [10].

N_2 and F_2 are immiscible with O_3F_2 at 77 K [2]. Gaseous F_2 did not react with O_3F_2. On passing F_2 through an electric discharge, O_3F_2 is fluorinated giving O_2F_2 [1, 2]. When liquid O_3F_2 came into contact with solid Br_2 or I_2 at 90 K, a white flash and mild explosions occurred [1, 2]. With an 8% O_3F_2–CF_3Cl solution, no reaction was observed with I_2. A 50% solution of O_3F_2 cooled to 90 K reacts visibly with I_2 crystals; a mild flash and gas evolution occur upon adding I_2 crystals, precooled to 195 K. IF_5, IF_7, and I_2O_5 are among the reaction products [2]. Cl_2 reacts with O_3F_2 at 113 K to give ClO_2, ClO_2F, and ClO_3F [11].

A mild explosion and a bright white flame result upon contact of a drop of liquid O_3F_2 with red phosphorus powder at 90 K, and an instantaneous blue flame is produced by adding liquid O_3F_2 to flowers of sulfur at 90 K which after a while turned white with occasional mild explosions. The addition of liquid O_3F_2 to powdered wood charcoal resulted immediately in a yellow flame at 90 K. On raising the temperature the mixture exploded [1, 2].

Reactions with Compounds

O_3F_2 mixes homogeneously with OF_2 or O_2F_2 at 116 K [2]. It is only slightly soluble in OF_2 at 90 K [1].

The addition of one drop of O_3F_2 to anhydrous NH_3 (both at 90 K) results in an instantaneous yellow-white flame accompanied by mild explosions. When one drop of O_3F_2 is added to solid N_2H_4 at 90 K an instantaneous powerful explosion occurs [1, 2]. No reaction is observed with NO at 90 or 195 K [11]. Mixing a 5% O_3F_2–CF_3Cl solution and pure FNO_2 at 90 K gives, without any reaction, a homogeneous solution. Pure O_3F_2 does not dissolve solid FNO_2 nor react with it at 90 K. At 116 K, the components are liquid and mix homogeneously forming a red-brown, very fluid solution. Above 125 K, O_2 evolution is observed due to the decomposition of O_3F_2 [2]. No reaction is observed between O_3F_2 and NF_3 at 77 or 90 K. O_3F_2 is immiscible with NF_3 at 90 K [2].

ClF and ClF_3 are immiscible with O_3F_2 at 90 K. ClO_3F mixes homogeneously with O_3F_2 at 127 K [2]. A spontaneous reaction with sparks and evolution of gas occurs on dropping liquid O_3F_2 onto solid ClF cooled in a liquid-oxygen bath. At 77 K, a very slow reaction between solid O_3F_2 and solid ClF gives unidentified blue and violet compounds [2], for remarks about these products, see [12].

The reaction of O_3F_2 with SO_2 yields, on warming the mixture from 90 to 147 K, 63.5% FSO_2F, 4.8% FSO_2OSO_2F, 19.0% FSO_2OOF, 12.7% FSO_2OF, and SOF_4 [13]. O_3F_2 reacts with BF_3 at 135 K by way of the O_2F radical to give O_2BF_4 [14, 15].

When one drop of O_3F_2 is added to a few drops of liquid CH_4 at 90 K an instantaneous, loud, powerful explosion occurs. O_3F_2 does not react with solid C_2H_5OH at 90 K. When removed from the liquid-oxygen bath, however, the mixture bursts immediately into a blue-white flame accompanied by mild explosions. O_3F_2 mixes homogeneously with CF_2Cl_2 or CF_3Cl at 116 K. At 90 K, CF_2Cl_2 and CF_3Cl dissolve about ⅓ of their volume of O_3F_2. Tetrafluoromethane is immiscible with O_3F_2 at 90 K. At 116 K, O_3F_2 is only slightly soluble in CF_4. Even in high dilution in liquid oxygen, O_3F_2 initiates spontaneous combustion when added to organic matter, for details, see [2].

A 1.5% O_3F_2–CF_3Cl solution does not react with KO_3 at 90 K. At higher temperatures, only decomposition of O_3F_2, but no reaction was observed with KO_3 [2]. No reaction occurs with $CsClF_4$ at 66 K. The reaction of O_3F_2 with AsF_5 at 113 K gives O_2AsF_6 [11].

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3.14 The O_2F Radical (OOF Isomer)

CAS Registry Numbers: O_2F *[15499-23-7]*, ^{17}OOF *[15891-85-7]*, $^{17}O_2F$ *[15844-91-4]*

Review

The O_2F radical was first detected as a paramagnetic impurity in O_2F_2. Electron spin resonance and infrared spectral techniques were applied toward its characterization. O_2F plays a key role in fluorine-oxygen chemistry.

3.14.1 Formation and Detection

Occurrence in O_2F_2, O_3F_2, and O_4F_2

As early as 1965, the radical was detected by its electron spin resonance (ESR) spectrum taken of neat O_2F_2 (for preparation of pure O_2F_2, see p. 84) and a solid solution of 3 vol% O_2F_2 in CF_3Cl, both at 77 K. The radical results from the decomposition process $O_2F_2 \rightarrow O_2F + F$. The radical concentration in O_2F_2 was estimated as $5 \times 10^{-4} \leq [O_2F]/[O_2F_2] \leq 5 \times 10^{-3}$ at 77 K [4]. This study was followed by similar ones with solid and liquid O_2F_2 [35, 36] and with liquid solutions of O_2F_2 in CF_3Cl [20, 37]. The O_2F radical was also detected by its IR absorption when O_2F_2 from a high-voltage glow discharge was slowly cocondensed with matrix gases at 20 K [40], by its mass spectrum when O_2F_2 was vaporized through a heated alumina tube [41], and by its UV absorption during the photolysis ($270 \leq \lambda \leq 390$ nm) of O_2F_2 dissolved in liquid Ar at 77 K [11]. O_2F formation by way of O_2F_2 decomposition is further supported by the chemical behavior of O_2F_2: Dioxygen difluoride acts as $O_2F + F$ [40] in reactions with SO_2, where lesser amounts of FSO_2OOF besides F_2SO_2 are formed [42, 43], with hexafluoropropene C_3F_6 [44], and with BF_3 forming the dioxygenyl salt O_2BF_4 [45], see also [32]. O_2F formation was assumed to be the primary step in the O_2F_2 thermal decomposition, $O_2F_2 + M \rightarrow O_2F + F + M$ [39].

In dilute samples of tetraoxygen difluoride, O_4F_2, in CF_4 at 77 K the O_2F radical was detected by ESR spectroscopy [37]. O_2F may be the major species in the vapor above liquid O_4F_2 and may be responsible for the rapid reaction of O_4F_2 with BF_3 [45], see also [32].

The equilibrium $O_4F_2 \rightleftharpoons 2O_2F$ was discussed [12] and later shown [46] to be of key importance in the preparation of the violet compound then believed to be ClF_3O_2 [47]. The mixture with components $O_4F_2 \rightleftharpoons 2O_2F$ and O_2F_2 was suggested to be the trioxygen difluoride, see p. 103 [32, 48].

O_2F was itself claimed to be a stable solid at 77 K with a melting point of 90 K (sic) [10]. The number density of molecules in the neat solid was quoted as 2.2×10^{22} cm^{-3}, which implies a density of 1.87 g/cm^3. From the method of preparation described [10] (electric discharge through a 2:1 O_2–F_2 mixture), the substance in question is likely to be O_4F_2 containing O_2F radicals, see p. 129.

Formation from $F + O_2$ and $F + O_3$

The radical was first detected by its IR absorption bands which appeared during the photolysis of F_2–O_2 or OF_2–O_2 mixtures in O_2, N_2, or Ar matrices at 4 K [1]. It is formed by the addition of F atoms, from photolyzed F_2 or OF_2, to O_2 molecules [2]:

$$(1)\quad O_2 + F \rightarrow O_2F$$

The identity of the radical was confirmed by further matrix IR studies at 20 K. The diffusion behavior was tested with photolyzed F_2–O_2 mixtures [2] and the isotopic splittings from all possible ^{16}O–^{18}O combinations were obtained with F_2 diluted in an O_2 matrix at the ratio 1:250

[3]. Numerous methods are given in the following two tables for the detection of the O_2F radical coming from reaction (1) or from the corresponding gas-phase reaction:

$$(1M)\quad O_2 + F + M \rightarrow O_2F + M$$

Formation with F from F_2 (phot. or rad. denotes photolysis or radiolysis):

F production	phot.	phot.	rad.	phot.	discharge	phot.	phot.	discharge
O_2F detection	ESR	IR	ESR, IR	ESR, UV	MS	UV	IR	IR
conditions	a)	b)	c)	d)	e)	f)	g)	h)
Ref.	[13]	[55]	[12]	[6, 7, 11]	[8]	[6, 7, 15]	[56]	[57]

a) O_2 and F_2 in Ar at 4.2 K. Photolysis by Hg lamp. – b) F_2 in O_2 or O_2–F_2 in Ar at 12 K. Photolysis by red and near-IR laser radiation. – c) F_2–O_2 mixture at 77 K, radiolyzed by 3-MeV bremsstrahlung. – d) F_2–O_2 in Ar at 87 K, photolyzed by Xe lamp. – e) Microwave discharge through F_2–He; products added to O_2 in a flow system at 272 to 362 K. – f) F_2–O_2 mixtures, flash photolyzed at 298 K. – g) F_2–O_2 mixtures, photolyzed at 200 K by an excimer laser ($\lambda = 350$ nm). Detection of O–O stretching mode ν_1. – h) Microwave discharge through F_2–He at 298 K. Products added to O_2 in a flow system.

Passing an F_2–O_2 mixture (1 to 6 Torr) through a quartz reactor heated to 513 to 773 K led to O_2F radicals, which were accumulated on a liquid-N_2 cooled finger and detected by ESR. The apparently low activation energy for the production of O_2F points toward a heterogeneous production of F atoms [17]. O_2F radicals, detected by IR, were also generated by photolysis of F_2 and NO_2 in N_2 at 8 K to give F and O_2, respectively, the latter coming from $NO_2 + h\nu \rightarrow NO + O$, $O + NO_2 \rightarrow NO + O_2$ [18] and by photolysis of F_2 and N_2O in Ar at 4 K, with O_2 present as an impurity in F_2 [19].

Formation with F from other sources (phot. or rad. denotes photolysis or radiolysis):

source	OF_2	NF_3	CF_4	CF_4	ClF_5	SF_6	WF_6	IF_7
F production	phot.	discharge	rad.	discharge	phot.	discharge	phot.	phot.
O_2F detection	ESR	IR	ESR	IR	UV	IR	—	UV
conditions	a)	b)	c)	d)	e)	d)	f)	e)
Ref.	[20]	[21]	[22]	[57]	[23]	[57]	[24]	[23]

a) OF_2–O_2 mixture at 95 K. O_2F is formed by $O_2 + F \rightarrow O_2F$ and possibly by $OF_2 + OF \rightarrow O_2F + F_2$. – b) The products of a microwave discharge through NF_3 in Ar are codeposited with O_2 at 14 K. – c) CF_4 containing trace amounts of O_2 is irradiated by electrons at 93 to 113 K. CF_4 with small amounts of O_2 enriched in ^{17}O was also studied. – d) Microwave discharge through CF_4–He or SF_6–He at 298 K. Products added to O_2 in a flow system. – e) ≤ 5 Torr ClF_5 or ≤ 0.8 Torr IF_7 in 300 to 600 Torr O_2 at 298 K. – f) The delay times between chemical pumping of an HF laser to threshold and the initial photolytic flash providing F atoms to produce HF were measured with and without addition of O_2 to a WF_6–H_2–He mixture in the laser resonator. Reaction (1M) increases the delay time.

Formation of O_2F by means of the addition reaction (1) or (1M) is assumed to take place in the following processes: thermal reaction of F_2–O_2 mixtures with AsF_5 and SbF_5 at 200 atm and $\leq 200°C$ [25], of SF_4 with F_2 in the presence of O_2 [54]; O_2-inhibited thermal reaction between H_2 and F_2 [26]; photochemical reaction of an F_2–O_2 mixture with AsF_5 and SbF_5 [27], of F_2 with O_2 at $-42°C$ [28], of F_2 with CO_2 (O_2 from the wall reaction of F) [29], of F_2 with F_2CO (O_2 added) [30], of F_2 with OSF_4 (O_2 added or from the wall reaction $2F_2 + SiO_2 \rightarrow SiF_4 + O_2$) [31]; reaction of F_2 with O_2 in electrical discharges [32 to 34].

Rate constant k of (1M) $O_2 + F + M \rightarrow O_2F + M$. A few data for the low-pressure, third-order limit k_0 are reported in "Fluorine" Suppl. Vol. 2, 1980, p. 140. A "preferred" value for k_0, multiplied by the third body concentration [M], is given in the most recent review on kinetic and photochemical data for atmospheric chemistry [51]: $k_0 = 1.3 \times 10^{-32} \cdot [N_2] \cdot (T/300)^{-1.4 \pm 1}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ from 200 to 300 K. The error in log k_0(300 K) is ±0.3. The numerical factor (k_0 at 300 K) is an average of a value measured at 298 K, $k_0 = (1.0 \pm 0.3) \times 10^{-32} \cdot [O_2]$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [24], and of another preferred value at 298 K, $k_0 = 1.6 \times 10^{-32} \cdot [N_2]$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, given in a previous review [60]. The temperature coefficient was taken [51] from a calculation [61] of third-order rate constants for recombination reactions, based on a theory by Troe [62] for second-order rate constants of unimolecular dissociation, and the equilibrium constant [51]. The preferred value [60] had been based upon an average of three measurements for M = He [8, 14, 52], an average of three determinations for M = Ar [9, 14, 52], and the relative efficiencies of N_2, He, and Ar [14]. A previous calculation [5] also used Troe's [62] theory. A preferred value for the high-pressure, second-order limit, $k_\infty = 3 \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ over the range 200 to 400 K, was estimated [16, 60] from calculated limits [53] for $NO + F + M \rightarrow FNO + M$.

Formation of O_2F in the $F + O_3$ reaction system was explained by the reaction $O_3 + F \rightarrow OF + O_2$, followed either by $2OF \rightarrow O_2 + 2F$ and (1M) or by $O_3 + OF \rightarrow O_2F + O_2$. Rotational spectra observed by far-IR laser magnetic resonance (LMR) were assigned to O_2F on chemical, kinetic, and qualitative spectroscopic grounds [58]. Detection by IR LMR in the range of ν_1 was also used [59].

Decomposition of Oxygenyl Salts

The gas-phase O_2F radical is formed by the thermal decomposition of solid O_2AsF_6 (UV [19] or Raman [63] detection), solid O_2SbF_6 (far-IR LMR detection) [58], or solid O_2BF_4 (^{18}F tracer study) [45].

Other Methods

The O_2F radical is formed in liquid OF_2 photolyzed by daylight [35] or by UV radiation [20, 35]. The radical was identified by its ESR spectrum which was identical with that of the paramagnetic species in higher oxygen fluorides [20, 36], see also [37]. O_2F was tentatively identified in the mass spectrum of an OF_2–SO_2 mixture at 77 K radiolyzed by 3-MeV bremsstrahlung [38]. The formation of O_2F in photolyzed OF_2 may be due to the primary step $OF_2 + h\nu \rightarrow OF + F$, followed by $OF_2 + OF \rightarrow O_2F + F_2$ [20]. O_2F is also obtained by UV photolysis of FSO_2OOF in solid $CFCl_3$ (ESR detection) [50].

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3.14.2 Enthalpy of Formation ΔH°_f in kcal/mol

$\Delta H^\circ_{f,298} = 3.0 \pm 5$ (12.6 ± 21 kJ/mol) and $\Delta H^\circ_{f,0} = 3.4 \pm 5$ were adopted [1] on the basis of two somewhat different figures for the enthalpy change ΔH of the reaction $O_2F_2 \rightarrow O_2F + F$. One, $\Delta H = 17.3$ kcal/mol had been estimated [2] from an older kinetic study [3] of the thermal decomposition of O_2F_2. Employing $\Delta H^\circ_{f,298}(O_2F_2) = 4.73$ kcal/mol [4] and neglecting the activation energy for the reverse reaction yielded $\Delta H^\circ_{f,298} = 3.2$. The other, $\Delta H = 16.5$ follows from the assumption ΔH for $O_2F_2 \rightarrow O_2F + F$ to be one half the enthalpy for $O_2F_2 \rightarrow 2F + O_2$. Then, $\Delta H^\circ_{f,298} = 2.4$ [1]. Other values include $\Delta H^\circ_{f,298} = 3.0$ [5] and $\Delta H^\circ_{f,298} = 3.5$ [2]. $\Delta H^\circ_{f,298} = 12.55$ kJ/mol (on the basis of the above JANAF value [1]) was used in a more recent calculation of the rate constant for the reaction $O_2 + F \rightarrow O_2F$. This $\Delta H^\circ_{f,298}(O_2F)$ implies an enthalpy change $\Delta H = -66.36$ kJ/mol for that reaction [6] (cf., however, below).

A distinctly larger formation enthalpy, $\Delta H^\circ_{f,298} = 12 \pm 3$ (50 ± 12 kJ/mol), was reported in a compilation [7] without the source of that value being clear and repeated in a review [8, 9] on kinetic data for atmospheric chemistry. In the last version [9], however, the enthalpy for

$O_2 + F \rightarrow O_2F$, $\Delta H = -66$ kJ/mol, was adopted (being incompatible with the reported [9] O_2F formation enthalpy).

A semiempirical SCF–MO procedure (MNDO) yields $\Delta H_f^\circ = 24.1$ [10].

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3.14.3 Molecular Properties and Spectra

3.14.3.1 Electronic Structure

Ground State

A weak O–F bond (compared to that in OF_2) and a strong O–O bond (close to that of O_2) were derived from the early matrix IR studies. Bond orders <0.5 and ~2 were given [1 to 3]. The correspondingly long O–F and short O–O bond distances were only recently verified by an IR diode laser spectrum [4]. Following the VB description of O_2F_2 [5], a contribution of the ionic form $\cdot O^+{=}O\ F^-$ was assumed [1]. A simple MO description [6, 7] was based on the analogous treatment of O_2F_2 [8]: A 2p orbital of fluorine can overlap with a lobe of a singly occupied π^* orbital of the oxygen molecule lying in the same plane to produce a weak O–F linkage ($(p\text{–}\pi^*)\sigma$ model). This picture was, however, criticized [9 to 12], since the interaction between F2p and the bonding π orbital of O_2 would be energetically more favorable. A more recent extended Hückel calculation [12] shows that bonding in O_2F is due mainly to the 2s rather than to the 2p orbitals of fluorine (see also below). The "Linnett structures" were reported for the radical [13]. For an "increased-valence formula", see [10, 14].

O_2F is a π radical; the highest MO containing the unpaired electron is perpendicular to the molecular plane (orbital 3a″, see below) [18, 19]. The ground term is $^2A''$ [15, 22]. One-electron energies were obtained by two ab initio calculations [16, 18] and are presented in the following table. The character of the orbitals, that is, their bonding, antibonding (marked with an asterisk), or nonbonding (n) properties [18] are also given.

orbital*⁾	3a″	10a′	2a″	9a′	8a′
$-\varepsilon_i$ in a.u. [16]	0.278	0.553	0.563	0.629	0.770
$-\varepsilon_i$ in a.u. [18]	0.105	0.381	0.525	0.528	0.635
orbital character [18]	π^*(O–O)	n	π(O–O)	σ(O–F)	σ(O–O)

*⁾ The orbital designations σ and π were used [16, 18]. It appears obvious, in particular from the definition given [18], that σ denotes in-plane orbitals (a′), while π are out-of-plane orbitals (a″).

One-electron energies were calculated and bonding properties of individual orbitals were also discussed according to the Hückel method [12, 17, 19].

The total energy was calculated by ab initio SCF methods [16, 20 to 22]. The lowest value obtained so far (unrestricted Hartree-Fock method) is $E_T = -248.928492$ a.u. [16]. Ab initio CI methods were also applied [22].

The atomic charge on F is given as −0.8 from a population analysis within a more recent extended Hückel calculation [12]. Two ab initio calculations [16, 22] and a CNDO calculation [15] agreed on a lower charge on F and a positive charge on the central O (charges on F and central O interchanged [16]). From simple Hückel calculations, the F atom has withdrawn 11% of an electronic charge from the O_2 molecule [19].

The electric dipole moment $\mu = 0.650$ D was calculated by the CNDO method [15]. Ab initio calculations gave $\mu = 0.4660$ and 0.7472 D [22] and 0.453 D (0.1783 a.u.) [16] (evaluated from components given in the original paper [16]). This latter value is believed to be an overestimate [16].

The components of the electric quadrupole moment were obtained from an ab initio calculation [16].

Excited States

Two relatively low-energy excitations, $n \rightarrow \pi^*$ and $\pi^* \rightarrow \sigma^*$(O–F), are assumed, since the isotropic $g = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$ from the ESR spectrum is close to the free electron value. The contribution of these excited states to the shift Δg have different signs and partly cancel each other [6, 18, 19, 25]. An absorption band observed at ~23800 cm^{-1} (see below) is assigned to the $n \rightarrow \pi^*$ transition on intensity grounds. A $\pi^* \rightarrow \sigma^*$(O–F) excitation energy of 9900 cm^{-1} will then be in accord with the measured g and its components, if no further excited states contributing to Δg exist below 40000 cm^{-1}. A low lying σ^*(O–F) orbital is also to be expected because of the small O–F bond dissociation energy in O_2F [18]. A band at 23800 cm^{-1} (420 nm) was observed upon radiolysis of a CF_4–O_2 system [25], O_4F_2 [26], and O_3F_2 [27], and was assigned to the O_2F radical [18].

A band at ~48000 cm^{-1} was assigned to a $\pi \rightarrow \pi^*$ transition on energy and intensity grounds [23]. The band was observed (at ~210 nm) in an F_2–O_2 photolytic system and was assigned to the O_2F radical by comparison of ESR spectra [28].

Excitation energies were also obtained by ab initio calculations for one [22] or two states [18], INDO calculations for two states [24], and CNDO calculations for three states [15].

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3.14.3.2 Ionization Potential E_i. Electron Affinity A. Polarizability α

$E_i = 12.6 \pm 0.2$ eV was measured from an electron impact study on O_2F by matching the ionization efficiency curve of O_2F^+ with that of Ar [1], see also [2, 3]. From the appearance potential of O_2F^+ in the mass spectrum of O_2F_2 (retarding potential difference method), $E_i \leq 13.2$ eV was estimated using an O–F bond dissociation energy of 0.8 eV for O_2F_2. With an estimated excess kinetic energy of 1.0 eV for the process $O_2F_2 \rightarrow O_2F^+ + F + e^-$, E_i was assessed as 12.2 eV [4]. $E_i = 12.19$ eV was calculated by the CI-CNDO method [5].

A = 1.91 eV was calculated by the CI-CNDO method [5].

$\alpha = 2.6243$ Å^3 was derived from the δ-function model of the chemical bond [6].

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3.14.3.3 Rotational Constants. Geometrical Structure

The O_2F radical is a near prolate symmetric top [1]. From the rotational constants given below, an asymmetry parameter $\varkappa = (2B - A - C)/(A - C) = -0.9667$ may be obtained. The setting of the principal inertial axes (corresponding to the order A>B>C for the rotational constants) [1] obviously implies the c axis to be perpendicular to the molecular plane. The following rotational ($\tilde{A}$, $\tilde{B}$, $\tilde{C}$), centrifugal distortion (Δ) and spin-rotation interaction (ε) constants were obtained from an IR spectrum of the ν_3 band (O–F stretching) taken with a tunable diode laser and using Zeeman modulation of the absorption lines. The constants (in cm^{-1}) are for the vibrational ground state; for data on the (001) vibrational state, see the original paper [1].

$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$10^7\Delta_N$	$10^6\Delta_{NK}$	ε_{aa}	$\varepsilon_{bb}+\varepsilon_{cc}$
2.619	0.334008	0.295365	5.3	−3.86	−0.02743	0.00018
±0.017	±0.000049	±0.000053	±1.9	±0.52	±0.00159	±0.00096

A reduced Hamiltonian [2] was used [1] for the rotational and centrifugal distortion constants (see also pp. 146/7). The spin-rotation splitting was analyzed [1] by an expression $\gamma(N+\frac{1}{2})$ [3] with $\gamma = [\varepsilon_{aa} - \frac{1}{2}(\varepsilon_{bb}+\varepsilon_{cc})] \cdot K^2/N(N+1) + \frac{1}{2}(\varepsilon_{bb}+\varepsilon_{cc})$ (N = rotational angular momentum excluding electronic spin, K = projection of N on the symmetry axis of the corresponding near prolate top).

Equilibrium internuclear distances r_e(O–O) = 1.200 ± 0.013 and r_e(O–F) = 1.649 ± 0.013 Å and a bond angle α_e(OOF) = 111.19° ± 0.36° were calculated from a preliminary analysis of the constants given above [1]. Prior to this measurement, the structural data of the O_2F_2 molecule had been used [4, 5], r(O–O) = 1.22, r(O–F) = 1.58 Å, and α(OOF) = 109.5°. Moments of inertia were reported for four isotopic species $^{16}O_2{}^{19}F$, $^{18}O_2{}^{19}F$, $^{16}O^{18}O^{19}F$, and $^{18}O^{16}O^{19}F$ [6]. A distance r(O–F) = 1.63 Å was inferred from force constants and from a comparison with O_2F_2 [7].

Bond lengths r(O–O) and r(O–F) and bond angle α(OOF) were also calculated by ab initio [8, 13], CNDO [9], INDO [11, 12], and MINDO [10] methods.

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3.14.3.4 Molecular Vibrations. Force Constants

The complete set of the three normal vibrations ν_1 (O–O stretch), ν_2 (bend), and ν_3 (O–F stretch), has only been observed by IR absorption of the radical isolated in various matrices. In the gas phase, the ν_1 band center (at 1489 cm^{-1}) was found with a Fourier transform IR spectrometer [2]. Only a small section of the ν_1 band around 1480 cm^{-1} was observed by tuning the Zeeman splittings of vibration-rotation transitions to selected lines of a CO laser (laser magnetic resonance, LMR) [1]. $\nu_3 = 579.31839 \pm 0.00035$ cm^{-1} (band origin) was measured with a tunable IR diode laser and using Zeeman modulation of absorption lines [3].

The matrix IR data in the following table result from studies of an O_2 matrix at 20 K [4] and an Ar matrix at 14 K [5]:

species	$^{16}O_2F$		$^{18}O_2F$		$^{18}O^{16}OF$		$^{16}O^{18}OF$	
matrix	O_2	Ar	O_2	Ar	O_2	Ar	O_2	Ar
ν_1 in cm^{-1}	1495.0	1490	1411.7	1407	(1454.6)	1449	(1453.1)	1449
ν_2 in cm^{-1}	376.0	—	366.6	—	(368.4)	—	(374.6)	—
ν_3 in cm^{-1}	584.5	583.5	560.1	559.0	581.2	581.0	563.4	562.0
remark		a)			b)		b)	

a) For an Ar matrix at 20 K: 1490 and 586 cm^{-1} [6]. – b) In parentheses: values calculated using a set of five force constants [4].

Some further values for $^{16}O_2F$ are: $\nu_1 = 1499.7$, $\nu_2 = 376.0$, and $\nu_3 = 586.4$ (O_2 and N_2 matrices at 20 K, $^{18}O_2F$ data in the original paper) [7]; $\nu_1 = 1494$, $\nu_3 = 584$ (Ar matrix at 4 K, $^{18}O_2F$ data in the original paper) [8]; $\nu_1 = 1501.2$, $\nu_3 = 589.2$ cm^{-1} (N_2 matrix at 8 K) [9]. An estimated value $\nu_2 = 290$ cm^{-1} [8] is incorrect [7].

The growth of the ν_1 bands of $^{16}O_2F$ (peaks at 1494.8 and 1490.2 cm^{-1}) and $^{18}O_2F$ (peaks at 1411.6 and 1406.9 cm^{-1}) was followed in O_2 matrices to obtain the laser excitation spectrum of the reaction between F_2 and O_2 in the red spectral region [10].

A Raman band at 1547 cm^{-1} was observed in the products of thermal decomposition of solid O_2AsF_6 at −142°C and identified as ν_1. The enlargement may be due to intermolecular interactions and electronic polarization [11].

Experimental fundamentals from the literature were also reported in a collection of vibrational energy levels of polyatomic transient molecules [12].

The following combination and overtone bands (in cm^{-1}) were observed in the IR absorption spectrum of O_2F isolated in an Ar matrix at 14 K [5]:

species	$\nu_2 + \nu_3$	$2\nu_3$	$2\nu_1$
$^{16}O_2F$	958	1153	2949
$^{18}O_2F$	925	1105	2786
$^{16}O^{18}OF$	—	—	2868

Root-mean-square amplitudes (in Å) at 298 K were calculated as u(O–O) = 0.0372, u(O–F) = 0.0696, and u(O···F) = 0.0785 [13].

Two sets of force constants of a generalized valence force field are given in the following table. The constants in the first row are derived from ν_3 (measured in the gas phase), the centrifugal distortion constants and the inertial defect, and the rotation-vibration constants α_3^X (X = A, B, C). The diagonal, third-order force constants F_{iii} (i = 1 to 3) were fixed at certain values (F_{333} was adjusted so as to reproduce the α_3^X) [3]. The constants in the second row are derived from O_2-matrix spectra [4]:

f_{OO} (mdyn/Å)	f_{OF} (mdyn/Å)	f_{OOF} (mdyn·Å·rad^{-2})	$f_{OO,OF}$ (mdyn/Å)	$f_{OF,OOF}$ (mdyn/rad)	Ref.
10.303 ±0.037	1.944 ±0.021	0.745 ±0.016	—	0.341 ±0.021	[3]
10.50	1.320	1.008	0.300	0.027	[4]

A restriction of the valence force field to only three diagonal constants does not warrant convergence [7], whereas inclusion of one nondiagonal constant does [7, 13]. A three-parameter force field reported elsewhere [8] was calculated with an estimated, incorrect bending frequency.

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3.14.3.5 **Bond Dissociation Energies** D in kcal/mol

$D(O_2–F) = 16$ (0.7 eV) may be derived from the relation $D(O_2–F) = D(FO–OF) + 2D(O–F) - D(FO_2–F) - D(O–O)$, if $D(FO–OF) = 2.1$ eV (see p. 94), $D(O–F) = 2.2$ eV (see p. 73), and $D(O–O) = 5.1$ eV are used and if $D(O_2–F) = D(FO_2–F)$ is assumed (as in [1, 2]). $D(O_2–F) = 18$ (0.8 eV) [1] is based on too high a value for D(FO–OF) and too low a value for D(O–F). $D(O_2–F) = 15$ is given [3 to 5] on the basis of $\Delta H_f(O_2F) = 3.5$ kcal/mol (see p. 113). $D(O_2–F) = 14 \pm 2$ follows from a kinetic study of the photochemical reaction between F_2 and CO_2 [6] and $D(O_2–F) = 13.5 \pm 2$ from similar studies with F_2 and SOF_4 [7]. $D(O_2–F) \approx 7$ [8] appears to be based upon $\Delta H_f(O_2F) = 12$ kcal/mol (see p. 113). $D(O_2–F) \approx 36$ was estimated from an approximate relation between bond order and bond length [9].

$D(FO–O) = 83$ (3.6 eV) may be derived from the relation $D(FO–O) = D(FO–OF) + D(O–F) - D(FO_2–F)$, if $D(FO–OF) = 2.1$ eV (see above), $D(O–F) = 2.2$ eV (see above), and $D(FO_2–F) \approx D(O_2–F) = 0.7$ eV (see above) are used. $D(FO–O) = 110$ (4.8 eV) [1] was based upon $D(FO–OF) = 4.5$ eV and $D(O–F) = 1.1$ eV, both values now believed to be in error.

The atomization enthalpy $\Delta H_{at}(O_2F) = 135$ kcal/mol [10] was probably based upon $D(O_2–F) = 18$ (see above) and $D(O–O) = 117$. $\Delta H_{at} = 136.9$ kcal/mol was deduced from a relationship between force constants and ΔH_{at} [11].

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3.14.3.6 Electron Spin Resonance Spectrum

Hyperfine Interactions. g Values

In liquid phases at low radical concentration ($\leq 5\times10^{19}$ cm^{-3} [1]), an isotropic doublet was observed which results from the hyperfine (hf) interaction with the ^{19}F nucleus. The ^{17}O hf structure was detected with samples enriched in ^{17}O: Due to the nuclear spin $I = 5/2$ of ^{17}O, each component of the central doublet is split into six lines of equal intensity for singly ^{17}O-labeled ^{17}OOF or $O^{17}OF$. For doubly labeled $^{17}O^{17}OF$, each component of the central doublet is split into 36 lines [4, 5]. The following table lists g values and isotropic hf coupling constants a in G measured in four different systems. The terminal O is denoted as O′. The two ^{17}O hf coupling constants were assigned to the central or terminal oxygen based on derived spin densities, the larger spin density being assigned to the terminal O [17]. The coupling constants are probably negative [5] (see also below).

system	T in K	g	a(^{19}F)	a(^{17}O)	a($^{17}O'$)	Ref.	rem.
OF_2 photolysis	77	2.0039 $\pm$0.0003	($\pm$)13.4$\pm$1.0	($\pm$)21.7$\pm$2.0		[3]	a)
O_2F_2 thermal decay	116	2.0033 $\pm$0.0003	($\pm$)15.9$\pm$0.1	($\pm$)14.9$\pm$0.5	($\pm$)22.4$\pm$0.3	[4]	b)
$CF_4(O_2)$ e^- irradiation	93 to 113	2.0038 $\pm$0.0001	($\pm$)12.83$\pm$0.05	($\pm$)14.50	($\pm$)22.17	[5]	c)
O_2F_2 solution in CF_3Cl	190 to 200	2.004 $\pm$0.0005	($\pm$)12.5$\pm$1	—	—	[6]	

a) OF_2 enriched to 1% ^{17}O. Spectrum ascribed to a radical O_nF with $n\geq2$. – b) Sample prepared from oxygen containing 51.2% ^{17}O. – c) Addition of small amounts of O_2 enriched to 27.7% ^{17}O.

In solid phases at low radical concentration (see above), an anisotropic spectrum is observed. The following table lists the components of the g tensor and the ^{19}F hf coupling tensor a in G measured in five systems. The isotropic constant $a_{iso} = -12.7$ G (-36.0 MHz) in solid Ar is in excellent agreement [8] with that obtained in liquid CF_4 (see above) [5].

system	O_2–F_2 photolysis	O_2–F_2 electrical discharge		O_2F_2 thermal decay	FSO_2OOF photolysis
matrix	Ar	O_2F_2	OF_2	O_2F_2	$CFCl_3$
T in K	4.2	77	25	77	93 to 113
g_1	2.0080	2.0083	—	2.0072	2.0080
g_2	2.0008	2.0001	—	2.0013	2.0024
g_3	2.0022	2.0022	—		
a_1	−102.6	(±)90.0	(±)112	(±)98.8	(±)98.3
a_2	+50.4	(±)43.7	(±)47	(±)24.0	(±)22.8
a_3	+14.0	(±)14.0	(±)12		
Ref.	[8]	[1]	[1]	[4]	[9]
remark	a)	b)		c), d)	d)

a) The spectrum had an additional complexity due to "forbidden" lines, in which an electron spin transition was accompanied by a nuclear spin flip. Thus, a determination of the relative signs of the hf coupling constants was possible: a_2 and a_3 must have a sign opposite to that of a_1. The same is true for the anisotropic contributions (b_1, b_2, b_3). The principal axes (assumed to be the same for the g and the hf coupling tensors) follow from semiquantitative considerations of the signs of the F2p spin densities and from a comparison of these signs with those of the b_i: Axis 1 is parallel to the O–F bond, axis 2 is perpendicular to the molecular plane. With the signs given above, the isotropic part of the coupling tensor becomes $a_{iso} = -12.7$ G (−36.0 MHz). $g_{iso} = 2.0037$. The components of a were given in MHz in the original paper [8], $a_1 = -288.4$, $a_2 = +141.1$, $a_3 = +39.2$, and subsequently converted into G [10]. – b) The appearance of the spectrum changed at higher radical concentrations: Only two asymmetric lines were observed at $\sim 5 \times 10^{20}$ cm^{-3}, and a singlet 25 to 30 G wide was observed at 2.2×10^{22} cm^{-3}. – c) Similar data were previously obtained [11], see also remarks in [12]. – d) Axial symmetry is assumed.

Components of the g tensor were calculated by ab initio SCF [13] and semiempirical (INDO) [14] methods. Ab initio UHF calculations seem to support a positive sign for $a_{iso}(^{19}F)$ and negative signs for $a_{iso}(^{17}O)$ and $a_{iso}(^{17}O')$ [15]. Ab initio RHF calculations, however, give negative signs for all isotropic coupling constants. The agreement between the calculated and the observed [11] anisotropic components of $a(^{19}F)$ is very poor and it was suggested that the species observed [11] was the radical O_3F rather than O_2F [16].

Spin Densities

The 2s densities in the following table were obtained from isotropic coupling constants. O′ denotes the terminal O:

F2s	O2s	O′2s	Ref.	remark
0.001	0.009	0.013	[17]	a)
0.00092	0.0093	0.014	[4]	b)

a) Based on earlier ESR data [5]. – b) The oxygen densities are assigned here to conform with those in the first row.

MINDO calculated 2s densities yield the isotropic coupling constants a = +12.81, −13.87, and −6.04 G for ^{19}F, ^{17}O, and $^{17}O'$, respectively [18]. A least-squares analysis of MNDO calculated F2s densities ϱ and observed ^{19}F coupling constants a (in G) of many F-containing radicals gives $a=2.04 \cdot 10^4 \cdot \varrho$; thus $|a|=6.7$ G for O_2F [19]. The F2p density is given as 0.077 [17], or 0.076 [4]. Strongly differing spin densities were calculated by a CNDO approximation under the assumption of a σ radical character for O_2F [2].

Total atomic spin densities at F, O, and O′ from two semiempirical calculations are 0.003, 0.282, and 0.715 (CNDO) [7] and 0.0055, 0.2039, and 0.7961 (INDO) [14].

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3.14.3.7 Visible and Ultraviolet Spectra

For IR spectra, see the section on molecular vibrations, p. 118.

A continuous absorption between 190 and 240 nm with a maximum at ~205 nm was obtained from the flash photolysis of a gaseous F_2–O_2 mixture at 298 K and partial pressures of 36 and 665 Torr. By comparison with the spectrum from a flash-photolyzed F_2–O_2 mixture in liquid Ar (see below), the absorption was ascribed mainly to the O_2F radical. Below 205 nm, O_2F_2 contributes to the absorption, too [1, 2]. The value of λ_{max} was also reported as 205 [3] and 206 nm [4]. O_2F absorption spectra were also observed with flash-photolyzed RF–O_2 mixtures (total pressure 300 Torr, RF partial pressures for R=F, 15 Torr; R=ClF_4, 3 Torr; R=IF_6, 0.5 Torr) [5] and with thermally decomposing O_2AsF_6 (λ_{max}=206 nm) [6]. Different numerical values are reported for extinction coefficients ε [2 to 4, 6]. An absorption cross section was given as 10^{-17} cm² at 220 nm [7].

The absorption spectrum of O_2F in liquid Ar at 87 K additionally shows a broad plateau in the >290 nm region and a weak maximum at 445 nm. The same spectral characteristics were observed with O_2F in liquid O_2 at 77 K or CF_4 [3]. The absorption of O_2F in liquid Ar was observed earlier between 190 and 260 nm. A shift of the maximum by ~3 nm to longer wavelengths (compared to the gaseous state) was noted. The spectrum could be ascribed to O_2F on the basis of ESR measurements. A small absorption maximum at 420 nm was observed [1, 2]. The absorption of electron-irradiated liquid CF_4 with trace amounts of O_2 began in the region 600 to 550 nm and increased down to <300 nm. But no conclusion could be drawn whether it was due to O_2F or O_4F_2 [8].

A photodecomposition threshold at 490 nm was observed for O_2F in solid Ar at 14 K from the decrease of IR absorption attributable to O_2F. But it was not possible to completely destroy O_2F even on prolonged irradiation with light of wavelengths shorter than 490 nm. The absorption maximum found in liquid media was supported [9].

The attribution of the observed maxima to excited states is discussed in the section on the electronic structure, p. 115.

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3.14.4 Thermodynamic Functions

The heat capacity C_p°, entropy S°, Gibbs free energy $(G^\circ - H_{298}^\circ)/T$, all in $cal \cdot mol^{-1} \cdot K^{-1}$, and the enthalpy $H^\circ - H_{298}^\circ$ in kcal/mol were calculated in intervals of 100 K [1] for the ideal gaseous state up to 6000 K on the basis of assumed geometrical parameters (see p. 117), vibrational frequencies for $^{16}O_2F$ [2] (see p. 118), and a spin multiplicity of two for the electronic ground state. Some values are listed below.

T	0	100	298	500	1000	2000	4000	6000
C_p°	0	8.242	10.611	11.843	13.132	13.688	13.853	13.884
S°	0	51.736	61.903	67.710	76.407	85.738	95.295	100.919
$-(G^\circ - H_{298}^\circ)/T$	∞	70.617	61.903	63.154	67.819	74.697	82.876	88.016
$H^\circ - H_{298}^\circ$	−2.688	−1.888	0	2.278	8.589	22.080	49.674	77.418

Similar values for C_p°, S°, and for $-(G^\circ - H_0^\circ)/T$ and $(H^\circ - H_0^\circ)/T$ were derived by Spratley et al. [3] between 100 and 1500 K in intervals of 100 K on the basis of their own frequency values. Some of the latter C_p° and S° data [3] are also reported in [4]. Thermodynamic functions were calculated for different isotopic species between 200 and 2000 K, but using a singlet electronic ground state [5].

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3.14.5 Chemical Behavior

ESR studies show the radical to be a key component in the reactions of dioxygenyl salts with substances like ClF, ClF_3, ClF_5, and ClF_3O [2]. Gaseous O_2F, detected by its UV absorption at ~210 nm, was used as a reagent in the chemical production of electronically excited species such as BrF and IF [3]. From these studies, bimolecular O_2F reactions are dynamically similar to three-body recombinations, the O_2 moiety playing the role of the third collision partner [4]. UV absorption was also employed in studying the radical decay in flash-photolyzed O_2–F_2 mixtures [5 to 7]. O_2F is assumed to be an intermediate in the synthesis of the dioxygenyl compounds O_2BF_4 [8], O_2AsF_6, and O_2SbF_6 [9, 10], see also the review [11] on oxygen fluorides and dioxygenyl compounds. The radical will also be involved in the synthesis of polyoxygen difluorides O_nF_2, $n \geq 2$: the reaction with atomic F leads to O_2F_2, and the dimerization gives O_4F_2 [11].

Specific radical reactions are listed below, which are assumed in the above mentioned systems or in some related ones.

The dissociation

$$(1)\quad O_2F + M \rightarrow O_2 + F + M$$

may be involved in the flash photolysis of O_2–F_2 mixtures [5] and in the thermal decomposition of O_2F_2 [12]. The ready decomposition $O_2F \rightarrow O_2 + F$, following certain displacement reactions between dioxygenyl salts and amphoteric molecules like ClF_3O, is a source of F atoms at low temperatures [2]. Second-order rate constants for the unimolecular decomposition were derived from theory [41]: $k_1 = 8.96 \times 10^{-19}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 300 K, 3.41×10^{-24} at 200 K; for k_{-1} see p. 111. Equilibrium constants from thermodynamic data are $K = 2.00 \times 10^{13}$ molecule/cm^3 at 300 K and 5.52×10^7 at 200 K [42]. The equilibrium, with concentrations $[F] \ll [O_2F]$, was assumed to be established in the thermal reaction of SF_4 with F_2 in the presence of O_2 [40]. $O_2F \rightleftharpoons O_2 + F$ was probably involved in the photolysis of liquid OF_2–O_2 mixtures [13].

The photodissociation $O_2F + h\nu \rightarrow O_2 + F$ was followed in an Ar matrix by IR absorption of O_2F. A threshold of 490 nm was measured [1]. The earlier results [14] with UV detection of the O_2F radical in liquid CF_4 or Ar were confirmed. The photodissociation was shown to be the limiting step in the photochemical transformation of O_2F into O_2F_2 [14].

The bimolecular decomposition

$$(2)\quad 2O_2F \rightarrow 2O_2 + F_2$$

is assumed to explain the kinetics of the thermal decomposition of solid O_2BF_4. An equilibrium $O_2BF_4(s) \rightleftharpoons O_2F(g) + BF_3(g)$ was established [8].

The disproportionation reaction

$$(3)\quad 2O_2F \rightarrow O_2F_2 + O_2$$

may be involved in the photolysis of liquid OF_2–O_2 mixtures at 95 K: A large concentration of O_2F radicals was observed, and O_2F_2 was possibly formed since specks of an insoluble solid were found after warming [13]. Reaction (3) was also stressed in an interpretation of NMR results for the liquid O_3F_2: This compound was thought to be composed of O_2F_2 and O_4F_2 which exists in equilibrium with O_2F (see p. 105). Reaction (3), then, should account for the irreversible decomposition of O_2F proceeding faster with increasing temperature [15, 16]. The gas phase equilibrium (3, −3) was assumed to account for the presence of O_2F radicals in O_2F_2, formed by laser flash photolysis of O_2–F_2 mixtures [43].

An $O_2F + O_2F$ reaction would explain the second-order decomposition of O_2F with an apparent rate constant $k = (1.5 \pm 0.5) \times 10^{11}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$, observed after the thermal decomposition of O_2AsF_6. Here an equilibrium $O_2AsF_6 \rightleftharpoons O_2F + AsF_5$, as in the similar O_2BF_4 case (see above), apparently is not involved [3].

The dimerization reaction

$$(4)\ 2O_2F \rightarrow O_4F_2$$

was based upon the early IR absorption studies with the matrix-isolated O_2F radical. Its absorption line at 1494 cm^{-1} disappeared during thermal cycling of the matrix to the diffusion temperature, and a new line at 1519 cm^{-1} appeared, which was ascribed to O_4F_2 [18]. Later studies have been interpreted by the formation of loosely bound aggregates $(O_2F)_n$ [19], see also [20 to 22]. The dimerization (4) probably also occurs when the products of a silent electric discharge through an O_2–F_2 mixture, O_2F and O_2F_2, are condensed in a cold trap at liquid-nitrogen temperature. The portion of the condensate having a composition "O_4F_2" increases with increasing temperature of the walls of the discharge tube. This is explained by an increase in formation of O_2F relative to thermally less stable O_2F_2 in the discharge. The O_2F radicals then undergo reaction (4) [23].

The equilibrium (4, −4) is part of the mechanism suggested [2] for the reactions of dioxygenyl salts with compounds like ClF_3, ClF_3O, HF, and others. It is responsible for the reversible blue↔brown color change, which intensifies with increasing starting temperature of the above reactions [2]. The equilibrium also accounts for the possible formation of O_4F_2 by sublimation of O_2AsF_6 followed by condensation of the vapor species at −196°C [33]. ESR studies in photolyzed liquid 1:1 mixtures of OF_2 and O_2 at 95 K showed the equilibrium favoring the reactants [13], while Raman studies with a 3:1 mixture at 90 K gave an equilibrium favoring the products [24]. Equilibrium constants were discussed [21] on the basis of ESR studies on electron-irradiated liquid $CF_4(O_2)$ [25] and on O_2F_2 and O_3F_2 [26]. The equilibrium was also considered elsewhere [15, 16].

The reaction $O_2F + H_2 \rightarrow O_2 + HF + H$, $\Delta H = -15.5$ kcal/mol, is considered to be a chain propagating step in the mechanism of the O_2-inhibited thermal H_2–F_2 reaction [36]. It must also occur in the H_2–F_2 photochemical system [28].

The reaction with O_2 may lead to the formation of O_4F [18], see also "Fluorine" Suppl. Vol. 2, 1980, p. 139. An equilibrium $O_2F + nO_2 \rightleftharpoons (O_2)_{n+1}F$ was indicated by ESR studies of the reaction chemistry of dioxygenyl salts and may be responsible for the frequently observed blue↔violet color change [2].

For the radical-atom process $O_2F + O \rightarrow O_2 + OF$, the rate constant is expected to approach the gas collision frequency, $k = 5 \times 10^{-11}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 298 K [39].

The reaction with atomic N was studied in view of the possibility of an NF chemical laser. Excited $N_2(B^3\Pi_g)$ molecules were observed, and the sequence of reactions $O_2F + N \rightarrow O_2 + NF(a^1\Delta, b^1\Sigma^+)$, $NF(a,b) + N \rightarrow N_2(B^3\Pi_g) + F$ was suggested [27].

The reaction $O_2F + F_2 \rightarrow O_2F_2 + F$ was part of a chain mechanism explaining the fast rate of the photochemical synthesis of dioxygenyl salts from O_2–F_2–MF_5 mixtures (M = As, Sb) [9]. The reactions with Br_2 and I_2 lead to chemiluminescence from electronically excited BrF and IF molecules. A two-step mechanism $O_2F + X_2 \rightarrow FX + X + O_2$, $X + O_2F \rightarrow FX + O_2$ ($X_2 = Br_2$, I_2) is probably involved [35].

The reaction with atomic F has frequently been discussed. For the termolecular reaction

$$(5a)\quad O_2F + F + M \rightarrow O_2F_2 + M$$

the third-order rate constant $k_{5a} = (3.3 \pm 1.2) \times 10^{16}\ cm^6 \cdot mol^{-2} \cdot s^{-1}$ was determined from UV absorption studies of flash-photolyzed O_2–F_2 mixtures at relatively high total pressures (350 Torr) and small O_2 pressures (0.15 to 0.95 Torr). A mechanism was assumed for production and consumption of O_2F, consisting of the formation reactions (−1) and (−5a) and the reactions (1), (5a), and (5b). An apparent second-order decay was found [5], see also [6, 7]. Reaction (5a) was also used [28] to explain the O_2F_2 formation from the photochemical reaction of O_2 and F_2 at −42°C.

The bimolecular reaction $O_2F + F \rightarrow O_2F_2$ was assumed in various photolytic systems with OF_2 [13, 14] or F_2 [18, 19].

For the bimolecular reaction

$$(5b)\quad O_2F + F \rightarrow O_2 + F_2$$

the rate constant $k_{5b} \leq 10^{10}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 298 K was estimated from a study of flash-photolyzed O_2–F_2 mixtures (see above) [5]. $k_{5b} = 10^{10}$ to $10^{11}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ is reported elsewhere [29]. Reactions (5b) together with (1) are expected to describe the O_2F decomposition at low total pressures (<1 Torr). The observed second-order decomposition of the radicals, generated from the thermal decomposition of O_2AsF_6, is, however, not in accord with this simple mechanism [3]. Reaction (5b) was assumed to be part of the mechanism of the photochemical reaction of F_2 with CO_2 [30], SOF_4 [31], and COF_2 [32].

The reactions with atomic halogens other than fluorine were studied with special interest in emission from electronically excited XF* species. The reaction $O_2F + Cl \rightarrow ClF + O_2$, $\Delta H = -46$ kcal/mol, is not sufficiently exothermic to produce ClF in the excited $B^3\Pi_0^+$ state. Rather, ground-state ClF undergoes rapid energy transfer with O_2 in excited $^1\Delta_g$ or $^1\Sigma_g^+$ states to produce ClF ($B^3\Pi_0^+$) [34]. For X = Br, an analogous behavior was found, because ΔH is −45 kcal/mol. For IF, the $A^3\Pi_1$ state was produced directly, because ΔH is nearly −52 kcal/mol [35].

The gas-phase reaction with atomic Mg gives a bright blue-white flame. The reaction $Mg + O_2F \rightarrow MgF + O_2$ is sufficiently exothermic ($\Delta H \approx -92$ kcal/mol) to produce MgF in the excited $A^2\Pi$ state. However, the intensity of the A→X emission band of MgF as a function of either O_2F or Mg flow rate shows that MgF($A^2\Pi$) is not produced directly. Rather, vibrationally excited $MgF^\dagger$ is probably formed as a long-lived intermediate and may react further with O_2F or be transferred to MgF($A^2\Pi$) by collisions [4].

The crude products from the reaction of N_2O_4 with O_2F at ~100 K gave ^{19}F NMR signals for FNO and FNO_2. After removal of the oxygen fluorides by thermal decomposition at ~200 K, the products condensable at 77 K included some $FONO_2$, as evidenced by IR spectra [17].

The reactions with ICl and HI lead to chemiluminescence from IF. The reaction mechanism is analogous to that postulated for the reactions with Br_2 and I_2, see above, [35].

The association of O_2F with the radical OF to give O_3F_2 was discussed [37], but rejected by others [16].

The reactions with BF_3 [8, 11, 16, 21] and with AsF_5 and SbF_5 [9, 10] give the dioxygenyl salts O_2BF_4, O_2AsF_6, and O_2SbF_6. Reactions were considered with SF_5 and SF_5O_2, leading to SF_6 and O_2 [40].

The surface reaction with CsI gave $CsF + I_2 + O_2$ [38].

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3.15 The O_2F Radical (OFO Isomer)

Ab initio SCF–MO calculations [1] predict a $^2B_2$ ground state with a total energy $E_T = -248.712952$ a.u. for OFO (point group C_{2v}). CI calculations [1] at the SCF optimized geometry show the isomer to be thermodynamically unstable relative to OOF by about 85 kcal/mol and give as lowest excited states $^2B_1$ at 0.136 eV, $^2A_2$ at 0.751 eV, and $^2A_1$ at 0.811 eV. Net atomic charges and electric dipole moments were calculated for all four states (F always negative). Optimized geometry parameters for $^2B_2$ were r(O–F) = 1.4635 Å and $\sphericalangle$OFO = 80°22′. Thus, OFO will be a highly strained system and may readily dissociate into O_2 and F or O and OF or may rearrange into the more stable OOF radical. This may explain, why OFO was not experimentally observed [1]. Previous nonempirical SCF calculations [2] were performed at an assumed bond length r(O–F) = 1.19 Å (sum of the covalent O and F radii). The calculation gave a $^2B_1$ ground state with a positive charge at F and a bond angle $\sphericalangle$OFO = 128°22′ [2].

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3.16 The O_2F^+ Ion

On the basis of an ionization potential of 12.6 eV for O_2F [1] (see p. 116), the enthalpy of formation is given as $\Delta H_f^\circ = 294$ kcal/mol [2]. The appearance potential of O_2F^+ from O_2F_2 (14.0 eV [3], see below) leads to $\Delta H_f^\circ = 308$ kcal/mol [2].

An appearance potential from O_2F_2 of 14.0 ± 0.1 eV was measured by the retarding potential difference method in an electrically discharged O_2–F_2 mixture at 25 to 35 Torr and 130 K. This figure indicates that the ion was produced directly by fragmentation of O_2F_2 and not from free O_2F radicals [3]. The same value was determined by matching the ion efficiency curve of O_2F^+ from O_2F_2 with that of Ar [1].

Wavenumbers were assigned to the fundamental vibrations on the basis of Raman studies of the reaction of O_2F_2 with polymeric VF_5. In this system, O_2F^+ may be assumed as a reaction intermediate. Thus, $\nu_1 = 1811$ (O–O stretching), $\nu_2 = 460$ (bending), and $\nu_3 = 642$ cm^{-1} (O–F stretching). These solid-state values lie between the values of O_2F (see p. 118) and those of FNO which is isoelectronic with O_2F^+ [4].

The bond dissociation energy $D(F\text{–}O_2^+) = 0.4$ eV was derived from $D(F\text{–}O_2^+) = D(F\text{–}O_2) + E_i(O_2) - E_i(O_2F) = (0.8 + 12.2 - 12.6)$ eV [1]. $D(O\text{–}OF^+) = 5.2$ eV was derived from $D(O\text{–}OF^+) = D(F\text{–}O_2^+) + D(O_2^+) - D(F\text{–}O^+) = (0.4 + 6.5 - 1.7)$ eV [1]. ($D(F\text{–}O^+) = 2.7$ eV, see p. 79, leads to $D(O\text{–}OF^+) = 4.2$ eV.)

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3.17 Tetraoxygen Difluoride, O_4F_2

CAS Registry Number: *[12020-93-8]*

Review

O_4F_2 is a reddish-brown solid which melts at about 82 K. Decomposition of the liquid occurs below the normal boiling point at about 194 K. At liquid-nitrogen temperature, however, pure O_4F_2 can be stored for weeks without noticeable decomposition. The compound that can be prepared from O_2–F_2 mixtures in an electric discharge is thought to result from the combination of two O_2F radicals. An experimental structure determination has not been carried out so far. The reactive behavior of O_4F_2 is similar to that of O_2F_2.

3.17.1 Preparation and Formation

O_4F_2 was first synthesized in 1958 from an O_2–F_2 mixture in a high-voltage electric discharge [1]. Under improved conditions, the 2:1 by volume mixture is passed at ~2 cm³/min through the discharge vessel made of copper and cooled to 90 K. The electric discharge operates at 4 to 6 mA and 1 to 1.5 kV. The maximum yield of O_4F_2 amounts to ~3 mg/min [2]. The product, which is a reddish-brown solid at 77 K and sometimes forms clusters of long, needle-like brown crystals [1], was collected either by melting at ~85 K or by dissolving and rinsing down with a solvent such as CF_4 or OF_2 [2]. Circulation of an F_2–O_2 mixture (100 to 400 Torr) through a silent discharge yielded a mixture of oxygen fluorides with the ratios O:F = ~1.1 to ~2.04, probably O_2F_2 and O_4F_2 [3]. O_4F_2 is also obtained (production rate 0.15 g/h) by passing a gaseous mixture (1:1.5 molar ratio) of OF_2 and O_2 (feed rate 82.5 cm³/h) through an electric discharge (maximum power 11 W) at 82 K and ≤8 Torr total pressure [4].

The compound is presumably formed as a result of the recombination of O_2F radicals (see p. 125), see e.g., experiments on the photolysis of O_2–F_2 and of OF_2–O_2 mixtures in solid matrices at 4 K [5] or on the radiolysis of O_2–F_2 mixtures at 77 K, which are interpreted assuming an $O_4F_2 \rightleftharpoons 2O_2F$ equilibrium [6]. The formation of O_4F_2 by dimerization of O_2F radicals is part of the mechanism suggested for the formation of the blue and violet compounds in the reaction of oxygen fluorides or O_2^+ salts [7]. Presumably, O_4F_2 is formed by sublimation of O_2AsF_6 followed by condensation of the vaporized species at 77 K [8].

Pure O_2F_4 or its solutions can be stored at liquid-N_2 temperature. O_2F_4 is an explosive compound. Therefore precautions must be taken in its preparation, handling, and storage [2].

A semiempirical SCF–MO calculation in the MINDO approximation gave the enthalpy of formation $\Delta H_f = 36.24$ kJ/mol [9].

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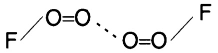
3.17.2 The Molecule and Spectra

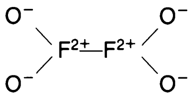
The O_4F_2 molecule appears to be composed of two O_2F radicals forming a weak bond between their outer O atoms [1, 2]:



This idea follows primarily from matrix IR absorption studies of the O_2F radical [3 to 5], see also [6], and from Raman solution studies of O_4F_2 [2]. The IR spectra obtained after heating the matrices to the diffusion temperature and the O_4F_2 Raman spectrum differ only slightly from the O_2F spectrum. Only the O=O stretching vibration is shifted to higher wave numbers, while the O–F stretching and the OOF bending frequencies remain practically the same. No IR absorption due to the central O···O bond could be found [4]. Weak O–F bonds, strong outer O–O bonds, and a weak central O–O bond may result from the following ionic structures in the valence bond theory (structures not equally important and to be supplemented by their respective mirror images) [3, 6]:

$$F^-O{=}O^+{-}O{-}O{-}F \leftrightarrow F{-}O^+{=}O\ O{=}O\ F^- \leftrightarrow F^-O{=}O^+{-}O^+{=}O\ F^- \leftrightarrow F{-}O^+{=}O\ O^-{-}O{-}F$$

An isomeric form, FO···O_2···OF, has been predicted [1] but is not in accord with the observations mentioned above. An arrangement has been suggested with a long weak F–F bond [7], see also [8]:



The total energy $E_T = -497.71374$ a.u. has been calculated by an ab initio SCF–MO method. This value implies the stability (by 0.05063 a.u.) of O_4F_2 with respect to the potential decomposition products O_2F_2 and O_2 ($^1\Delta_g$) [9].

The dipole moment $\mu = 0.03703$ D was also calculated [9].

Geometrical parameters have been calculated by an ab initio [9] and a semiempirical (MINDO, see [11]) SCF–MO method [10]. Distances r in Å, bond angles α and dihedral angles Φ in degrees (the point group is C_2 [9, 10]):

r(O–F)	r(O–O)	α(OOF)	α(OOO)	Φ(OOOF)	Φ(OOOO)	Ref.
1.3564[a)]	1.4069[a)]	103.77	102.76	180[c)]	88.12	[9]
1.487	1.312, 1.421[b)]	112.0	121.0	79.6	53.3	[10]

[a)] Value taken from the corresponding calculation for the O_3F_2 molecule. – [b)] 1.312 for the outer, 1.421 for the inner O atoms. – [c)] Assumed.

r(O–F) = 1.63 Å, r(O–O) = 1.22 Å, and α(OOF) = 100° were assumed for the calculation of force constants [3].

Wavenumbers assigned to the molecular vibrations ν(O–O), ν(O–F), and δ(O–O–F) are given in the following table. They are based upon IR or Raman spectra observed for various liquid or solid systems at low temperatures:

ν(O–O) in cm^{-1}	1516.2 ± 1	1515	1514	1523, 1517	1519
ν(O–F) in cm^{-1}	584.6 ± 1	586	589	586	588
δ(O–O–F) in cm^{-1}	376.8 ± 1	—	(376)	376	—
spectrum	Raman	IR	IR	IR	IR
system	OF_2–O_2 photolysis	F_2–O_2–Ar photolysis	O_2F_2–Ar	F_2–O_2 radiolysis	F_2–O_2 photolysis
T in K	90	20	20	77	4
Ref.	[2]	[5]	[5]	[12, 13]	[3]
remark	a)	b)	c)	d)	e)

a) Depolarization ratios in the above order are 0.6, 0.5, and ~0.7. – b) Similar studies [4] led to ν(O–O) = 1510 cm^{-1} and the isotopic data $\nu(^{16}O{-}^{18}O) = 1470$ and $\nu(^{18}O{-}^{18}O) = 1425\ cm^{-1}$. – c) The δ value is given as 316 cm^{-1} in the text. For a CO_2 matrix, ν(O–O) = 1530 cm^{-1}. The bands are narrowed compared to those observed in solid O_2F_2 at 77 K: ~1511, 587, and 375 cm^{-1} (shoulder) from the IR spectrum, 1516 and 593 cm^{-1} from the Raman spectrum [5]. ν(O–F) = 588 cm^{-1} from the solid O_2F_2 Raman spectrum [14]. – d) The bands were observed after warming the formed solid, O_2F_2, to 85 K and cooling to 77 K again. – e) The O_4F_2 absorption was observed after the diffusion operation: warming to 45 K and recooling to 4 K. Isotopic data are $\nu(^{16}O{-}^{18}O) = 1479$, $\nu(^{18}O{-}^{18}O) = 1432$, and $\nu(^{18}O{-}F) = 564\ cm^{-1}$. Bands at 1520 and 590 cm^{-1} were observed in irradiated solid solutions of OF_2 in O_2 and of F_2 in O_2 [3].

Force constants were derived from the observed wavenumbers ν(O–O) and ν(O–F) and an estimated value δ(O–O–F) = 290 cm^{-1}. However, the latter is in error, see table above: $f_{OO} = 10.80$ mdyn/Å, $f_{OF} = 1.62$ mdyn/Å, $f_{OOF} = 0.54$ mdyn·Å [3].

The bond dissociation energy $D(FO_2{-}O_2F) \approx 3$ kcal/mol was obtained from estimated values for the dissociation equilibrium constant at 80 to 90 K and the dissociation entropy [12], see also [15].

The ^{17}O and ^{19}F NMR spectra apparently have not been observed, although the O_3F_2 spectra were ascribed to a mixture of O_2F_2 and O_4F_2; the latter was assumed to be in equilibrium with O_2F [16, 17]. The signal of O_4F_2, in equilibrium with O_2F, should be as broad as that of O_2F, the broadening in this case coming from relaxation processes [6], see also [18, 19].

The electronic absorption of a 0.05 ± 0.01 mol/L solution of O_4F_2 in CF_4, with 3% O_2 added to avoid solidification, was studied at 77 K between 350 and 750 nm [20], see also [8, 21]. The extinction coefficients [20], however, reportedly pertain to a mixture of O_2F and O_2F_2 [22]. Absorption studies show that in solutions with concentration $\leq 10^{-3}$ mol/L, a compound O_4F_2

does not exist but rather the O_2F radical [22]. An additional absorbing species, perhaps the radical O_4F, was claimed [12] to have complicated the visible and UV spectra [20].

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3.17.3 Thermal Properties

The van der Waals constants $a = 2.16 \times 10^6$ atm·cm^6·mol^{-2} and $b = 48.5$ cm^3/mol were calculated by using the theorem of corresponding states [1].

O_4F_2 melts at 82 ± 2 K. Its vapor pressure at 90 K is 0.25 Torr. The extrapolated normal boiling point is 194 K; the compound decomposes below this temperature [2]. The enthalpy of vaporization $\Delta H_v = 1749$ cal/mol, the entropy of vaporization $\Delta S_v = 17.5$ cal·mol^{-1}·K^{-1}, and the critical constants $T_{cr} = 163.1$ K, $p_{cr} = 34.9$ atm, $V_{cr} = 170.6$ cm^3/mol, $\varrho_{cr} = 0.605$ g/cm^3 have been calculated [1].

References:

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3.17.4 Chemical Behavior

O_4F_2 dissociates presumably by the cleavage of the weak O–O bond forming O_2F radicals. This follows from investigations of the O_4F_2 molecule, see p. 130, and of the O_2F radical, see pp. 109, 125. The equilibrium $O_4F_2 \rightleftharpoons 2O_2F$ is discussed in connection with the radiolysis of a liquid 3:1 F_2–O_2 mixture at 77 K [1], with the interpretation of the structure of the trioxygen difluoride (see p. 105) [2, 3], and with the formation of the violet and blue species observed in the reaction of oxygen fluorides or dioxygenyl salts [4]. O_4F_2 decomposes at 90 K with about a 16-days half-life into O_3F_2 and oxygen. O_3F_2 decomposes, in turn, at 90 to 115 K into O_2F_2 and finally into O_2 and F_2. Pure O_4F_2, or its solidified solutions containing about 1 mol% of O_4F_2 in CF_4, has been kept at liquid-nitrogen temperature for weeks without noticeable decomposition. O_4F_2 explodes on rapid warming [5].

Solid O_4F_2 is practically insoluble in liquid N_2 at 77 K and in liquid Ar at 85 K (solubility <0.01 mol%). In liquid O_2 at 77 K, the solubility of O_4F_2 is ~ 0.05 mol%. CF_4 dissolves appreciable amounts of O_4F_2 at 90 K. The solution containing 1 mol% O_4F_2 is reddish-brown. Reddish-brown solutions of O_4F_2 were obtained in CF_3Cl at 90 K. O_4F_2 is readily soluble in liquid OF_2. At 77 K, the solubility is $\sim 2\%$ by weight; at 90 K, OF_2 dissolves $\geq 5\%$ by weight of O_4F_2 [5].

If a mixture of O_4F_2 and xenon is warmed slowly from 77 to 195 K, O_4F_2 decomposes and some of its decomposition products react with xenon to form xenon fluorides. At 116 K, O_4F_2 explodes on contact with concentrated O_3. With N_2F_4, tetraoxygen difluoride (dissolved in OF_2) reacts at 77 K to produce O_2F_2, NF_3, and O_2 [5]. The reaction of O_4F_2 in $CFCl_3$ with SO_2 at 77 K gave SO_2F_2, FSO_2OOF, FSO_2OSO_2F, O_2, and traces of F_2. The comparison with the analogous reaction of O_2F_2 showed that the reaction is similar; that is, simple fluorination predominates. However, O_4F_2 appears to be the better source of O_2F than O_2F_2, since the yield of FSO_2OOF is higher for O_4F_2 (32%) than for O_2F_2 (5%) [6]. Like O_2F_2, tetraoxygen difluoride reacts with BF_3 at 135 K to form the dioxygenyl salt O_2BF_4 [7].

References:

[1] C. T. Goetschel, V. A. Campanile, C. D. Wagner, J. N. Wilson (J. Am. Chem. Soc. **91** [1969] 4702/7).

[2] I. J. Solomon, J. K. Raney, A. J. Kacmarek, R. G. Maguire, G. A. Noble (J. Am. Chem. Soc. **89** [1967] 2015/7).

[3] I. J. Solomon, J. N. Keith, A. J. Kacmarek, J. K. Raney (J. Am. Chem. Soc. **90** [1968] 5408/11).

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3.18 Pentaoxygen Difluoride, O_5F_2, and Hexaoxygen Difluoride, O_6F_2

CAS Registry Numbers: O_5F_2 *[12191-79-6]*, O_6F_2 *[12191-80-9]*

Little is known about these compounds which were prepared by electric discharges through F_2–O_2 mixtures of the appropriate molar ratio at 60 to 77 K [1]. The analysis of the products gave the molar ratios 5:2 and 6:2 [1], but no conclusive evidence for existence of these oxygen fluorides seems to exist (see, e.g. [2, 3]). A mixture of oxygen fluorides, one of the components might have been O_6F_2, was prepared by radiolysis of liquid mixtures of O_2 and F_2 at 77 K [2]. Valence bond models were discussed for the compounds [1].

O_5F_2 is a reddish-brown liquid at 90 K and appears to be an oil at 77 K. At 77 K, it is insoluble in liquid N_2, soluble in liquid O_2 ($\leq$0.02 mol% O_5F_2) and in CF_4 ($\geq$0.1 wt% O_5F_2 + 3 wt% O_2), and soluble in liquid OF_2 at 65 K (~5 wt% O_5F_2). The ESR spectrum (no details) is substantially different from that of O_4F_2 [1].

O_6F_2 is dark brown and a crystalline solid at 60 K. There is no noticeable decomposition (<0.1 mol%) at 60 K during 4 h. On warming slowly (rate ~10 K/h) it decomposes quickly, forming lower oxygen fluorides and ozone. On rapid warming to 90 K it explodes to give O_2 and F_2. Accumulation of amounts of O_6F_2 greater than ~20 mg during preparation or the irradiation of O_6F_2 by a flashlight led to explosions. O_6F_2 is insoluble at 60 K in a liquid mixture of 95 vol% N_2 + 5 vol% O_2. At 60 K, traces of O_6F_2 are soluble in liquid O_2 and amounts of ~5 wt% O_6F_2 are soluble in liquid OF_2 [1].

References:

[1] A. G. Streng, A. V. Grosse (J. Am. Chem. Soc. **88** [1966] 169/70).

[2] J. J. Turner (Endeavour **27** [1968] 42/7).

[3] C. T. Goetschel, V. A. Campanile, C. D. Wagner, J. N. Wilson (J. Am. Chem. Soc. **91** [1969] 4702/7).

3.19 The O_3F Radical

The radical might have been detected by matrix IR absorption studies. A peak at 1503 cm^{-1}, observed during the photolysis of F_2 in an O_2 matrix at 4 K, was assigned to O_3F, which could have been formed [1] by

$$O_4F + h\nu \rightarrow O_3F + O$$

The formation of the radical was assumed to occur in the photochemical reaction between F_2 and O_3 [2] by

$$F + O_3 \rightarrow O_3F$$

From a comparison of the observed [3] and calculated anisotropic ^{19}F hyperfine coupling constants of the O_2F radical, it was suggested that the radical observed in [3] was really O_3F [4].

The formation enthalpy $\Delta H_f^\circ = 107.69$ kJ/mol was semiempirically calculated [5].

The bonding has been qualitatively treated (for the series $(O_2)_nOF$, n = 0, 1, ...) [6].

Structural parameters from a semiempirical SCF–MO calculation (r in Å, α = bond angle and Φ = dihedral angle; O_1 atom at F) [5] are:

r(O–F)	r(O_1–O_2)	r(O_2–O_3)	α(OOF)	α(OOO)	Φ(OOOF)
1.489	1.314	1.257	116.2°	124.2°	53.1°

References:

[1] A. Arkell (J. Am. Chem. Soc. **87** [1965] 4057/62).

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3.20 The O_4F Radical

The radical has probably been detected by matrix IR absorption studies. A peak at 1512 cm^{-1}, observed during the photolysis of F_2 in an O_2 matrix at 4 K, was assigned to O_4F, which could have been produced by either of the two reactions [1]

$$O_2F \text{ (from } O_2 + F) + O_2 \rightarrow O_4F \quad \text{or} \quad O_4 + F \rightarrow O_4F$$

The radical has possibly also been formed during the radiolysis of O_2–F_2 mixtures at 77 K [2]. From a quantitative comparison of the visible and near UV absorption data [3] of O_2F_2, O_3F_2, and O_4F_2, it was supposed that O_4F may have been present in the O_4F_2 sample [2]. An equilibrium $O_2F + nO_2 \rightleftharpoons (O_2)_{n+1}F$, involving O_4F for n = 1, is assumed to be responsible for the color change blue ⇌ violet, frequently observed in the reactions of oxygen fluorides or of dioxygenyl salts or in the photolytic reactions of oxygen and fluorine compounds [4].

The formation enthalpy $\Delta H_f^\circ = 134.01$ kJ/mol was semiempirically calculated [5].

The bonding has been qualitatively treated (in the series $(O_2)_nF$) [6].

Structural parameters from a semiempirical SCF–MO calculation (r in Å, α = bond angle and Φ = dihedral angle; O_1 atom at F) [5] are:

$r(O_1–F)$	$r(O_1–O_2)$	$r(O_2–O_3)$	$r(O_3–O_4)$	$\alpha(OOF)$	$\alpha(O_1O_2O_3)$	$\alpha(O_2O_3O_4)$	$\Phi(OOOF)$	$\Phi(OOOO)$
1.488	1.312	1.439	1.253	110.1°	122.0°	123.3°	80.4°	47.8°

References:

[1] A. Arkell (J. Am. Chem. Soc. **87** [1965] 4057/62).

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3.21 Helium Oxide Fluoride, HeOF

CAS Registry Number: *[62462-53-7]*

MO calculations show that linear helium oxide fluoride should be stable. The He–O bond distance was fixed at 2.15 a.u. (1.14 Å). Orbital energies (in 1000 cm^{-1}, omitting O1s and F1s) are: −359.53 for 1σ, −273.43 for 2σ, −207.87 for 3σ, −176.77 for π, −140.97 for 4σ, and −97.95 for π^*. The atomic populations were calculated.

Reference:

R. J. Fereday, S. P. Sinha (J. Chim. Phys. **74** [1977] 87/91).

3.22 F–O–Xe Compounds

These compounds were dealt with in "Edelgasverbindungen" 1970, pp. 93/101. More recently, graphite intercalation compounds of $XeOF_4$ [1] and reactions of $XeOF_4$ with KrF^+ [2] were studied.

References:

[1] H. Selig, O. Gani (Inorg. Nucl. Chem. Letters **11** [1975] 75/7).
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3.23 The HOF_2^+ Ion

Ab initio SCF calculations with an STO basis indicate a pyramidal structure of the ion with an apical H atom; total energy $E_T = -273.7362$ a.u. The inversion barrier is given as 18.1 kcal/mol. The internuclear distances and bond angles are r(O–F) = 1.355 Å, r(O–H) = 0.995 Å, $\sphericalangle$FOH = 105.1°, and $\sphericalangle$FOF = 106.0°. For the planar configuration parameters, see the original paper.

Reference:

D. S. Marynick, D. A. Dixon (J. Phys. Chem. **87** [1983] 3430/3; Erratum: **89** [1985] 3946).

3.24 Hypofluorous Acid, HOF

CAS Registry Numbers: HOF *[14034-79-8]*, DOF *[28054-69-5]*, $H^{18}OF$ *[41968-13-2]*

Review

HOF was first prepared and isolated at the beginning of the 1970s by passing fluorine over cold water. At low temperature, HOF is a white solid that melts at −117°C forming a pale yellow liquid and boils below room temperature. The compound has a strong tendency to decompose into HF and O_2.

Throughout this chapter, the formula of the compound is written as HOF in accordance with the structure of the molecule where the central atom is oxygen. Two isomeric forms, HFO (bent) and FHO (linear) were predicted and are treated in Chapter 3.25, p. 157.

A review on HOF is contained in the article on fluorinated hypofluorites and hypochlorites by J. M. Shreeve (Advan. Inorg. Chem. Radiochem. **26** [1983] 119/68, 121/3).

3.24.1 Formation and Detection. Handling

HOF was synthesized by reacting F_2 with H_2O (solid or liquid) and was detected in a time-of-flight mass spectrometer. It may be prepared in mg amounts by slowly pumping F_2 at 300 Torr or less over water at 0°C in a Kel-F (polytrifluorochloroethylene) U tube. Two further U tubes at

−50 and −79°C are used to trap water and another at −183°C to trap the HOF as a white solid [1 to 3]. To rapidly remove the HOF formed in the reaction zone and to simultaneously provide intimate contact of the reactants, F_2 is circulated at a rate of ~10 L/min through a system containing ice at −40°C, two traps at −55 and −79°C for H_2O and HF and one trap at −183°C for HOF [3, 4]. Thus, about 50 to 200 mg HOF can be prepared with yields approaching 50% based on charged F_2 [3].

In an N_2 matrix at 14 and 20 K, HOF was formed by the photolysis of a mixture of fluorine and water and was detected by its IR absorption bands [5]. For the reaction steps involved, see "Fluorine" Suppl. Vol. 2, 1980, p. 164. HOF and DOF are formed as secondary reaction products in the gas-phase reaction $F + H_2O(D_2O) \rightarrow HF + OH(OD)$ and are detected by photoelectron spectroscopy. More DOF appeared to be generated than HOF [18]. The formation of HOF as an intermediate complex in the reaction $F + OH \rightarrow HF + O$ was suggested from the vibrational energy distribution of HF product molecules [19]. The intermediate formation of HOF was considered in an anode reaction in the system H_2O–HF [6].

Solid HOF appears white [1]. The vapor is colorless, and the liquid is described as pale yellow [3], previously as colorless [1].

The handling of HOF requires adequate shielding [7] since minor detonations were observed [8], resulting from the spontaneous decomposition into O_2 and HF (see p. 155).

HOF may be stored at liquid-N_2 temperature [4].

Enthalpy of Formation ΔH_f° in kcal/mol. $\Delta H_{f,0}^\circ = -22.8 \pm 1$ and $\Delta H_{f,298}^\circ = -23.5 \pm 1$ were determined [10] by photoionization mass spectrometry of HOF: The O^+ appearance potential from HOF, 14.34 eV, was used with $\Delta H_{f,0}^\circ$ of O^+ and HF, 373.02 and −65.13 kcal/mol, respectively. The activation energy for the reorganization reaction $HOF + h\nu \rightarrow O^+ + HF + e^-$ was assumed zero. The OH^+ appearance potential, 15.07 eV, led to the similar value $\Delta H_{f,0}^\circ = -21.6$, if $\Delta H_{f,0}^\circ(F) = 18.36$ from the JANAF Tables [13] and $\Delta H_{f,0}^\circ(OH^+) = 307.5 \pm 0.5$ due to Dibeler et al. [9] were used (instead of $\Delta H_{f,0}^\circ(OH^+) = 313.3 \pm 2.5$ [13]). $\Delta H_{f,0}^\circ = -22.8 \pm 1$ and $\Delta H_{f,298}^\circ = -23.5 \pm 1$ are adopted in a supplement to the JANAF Tables [11]. The older approximate values $\Delta H_{f,0}^\circ = -30 \pm 10$, $\Delta H_{f,298}^\circ = -31 \pm 10$ were derived from an estimated heat of atomization: $\Delta H_{at} = 161.6$ kcal/mol for the reaction $HOF \rightarrow H + F + O$ was assumed to be the sum of the F–O and H–O bond energies, which were obtained from the corresponding bond energies in OF_2 and H_2O [13]. $\Delta H_{f,298}^\circ = -27.7$ was estimated by comparison with the isoelectronic species CH_3OH, NH_2OH, and HOOH [14]. A comparison with HOOH was later made [12] using $\Delta H_{f,298}^\circ = -23.5$ of Berkowitz et al. [10].

ΔH_f was also calculated by the semiempirical SCF methods MINDO [15] and MNDO [16, 17].

The Gibbs free energy of formation is $\Delta G_{f,298}^\circ = -20.5 \pm 1$ kcal/mol [10].

References:

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[9] V. H. Dibeler, J. H. Walker, H. M. Rosenstock (J. Res. Natl. Bur. Std. A **70** [1966] 459/63).
[10] J. Berkowitz, E. H. Appelman, W.A. Chupka (J. Chem. Phys. **58** [1973] 1950/4).

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3.24.2 Molecular Properties and Spectra

3.24.2.1 Point Group. Isomerism. Electronic Structure

The nonlinear molecular structure (C_s symmetry, see e.g. [1]) was proved by microwave (MW) [2, 3] and infrared (IR) spectra [4] in the gas phase. It was also obtained by ab initio [5 to 9] and by semiempirical (INDO) calculations [10] and by the extended Hückel theory [11].

Besides this equilibrium structure, two metastable minima of an analytical potential energy function for the 3-dimensional coordinate space of internuclear distances of H, O, and F were predicted [5]. These minima correspond to a bent HFO and to a linear FHO molecule. The relative energies of these different isomers and their spin-allowed dissociation products are shown in **Fig. 3**. The potential energy surface was constructed from spectroscopic data including those of the diatomics OH, HF, and OF by the method given in [12]. Two ab initio calculations show the same trends of relative stabilities. Energies of HFO (bent) and FHO (linear), referenced to HOF (bent) are: 2.78 and 3.47 eV from a calculation [27] including correlation energy by the Møller-Plesset [26] method, and 2.425 and 2.467 eV from a calculation with configuration interaction [5]. The calculations of Pople et al. [28] apply to FHO as a cyclic transition structure (point group C_s) in the rearrangement transition between HOF and HFO and add correlation corrections only at the SCF-optimized geometry. From the relative energies, 2.53 and 1.95 eV for HFO and FHO, it was concluded that HFO would not correspond to a minimum [28]. An earlier calculation without correlation gave 1.13 eV for HFO [7].

The electronic configuration of the HOF X^1A' ground state, written in a presumed order of decreasing binding energy, is $(1a')^2(2a')^2\ldots(6a')^2(1a'')^2(7a')^2(2a'')^2$ [5]. The order of the three outermost orbitals agrees with that obtained from calculations of vertical ionization potentials by perturbation corrections to Koopmans' theorem [13] and of orbital energies by the extended Hückel theory [11]. It disagrees, however, with the order of the orbital energies from the other ab initio and semiempirical calculations (see below).

Orbital energies ε_i, total energy E_T. An ab initio SCF-MO calculation with a contracted Gaussian basis yielded $E_T^{SCF} = -174.266420$ a.u. and the following energies of the occupied orbitals at the optimized geometry (the original designations are a and a') [8]:

orbital	1a'	2a'	3a'	4a'	5a'	1a"	6a'	7a'	2a"
$-\varepsilon_i$ in a.u.$^{a)}$ ...	26.235	20.62	1.585	1.245	0.7113	0.6802	0.6309	0.5493	0.5137
$-\varepsilon_i$ in eV$^{b)}$	713.88	561.09	43.12	33.89	19.35	18.51	17.17	14.95	13.98

a) Rounded. – b) The data in [8] were converted to eV by Chong et al. [13].

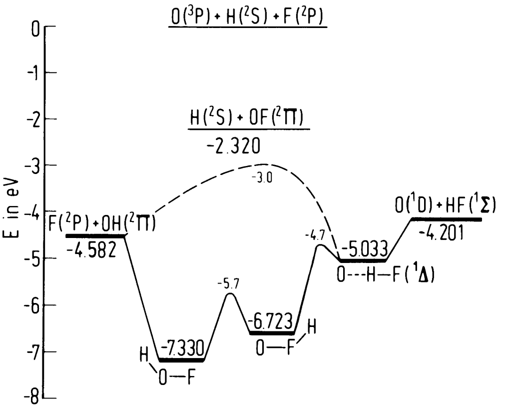

Fig. 3. Relative energies E of different isomers and spin-allowed dissociation products of the HOF molecule according to an analytical potential energy function (from [12]). Barriers between different isomers are shown along the lowest energy path. The barrier at −3.0 eV between O···H–F and OH + F is along the collinear reaction path. (Note that $^1\Delta$ is not the ground state of O···H–F, cf. p. 157.)

Orbital energies from other ab initio calculations pertain to assumed bond lengths [9] or to the experimental geometry [13, 14]. Orbital energies were also calculated semiempirically by the extended Hückel method [11], by CNDO [15], INDO [15, 16], MNDO [17], and SINDO [18] (symmetrically orthogonalized INDO, see [19]).

Apparently, the lowest total energy was calculated by Murrell et al. [5], $E_T^{SCF} = -174.78728$ a.u. Total energies were also calculated in [7, 24, 27 to 30], at assumed bond lengths in [9], at the "standard model geometry" (reported in [20]) in [21, 22], and at the experimental geometry in [5, 14, 23]. For total energies including correlation corrections, see [5, 25, 27 to 29].

The influence of surrounding dielectrics upon orbital and total energies of the solute HOF molecule was calculated [31].

Orbital bonding properties. Ab initio and semiempirical calculations show 2a″ to be an antibonding combination of 2p orbitals on O and F out of the molecular plane. The antibonding character is confirmed by the photoelectron spectrum, since the O–F stretching frequency of the cation is higher than that of the neutral molecule (see pp. 149, 158). 7a′ is primarily an in-plane antibonding combination of O2p and F2p and a bonding combination of O2p and H1s. 6a′ is primarily a bonding combination of O2p and F2p of pσ type and a slightly bonding combination between O2s and 2p and H1s [15]. 1a″ is dominated by an in-plane (sic) F2p orbital (F lone pair) [13].

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3.24.2.2 Ionization Potentials. Photoelectron Spectrum

The adiabatic first ionization potential $E_i = 12.71 \pm 0.01$ eV was measured for HOF by photoionization mass spectrometry [1], and for HOF and DOF by photoelectron (PE) spectroscopy [8]. $E_i = 12.69 \pm 0.03$ eV from an older PE study may be affected by a small H_2O impurity [2], and therefore the former value [1] is preferred [2]. The vertical ionization potential is about 13.0 eV [2]. HOF does not fit into a linear relation between vertical ionization potentials and atomic charges (calculated semiempirically) for HOX molecules [9].

The first band in the PE spectrum shows a vibrational structure with an average interval of 1050 cm^{-1} for both HOF and DOF, due to the O–F stretching frequency of the HOF^+ (DOF^+) ion, see p. 158, [8]. A 946 cm^{-1} interval [2] may be in error [8].

Higher adiabatic ionization potentials (in eV) from the PE spectrum are 14.50 ± 0.03 and 15.95 ± 0.05. The corresponding vertical values are ~14.8 and ~16 [2]. $E_i = 14.8$ eV (vertical) was later obtained for both HOF and DOF [8]. The band at 14.5 eV is ~0.5 eV broad and shows little if any structure [2].

The following MO assignment of the PE peaks was reached on the basis of calculated values from a perturbation correction to Koopmans' theorem (see [3]) and of the bonding properties of the respective MOs (see p. 139) [4]:

vertical ionization potential in eV [2]	13.0	14.8	16
orbital (cationic state)	$2a''(^2A'')$	$7a'(^2A')$	$1a''(^2A'')$

The calculated vertical ionization potentials are 13.07 (2a″), 15.09 (7a′), 16.94 (1a″), and 17.97 eV (for the unobserved 6a′) [4]. The differing assignment of the 16 eV peak to 6a′ [2] was based upon ab initio [5] and semiempirical [2] orbital energy calculations (see p. 138). Ionization potentials calculated as differences of the total energies of the neutral molecule and of the HOF^+ ion are 14.2 (2a″), 15.8 (7a′), 21.1 (6a′), and 21.6 eV (1a″) [6].

Core binding energies calculated by ab initio methods including electronic relaxation were: O1s 4.52 eV relative to $HOCH_3$, F1s 0.89 eV relative to FCH_3 [7].

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3.24.2.3 Proton Affinity A_p

$A_p = 139.3$ for protonation at O and $A_p = 125.8$ kcal/mol for protonation at F follow from an ab initio MO calculation [2] using the Møller-Plesset method [1] to include correlation energy. A Hartree-Fock calculation yields 137.2 and 124.7 kcal/mol [2]. Thus, protonation at O is energetically favored over that at F, which is also indicated by previous ab initio calculations [3, 4] and by combining the frontier orbital concept (see [5]) with data from the UV photoelectron spectrum [6].

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3.24.2.4. Electric Moments. Atomic Charges. Electric Field Gradient

Dipole Moment μ in D

The absolute value $|\mu| = 2.23 \pm 0.10$ was derived from the Stark effect in the microwave (MW) spectrum. Components along the principal inertial axes (a nearly along O–F, c perpendicular to the molecular plane) are: $|\mu_a| = 0.37$, $|\mu_b| = 2.20$ for HOF, and $|\mu_a| = 0.28$, $|\mu_b| = 2.22$

for DOF, all ± 0.10 D. The $1_{0,1} \leftarrow 0_{0,0}$ rotational transition was studied in both HOF and DOF, and the $2_{0,2} \leftarrow 1_{1,1}$ transition in DOF. μ_b of HOF was determined by assuming that the total electric dipole moment has the same magnitude for both isotopic species [1]; for the components, see also the MW spectral tables [2]. $|\mu_a| = 0.37$, $|\mu_b| = 2.20$ for both HOF and DOF were adopted in [3], since the above components [1] were not believed to be internally consistent due to experimental uncertainties. Both μ_a and μ_b have the same sign (adopted negative) [3] in accordance with the atomic charges derived from the NMR spectrum [4] and with a calculated charge distribution [6].

Several quantum mechanical methods were applied to the calculation of the dipole moment or its components: $|\mu| = 1.47$ to 2.72 (ab initio) [5 to 9, 26], 1.51 (SINDO = symmetrically orthogonalized INDO, see [10]) [5], 1.81 (MNDO) [11].

The influence of surrounding dielectrics on μ was also calculated [26].

Dipole moment derivatives. Rotational contributions to the derivatives with respect to the symmetry coordinates (see [12]) were calculated for HOF and DOF [3, 13]. The derivatives of the components of μ with respect to atomic Cartesian coordinates ("atomic polar tensor" [27]) were calculated for both the F and the H atom from different contributions (i.e., atomic charge, "charge flux" [28], and overlap) [29].

Quadrupole Moment Q in 10^{-26} esu·cm^2

The components along the principal inertial axes were derived from the molecular g values, the magnetic susceptibility anisotropies, and the rotational constants [1]:

Q_{aa}	Q_{bb}	Q_{cc}
0.2 ± 0.4	1.9 ± 0.8	−2.1 ± 1.1

The components $Q_{aa} = 22.0$, $Q_{bb} = -16.4$, and $Q_{cc} = -5.6$, which are calculated for the opposite signs of the molecular g values, are too large when compared to the moments of H_2O and OF_2. Theoretical values from a point charge model, using the atomic charges given in [4] are: $Q_{aa} = -0.1$, $Q_{bb} = +2.9$, $Q_{cc} = -2.8$. With the exception of Q_{bb}, they lie within the experimental error [1].

Atomic Charges

The ^1H and ^{19}F chemical shifts of liquid HOF and the ^1H shift of gaseous HOF indicate that the F atom carries a negative charge (~ −0.5e) and the H atom a positive charge (~ +0.5e) [4]. This charge distribution is supported by the apparent agreement of the corresponding Q tensor with the measured one [1], and by the reaction of CrN_3^{2+} with HOF yielding $CrNO^{2+}$, indicating that the N bound to Cr must add a formally neutral O [14]. The polarity $(HO)^{\delta+}-F^{\delta-}$ is supported by the observation [15] that HOF hydroxylates rather than fluorinates aromatic compounds [16]. See also the polemics on the oxidation number of F in HOF [17 to 20].

A charge distribution $H^{\delta+}-(OF)^{\delta-}$ with a nearly neutral F atom, however, would be in accordance with the closeness of the OF stretching frequency of matrix-isolated HOF to the fundamental frequency of gaseous F_2, and also with the closeness of the OH frequency to that of the neutral OH radical [21]. Yet this distribution is not in accordance with the measured Q tensor [1].

Theoretical data from Mulliken population analyses applied to wave functions from ab initio calculations cover the ranges (in units of e) −0.045 to −0.22 for F, −0.13 to −0.31 for O, and +0.20 to +0.50 for H [6, 9, 22, 23, 26, 30]. For O2s and O2p orbital populations, see [31]. For charges from an MNDO and a CNDO calculation, see [32] and [33]. The charges −0.13, −0.13, and +0.26 were derived from calculated 1s orbital energies using an empirical correlation between the charges and the 1s energies of an atom in several molecules [24]; the charges used in obtaining these relations were determined by an integration procedure in [25].

Electric Field Gradient

The components of the tensor at the F nucleus from an ab initio calculation are reported in [9].

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3.24.2.5 Polarizability α

$\alpha = 1.89$ Å^3 was derived [1, 3] from the δ-function potential model of chemical binding proposed in [2]. The parallel and perpendicular components of α to the bond are given [1, 3].

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3.24.2.6 Magnetic Constants

Susceptibility χ in 10^{-6} erg·G^{-2}·mol^{-1}

$\chi = \frac{1}{3}(\chi_{aa} + \chi_{bb} + \chi_{cc}) = -13.0 \pm 1.3$ follows from the susceptibility components along the principal inertial axes (see p. 146), $\chi_{aa} = -19.7 \pm 2.1$, $\chi_{bb} = -8.6 \pm 2.1$, and $\chi_{cc} = -10.8 \pm 2.4$. Besides the two anisotropies of χ given below, a third piece of information to determine the principal components and to partition them into diamagnetic and paramagnetic contributions was an assumed value for the expectation value $\langle c^2 \rangle$ of the charge distribution (electronic + nuclear; the electronic part was estimated from free-atom values). This is directly related to $2\chi_{cc} - \chi_{bb} - \chi_{aa}$. The paramagnetic and diamagnetic contributions, χ^p_{ii} and χ^d_{ii}, to these components were obtained as follows:

χ^p_{aa}	χ^p_{bb}	χ^p_{cc}	χ^d_{aa}	χ^d_{bb}	χ^d_{cc}
1.1 ± 0.1	50.3 ± 0.1	49.5 ± 0.1	-20.8 ± 2.1	-58.9 ± 2.1	-60.3 ± 2.4

Two magnetic susceptibility anisotropies were directly measured by the molecular rotational Zeeman effect as $2\chi_{aa} - \chi_{bb} - \chi_{cc} = -19.6 \pm 0.6$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc} = +12.8 \pm 1.2$ [1]. Also see the microwave spectral tables [11]. The effect of intramolecular charge transfer on the diamagnetic components χ^d_{ii} was studied [2]. $\chi = -13.19$ and the components $\chi_{xx} = -16.74$, $\chi_{yy} = -11.53$, and $\chi_{zz} = -11.30$ (x $\parallel$ OH, molecule in xz-plane) were calculated by a finite perturbation method (see below) with a gauge invariant Gaussian basis set. $\chi \approx -16$ follows from the Pascal additivity rule [3].

Molecular g Values

Elements of the g tensor for the rotational magnetic moment in units of the nuclear magneton and referred to the principal inertial axes from the linear and quadratic rotational Zeeman effect [1, 11]:

g_{aa}	g_{bb}	g_{cc}
$+0.642 \pm 0.001$	-0.119 ± 0.001	-0.061 ± 0.001

The signs are chosen to obtain reasonable values for the Q tensor [1], cf. p. 142.

Chemical Shifts δ, Nuclear Magnetic Shielding Constants σ, in ppm

The ^{19}F chemical shift was measured for liquid HOF at -80 to -102°C. Referenced to gaseous F_2 at 25°C, $\delta = +402$ (-80 and -90°C), $+403$ (-102°C); the positive sign denotes a shift to higher field [4].

The shielding constant $\sigma = 187 \pm 20$ [5] is based upon the "absolute" ^{19}F scale reported in [6]; on that scale, $\sigma = 410.0$ (± 6) is assigned to HF, leading to $\sigma = 363.2$ for the often used reference compound SiF_4. The HOF shielding constant then results from a comparison of $\delta(HOF) = 402$ [4] with $\delta(HF) = 625$ [7, 8], both referenced to F_2 [5]. For calculated values, see below.

The ^1H chemical shift was measured relative to gaseous CH_4 (external standard) at 25°C (positive to higher field): $\delta = -12.1$ for gaseous HOF at 0 to 20°C and $\delta = -16.0$ for liquid HOF at −80°C. The latter value was obtained from a signal broadened by rapid exchange between HF and HOF protons, the HF impurity being present to ~20 mol% [4].

Theoretically calculated shielding constants for ^{19}F, ^{17}O, and ^1H nuclei are given in the following table. Part (or all) of the calculations based on the perturbed Hartree-Fock (HF) model [12, 13] used the finite perturbation method described by Pople et al. [14]. The gauge invariance of the vector potential associated with the perturbing field was approached by some authors by making use of gauge invariant atomic orbitals (GIAO, always expressed by Gauss functions):

^{19}F	^{17}O	^1H	method	gauge	remark	Ref.
206.45	−150.40	6.03	sum over states [15]		a)	[17]
—	—	21.99	perturbed HF	GIAO	b)	[18]
—	—	24.1	perturbed HF	GIAO	b)	[10]
190.5	172.4	28.2	finite perturbation	GIAO		[3]
−81.5	—	—	finite perturbation	origin = center of mass	c)	[5]

a) A simple sum-over-states formula was used for the second-order energy of the perturbed HF theory due to [15]. A criterion for the best choice of the gauge origin was developed in [16]. – b) For the method used, see [19], for the use of GIAO, see [20]. Components of σ in its principal axis system are $\sigma_{11} = 31.21$, $\sigma_{22} = 21.74$, and $\sigma_{33} = 13.02$ [18]. – c) Unpublished work of Ditchfield et al. [9], cited in [5]. The method probably was that published in [21]. For a comparison of the method with the sum-over-states perturbation theory, see [22].

Nuclear spin-spin coupling constants ^1J and ^2J were calculated [17] on the basis of the sum-over-states formula given by Nakatsuji [15].

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3.24.2.7 **Rotational and Centrifugal Distortion Constants** in MHz

The Kivelson and Wilson [1] constants for a planar asymmetric rotor in the notation of Kirchhoff [2] are $A' = A - \frac{1}{2}\tau_{abab}$, $B' = B - \frac{1}{2}\tau_{abab}$, $C' = C + \frac{3}{4}\tau_{abab}$ (the definition of C′ is misprinted in "Schwefel" Erg.-Bd. 3, 1980, p. 81), $\tau'_{\alpha\alpha\alpha\alpha} = \tau_{\alpha\alpha\alpha\alpha}$, $\tau'_{\alpha\alpha\beta\beta} = \tau_{\alpha\alpha\beta\beta} + 2\tau_{\alpha\beta\alpha\beta}$, where the indices α or β denote the principal inertial axes a, b, c and are constrained to $\alpha \neq \beta$. The a axis is nearly along the O–F bond and c is perpendicular to the molecular plane. A, B, and C are related to the effective moments of inertia I in the usual manner (e.g., $A = h/8\pi^2 I_a$). Since, in the general case, the six distortion constants (τ') cannot be determined from the observed energy levels, two sets of "determinable parameters" were suggested by Watson [3, 4]. The first set, again in Kirchhoff's notation [2], is $A'' = A' - \frac{1}{2}\tau'_{bbcc}$, $B'' = B' - \frac{1}{2}\tau'_{aacc}$, $C'' = C' - \frac{1}{2}\tau'_{aabb}$, $\tau_{\alpha\alpha\alpha\alpha}$ (α = a, b, c), $\tau_1 = \tau'_{aabb} + \tau'_{bbcc} + \tau'_{aacc}$, and $S \cdot \tau_2 = A'\tau'_{bbcc} + B'\tau'_{aacc} + C'\tau'_{aabb}$ $(S = A' + B' + C')$. For the second set ($\tilde{A}$, $\tilde{B}$, $\tilde{C}$, Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K), see [3]. The rotational constants (see below) show HOF and DOF to have asymmetry parameters $\varkappa = -0.99555$ and $\varkappa = -0.98630$, that is, to be nearly prolate symmetric tops.

Microwave rotational spectra of HOF and DOF [5] were reanalyzed by Lovas [6], who obtained the following constants for the molecular ground state (the τ's are rounded):

molecule	A″	B″	C″
HOF	585631.428 ± 0.159	26760.6692 ± 0.0120	25515.0321 ± 0.0095
DOF	316096.061 ± 0.045	25593.2238 ± 0.0030	23589.5489 ± 0.0027

molecule	τ_{aaaa}	τ_{bbbb}	τ_{cccc}
HOF	−340.3 ± 0.4	−0.4112 ± 0.0003	−0.3422 ± 0.0006
DOF	−106.50 ± 0.03	−0.36328 ± 0.00005	−0.26839 ± 0.00004

molecule	τ_1	τ_2
HOF	−10.785 ± 0.002	−0.7635 ± 0.0005
DOF	−7.884 ± 0.002	−0.7571 ± 0.0001

The following parameters were derived assuming planarity conditions (see [2]). τ_{aabb} and τ_{abab} in the following table were obtained from τ_1 and τ_{cccc}; they may be obtained also from τ_2 and τ_{cccc}, or from τ_1 and τ_2, see the original paper [6]:

molecule	A'	B'	C'
HOF	585631.24 ± 0.16	26760.264 ± 0.053	25510.233 ± 0.050
DOF	316095.907 ± 0.044	25593.117 ± 0.003	23585.868 ± 0.003

molecule	τ'_{aabb}	τ'_{bbcc}	τ'_{aacc}
HOF	−9.6 ± 0.1	−0.3764 ± 0.0003	−0.8 ± 0.1
DOF	−7.362 ± 0.003	−0.30817 ± 0.00005	−0.214 ± 0.003

molecule	τ_{aabb}	τ_{abab}
HOF	0.9 ± 0.1	−5.7 ± 0.1
DOF	0.150 ± 0.002	−3.614 ± 0.001

The second set of determinable parameters was derived by Pearson and Kim [5] from their microwave measurements:

molecule	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$
HOF	585631.20 ± 0.14	26760.31 ± 0.12	25510.19 ± 0.12
DOF	316096.02 ± 0.06	25593.91 ± 0.01	23585.28 ± 0.01

molecule	Δ_J	Δ_{JK}	Δ_K
HOF	0.09414 ± 0.00009	2.4146 ± 0.0006	82.52 ± 0.08
DOF	0.07904 ± 0.00003	1.7349 ± 0.0009	24.82 ± 0.01

molecule	δ_J	δ_K
HOF	0.00432 ± 0.00001	1.12 ± 0.06
DOF	0.00593 ± 0.00001	1.183 ± 0.002

This set is also reported in [6, 7]. For the constants A, B, and C, see [5, 8]. A centrifugal distortion analysis in the symmetric-top approximation of several a-type transitions in the microwave rotational spectrum yields the HOF(DOF) constants $D_J = 0.0934 \pm 0.0015$ (0.0775 ± 0.0021) and $D_{JK} = 2.417 \pm 0.005$ (1.746 ± 0.007) [8]. The constants A, ½(B + C), and D_K were evaluated from the IR absorption spectrum of gaseous HOF and DOF [9].

Several centrifugal distortion constants were also derived from force fields [10, 11, 12].

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3.24.2.8 Moments of Inertia. Geometrical Structure

Moments of Inertia I

I_x in 10^{-40} g·cm^2 (x = a, b, c) was evaluated for HOF [1] from the atomic coordinates reported in [2]: $I_a = 1.433$, $I_b = 31.368$, and $I_c = I_a + I_b = 32.801$.

Moments of inertia in amu·Å^2 for HOF (DOF) may be obtained from effective rotational constants X = A, B, C [2] using $I_x \cdot X = 505391$ amu·Å^2·MHz: $I_a = 0.8630$ (1.5990), $I_b = 18.8878$ (19.7481), and $I_c = 19.8083$ (21.4257). The resulting inertial defect $\Delta = I_c - I_b - I_a$ is 0.058 amu·Å^2 for HOF and 0.079 for DOF [2]. $\Delta = 0.0546$ (0.0721) [4], 0.0567 [5], and 0.0552 [22] were derived from molecular force fields.

Bond Distances r in Å, **Bond Angle**

Values from the rotational constants A, B, C are [1, 2, 6]: r(O–H) = 0.966, r(O–F) = 1.442, and ∢HOF = 96.78° (effective structure). The following uncertainty ranges were assigned to these parameters in a critical compilation of molecular structures [7]: 0.010 to 0.020 Å to the O–H distance, 0.002 to 0.005 Å to the O–F distance, and 0.5 to 1.0° to the bond angle.

Atomic coordinates (in Å) in the principal axis system [2]:

axis	H	O	F
a	+0.9181	+0.7555	−0.6848
b	+0.8875	−0.0652	+0.0078

A similar set of molecular constants (moments of inertia, molecular structure, and atomic coordinates) as presented in [2] was previously derived by the same group of workers from a smaller number of rotational microwave transitions (a-type transitions only) [3].

Bond length changes which occur on substituting H by F, or vice versa, in HMF compounds with elements M of the first or second period have been considered [9].

Theoretical equilibrium distances and angles were obtained from ab initio [10 to 14, 21, 23 to 25] and several types of semiempirical calculations [15 to 17, 19, 20, 26]. For ab initio calculations of the O–F distance, see also [8, 18, 27].

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3.24.2.9 Molecular Vibrations

Fundamental Frequencies

Wavenumbers (in cm^{-1}) of the O–H stretching (ν_1), the bending (ν_2), and the O–F stretching (ν_3) mode, all of symmetry type a′, from the analysis of the rotational subbands observed in the gas-phase IR spectra of HOF and DOF [1] are:

molecule	ν_1	ν_2	ν_3
HOF	3578.5	1354.8	889.0
DOF	2643.5	1003.9	891.1

$\nu_1 = 3537.1$, $\nu_2 = 1359.0$, and $\nu_3 = 886.0$ were observed in the IR spectrum of HOF isolated in an N_2 matrix [3]. These latter ν_1 and ν_3 together with $\nu_2 = 1393.0$ from an older N_2 matrix study [4] (see below) are listed in a table [5] of selected values of fundamental vibrations (numbering of ν_2 and ν_3 interchanged).

According to [3], the wavenumbers of the matrix study [4] actually refer to a H-bonded complex HF···HOF, where HF was a product of thermal decomposition of HOF: $\nu_1=3483\pm1$ and $\nu_3=884.0\pm0.5$ were reported; for ν_2, see above. For DOF ($H^{18}OF$ in parentheses): $\nu_1=2573$ (3472), $\nu_2=1029.5$ (1390.3), and $\nu_3=885.5$ (857.0) [4].

Fundamentals of three isotopic species were derived from an anharmonic potential energy function, which was based on an ab initio calculation and on experimental information for the most common isotopic HOF species (for the fundamentals, see table above) [6]. Later calculations for HOF and DOF [15], using both SCF and CI methods, were based upon the same potential energy function.

Harmonic Frequencies ω_i in cm^{-1}

molecule	ω_1	ω_2	ω_3	remark	Ref.
HOF	3744.1	1420.1	899.0	a)	[8]
HOF	3735.6	1405.2	933.5	b)	[6]
DOF	2724.2	1044.1	901.1	a)	[8]
DOF	2722.1	1034.0	931.0	b)	[6]

a) ω_1 was derived from the experimental ν_1 (see the first table in this section) using the OH and OD anharmonicity constants [9] $x_{11}=-82.8$ and $-40.4\ cm^{-1}$ for HOF und DOF, respectively. For ω_2, the Teller-Redlich product rule was applied. ω_3 was estimated as $\omega_3=\nu_3+10$ [8]. Improved wavenumbers ω_1 were obtained using apparently more recent values $\omega_ex_e=-85$ for OH and $-45\ cm^{-1}$ for OD: $\omega_1(HOF)=3748.5$ and $\omega_1(DOF)=2733.5$ [2]. – b) Derived from the harmonic part of an anharmonic potential function (see above). The same ω_i (rounded) are given in [15].

Ab initio SCF calculations give widely differing harmonic frequencies for HOF [16, 17]. Inclusion of electron correlation by the Møller-Plesset procedure [7] leads to $\omega_1=3710$, $\omega_2=1407$, and $\omega_3=986$ [16].

Overtones and Combinations, in cm^{-1}

$2\nu_2=2686.8$ and 1993.9 (band centers) for HOF and DOF, respectively, and $2\nu_3=1763.8$ (Q branch peak) for DOF have been observed in the gas-phase IR spectrum. (Assignment $2\nu_3$ from [6], assignment in original paper [1] was $\nu_1-\nu_3$.) $2\nu_2$ of HOF may be in Fermi resonance with $\nu_1-\nu_3$ [1]. Theoretical data for $2\nu_1$, $2\nu_2$, $2\nu_3$, $3\nu_3$, $4\nu_3$, $\nu_2+\nu_3$, $2\nu_2+\nu_3$, and $\nu_2+2\nu_3$ of the 4 isotopic species HOF, DOF, $H^{18}OF$, and $D^{18}OF$ were derived from an anharmonic potential function [6].

Vibrational Amplitudes

Root-mean-square amplitudes of vibration u in Å were generally derived from the gas-phase frequencies given in [1]. Amplitudes at 298 K [12, 14] follow:

molecule	u(H–O)	u(O–F)	u(H···F)
HOF	0.0705	0.0466	0.1064
DOF	0.0594	0.0457	0.0905

Similar values for HOF are given in [13, 18]. The amplitudes for HOF and DOF in [10] (at 0, 298, and 500 K) differ more widely from those in the table above. The data for HOF, DOF, and

$H^{18}OF$ at 298 K in [11] were based upon the frequencies [4] of the H-bonded complex HF···HOF. For amplitudes calculated by SCF and CI procedures applied to a vibrational Hamiltonian, see [15].

Coriolis Coupling Constants ζ

The ζ's obey the sum rule $\zeta_{12}^2+\zeta_{13}^2+\zeta_{23}^2=1$. Two sets of absolute values $|\zeta_{12}|$, $|\zeta_{13}|$, and $|\zeta_{23}|$ were derived from different force fields: 0.0087, 0.2094, and 0.9777 [13] and 0.1987, 0.2130, and 0.9566 [18].

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3.24.2.10 Force Constants

Using internal coordinates the general quadratic potential function may be written as $2V = f_{OH}\Delta r_{OH}^2 + f_{OF}\Delta r_{OF}^2 + f_{\alpha}\Delta\alpha^2 + 2f_{OH,OF}\Delta r_{OH}\Delta r_{OF} + 2f_{OH,\alpha}\Delta r_{OH}\Delta\alpha + 2f_{OF,\alpha}\Delta r_{OF}\Delta\alpha$. The constants reported in the literature differ since different assumptions regarding the interaction constants were made:

f_{OH} mdyn/Å	f_{OF} mdyn/Å	f_{α} mdyn·Å	$f_{OH,OF}$ mdyn/Å	$f_{OH,\alpha}$ mdyn	$f_{OF,\alpha}$ mdyn	input parameters	remark	Ref.
7.7936	4.4184	1.0278	0	−0.1564	0.5226	ω_1, ω_2, ω_3 of HOF and DOF	a)	[1]
7.839 ±0.226	4.535 ±0.060	0.931 ±0.010	−0.303 ±1.743	−0.051	0.638 ±0.069	ω_1, ν_2, ν_3 of HOF and DOF	b)	[2]

f_{OH} mdyn/Å	f_{OF} mdyn/Å	f_α mdyn·Å	$f_{OH,\,OF}$ mdyn/Å	$f_{OH,\,\alpha}$ mdyn	$f_{OF,\,\alpha}$ mdyn	input parameters	remark	Ref.
7.142	4.270	0.922	—	—	0.827	ν_1, ν_2, ν_3 of HOF and DOF	c)	[3]
7.8353	4.2727	0.9293	—	+0.100	0.416	ω_1, ν_2, ν_3 of HOF and DOF	d)	[5]

a) The ω_i used may be found in the first and third rows of the table on p. 150. $f_{OH,OF}$ was constrained to be zero [1]. – b) For ω_1, the improved wavenumbers mentioned in footnote a) of the table on p. 150 were used. ν_2 and ν_3 were taken from the gas-phase measurement [4]. $f_{OH,\alpha}$ was constrained to the value of an ab initio calculation [2]. – c) The measured ν_i [4] were used. For an ab initio calculation of the constants, see the original paper [3]. – d) Wavenumbers for the ν_1 fundamentals [4] were corrected for anharmonicity by factors of 1.0456 and 1.0331 for HOF and DOF, respectively. Wavenumbers for the ν_2 and ν_3 vibrations were directly taken from [4]. Force constants were converted from $N \cdot m^{-1}$ used throughout the original reference [5] to mdyn, Å units by applying the rules and using the values for the internuclear distances r(OF) and r(OH) given therein.

Sets of six force constants were also given [6, 8, 9]. Two different sets for HOF and DOF containing six constants each are reported [7].

The constants f_{OH}, f_{OF}, f_α, and $f_{OF,\,\alpha}$ in [10] were based upon HOF, DOF, and $H^{18}OF$ vibrations, which, however, as outlined on p. 150, proved to be perturbed by H-bonding to HF.

Constants of the simple valence force field. Least-squares calculations with six HOF and DOF fundamentals of a simple three-parameter force field did not yield a converging set of force constants. With the addition of the OF stretch-bend interaction constant, an acceptable set of converging values was obtained [3]. (They comprise the third set of the table above.) The measured ν_i of HOF alone yielded $f_{OH} = 7.10$, $f_{OF} = 4.27$, and $f_\alpha = 0.87$ (all in mdyn/Å) [4]. For similar data, see [11].

Constants of the Urey-Bradley force field were calculated [7].

An anharmonic force field was derived from quantum mechanical calculations and experimental data for the equilibrium geometry and the HOF fundamentals [12].

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3.24.2.11 **Bond Dissociation Energies** D in kcal/mol

$D^\circ_0(\text{HO–F}) = 50.4$ (2.18_6 eV) follows from the heats of formation of HOF (see p. 137), of OH(g) and of F(g) [1]. Within experimental error, $D^\circ_{298} = 51.7$ equals the dissociation energy D(HO–OH) = 51.2 kcal/mol of H_2O_2, isoelectronic with HOF [2]. D(FO–H) = 100 ± 15 was calculated from JANAF estimates (sic) [3].

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3.24.2.12 Spectra

Microwave Spectrum

The microwave spectral tables for triatomic molecules [3] contain 47 transitions for HOF with frequencies from 52269.90 to 370057.77 MHz and 42 transitions for DOF from 83295.86 to 250799.63 MHz. 24 of these transitions, with $\Delta K_{-1} = 0$, $J'' = 1$ to 4, for both HOF and DOF, were measured by [4]. 9 additional HOF transitions with $\Delta K_{-1} = 0$, in the range 361349.55 to 370057.77 MHz, and 13 further HOF transitions with $\Delta K_{-1} = \pm 1$ as well as 18 DOF transitions with $\Delta K_{-1} = \pm 1$ are due to [5]. The lowest frequency transition of HOF is reported in [6]. The assignments HOF $7_{1,7} \leftarrow 6_{1,6}$ at 361349.55 and DOF $5_{3,2} \leftarrow 4_{3,1}$ at 245734.60 MHz were excluded from the reanalysis of the spectrum. The calculated frequencies are 361350.22 and 245735.11 MHz [3].

The Zeeman effect was observed for the four HOF lines at 52269.90 ($1_{0,1} \leftarrow 0_{0,0}$), 103282.89 ($2_{1,2} \leftarrow 1_{1,1}$), 104536.04 ($2_{0,2} \leftarrow 1_{0,1}$), and 105773.90 MHz ($2_{1,1} \leftarrow 1_{1,0}$) [6] (frequency values from [3]).

Infrared and Raman Spectra

In the IR spectrum of the gas at 60 to 400 Torr, the rotational subbands of the three fundamental vibrations and of the overtone $2\nu_2$ (see p. 150) of HOF and DOF were observed [7]. The spectrum of matrix-isolated HOF was studied at HOF : N_2 ratios of ~1 : 3000 and ~1 : 20000. The fundamental vibrations (see p. 149) were observed as well as a small band at 1393 cm^{-1}, definite only in the more concentrated matrix and presumably due to the bending mode of an HOF molecule hydrogen-bonded to HF, a product of thermal decomposition of HOF [8]. The complex spectra in N_2 and Ar matrices are also partly due to HF···HOF [9]. IR spectra of solid films were studied at −195°C, and the intramolecular vibrations ν_1, ν_2, ν_3, $2\nu_2$, and $2\nu_3$ of HOF, DOF, and $H^{18}OF$ were found. Bands at 628 and 448 cm^{-1} for HOF were ascribed to a simple cyclic dimer. But infinite planar zigzag chains could not be ruled out [10], and this latter interpretation is supported by the Raman spectrum (see table p. 154).

The Raman spectrum of the solid was excited at liquid-N_2 temperature by the 5145 Å line of an Ar^+ laser. It is interpreted by a H-bonded structure consisting of planar zigzag chains with two HOF molecules per primitive unit cell (similar to the structure of solid HF, see "Fluorine" Suppl. Vol. 3, 1982, pp. 88/9). Thus, by analogy with the crystal structures of HF and HCOOH, the factor group is considered isomorphous with the C_{2v} point group. The eighteen eigenmodes at zero wave vector of a planar infinite zigzag chain consisting of repeating $(HOF)_2$ units then factorize as $6a_1 + 6b_1 + 3a_2 + 3b_2$. Modes of a_1 and b_1 symmetry are in-plane, while a_2 and

b_2 are out-of-plane. One mode in each species belongs to the acoustical branch, that is, has zero frequency at zero wave vector [11]. The following table shows the wavenumbers in cm^{-1} of the optical modes observed for HOF in the Raman [11] and in the IR spectrum [10]:

a_1 modes	O–H stretch	HOF bend	O–F stretch	libration	rotation
Raman [11]	3359	—	884	154	79
IR [10]	3370	1397	885	—	—

b_1 modes	O–H stretch	HOF bend	O–F stretch	libration	libration
Raman [11]	3283	—	884	123	104
IR [10]	3285	1397	885	—	—

a_2 modes	libration	rotation
Raman [11]	—	72
IR [10]	628	—

b_2 modes	libration	libration
Raman [11]	—	227
IR [10]	448	—

Visible and Ultraviolet Spectra

Significant absorption of the colorless vapor starts below 400 nm [1]. The absorption cross section of the continuum between ~400 and 200 nm was measured at 295 K. It rises from $\sim 8 \times 10^{-22}\ cm^2$ at 375 nm to $\sim 3 \times 10^{-19}\ cm^2$ at 200 nm. The continuous nature indicates absorption to unbound states [2].

References:

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3.24.3 Thermal Properties

The vapor pressure is ~5 Torr at −64°C [1] and <1 Torr at −79°C [1, 2]. The normal boiling point lies somewhat below room temperature (sic) [2]. The melting point is at −117°C [1, 2].

Thermodynamic functions for the ideal gas (molar heat capacity C_p°, entropy S°, Gibbs free energy function $(G^\circ - H_{298}^\circ)/T$, all in $cal \cdot mol^{-1} \cdot K^{-1}$, enthalpy $H^\circ - H_{298}^\circ$ in kcal/mol) were calculated from the molecular constants between T = 0 and 6000 K at 100 K intervals [3]. Some values are given on the following page.

T	0	100	298	600	1000	2000	4000	6000
C°_p	0	7.950	8.587	10.236	11.457	12.882	13.601	13.768
S°	0	45.323	54.174	60.729	66.274	74.739	83.959	89.511
$-(G^\circ - H^\circ_{298})/T$	∞	61.483	54.174	55.965	59.053	64.981	72.409	77.245
$H^\circ - H^\circ_{298}$	−2.411	−1.616	0	2.859	7.221	19.516	46.199	73.599

$S^\circ_{298} = 54.15$ cal·mol^{-1}·K^{-1} was previously calculated [4]. The older data for 100 to 2000 K [5] and 0 to 6000 K [6] were based upon assumed molecular structures.

References:

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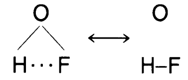
3.24.4 Chemical Behavior

Generally, HOF acts as a donor of atomic oxygen or of its conjugate acid OH^+. The oxygen transfer may be interpreted in terms of the great affinity between the proton and the F atom [1]:



The oxidizing properties of HOF in aqueous solution are similar to those of F_2 [2].

A rapid proton exchange with D_2O was observed at room temperature with some evidence of exchange even at much lower temperature, as expected for an acidic H atom [3].

The thermal decomposition products are HF and O_2 [3 to 5]. The half-life varies from 5 min to >1 h at room temperature and may be affected by pressure and by traces of impurities such as H_2O [4]. A half-life of 30 to 50 min in a Kel-F cell was reported [6]. The decomposition in such a vessel is affected by HOF attacking the Kel-F [3]. The reaction $2HOF \rightarrow 2HF + O_2$ should be exothermic by 84.7 kcal/mol. An exothermicity of about 75 kcal/mol was previously estimated from the OH and OF bond energies which were taken from H_2O and OF_2. A rapid decay reaction is also suggested by the H-bonding properties of HOF. In a H-bonded collision complex, H transfer is facilitated by the charge displacement from H to F [7].

Photodissociation was observed at wavelengths below ~400 nm. Solar photodissociation coefficients were calculated as a function of altitude from the measured absorption cross sections. The maximum photolytic lifetime for HOF in the stratosphere was estimated to be on the order of hours [17].

Association reaction with H^+: For calculated energy changes, see pp. 141, 160.

An energy change for the reaction

$$HOF + H_2 \rightarrow HF + H_2O$$

was calculated by ab initio SCF methods and compared to the corresponding reactions of FCH_3, NH_2F, and F_2 [16].

The rate constant for the H abstraction reaction

$$HOF + F \rightarrow HF + OF$$

was estimated to be $>2\times10^{-10}$ $cm^3\cdot molecule^{-1}\cdot s^{-1}$ ($>1.2\times10^{14}$ $cm^3\cdot mol^{-1}\cdot s^{-1}$ [15]) at 300 K on the basis of a mass-spectrometric discharge-flow study. Since OF decomposes to reform F atoms, $2OF \rightarrow O_2 + 2F$, the whole process can be termed an F-catalyzed decomposition of HOF [9, 14].

The reaction

$$HOF + F_2 \rightarrow OF_2 + HF$$

may be responsible for the production of small quantities of OF_2 observed in the reaction of F_2 with acidic aqueous solutions [2, 19].

The reaction with I^-

$$HOF + 3I^- \rightarrow I_3^- + OH^- + F^-$$

was used for a quantitative analysis of HOF [3].

Association reaction with Li^+. An energy change of −24 kcal/mol was calculated by ab initio SCF methods for the attachment of Li^+ at F. Attachment at O is predicted to give an unstable product [18].

The Ag^+ ion is oxidized by HOF to Ag^{2+} [2, 5].

The rapid reaction of HOF with H_2O gives HF, O_2, and H_2O_2 [1 to 5]. A steady-state concentration of H_2O_2 was found when HOF reacted with H_2O containing 0.01 M HF (to minimize pH changes). For the two reactions

$$(1)\ HOF + H_2O \rightarrow H_2O_2 + HF \quad \text{and} \quad (2)\ HOF + H_2O_2 \rightarrow HF + H_2O + O_2$$

the ratio $k_1/k_2 = 0.86\,M$ could be directly taken as the steady-state concentration of H_2O_2. The reaction with H_2O_2 (9M solution in H_2O) was studied with ^{18}O as a tracer. The O_2 produced (besides HF and H_2O) contains substantial amounts of oxygen from HOF. A possible sequence is then

$$HOF + H_2O_2 \rightarrow H_2O_3 + HF \quad \text{and} \quad H_2O_3 \rightarrow H_2O + O_2$$

The amounts of oxygen in O_2 transferred from HOF were, however, badly reproducible and thus, the following chain reaction may also be involved

$$\begin{aligned} H^{18}OF + H_2O_2 &\rightarrow HF + {}^{18}OH + HO_2 \\ HO_2 + H^{18}OF &\rightarrow O_2 + HF + {}^{18}OH \\ H_2O_2 + {}^{18}OH &\rightarrow HO_2 + H_2{}^{18}O \end{aligned}$$

recombination of ^{18}OH with HO_2 being apparently unimportant [19].

In solid matrices, HF may form the H-bonded complex $HF\cdots HOF$ [8, 10].

The BrO_3^- ion is oxidized by HOF to BrO_4^- in alkaline solution [2, 4, 5].

The reaction of HOF with HSO_4^- produces a mixture of HSO_5^- and H_2O_2. ^{18}O tracer studies show that HOF reacts predominantly via the direct transfer of an oxygen atom to a hydrogensulfate ion and this transfer proceeds much faster than the exchange of oxygen between HOF and water [1].

The reactions of HOF with various complexes of Cr^{III} were studied in aqueous perchloric acid solutions. $R(H_2O)^{3+}$ and RF^{2+}, where R represents $Cr(H_2O)_5$, are unreactive with HOF. $R(ClO_3)^{2+}$, $R(NO)^{2+}$, RCl^{2+}, and RBr^{2+} show increasing reactivity in this order, the principal product being Cr^{3+}. The most reactive complex $R(N_3)^{2+}$ forms $R(NO)^{2+}$ [2]:

$$HOF + Cr(H_2O)_5(N_3)^{2+} \rightarrow Cr(H_2O)_5(NO)^{2+} + N_2 + HF$$

^{18}O tracer studies with $Cr(NH_3)_5(N_3)^{2+}$ show that $Cr(NH_3)_5(NO)^{2+}$ is formed by the direct transfer of an O atom [1].

Reactions with organic compounds. HOF converts alkenes into α-fluoro alcohols, acetylenes mainly into α-fluoro carbonyl compounds [11], aromatic compounds (benzene and its monosubstituted derivatives, p-xylene, naphthalene) into phenolic products [12], and octaethylporphyrin into the N-oxide [13].

References:

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3.25 The Isomers of Hypofluorous Acid, FHO and HFO

CAS Registry Number: HFO *[86825-58-3]*

Both species are predicted to be metastable and to represent local minima of an analytical potential function [1], see p. 138 and Fig. 3, p. 139.

FHO

A $^3\Sigma^-$ ground state of the H-bonded linear species $O\cdots HF$, bound with respect to $O(^3P)+HF(^1\Sigma^+)$, is predicted from an ab initio SCF calculation. The electron configuration is $1\sigma^2\cdots5\sigma^2 1\pi^4 6\sigma^2 2\pi_x 2\pi_y$. The $O\cdots H$ bond length and dissociation energy are calculated as $r(O\cdots H)=2.10$ Å (at $r(H\text{–}F)=0.906$ Å, taken from the $^1\Delta$ calculation, see below) and 0.0040 a.u. (0.11 eV) [1].

The lowest singlet is $^1\Delta$, bound with respect to $O(^1D)+HF(^1\Sigma^+)$. Bond lengths from an SCF and from a CI calculation are $r(O\cdots H)=2.123$ and 2.090 Å, and $r(H\text{–}F)=0.906$ and 0.921 Å [1]. Another ab initio calculation [7] including correlation energy according to the Møller-Plesset method [6] predicts $r(O\cdots H)=1.956$, $r(H\text{–}F)=0.959$ Å, and $\sphericalangle OHF=179.9°$. The neutral FHO is termed a "complex" between O and HF [7]. The next higher singlets are $^1\Pi$ and $^1\Sigma^+$ [1].

The molecular vibrations were calculated from a potential surface by a variational procedure due to [2]. For the O···F stretching mode ν_1, the bending mode ν_2, and the H atom vibration between the heavy atoms ν_3, the wavenumbers 454, 605, and 3319 cm^{-1} were obtained [1]. An extension of that potential function by inclusion of parameters calculated previously [1] for FHO and HFO which correspond to local minima on that potential surface gave $\nu_1 = 439$, $\nu_2 = 555$, and $\nu_3 = 3897$ cm^{-1} [3]. In both cases ν_2 is taken as one-half of the energy of the (02^00) vibrational level.

HFO

The species contravenes the normal valencies of O and F. If, however, the F in the OF radical carries ~25% of the unpaired electron, as shown by calculations [4], then there could be some attraction between F and an approaching H. SCF + CI calculations show bent $HFO(^1A')$ to be bound with respect to $O(^1D) + HF(^1\Sigma^+)$ [1]. An enthalpy of formation of +47.4 kcal/mol was calculated by the MNDO method [9]. Bond lengths r(H–F), r(F–O) (in Å) and the bond angle $\sphericalangle$HFO in the $^1A'$ state from a CI calculation are 0.929, 1.675 and 96.0° [1]. From a Møller-Plesset [6] calculation 0.970, 1.667 and 94.0° [7], and from an SCF calculation 0.956, 1.592 and 107.3° [5] were obtained. r(F–O) = 1.928 was also calculated [8].

References:

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3.26 The Ions HOF^+, HOF^-, HFO^+, and FHO^+

CAS Registry Numbers: HOF^+ *[90243-22-4]*, HOF^- *[36505-07-4]*, HFO^+ *[90176-63-9]*

The HOF^+ Ion

The formation enthalpy $\Delta H^\circ_{f,0} = 270.3$ kcal/mol was derived from $\Delta H^\circ_{f,0}(HOF) = -22.8$ kcal/mol and the ionization potential $E_i(HOF) = 12.71$ eV [1]. For the ground state $^2A''$, the total energy, charge densities, and the optimized bond distances r(O–H) = 1.053, r(O–F) = 1.337 Å, and the bond angle $\sphericalangle$HOF = 105.4° were obtained from an ab initio calculation including correlation energy [10] by the Møller-Plesset procedure [9]. For an SCF calculation, see [2]. An O–F stretching vibration of 1050 cm^{-1} was observed in the HOF photoelectron (PE) spectrum [11]. The value 946 cm^{-1} [3] is probably in error [11]. The electronically excited states $^2A'$ and $^2A''$ are 14.8 and ~16 eV above the ground state of neutral HOF for vertical excitation [4] as indicated by the PE spectrum [3] (cf. p. 140). A calculation with perturbation corrections to Koopmans' theorem gives 15.09 and 16.94 eV (and 17.97 eV for the next higher $^2A'$ state) [4].

The HOF^- Ion

The ion was identified by its ESR spectrum in glassy aqueous solutions of KF after γ-irradiation at 77 K. Observed g values (z‖O–H) were $g_z = 2.1$ and $g_x = g_y = 2.009$. Hyperfine (hf) coupling constants (in G) for ^{19}F were $a_z = (\pm)7$, $a_x = 33$, $a_y = (\pm)7$, $a_{iso} = 15.8$ if $a_z > 0$, $a_y > 0$ or 6.4 if $a_z < 0$, $a_y < 0$; likewise the hf coupling constants for ^1H were $a_z \approx 0$, $a_y = -40$, and $a_x = -25$ [5], see also preliminary data in [6] and the tabulation [7] of g and a. The spectra of HOF^- and DOF^- can be interpreted in terms of a hydroxyl radical weakly interacting with an F^- ion through an O2p orbital perpendicular to the OH bond. This is consistent with a low spin density at the F^- ion as derived from the ^{19}F hf coupling constants [5], and was also predicted by analogy with $BrOH^-$ and IOH^- [8].

The Ions HFO^+ and FHO^+

The ground states $^2A''$ of bent HFO^+ and $^2\Pi$ of linear FHO^+ are calculated to lie 20.8 and 34.8 kcal/mol above the HOF^+ ground state. Bond distances and angles from these calculations were r(H–F) = 1.022, r(F–O) = 1.474 Å, and $\sphericalangle$HFO = 110.1° for HFO^+ and r(F–H) = 1.460, r(H–O) = 1.134 Å, and $\sphericalangle$FHO = 179.4° for FHO^+. Thus, FHO^+ shows a strong H-bond between F and OH^+ [10]. For an SCF calculation of HFO^+, see [2].

References:

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[10] G. Frenking, W. Koch (Chem. Phys. Letters **105** [1984] 659/62).

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3.27 Dimeric Hypofluorous Acid, $(HOF)_2$

Low-frequency IR absorption data of solid HOF were believed to be consistent with the formation of a planar cyclic dimer (point group C_{2h}) [1]. The Raman spectrum showed, however, that an isolated dimeric structure in the solid is not in accord with the spectral features [2]. Ab initio calculations point to an open chain structure. The distance between the two HOF is given as 2.81 Å. Two stable structures of comparable energies were found [3].

References:

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3.28 Protonated Hypofluorous Acid

CAS Registry Number: *[81128-65-6]*

Ab initio calculations with correlation energy [1] and without it [1, 2] were performed for both H_2OF^+ and $HOFH^+$, corresponding to protonation of HOF at either O or F. The assumed structures are nonplanar H_2OF^+ with two equal OH bond lengths and planar $HOFH^+$, the point group is C_s in each case. The total energies of the respective ground states $^1A'$ show H_2OF^+ to be the more stable species, the energy difference is ≥ 13.5 kcal/mol [1, 2]. The barrier to proton transfer amounts to 20.9 kcal/mol [1]. Another ab initio calculation [3] is concerned with the use of O2s and O2p orbitals in the bonding in several H_2OX^+ ions (X = H, CH_3, NH_2, OH, and F).

Geometrical parameters (r in Å) from the SCF-MO calculations for H_2OF^+ and for trans-$HOFH^+$ (for the somewhat less stable cis-$HOFH^+$, see original paper) [2] follow:

species	r(O-F)	r(O-H)	r(F-H)	∢HOF	∢OFH	∢HOH
H_2OF^+	1.371	1.011	—	128.3°	—	112.2°
trans-$HOFH^+$	1.427	1.026	0.980	98.2°	107.6°	—

For the O-F bond length, see also [1].

References:

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3.29 Fluorohydroperoxide, HO_2F

CAS Registry Number: *[36336-12-6]*

HO_2F is assumed to be an intermediate in the reaction of F_2 with H_2O_2 in aqueous solution [8]:

$$F_2 + H_2O_2 \rightarrow HO_2F + HF, \qquad HO_2F \rightarrow O_2 + HF$$

The standard enthalpy of formation $\Delta H_f^\circ = -8.7$ kcal/mol was derived from a calculated value of 6.3 kcal/mol for the enthalpy of the (hypothetical) reaction $HO_2F(g) + H_2O(g) \rightarrow H_2O_2(g) + HOF(g)$. This reaction enthalpy was derived from SCF total energies of the reactants and products [3] and is called a "bond separation energy", since a molecule with three heavy atoms (HO_2F) is converted into molecules with two heavy atoms and the same type of formal bonds [1, 2, 3]. For ΔH_f°(HOF), an estimated value of −27.7 kcal/mol was inserted, cf. p. 137, [3]. $\Delta H_f^\circ(HO_2F) = -25.6$ kcal/mol (−107.12 kJ/mol) was calculated by a semiempirical SCF-MO method (MINDO) [4].

The total energy was calculated by ab initio methods [3, 5, 7]. The energy in [3] is for a "standard geometry": bond lengths r(O-H) = 0.96, r(O-F) = 1.42, r(O-O) = 1.48 Å, bond angles ∢OOH = ∢OOF = 109.47° [6], and dihedral angle Φ(HOOF) = 90° [3].

The dipole moment $\mu = 2.64$ D (presumably for the standard geometry from [3]) and the ionization potential $E_i = 14.75$ eV were calculated in [5]; for atomic charges, see the original paper.

Structural parameters (r in Å) from a semiempirical calculation [4] are:

r(O–H)	r(O–F)	r(O–O)	∢OOH	∢OOF	Φ(HOOF)
0.970	1.490	1.319	109.9°	109.9°	81.3°

A dihedral angle $\Phi = 75°$ follows from an ab initio calculation [7], in which the residual structural parameters had their "standard" values.

For the potential function of the internal rotation about the O–O bond, a Fourier expansion of the form $2V(\Phi) = V_1 \cdot (1 - \cos \Phi) + V_2 \cdot (1 - \cos 2\Phi) + V_3 \cdot (1 - \cos 3\Phi)$ was used. The constants $V_1 = 4.20$, $V_2 = -5.17$, and $V_3 = -0.13$ kcal/mol were calculated (this gives a minimum at $\Phi = 77°$) [7], see also comparison with the constants for related molecules [5]. Rotational barriers ΔV(cis) and ΔV(trans) from semiempirical [4] and ab initio [7] calculations are compiled below. These are relative energies of the cis conformation at $\Phi = 0°$ and the trans conformation at $\Phi = 180°$ with respect to the minimum; units are kcal/mol:

ΔV(cis)	ΔV(trans)	Ref.
6.8	10	[4]
3.33	7.39	[7]

A rotational barrier (energy difference between the cis conformation and the standard-geometry conformation (i.e. $\Phi = 90°$) was calculated [9] using a concept of bond orbitals [10].

The bond dissociation energy D(HO–OF) = 284 kJ/mol was derived from ΔH_f° of OH and HO_2F, calculated by a semiempirical MO method (MINDO), and from ΔH_f°(OF) = 106 kJ/mol (see p. 66) [4]. This D correlates better with the calculated O–O bond length than does D = 215.7 kJ/mol obtained [4] with ΔH_f°(OF) = 38 kJ/mol [11].

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3.30 Fluorohydrotrioxide and -tetraoxide, HO_3F and HO_4F

CAS Registry Numbers: HO_3F *[75968-90-0]*, HO_4F *[75968-91-1]*

The formation enthalpies $\Delta H_f^\circ = -50.44$ and $+9.50$ kJ/mol for HO_3F and HO_4F, respectively, and the structural parameters were calculated by a semiempirical MO method, C. Glidewell (J. Mol. Struct. **67** [1980] 35/44).

4 Fluorine and Nitrogen

The field of fluorine-nitrogen chemistry received much attention when in the middle of the 1950s interest in its compounds as possible high-energy oxidizers for rocket fuels began to grow. Numerous new compounds were synthesized since that time as impressively demonstrated by comparing this volume with "Fluor" Erg.-Bd. 1, 1959, where only eight compounds had been considered under the same heading.

4.1 Binary Fluorine-Nitrogen Compounds

Review

The known binary fluorine-nitrogen compounds are nitrogen trifluoride, NF_3; dinitrogen tetrafluoride, N_2F_4; dinitrogen difluoride, N_2F_2; and trinitrogen fluoride, N_3F. There are also a number of radicals and ions, namely NF_2, NF, NF_4^+, NF_3^+, NF_2^+, NF_2^-, NF^+, NF^-, $N_2F_3^+$, and N_2F^+. NF_5, NF_4, and $N_2F_5^+$ are hypothetical species.

Nitrogen trifluoride, first synthesized in 1928 by electrolysis of molten $NH_4F \cdot HF$, is the only nitrogen fluoride which has attained some commercial importance. It is presently produced by the direct fluorination of ammonia with fluorine in the presence of molten ammonium fluoride. Since about 1975, NF_3 has been used as the fluorine source in high-power HF/DF chemical lasers.

The synthesis of dinitrogen tetrafluoride in 1958 was the beginning of a period where numerous previously unknown substances were synthesized. The preparations, properties, and reactions of N_2F_4 have been intensively studied. The most remarkable property is its reversible dissociation into NF_2 radicals, $N_2F_4 \rightleftharpoons 2NF_2$, which explains many of the chemical properties of N_2F_4. Due to the relative stability of the NF_2 radical, its molecular properties and spectra are well investigated.

Dinitrogen difluoride has been known since 1942 when it was detected as a product of the thermal decomposition of trinitrogen fluoride. Most methods of preparation yield a mixture of cis- and trans-N_2F_2 which can be separated.

Only a few studies have been carried out with the highly explosive trinitrogen fluoride since its first preparation in 1942.

The free NF radical is generated in three electronic excited states by a number of gas-phase reactions. In particular, the spectral properties were intensively studied.

Among the binary fluorine-nitrogen ions the most significant one is the perfluoroammonium cation. In 1966, the first synthesis of two NF_4^+ salts, NF_4AsF_6 and NF_4SbF_6 (by the activation of NF_3, F_2, and a Lewis acid with a suitable energy source), was simultaneously reported by two groups of workers. More than 30 salts, synthesized by various methods, were known at the end of 1985. These salts are convenient solid sources of F_2 and NF_3, since they are stable up to about 200°C, but rapidly decompose above 300°C to yield F_2 and NF_3.

Other ions which are stable as salts are $N_2F_3^+$ and N_2F^+.

The systematic names of the binary fluorine-nitrogen compounds are only used for a few substances, whereas the organic substitutional type of nomenclature is widely used. Thus, NF_3 is called by its systematic name nitrogen trifluoride (and not trifluoroamine), but N_2F_4 is generally named tetrafluorohydrazine instead of dinitrogen tetrafluoride and N_3F fluorine azide instead of trinitrogen fluoride. Subsequently, there are sometimes up to three names for a particular compound. Here, the systematic names are reserved for the titles, and the names in common use are applied in the texts.

4.1.1 Nitrogen Pentafluoride, NF_5

CAS Registry Number: *[13706-13-3]*

The hypothetical NF_5 molecule, the conjugate base of NF_4^+, has been assumed to exist in an equilibrium of the type $NF_4AsF_6(s) \rightleftharpoons NF_5(g) + AsF_5(g)$ established during the thermal decomposition of NF_4AsF_6 to NF_3, F_2, and AsF_5 [1]. However, neither matrix isolation techniques to trap the intermediate [1], nor isotopic exchange studies with NF_4AsF_6 [2] could confirm the existence of NF_5. According to non-empirical valence-shell SCF-MO calculations, the NF_5 molecule should be unstable with respect to decomposition to NF_3 and F_2 by +824 kJ/mol [3].

Previous attempts to prepare a stable salt $NF_4^+F^-$ from NF_3 and F_2 by UV photolysis [5] or γ radiation [6] at $-196°C$ were also unsuccessful. Estimations on the basis of a thermochemical cycle, where only the $NF_4^+F^-$ lattice enthalpy was unknown, indicate that solid $NF_4^+F^-$ is unstable with respect to NF_3 and F_2 by about $+36 \pm 40$ kJ/mol [4]. This value combined with the enthalpy of formation of $NF_3(g)$, -131 kJ/mol, leads to an exothermic enthalpy of formation for solid $NF_4^+F^-$ of -95.4 kJ/mol [7]. An almost identical value, -91 kJ/mol, was derived from an estimate of the enthalpy of formation for $NO_2^+F^-$ using the observation that the enthalpies of solid NF_4^+ salts are close to those of the corresponding NO_2^+ salts [8].

Ab initio electronic structure calculations indicate that NF_5 as a covalent or ionic species is unstable and unlikely to exist [9].

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4.1.2 Nitrogen Tetrafluoride, NF_4

CAS Registry Number: *[82621-13-4]*

The possible existence of NF_4 as a reaction intermediate in the formation mechanism of NF_4^+ salts such as NF_4AsF_6 has been suggested by Christe et al. [1]. However, ab initio molecular orbital calculations indicated that NF_4 is energetically unfavorable and cannot be formed from NF_3 and F [2]. This fact prompted Christe et al. [3] to revise their proposed mechanism for the formation of NF_4AsF_6.

References:

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4.1.3 The Perfluoroammonium Ion, NF_4^+

CAS Registry Number: *[30494-78-1]*

General References:

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K. O. Christe, Research Studies in NF_4^+ Salts, AD-A086981 [1980] 1/124; C.A. **94** [1981] No. 113664 (the appendix contains copies of 13 papers published by the author's research group in the years 1978 through 1981).

Review

The perfluoroammonium cation can be stabilized with a large number of different anions in the form of stable salts; these anions are derived mainly from perfluorinated Lewis acids. The NF_4^+ salts are prepared directly from NF_3 or by conversion of readily accessible NF_4^+ salts. They are crystalline, moisture-sensitive materials, and usually soluble in HF. Various techniques have been applied to characterize them: Infrared, Raman, ^{19}F NMR, and ESR spectroscopy, X-ray diffraction, calorimetry, and elemental analysis. Decomposition to NF_3, F_2, and a Lewis acid takes place at elevated temperatures. Therefore, NF_4^+ salts are principal ingredients in solid NF_3–F_2 gas generators, for example, for HF chemical lasers and in high detonation pressure explosives.

4.1.3.1 Preparation. Enthalpy of Formation

Preparation

In 1966, the first reports on the successful syntheses of NF_4^+ salts were published by two research groups, Tolberg et al. [1] and Christe et al. [2]. Previously, it was concluded from theoretical considerations that NF_4^+ could not form crystalline salts [3] or that only the fluoroborate, NF_4BF_4, might exist at low temperatures. Thus, no other hypothetical salts such as perfluoroammonium perchlorate, -sulfate, and -fluoride were thought to exist [4]. Since the first reports, numerous NF_4^+ salts have been prepared and characterized containing counterions which are derived mainly from perfluorinated Lewis acids.

The NF_4^+ salts can be prepared directly from NF_3 or indirectly by conversion of the readily accessible NF_4^+ salts into new NF_4^+ salts. In the following paragraphs, the methods used for syntheses and the NF_4^+ salts produced so far are summarized.

Method I. NF_3 is reacted directly with F_2 in the presence of a fluoride ion acceptor and under the action of a suitable activation energy source

$$NF_3 + F_2 + XF_n \xrightarrow{E} NF_4^+XF_{n+1}^-$$

This method is suitable for the preparation of NF_4^+ salts derived from volatile, strong Lewis acids. Four different sources of energy were used to synthesize the following NF_4^+ salts:

(a) Heating under high pressure: NF_4AsF_6 [1, 5], NF_4SbF_6 [1, 5 to 8], NF_4BiF_6 [7], and $NF_4TiF_5 \cdot xTiF_4$ [9].

(b) Glow discharge at temperatures below 200 K: NF_4BF_4 [10, 11] and NF_4AsF_6 [2, 12].

(c) UV photolysis at 77 K: NF_4BF_4 [13, 14], NF_4GeF_5 [14], NF_4PF_6 [14], NF_4AsF_6 [13, 14], and $NF_4SbF_6 \cdot xSbF_5$ [13].

(d) 3 MeV bremsstrahlung at 77 K: NF_4BF_4 [15].

The preferred starting material of the metathetical reaction (Method III) for the synthesis of NF_4^+ salts by indirect methods, NF_4SbF_6, is most conveniently prepared by a thermal reaction [1, 5 to 8]. However, for the synthesis of pure NF_4^+ salts on a small scale, UV photolysis is recommended [14].

Method II. NF_3 is reacted directly with a KrF^+ salt containing the desired anion (or KrF_2 and the Lewis acid) in anhydrous HF

$$NF_3 + KrFXF_{n+1} \rightarrow NF_4XF_{n+1} + Kr$$

This method has been used to synthesize NF_4BF_4 [16, 17], NF_4PF_6 [17], NF_4AsF_6 [16], $NF_4SbF_6 \cdot SbF_5$ [16, 17], $NF_4TiF_5 \cdot xTiF_4$ [16, 17], and NF_4NbF_6 [17].

Method I is given preference over Method II due to its high yields, relative simplicity, and scalability [18].

Method III. A highly soluble NF_4^+ salt and an alkali metal salt, containing the desired anion, undergo metathesis in a suitable solvent such as anhydrous HF or BrF_5. The general principle is to choose the alkali metal in such a manner that the starting materials and the desired NF_4^+ salt product are highly soluble and the alkali metal salt formed is of very low solubility. The best product yields and purities are obtained using Cs salts and NF_4SbF_6 as starting materials in HF (for NF_4BiF_6 as a possible alternative, see [19])

$$CsXF_{n+1} + NF_4SbF_6 \xrightarrow{HF} CsSbF_6\downarrow + NF_4XF_{n+1}$$

This method requires anions which are stable in the solvent and leads to an impure product. The syntheses of NF_4HF_2 [20], NF_4BF_4 [6, 19], NF_4SnF_6 [21], NF_4SO_3F [22], NF_4ClO_4 [20], $(NF_4)_2TiF_6$ [9], $(NF_4)_2MnF_6$ [23], and $(NF_4)_2NiF_6$ [24] were carried out using this procedure.

Method IV. NF_4HF_2 is reacted with a nonvolatile Lewis acid. In cases where due to the low solubility of the salts or their instability in the solvent the metathetical reaction (Method III) fails, the reaction of the Lewis acid with a large excess of NF_4HF_2 in an HF solution leads to the desired NF_4^+ salt at room temperature or below. NF_4HF_2 is readily accessible by metathesis from NF_4SbF_6 and $CsHF_2$, and unreacted NF_4HF_2 is easily decomposed at room temperature

$$\begin{aligned} NF_4SbF_6 + CsHF_2 &\rightarrow CsSbF_6\downarrow + NF_4HF_2 \\ NF_4HF_2 + XF_n &\rightarrow NF_4XF_{n+1} + HF \end{aligned}$$

NF_4^+ salts accessible in this manner include $NF_4Be_2F_5$ [25], NF_4BF_4 [41, 42], NF_4AlF_4 [25], NF_4CrF_6 [26], NF_4WOF_5 [27], and NF_4UOF_5 [28].

Method V. Solid $NF_4HF_2 \cdot xHF$ is reacted with a weak volatile Lewis acid. NF_4^+ salts of anions, which are derived from a Lewis acid weaker than the solvent itself and therefore, unstable in a solvent such as HF, can be prepared by shifting the equilibrium

$$m\,NF_4HF_2 \cdot xHF + XF_n \rightleftharpoons (NF_4)_mXF_{n+m} + m(x+1)HF$$

to the right. This is achieved by repeatedly treating $NF_4HF_2 \cdot xHF$ with a large excess of the

Lewis acid and continuously removing the HF and the excess Lewis acid. $NF_4HF_2 \cdot xHF$ was synthesized from a solution of NF_4HF_2 in HF by removing as much HF as possible without decomposing the $NF_4HF_2 \cdot xHF$. Some NF_4^+ salts prepared in this manner include $(NF_4)_2SiF_6$ [29], NF_4WF_7 [30], NF_4UF_7 [30], and NF_4XeF_7 [31].

Method VI. The Lewis acid in the readily available NF_4BF_4 is displaced by a stronger Lewis acid

$$NF_4BF_4 + XF_n \rightarrow NF_4XF_{n+1} + BF_3$$

The reaction takes place without a solvent at elevated temperatures or in HF solutions at ambient temperature and is complete after repeated treatment with the Lewis acid. The salts NF_4GeF_5 [14], NF_4SnF_5 [21], NF_4PF_6 [14], NF_4BiF_6 [7], and $NF_4TiF_5 \cdot xTiF_4$ [9] were prepared by this procedure.

Miscellaneous Methods. A large excess of NF_3 and F_2 reacts with PtF_6 at 125°C under an autogenous pressure of about 140 atm to give NF_4PtF_6 in high yield

$$2NF_3 + F_2 + 2PtF_6 \rightarrow 2NF_4PtF_6$$

The reaction of NF_3 with PtF_6 in HF solutions or UV irradiation of a gaseous NF_3–PtF_6 mixture led to the formation of some NF_4^+ salts, the anions of which were not very well defined [16].

$(NF_4)_2GeF_6$ is accessible from NF_4GeF_5 via the equilibrium

$$2NF_4GeF_5 \xrightleftharpoons{HF} (NF_4)_2GeF_6 + GeF_4$$

This equilibrium is completely shifted to the right by repeated treatment of NF_4GeF_5 with HF and removal of GeF_4 [14].

Solvolysis of NF_4WOF_5 in HF or vacuum pyrolysis of NF_4WOF_5 at 180°C both result in $NF_4W_2OF_9$ as a stable salt [27].

NF_4BF_4 forms in a CO_2 laser-initiated reaction of an NF_3–BF_3–SF_6 mixture [32].

A small amount of $(NF_4)_2XeF_8$ was obtained by prolonged irradiation of NF_4XeF_7 with blue (488 nm) laser light [31].

A summary of the synthetic methods for the preparation of NF_4^+ salts is given in [18].

Three different formation mechanisms for the NF_4^+ cation which consider all of the experimental evidence available so far have been formulated. They are connected with the action of the three fluorinating agents known to be capable of oxidizing NF_3 to NF_4^+: (1) F_2 in the presence of a Lewis acid, (2) PtF_6, and (3) KrF^+ salts [16]. For alternative mechanisms previously postulated, see [2, 12, 13, 17, 33].

Enthalpy of Formation

The enthalpy of formation of gaseous NF_4^+ was estimated from formation enthalpies of NF_4^+ salts to be $\Delta H^\circ_{f,298} = +784 \pm 30$ kJ/mol [34]. A previous estimate was $\Delta H^\circ_{f,298} = +854 \pm 42$ kJ/mol [15]. Other estimated values, +828 and +895 kJ/mol, were obtained by combining core binding energies and enthalpies of formation of the isoelectronic species CF_4 and F_3NO, respectively [35].

For heats of formation of a number of NF_4^+ salts, see [34, 36, 37].

For references, see p. 170.

4.1.3.2 Physical Properties

Structure. Bonding. Bond Distance

The suggested structure of the cation in all NF_4^+ salts prepared so far is a regular tetrahedron, point group T_d. Spectroscopic evidence has explicitly shown this to hold true for NF_4AsF_6 [43] and NF_4SbF_6 [5] in the solid state and in HF solution: The number of fundamentals occurring in the IR and Raman spectra nicely fits the pattern for a point group T_d [43]. The ^{19}F NMR spectrum of NF_4^+ in liquid HF shows a triplet of narrow lines of equal intensity, indicating that the fluorine atoms are equivalent. Further, since relaxational broadening induced by the ^{14}N nuclear quadrupole moment is absent, the nitrogen atom should be located in a spherically symmetrical environment [5, 43]. The T_d assignment for NF_4^+ was imposed on the vibrational spectra of all salts, although in the solids a splitting of some modes which are degenerate in the point group T_d frequently occurs.

There is some controversy about the nature of the N-F bond in NF_4^+. The relative intensities of the ν_1 Raman bands of NF_4^+ and BF_4^- (observable under identical conditions in NF_4BF_4) [15] and, furthermore, the comparatively high value of the 1s binding energy of fluorine bound to nitrogen in NF_4BF_4 [11] point towards a higher degree of covalency of the N-F bond than, for example, of the B-F or C-F bond [11, 15]. On the other hand, the valence force constant in the isoelectronic series BF_4^-, CF_4, NF_4^+ does not increase regularly, as expected if only single bonds are involved, but actually decreases from CF_4 to NF_4^+. This is attributed to a considerable polarization of the N-F bond in NF_4^+ [43]. Ab initio calculations for NF_4^+ and NF_3 indicate that the bond is more covalent in NF_4^+ than in NF_3 [39].

Incomplete X-ray structural data [38, 44] indicate that the N-F bond length in NF_4^+ is 1.25 to 1.30 Å. A bond length of 1.31 Å [57] (preliminary result: 1.24 Å [45]) was obtained by comparing the N-F stretching force constants of NF_4^+, FNO, and NF_3 and relating them to the well known bond distances for the latter two molecules [45, 57]. An X-ray analysis of $(NF_4)_2NiF_6$ gave N-F bond lengths in a distorted NF_4^+ tetrahedron between 1.30 and 1.40 Å [56]. Based on ab initio calculations for NF_4^+ and NF_3, the bond length was estimated to be 1.322 Å, assuming that the error of the calculated value was same as that for NF_3 [39].

Nuclear Magnetic Resonance

The ^{19}F NMR spectrum of NF_4^+ in solution (solvents HF or BrF_5) at room temperature has been measured for salts with anions PF_6^- [14], AsF_6^- [43], SbF_6^- [1, 5], GeF_6^{2-} [14], SnF_6^{2-} and SnF_5^- [21], SO_3F^- [22], XeF_7^- [31], TiF_6^{2-} [9], CrF_6^- [26], WOF_5^- and $W_2O_2F_9^-$ [27], WF_7^- and UF_7^- [30], and MnF_6^{2-} [23]. Typically, it consists of a triplet having lines of equal intensity downfield from $CFCl_3$. The triplet structure is due to spin coupling of the four equivalent ^{19}F nuclei to ^{14}N, although spin coupling was absent in $(NF_4)_2MnF_6$, which was attributed to the presence of the paramagnetic anion [6]. The ^{19}F NMR data of three NF_4^+ salts are presented below. The solvent was HF and the shifts refer to $CFCl_3$ (downfield negative) as an external standard (Φ scale):

salt	$\Phi(NF_4^+)$ in ppm	$^1J(N\text{-}F)$ in Hz	Ref.
NF_4PF_6	−217.0	230	[14]
NF_4AsF_6	−213.5	234	[43]
NF_4SbF_6	−214.7	231	[1, 5]

The ^{14}N NMR spectrum, at room temperature, of NF_4^+ dissolved as NF_4BF_4 and NF_4AsF_6 in HF is characterized by a shift of 92.3 ppm upfield from neat liquid CD_3NO_2 and $J(^{14}N\text{-}F) = 230.5$ Hz [46]. For INDO calculations of ^{19}F screening constants, see [47, 48, 49], of J(N-F), see [50].

Vibrational Spectra. Force Constants

Nearly all perfluoroammonium salts which have been synthesized so far show IR and Raman bands characteristic of a tetrahedral NF_4^+ ion, i.e., the fundamentals ν_1 (a_1; Ra), ν_2 (e; Ra), ν_3 (f_2; IR, Ra), and ν_4 (f_2; IR, Ra). The symbols in parentheses denote symmetry species of the point group T_d and occurrence of the mode in the IR and/or Raman spectrum. The salts, listed by their anions, were the following (all studied as neat solids): $Be_2F_5^-$ [25], BF_4^- [10, 14, 15, 17], SiF_6^- [29], PF_6^- [14, 17], AsF_6^- [14, 43, 45, 51], SbF_6^- [5, 7, 17], $Sb_2F_{11}^-$ [14], BiF_6^- [7], GeF_6^{2-} and GeF_5^- [14], SnF_6^{2-} and SnF_5^- [21], HF_2^- [20], SO_3F^- [22], ClO_4^- [20], XeF_7^- and XeF_8^{2-} [31], TiF_6^{2-} [9, 17], NbF_6^- [17], CrF_6^- [26], WOF_5^- and $W_2O_2F_9^-$ [27], WF_7^- and UF_7^- [30], UOF_5^- [28], MnF_6^{2-} [23], NiF_6^{2-} [24], and PtF_6^- [16]. In the solids, a splitting of the ν_2, ν_3, and ν_4 modes, which are degenerate in T_d, is frequently observed. Also, the virtually forbidden ν_1 and ν_2 modes sometimes appear as weak features in the IR spectrum, indicating that the actual site symmetry of NF_4^+ may be lower than T_d. However, due to the lack of knowledge of the full crystal structure, the T_d assignment was adopted in all cases. From IR and Raman spectra of $^{14}NF_4AsF_6$ and $^{15}NF_4AsF_6$, where from X-ray diffraction the site symmetry of NF_4^+ is assumed to be S_4, Christe [45] has taken averages of the frequencies which he assigned as components of the e and f_2 modes of NF_4^+ split under S_4 site symmetry. He thus obtained the following wave numbers, in cm^{-1}, of the NF_4^+ fundamentals:

ion	ν_1	ν_2	ν_3	ν_4
$^{14}NF_4^+$	848.2	443.3	1158.95	611.15
$^{15}NF_4^+$	848.2	443.3	1129.7	609.35

These values were then used to calculate a unique set of symmetry force constants, in mdyn/Å:

F_{11}	F_{22}	F_{33}	F_{44}	F_{34}
8.053	0.733	5.52 ± 0.08	1.00 ± 0.02	0.73 ± 0.03

The symmetry force constants were written in terms of seven constants of a general valence force field for which the values $f_r = 6.153 \pm 0.1$ and $f_{rr} = 0.633 \pm 0.03$ mdyn/Å were given explicitly [45]. Several approximate methods were used to obtain force constants from only four vibrational frequencies of $^{14}NF_4^+$ [43, 51 to 53]. From force fields so obtained, vibrational amplitudes were derived [52, 53].

Bond Dissociation Energy. Electron Affinity

The first dissociation energy $D(F\text{-}NF_3^+)$, 347 ± 42 kJ/mol [15] or 419 kJ/mol [34], was calculated from standard enthalpies of formation ΔH_f°, viz. by $-\Delta H_f^\circ(NF_4^+, g) + \Delta H_f^\circ(NF_3^+, g) + \Delta H_f^\circ(F, g)$. The last two were taken from the literature, and $\Delta H_f^\circ(NF_4^+, g)$ as 854 ± 42 kJ/mol [15] or 784 ± 30 kJ/mol [34], cf. p. 166.

The electron affinity of NF_4^+ was estimated as ≤ 10 eV (NF_4 unstable with respect to NF_4^+) on the basis of a comparison of thermochemical cycles leading to O_2BF_4 or NF_4BF_4 [17].

For references, see p. 170.

4.1.3.3 Chemical Behavior

Thermal Decomposition

Most NF_4^+ salts are stable at room temperature and, in many cases, the thermal stability extends to 200°C and above. The thermal decomposition of NF_4BF_4 [33], $(NF_4)_2SiF_6$ [29], NF_4AsF_6 [33, 54], and $(NF_4)_2NiF_6$ [24] was quantitatively studied by total-pressure measurements over temperature ranges of 10°C [29], 35°C [33], and 50°C [24, 54]. The decomposition follows the general equation

$$NF_4XF \rightarrow NF_3 + F_2 + X$$

Reaction orders of 1.5 (NF_4BF_4, NF_4AsF_6) and 1.12 ($(NF_4)_2SiF_6$) were obtained from the decomposition kinetic data, and Arrhenius plots gave global decomposition activation energies $E_\alpha(NF_4BF_4) = 153.1 \pm 3.3$ [33], $E_\alpha((NF_4)_2SiF_6) = 111.3$ [29], $E_\alpha(NF_4AsF_6) = 187.0 \pm 17.6$ [33] and 172 [54] kJ/mol. The decomposition rate constants (in s^{-1}) for $(NF_4)_2NiF_6$ between 80 and 128°C are represented by the equation $k = 4.840 \times 10^{14} \exp(-147.114\ kJ \cdot mol^{-1}/RT)$ [24].

Enthalpies of dissociation (in kJ/mol) of some NF_4^+ salts obtained from differential scanning calorimetry (DSC) measurements are listed in the following table:

NF_4^+ salt	NF_4BF_4	NF_4GeF_5	$(NF_4)_2GeF_6$	NF_4PF_6
$\Delta H(NF_4XF(s) \rightarrow NF_3(g) + F_2(g) + X(g))$	142	150	151	132
Ref.	[34]	[34]	[34]	[34]
NF_4^+ salt	NF_4AsF_6	NF_4SbF_6	$(NF_4)_2NiF_6$*)	NF_4XeF_7*)
$\Delta H(NF_4XF(s) \rightarrow NF_3(g) + F_2(g) + X(g))$	169	246	134.7 ± 13.0	64.6 ± 5
Ref.	[34]	[34, 36]	[36]	[37]

*) Decomposition into $NF_3(g) + F_2(g) + X(s)$.

Hydrolysis

The hydrolysis of NF_4^+ is highly exothermic and results in rapid quantitative evolution of NF_3.

$$2NF_4^+ + 2H_2O \rightarrow 2NF_3 + O_2 + 2H_2F^+ \quad [5]$$

The oxygen evolution was less than quantitative due to side reactions leading to H_2O_2, HOF [14], and O_3 [34]. The quantitative evolution of NF_3 serves to determine the NF_4^+ content of complex fluoro anion salts using gas volumetric methods or gas chromatographic methods [55].

Reactions with Aromatic Compounds

NF_4^+ salts can be used as powerful reagents for the fluorination of aromatics [40]. Fluorinations were carried out by reacting NF_4BF_4 with benzene, toluene, and nitrobenzene in anhydrous HF at temperatures between −78 and +25°C. Up to four hydrogens can be substituted by fluorine in the aromatic rings in rapid electrophilic reactions. These rapid reactions are followed by much slower fluorine addition reactions to give the corresponding cyclohexadienes and -hexenes in high yields. In separate experiments using tetra-, penta-, and hexafluorobenzene as educts, the first two fluorines added para to each other (1,4 addition) and ortho to any hydrogen, if present, to yield a cyclohexadiene. The second pair of fluorines underwent a 1,2 addition, resulting in a cyclohexene [40].

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4.1.4 Nitrogen Trifluoride, NF_3

CAS Registry Numbers: NF_3 *[7783-54-2]*, $^{15}NF_3$ *[21641-14-5]*

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Review

Nitrogen trifluoride is a colorless, toxic gas with a boiling point of −129.0°C and a melting point of −206°C. High-purity NF_3 has little odor, but the gas containing traces of active fluorides has a pungent, musty odor. On the industrial scale, NF_3 is produced by electrolysis of molten ammonium hydrogen difluoride or by the direct fluorination of ammonia in the presence of molten ammonium hydrogen difluoride. The reactivity of NF_3 is low at ambient conditions; no reaction occurs with water, acidic, or basic solutions. However, at elevated temperatures, its reactivity is similar to that of fluorine because of the appreciable dissociation into NF_2 and F.

The results of previous investigations are given in "Fluor" Erg.-Bd. 1, 1959, pp. 238/46.

4.1.4.1 Preparation. Formation

Although NF_3 has been known since 1928, it first became of commercial interest in the late 1950s. Only two processes are of technical and economic importance for the large-scale production of NF_3: (1) the electrolysis of molten ammonium hydrogen difluoride, and (2) the direct fluorination of ammonia in the presence of molten ammonium hydrogen difluoride. The electrolytic process has also been recommended and widely used for the preparation of NF_3 in the laboratory.

4.1.4.1.1 Electrolysis of Ammonium Hydrogen Difluoride

Ruff et al. [1] first prepared NF_3 in 1928 by the electrolysis of molten anhydrous ammonium hydrogen difluoride. The electrolysis was carried out at 125°C, with a voltage of 7 to 9 V, and a current of 10 A in a cell made of copper. NF_3 and other gaseous products were formed at the carbon anode and H_2 was eliminated at the copper cathode. All the essential aspects of Ruff's work have been described in "Fluor" Erg.-Bd. 1, 1959, pp. 238/40. In this section, only the work published since 1950 will be reported. Several papers dealing with improvements of Ruff's process have been published, especially in the 1960s.

The best yields of NF_3 are obtained if the electrolyte has the composition $NH_4F \cdot 1.1HF$ to $NH_4F \cdot 1.8HF$ and the electrolysis is carried out between 100 and 130°C [2 to 5]. Pierce and Pace [6] were the first to substitute the original carbon anode with a nickel anode. By using a nickel anode, the contamination of NF_3 with CF_4 and other fluorinated carbon compounds was avoided. A disadvantage of nickel anodes is that they degrade by forming nickel fluorides [2].

The electrolytic cells used are very similar to the cells used for the production of elemental fluorine [4, 5, 7]; cf. "Fluorine" Suppl. Vol. 2, 1980, pp. 4/10. An electrolytic cell suitable for NF_3 production on a pilot-plant scale having a capacity of about 25 kg of electrolyte was described by Massonne [5]. The cell and the gas separation skirt were made of Monel; the cell cover and the cathode were made of mild steel. The anode was composed of nickel or carbon with an efficient surface of ca. 800 cm^2. Thus, a current density of 0.15 A/cm^2 was possible at a current of 120 A. On the top of the cell cover there were holes for the release of H_2, the anode gas, inlets for HF, NH_3, and N_2, and for the electrodes. The cell was electrically heated and a water-cooling system was attached to remove the heat at high current densities.

The product gas mixture was expected to contain the following substances: H_2, NF_3, N_2, N_2F_2, NH_2F, NHF_2, N_2O, O_2, F_2, and HF. CF_4 occurred when carbon anodes were used [4, 5]. Additionally, the formation of NO [8, 9] and NO_2 [4] was reported. O_2 and N_2O result from the water content of the electrolyte [3 to 5]. The formation of F_2 occurred only at high HF concentrations in the electrolyte, i.e., at a composition of $NH_4F \cdot (1.8\text{ to }1.9)HF$ [5].

Explosions often occurred in the electrolytic cell or during the purification of the anode gas. Mixtures containing NF_3 and other components, especially H_2, are explosive. To reduce the explosion hazard, the anode and the cathode compartments were separated by a diaphragm [4, 5]. Moreover, gaseous N_2 was introduced into the cell to maintain the concentration of NF_3 at a value lower than 9.4% or larger than 95%. Outside this range, NF_3–H_2 mixtures were nonexplosive [7]. The by-products NHF_2 and NH_2F that were responsible for explosions during condensation of the anode gas were removed by oxidation using $MnO_2 + KMnO_4$ [2], MnO_2, $KMnO_4 + Na_2O_2$ [3], or an alkaline $KMnO_4$ solution [4].

Massonne [5], in his study of the electrolysis in a pilot plant, determined the composition of the anode gas at various temperatures, current densities, and compositions of the electrolyte. He showed that the NF_3 production is nearly independent of these parameters within a relatively large range. The optimum conditions were: temperature 100 to 120°C, current density 0.12 to 0.15 A/cm^2, and an electrolyte $NH_4F \cdot (1.1\text{ to }1.5)HF$. Under these conditions, and after it had passed through an adsorber with NaCl and had been washed with alkali, the anode gas had the following composition (in vol%):

NF_3	72 to 76	N_2F_2	0.2 to 1.3	O_2	0.1 to 0.2
N_2	23 to 26	N_2O	0.4 to 0.6	CF_4	<0.1

The current yield for NF_3 was about 70% and referred to the formal equation $NH_4F \cdot 2HF \rightarrow NF_3 + 3H_2$.

Watanabe, Tasaka et al. [8 to 13] studied NF_3 formation in the electrolysis of the molten potassium hydrogen difluoride-hydrogen fluoride-ammonium fluoride system. NF_3 in up to 75% current yields, N_2, and small quantities of N_2O and F_2 were produced in this system. The addition of a few wt% of fluorides such as LiF, CoF_2, NiF_2, or AlF_3 to the electrolyte prevented anode polarization ("anode effect"). The electrode kinetics of the formation of NF_3 have been thoroughly discussed.

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4.1.4.1.2 Direct Fluorination of Ammonia

The direct fluorination of ammonia by fluorine in the gas phase is not feasible for technical use, cf. p. 176. However, the direct fluorination in the presence of molten ammonium hydrogen difluoride is feasible and was commercialized in a production plant by Air Products and Chemicals, Inc. [1, 2].

A mixture of gaseous F_2 diluted with N_2 and NH_3 is introduced into a liquid $NH_4F \cdot HF$ bath heated to 125 to 130°C. Fluorine reacts with the NH_3 that is presumably generated in situ from the decomposition of $NH_4F \cdot HF$. The molten $NH_4F \cdot HF$ acts as a transport medium for supplying NH_3 to the reaction zone and as a heat sink for the intense heat of reaction. NH_3 is added in excess to maintain a mole ratio of HF to NH_3 of 2.0 to 2.5, thereby replacing the NH_3 consumed and avoiding the formation of NH_4F contaminant. Impurities in the reactor gas such as NH_4F, HF, and H_2O are removed by passing the gas stream through suitable adsorbers. Thereafter, the gas is cooled to liquid-nitrogen temperature and residual N_2 produced in side reactions is removed by vacuum pumping.

The process yields a high-purity product (>99.5%) that is substantially free of dinitrogen difluroride contaminant. Reasonably high yields of NF_3 were obtained on a pilot-plant scale. The advantages of this process compared to the electrolytic process are: (1) a product is produced in a reasonably high yield that is essentially free of N_2F_2 and other contaminants; (2) there is a 20 to 30% energy savings over the electrolytic process; (3) H_2 is not evolved so explosive NF_3–H_2 mixtures cannot form [1, 2].

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4.1.4.1.3 Electrochemical Fluorination

Electrochemical methods of fluorination (electrofluorination) involve the electrolysis of a liquid hydrogen fluoride solution or a molten alkali metal fluoride-hydrogen fluoride mixture containing the appropriate nitrogen compounds. The electrolysis is usually carried out at a voltage of 5 to 7 V (which is too low to liberate elemental fluorine) and at temperatures between −15 to +20°C for the HF solution or above 100°C for the fused salt. The elimination of NF_3 at the anode is always accompanied by the formation of other products, the amount of which is dependent on the conditions of the electrolysis. Table 1 lists a number of substances that give NF_3 in good yields and, therefore, were proposed for preparation of NF_3 in the laboratory.

Engelbrecht et al. [9] studied the electrochemical fluorination of a number of inorganic compounds in HF or molten KHF_2. NF_3 was one of the products in the fluorination of $(NH_2)_2SO_2$, $(NH_2)HSO_3$, $(NH_4)_2SO_4$, N_4S_4, NH_4ClO_4, $[NP(NH_2)_2]_3$, and $Hg(CN)_2$.

Only small quantities of NF_3 were identified when NH_3 (as a 5% solution of NH_4F) in HF [1] and N_2H_4 in HF [1] or in the molten KF–HF system [4, 6] were electrolyzed; the main product was N_2.

Table 1
Preparation of NF_3 by Electrofluorination.

substance	current yield of NF_3	principal by-products	remarks	Ref.
urea (10%) in HF	38%	N_2, COF_2, CO_2, CF_4, OF_2	$NF_3:CF_4 \approx 11:1$	[1, 2]
urea in HF	—	N_2, COF_2, CF_4, N_2O, CO_2, N_2F_4	$NF_3:CF_4:N_2O = 1:0.3:0.43$	[3]
urea (2.4 mol%) in KHF_2–HF	55%	N_2(21%), CO_2(13%), CF_4(4%), N_2O(4%), F_2(3%)	in parentheses: current yield	[4, 5, 6]
guanidine (40%) in HF	47%	N_2, CF_4	$NF_3:CF_4:N_2 = 6:2.22:1$	[7]
guanidine (5%) in HF	16%	CF_4, N_2, NO_x, CO_2, COF_2, CF_3NF_2	$NF_3:CF_4 \approx 2:1$; aminoguanidine and semicarbazide also form NF_3 in preparative amounts	[1]
guanidine(12%) in HF	—	CF_4, N_2O	$NF_3:CF_4:N_2O = 1:0.7:0.1$	[3]
pyridine (32%) in HF	27%	C_5F_{12}, other perfluorinated hydrocarbons	$NF_3:CF_4 \approx 2:1$	[1]
thiourea (7%) in HF	—	CF_4, CF_3NF_2, SF_6, CF_3SF_5	$NF_3:CF_4 \approx 3:1$	[8]

NF_3, in 2% current yield, was formed from the electrolysis of an N_2O solution in HF containing NaF as a conductivity additive [10].

NF_3 (92 mol%), together with a relatively large amount of N_2F_2 (3.5 mol% of each isomer) and N_2F_4, were obtained from the electrolysis of a molten mixture of NH_4HF_2 in the presence of an F^- acceptor such as BF_3, AlF_3, PF_3, or AsF_5 [11].

The formation of NF_3 from the electrolysis of dicyanodiamide [12], acetonitrile [13], and cyanamide [5] in molten KF–HF systems was studied.

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4.1.4.1.4 Miscellaneous Methods of Formation

From the Elements

The formation of NF_3 from the elements occurs under the action of an electric discharge on an F_2–N_2 mixture in a discharge tube immersed in liquid nitrogen or with the reaction mixture trapped in a vessel that is cooled with liquid nitrogen [1 to 4]. The conversion of a stoichiometric F_2–N_2 mixture into NF_3 increased with increasing specific energy (= ratio of the power of the discharge to the flow rate of the gases) between 200 to 450 Wh/L at current strengths of 8 to 25 mA [4]. Degrees of conversion of up to 70% were reported [2].

If F_2 is introduced into a nitrogen plasma and the resulting gas stream ($\sim$3500 K) immediately quenched with liquid nitrogen, NF_3 and N_2F_4 are formed. NF_3 can be exclusively produced by varying the F_2 to N_2 ratio [5].

The synthesis of NF_3 can also be carried out with the uranium-fission products of a nuclear reaction. Mixtures of fluorine and nitrogen containing UF_6, enriched with ^{235}U, were exposed to neutron radiation from a nuclear reactor [6 to 8]. The main product was NF_3; the amount of which was dependent on the total energy deposited [6]. Other products identified in minor quantities were cis- and trans-N_2F_2 [6, 8]. Irradiation of a mixture containing N_2 (306 Torr partial pressure), F_2 (294 Torr), and UF_6 (52 Torr) for 84 h produced 103.5 g NF_3 (mean flux of thermal neutrons in the reactor $\sim 2\times10^{10}$ neutrons$\cdot$cm$^{-2}\cdot$s^{-1}) [7]. The action of a beam of 30 MeV electrons from a linear electron accelerator also produced NF_3 along with N_2F_2 [9]. Radiolysis of a liquid mixture of N_2 and F_2 with ^{60}Co γ-radiation (dosage up to 50 Mrad) at 77 K resulted in the formation of NF_3 with a radiation-chemical yield of $\sim$0.4 molecules per 100 eV absorbed by the sample [34].

From Nitrogen and Carbon Tetrafluoride or Sulfur Hexafluoride

The introduction of CF_4 or SF_6 into a nitrogen plasma and subsequent quenching of the gas stream from about 3500 K to room temperature yielded small quantities of NF_3 together with N_2F_4 and F_3CNF_2 and trace quantities of N_2F_2 and C_2F_4 [10].

From Ammonia or Nitrogen Oxides

The direct fluorination of NH_3 to NF_3 in the gas phase was studied in a copper-packed reactor. With an excess of fluorine, NF_3, in a yield of about 20% (based on F_2), and NH_4F were formed (40 to 60% yield according to Lawless and Smith [11]). With an excess of ammonia, NF_3 (10 to 25%) along with N_2F_4 (up to 11%), N_2F_2, and NHF_2 were obtained [12]. For the mechanism, see also "Fluorine" Suppl. Vol. 2, 1980, p. 165. Problems associated with this process as an industrial process are listed by Woyteck and Lileck [13]. They include (a) the competing decomposition of NF_3 to N_2 and F_2, (b) the heat removal and temperature control, and (c) the generation of NH_4F that can cause plugging in the recovery system downstream.

The combustion of NH_3 in a stream of F_2 (in excess) gave no NF_3 [14].

The fluorination reaction was also carried out with solid NH_3 at about −110°C or liquid NH_3 at −80 to −70°C. Besides NH_4F and NHF_2 as the main products, NF_3, N_2F_4, N_2F_2, and N_2 were formed [37].

According to a patent [15], N_2O can be fluorinated yielding NF_3 and FNO, and small quantities of N_2F_2 and FNO_2. The reaction represented by the equation

$$N_2O + 2\,F_2 \rightarrow NF_3 + FNO$$

was carried out as a flow process in a nickel reactor at 400 to 700°C. Another process described in the patent literature uses CF_4 or COF_2 as the fluorinating agent to convert NO into NF_3, N_2F_2, and FNO. The reaction was carried out by passing the reactants through an electric arc at about 2000°C, after which the gas was quenched very quickly to a temperature below 100°C [16]. When a mixture of nitric oxide and fluorine is passed at 650°C through a tube filled with CaF_2, NF_3 is produced according to

$$2\,NO + 2\,F_2 \rightarrow NF_3 + FNO_2 \quad [35]$$

From Ammonium or Hydrazinium Fluorides

The fluorination of solid NH_4F at about 20 to 70°C proceeds according to the overall equations

$$NH_4F + 3\,F_2 \rightarrow NF_3 + 4\,HF \text{ and } 2\,NH_4F + 3\,F_2 \rightarrow N_2 + 8\,HF$$

Yields of NF_3 up to 70% (based on the first equation) were reported [17, 18]. Only small quantities of NF_3 were obtained from NH_4F or $N_2H_6F_2$ at room temperature [19]. For more details concerning the by-products, see "Fluorine" Suppl. Vol. 2, 1980, p. 184. In an analogous process

$$NH_4AlF_4 + 3\,F_2 \rightarrow NF_3 + AlF_3 + 4\,HF$$

the yield of NF_3 was reported to reach 70% [18]; also see [36].

An attempt to fluorinate NH_4F with XeF_2 or KrF_2 gave only negligible amounts of NF_3 [20].

From Amines, Amides, or Cyano Compounds

A patent [21] describes the fluorination of substances containing N–H bonds. Substances such as alkali metal amides, urea, biuret, hydrazine, and others were reported to react with elemental fluorine in the presence of fluorides of metals which form acid salts with HF. These salts, e.g., NaF or LiF, act as catalysts under the conditions used. Good yields of NF_3 as well as of N_2F_2 and N_2F_4 were obtained when the external temperature of the reactor was maintained between 0 and 100°C.

A group of Russian workers [22 to 27] reported on the fluorination of mixtures of solid amines, amides, or cyano compounds with KF or CaF_2. The reactions were carried out in a stream of F_2 diluted with N_2 at about −10 to +10°C. NF_3 was one of the main products and was accompanied by fluorinated fragments of the compounds treated. The N-containing compounds studied include aliphatic amine hydrochlorides [22, 23], the amides of trifluoro- and difluoro acetic acid [24], potassium cyanate [25], silver and potassium thiocyanate [26], and a acetonitrile boron trifluoride complex [27].

The fluorination of alkali metal amides according to the overall reaction

$$2\,MNH_2 + 3\,F_2 \rightarrow NF_3 + 2\,MF + NH_4F$$

occurs at room temperature after several days (e.g., 0.3 g $LiNH_2$ react in 3 d) and leads to an NF_3 yield of 60 to 65% based on the amide [28]. In an earlier publication [29], the fluorination of $NaNH_2$ diluted with NaF in a ratio of 1:10 at 40 to 50°C gave NF_3 in a yield of ca. 30% and also some N_2F_2.

From Nitrides

When a mixture of a halogen fluoride, e.g., ClF_3, and a metal nitride such as Li_3N, Ca_3N_2, Mg_3N_2, BN, or Si_3N_4 is heated to about 160°C for 12 to 16 h, the major product is NF_3. The best results were obtained in the reaction of Mg_3N_2 with ClF_3, where up to 70% of the total available nitrogen was converted into NF_3 [30]. The reaction of metal nitrides with elemental fluorine yielded chiefly N_2 and only negligible amounts of NF_3 [19]. Some reactions between metal nitrides and fluorinating agents are very vigorous [19, 30].

From Azides

A patent describes a process for the formation of NF_3 by passing elemental fluorine through an aqueous solution of NaN_3 at 5 to 10°C [31].

FN_3 reacts with OF_2 yielding NF_3 when the gases are passed through a reactor and subjected to UV irradiation (250 to 400 nm) at room temperature for 2 to 7 s. The overall reaction is thought to be

$$2FN_3 + 2OF_2 \rightarrow 2NF_3 + 2N_2 + O_2 \text{ [33]}$$

NF_3 is also formed when FN_3 is introduced into liquid FNO or ClF_3 at −70 to −60°C [32].

From Tetrafluorohydrazine

NF_3 is formed in reactions of N_2F_4 or NF_2 with fluorinating agents such as F_2, ClF_3, or OF_2 or with other reactants. More details are given on pp. 350/2 and in Section 4.1.12.6.8, pp. 356/81.

From Tetrafluoroammonium Salts

NF_3 is evolved on heating or hydrolyzing NF_4^+ salts. For more details, see p. 169.

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4.1.4.1.5 Purification

Typical by-products and impurities in NF_3 produced by the electrolysis of molten ammonium hydrogen difluoride are HF, N_2, O_2, H_2, N_2F_2, NHF_2, N_2O, and CF_4. Gas chromatography is used to analyze the volatile impurities, and the active fluorides are determined by wet-chemical analysis, see e.g., [1, 2].

HF is condensed and/or adsorbed on solid alkali fluorides [3, 4, 6]. Oxidizable compounds such as NHF_2 are eliminated by passing the gas over solid oxidizing agents, e.g., $MnO_2 + KMnO_4$ [5], $MnO_2 + KMnO_4 + Na_2O_2$ [3], or through an alkaline $KMnO_4$ solution [6]. Washing the gas with an aqueous alkali hydroxide solution removes acidic and hydrolyzable impurities [1, 4]. Thereafter, the NF_3 contains N_2F_2, N_2O, CF_4, O_2, N_2, and H_2 [1]. Oxidizing impurities, e.g., N_2F_2, can be removed by treatment with a KI solution [1, 3, 7], solid KI [3], sulfide, or sulfite solutions [1]. Patents [8, 9] describe the decomposition of N_2F_2 in NF_3 by contact with nickel balls in a nickel pipe at about 240°C. The remaining gas products are cooled to liquid-nitrogen temperature. While maintaining a vacuum, O_2, N_2, and H_2 pass through the condensation traps leaving liquified NF_3, solid N_2O, and small quantities of CF_4. The N_2O can be separated by low-temperature filtration [4, 10] or by fractionation [14]. Small quantities of N_2F_2 and N_2O can also be removed by molecular sieves at room temperature [1]. Activated carbon completely adsorbs N_2F_2 and N_2O at $-80°C$ and only N_2O at $+20°C$. However, this adsorption process may cause powerful explosions [11]. The removal of CF_4 is very difficult because the physical properties of NF_3 and CF_4 are quite similar (e.g., boiling points, $-129.0°C$ for NF_3, $-128°C$ for CF_4).

The following impurities were given in the two commercially available specifications of NF_3 (from Air Products and Chemicals, Inc.) [12]:

NF_3 in wt%	typical analysis ppm by weight						
	O_2	N_2	CF_4	N_2O	SF_6	reactive fluorides	H_2O
laser grade 98.0	3000	1000	2000	1500	1000	1000	1
etchant grade 99.9	300	100	500	—	20	—	0.1

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4.1.4.1.6 Thermodynamic Data of Formation

ΔH_f° and ΔG_f° are the standard enthalpy and the Gibbs free energy, respectively, for the formation of gaseous NF_3 from the gaseous elements in their standard states.

Enthalpies of formation were derived from enthalpies of reaction measured for reactions of NF_3 with various partners in bomb calorimeters and enthalpies of formation of the various reactants from the literature. The following table lists the studied reactions along with the enthalpies of reaction and enthalpies of formation calculated from each reaction.

reaction	$-\Delta H^\circ_{298}$ in kcal/mol	$-\Delta H^\circ_{f,298}$ in kcal/mol	Ref.
$NF_3(g) + {}^3\!/_2 H_2(g) \rightarrow 3HF(aq, a=1) + {}^1\!/_2 N_2(g)$	196.3 ± 6.4*)	30.92 ± 1.72*)	[1]
$NF_3(g) + {}^3\!/_2 H_2(g) \rightarrow 3HF(123H_2O) + {}^1\!/_2 N_2(g)$	199.49 ± 0.22		[2]
$NF_3(g) + {}^3\!/_2 H_2(g) \rightarrow 3HF(\infty H_2O) + {}^1\!/_2 N_2(g)$	196.23 ± 0.77*)		[3]
$2NF_3(g) + S(c, rh) \rightarrow SF_6(g) + N_2(g)$	228.26 ± 0.2	31.75 ± 0.2	[4]
$NF_3(g) \rightarrow {}^1\!/_2 N_2(g) + {}^3\!/_2 F_2(g)$	-31.44 ± 0.3	31.44 ± 0.3	[5]
$8NF_3(g) + 3C_2N_2(g) \rightarrow 6CF_4(g) + 7N_2(g)$	1308.8 ± 1.3	31.4 ± 4.4	[6]
$NF_3(g) + B(c) \rightarrow BF_3(g) + {}^1\!/_2 N_2(g)$	239.7 ± 1.2	31.7 ± 1.6*)	[7]
$NF_3(g) + 4NH_3(g) \rightarrow 3NH_4F(g) + N_2(g)$	259.5 ± 1.0	29.0 ± 3.0*)	[1]

*) Value recalculated by Chase et al. [8].

The values $\Delta H^\circ_{f,298} = -31.57 \pm 0.27$ kcal/mol ($\Delta H^\circ_{f,0} = -30.20 \pm 0.27$ kcal/mol), as the weighted mean of values from the table above, and $\Delta G^\circ_{f,298} = -21.66$ kcal/mol are recommended by JANAF Thermochemical Tables (Suppl. 1982) [8]. ΔH°_f and ΔG°_f values at temperature intervals of 100 K, from 0 to 6000 K, are also given. For a critical discussion of ΔH°_f values and their calculation in previous publications, see [9, 10].

Combining the appearance potential and the enthalpy of formation of NF_3^+ gives a value of -29.4 kcal/mol for $\Delta H_f(NF_3)$ [11]. $\Delta H^\circ_{f,298} = -34.1$ [12] and -34.2 kcal/mol [13] were computed using the quantum chemical method MNDO.

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4.1.4.2 Handling

Nitrogen trifluoride gas is shipped as a compressed gas in steel cylinders and can also be provided by tube trailer. Metals suitable for use in NF_3 systems at ambient temperatures are stainless steel, steel, brass, aluminium, copper, and nickel. Corrosion rates of less than 0.0025 mm/a at about 70°C have been measured for these materials [1, 2]. However, the corrosion rate increases significantly in the presence of moisture or HF [2]. Fluorinated polymers such as Teflon, Kel-F, and Viton are not attacked by NF_3 at ambient [1, 2] and elevated temperatures [3]. These materials are recommended for flexible lines and fittings [1]. At elevated temperatures, where the reactivity is similar to that of fluorine, nickel and Monel are recommended as suitable materials for handling NF_3 [1].

Mixtures containing NF_3 and H_2 are explosive in the range 9.4 to 95 mol% NF_3. The explosion hazard is reduced by diluting the mixture with a gas such as N_2, Ar, or He [4]. Nitrogen trifluoride–n-butane mixtures with 25 to 98.5 mol% NF_3 explode violently when sparked. The ranges of flammability for methane, ethane, and propane can be anticipated to lie between those of hydrogen and butane. Mixtures of nitrogen trifluoride and 26 to 52 mol% perfluoroethane burn, but do not explode when sparked [3].

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4.1.4.3 Disposal

Disposal of nitrogen trifluoride by exhausting it into water is impractical because it hydrolyzes very slowly and its solubility in water is very low. Venting into the atmosphere also should be avoided. Since nitrogen trifluoride is approximately three times as dense as air, it can settle out and cause local areas of high NF_3 concentration [1].

The most promising method for the disposal of NF_3 appears to be combustion with an excess of fuels such as hydrocarbons or fluorocarbons [1, 2]. A modified laser combustor might serve as the disposal unit [1]. The gaseous products formed, such as HF (in the case of hydrocarbons) and NO_x, must be removed in a subsequent process [1, 2].

Disposal of NF_3 via reaction with activated charcoal (forming N_2 and CF_4) has to be done in a fluidized bed to assure the transfer of the heat of reaction and to prevent gas adsorption [1, 2]. A disadvantage is, however, the formation of toxic and hazardous N_2F_4 [1] which also may take place when NF_3 is destroyed by introducing the gas through a bed of nickel or Monel turnings maintained above 550°C [2].

A device consisting of a solid propellant (ejector) impregnated with particles of Mg and MgO (scrubbers) has been proposed for NF_3 disposal. In this disposal method, ignition of the solid would generate gases sufficiently hot to dissociate any NF_3. The fluorine produced would then react with Mg and MgO [1].

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4.1.4.4 Toxicity

Nitrogen trifluoride is a toxic substance and is most hazardous by inhalation. The lethal effects of NF_3 are due to anoxia caused by extensive conversion of hemoglobin to methemoglobin, as demonstrated by studies on the inhalation toxicity of NF_3 on rats, mice, dogs, and monkeys; see [1 to 3] and the review [4]. Based on these experiments, emergency exposure limits (EEL) have been proposed for NF_3. The National Academy of Sciences, National Research Council, Committee on Toxicology recommends the following EELs: 2250 ppm for 10 min, 750 ppm for 30 min, and 375 ppm for 60 min. An EEL is a concentration which is believed not to result in a period of disability or interfere with the performance of tasks. It may well produce injury, but this injury is reversible [5]. An individual exposed to massive concentrations of NF_3 should be treated with oxygen therapy for periods up to six hours [4].

A threshold limit value (TLV) of 10 ppm has been set by the American Conference of Governmental Industrial Hygienists (ACGIH) [4, 6, 7]. This is the concentration of NF_3 in the workplace atmosphere which is believed to cause no evident harm to most workers. Since NF_3 is nearly odorless, it cannot be detected by its odor at concentrations within the TLV [6, 7].

Nitrogen trifluoride is considered to be innocuous to the skin and a minor irritant to the eyes and mucous membranes [6, 7].

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4.1.4.5 Uses

Nitrogen trifluoride was used as an high-energy oxidizer in rocketry in the early 1960s. But this application was limited because of the relatively costly production (via electrolysis), the reactivity, and toxicity of NF_3 [1 to 3]. At present, the most significant use for NF_3 is as a fluorine source for hydrogen fluoride and deuterium fluoride high-energy chemical lasers. Its advantage over elemental fluorine is its relative inertness at ambient temperature which allows easier storage and handling of large quantities [3, 4]. Small amounts of NF_3 are used as educts for the preparation of N_2F_4 (see p. 300) and perfluoroammonium salts (see p. 164) and as a fluorine source in the preparation of fluorocarbons (see p. 227). The use of NF_3 as a dry gas etchant for semiconductors is currently being discussed. It has the advantage that it liberates fluorine species without the polymer deposition resulting from the use of carbon tetrafluoride, see, for instance, [5 to 8]. NF_3 as a convenient surface fluorinating agent for plastics in glow discharge is described by [9].

The application of NF_3 as a filling gas with a metal in flash lamps has been proposed [10]. A high-temperature hydrogen-nitrogen trifluoride torch, useful for welding, brazing, and cutting metals has been described [11, 12].

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4.1.4.6 Molecular Properties and Spectra

4.1.4.6.1 Electronic Structure. Bonding

Although the pyramidal structure of the molecule (point group C_{3v}) is well established, apparently no unique picture for the bonding in NF_3 exists consistent with the bond length and angle, the molecular dipole moment, and the ^{14}N nuclear quadrupole coupling constant. According to Kisliuk [1], both the bond length (as compared to N_2F_2) and the nuclear quadrupole coupling constant, eqQ, point towards a contribution of multiple bonding. However, interpretation of eqQ was ambiguous at that time because the key value of eqQ for one unbalanced electron in a p orbital of nitrogen was not sufficiently well known. Taking this to be ~10 MHz, as established later, Kaufman [2] showed that eqQ in NF_3 could only be reconciled with little, if any, multiple bonding in NF_3. This she accounted for by the fact that the only orbital of nitrogen suitable for π-bond formation is occupied by two electrons and thus should show little tendency for a bonding interaction [2]. An ionic character of 35% and an s character of 10% for the NF bonds have been calculated from the observed dipole moment using the model of directed valence [3]. A similar calculation, but without ionic character taken into account, gave an s character of 53% [4] which, however, was believed to be unreasonable [5].

The significant difference between the bond angles in NH_3 ($\sphericalangle HNH = 106.7°$) and NF_3 ($\sphericalangle FNF = 102.4°$) is explained within the valence-shell electron-pair repulsion model of Gillespie (or its earlier variants) by a smaller repulsion of bonding electron pairs in NF_3 as compared to

NH_3, since in the former, the electrons are drawn towards the more electronegative fluorine atoms [6, 7, 8]. In the valence bond model, the same effect is explained on spatial grounds by a repulsion between nonbonded atoms which is smaller in NF_3 than in NH_3 [9].

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4.1.4.6.2 Molecular Orbitals. Ionization Energies

The electron configuration of the ground state is $1a_1^2 1e^4 2a_1^2 3a_1^2 2e^4 4a_1^2 3e^4 5a_1^2 4e^4 1a_2^2 5e^4 6a_1^2$ [1 to 4]. The first three orbitals are built from the 1s cores of the atoms [4].

The following adiabatic (ad) and vertical (vert) ionization energies E_i in eV were obtained from photoelectron spectra with He I and He II resonance radiation:

E_i(ad) [1]	12.97	15.49	—	17.16	19.24	—
E_i(vert) [1, 2]	13.73	16.15	16.55	17.52	19.71	21.14
E_i(vert) [3]	13.73	15.95	15.95	17.40	19.73	—
orbital assignment [1, 3]	$6a_1$	5e	$1a_2$	4e	$5a_1$	3e
approximate orbital description [1]	N lone pair	Fpπ, nonbonding			Np_z + Fpσ, pπ, bonding	Np_x, p_y + Fpσ, bonding

The $1a_2$ band appeared only as a shoulder on the strong 5e band [1, 2] or was even left completely unresolved [3]. Values of the first ionization energy from mass spectra following electron impact or photoionization are in the range 13.1 ± 0.1 eV [5 to 9]. The onset of strong absorption in the vacuum ultraviolet region suggests an ionization limit of 12.92 eV (104170 cm^{-1}) [10].

An ionization energy of 414.1 eV for the 1s shell of nitrogen was estimated from a Rydberg series comprising three members in the K absorption spectrum of nitrogen in NF_3 [11]. From X-ray excited photoelectron spectra, the N1s ionization energy was found to be 4.3 eV larger than in N_2 [12], which, when combined with Siegbahn's [13] value of 409.9 eV for N1s in N_2, gives 414.2 eV for NF_3. The 1s ionization energy of fluorine in NF_3 was estimated as 694 eV [11] by adding the first ionization energy from photoelecton spectra [2] to the energy of the FKα line in various fluorine compounds where it is approximately constant.

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4.1.4.6.3 Electric Dipole Moment and Derivatives. Polarizability and Derivatives

From the Stark effect of the $J=1 \leftarrow 0$, $F=2 \leftarrow 1$ rotational transition in the microwave spectrum, a dipole moment $\mu = 0.235 \pm 0.007$ D was obtained [1] which nicely agrees with an earlier measurement by the same method, see "Fluor" Erg.-Bd. 1, 1959, p. 242. The sign of μ cannot be determined unambiguously because μ results from a near cancellation of the N–F bond moments and the moment of the lone pair at the nitrogen atom. Either sign of μ leads to a reasonable value of the lone-pair moment. From IR intensities of the $\nu_1(a_1)$ and $\nu_2(a_1)$ fundamental bands, the bond moment μ(N–F) and its derivative $\partial\mu$(N–F)/∂r have been placed at 0.9 D $\leq \mu$(N–F) $\leq$ 1.2 D (negative end at F atom), and 1.5 D/Å $\leq \partial\mu$(N–F)/∂r $\leq$ 2.0 D/Å. A distinctly different value, $\partial\mu$(N–F)/∂r $\approx$ 4.7 D/Å, was obtained from the IR intensities of the $\nu_3(e)$ and $\nu_4(e)$ fundamentals [2].

A total of 16 different combinations of values for μ, μ(N–F), and $\partial\mu$(N–F)/∂r, corresponding to the 16 possible sign combinations of $\partial\mu/\partial Q_i$, where Q_i, i = 1 to 4, are the normal coordinates, have been determined [3] from IR intensities [2] and from a force-field calculation [3]. For an earlier evaluation of μ(N–F) and $\partial\mu$(N–F)/∂r from IR intensities, see [4].

The (optical) polarizability $\alpha = 27.86 \times 10^{-25}$ cm^3 was calculated from the refractive index (see "Fluor" Erg.-Bd. 1, 1959, p. 243) using the Debye equation [5]. The anisotropy $\alpha_{\parallel} - \alpha_{\perp} = (-9.5 \pm 0.2) \times 10^{-25}$ cm^3 was derived from the depolarization ratio of Rayleigh scattered light at $\lambda = 514.5$ nm (the "$\parallel$" and "$\perp$" indices refer to the molecular C_3 axis) [6]. Raman intensities of the $\nu_1(a_1)$ and $\nu_2(a_1)$ fundamental bands gave the derivatives with respect to bond distance and angle, r and Θ, $\partial\alpha/\partial r = 1.15$ Å^2 and $(1/r) \cdot \partial\alpha/\partial\Theta = -0.085$ Å^2 [7].

References:

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4.1.4.6.4 Nuclear Quadrupole Coupling Constant eqQ

Values in MHz from rotational microwave spectra are: eqQ(^{14}N) = −7.067 ± 0.018 [1], −7.01 ± 0.06 [2], −7.09 [3], and −7.07 ± 0.10 [4]; eqQ in vibrationally excited states ν_1 to ν_4 and $2\nu_4$ have been determined as well [2]. Pure quadrupole resonance spectra in solid NF_3 below 35 K gave eqQ(^{14}N) = (±)7.0681 ± 0.0005 MHz, and a small asymmetry parameter, $\eta = (1.12 \pm 0.02) \times 10^{-3}$ [5]. The temperature dependence of the ^{14}N quadrupole resonance frequencies in solid NF_3 above 35 K has been analyzed in terms of hindered rotations, see p. 201. The quadrupole coupling constant of ^{19}F in the $I = 5/2$ excited nuclear state at 197 keV has been measured by perturbed angular correlations of γ rays with a sample of NF_3 held at 10 K [6].

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4.1.4.6.5 Nuclear Magnetic Resonance

Values of the chemical shift δ and the spin coupling constant J(^{14}N-^{19}F) are compiled below; δ is defined positive in the high field direction, RT = room temperature.

nucleus	δ in ppm	standard	T in K	J(^{14}N-^{19}F) in Hz	Ref.
^{14}N	8	NO_3^- in 3 M HCl	121	158 ± 5	[1]
^{14}N	238	NO_2^- (aq.)	143	—	[2]
^{19}F	−312.80*) ± 0.06	SiF_4	300	—	[3]
^{19}F	−146.9	$CFCl_3$	—	155	[4]
^{19}F	−142	$CFCl_3$	77	—	[5]
^{19}F	−138	$CFCl_3$	RT	—	[5]
^{19}F	−145 ± 1	$CFCl_3$	—	—	[6]
^{19}F	−219	CF_3COOH	68 to 293	160	[7]
^{19}F	285	F_2(gas)	125	—	[8]

*) Value refers to the isolated molecule and was obtained by extrapolation of gas phase values to zero density by means of virial coefficients for σ, see below.

A study of ^{19}F NMR spectra of gaseous samples at different densities ϱ and temperatures T served to obtain the virial coefficients of the shielding constant σ, defined by the power series expansion $\sigma(T,\varrho) = \sigma_0(T) + \sigma_1(T)\cdot\varrho + \sigma_2(T)\cdot\varrho^2 + \cdots$. The densities were kept sufficiently low so that only the first two terms had to be taken into account. The virial coefficients σ_0 and σ_1 were represented by expansions in powers of (T−300), T in K:

$$\sigma_0(T) - \sigma_0(300) = a_1^\circ(T-300) + a_2^\circ(T-300)^2 + a_3^\circ(T-300)^3$$
$$\sigma_1(T) = a_0^1 + a_1^1(T-300) + a_2^1(T-300)^2$$

These expansions gave the following parameter set from a fit to observed shifts in the temperature range 220 to 370 K (a_1°, a_2°, a_3° in ppm, a_0^1, a_1^1, a_2^1 in ppm/amagat; 1 amagat = 0.044617 mol/L) [9]:

$10^3 a_1^\circ$	$10^5 a_2^\circ$	$10^8 a_3^\circ$	$10^3 a_0^1$	$10^5 a_1^1$	$10^7 a_2^1$
−19.96	−5.23	5.87	−6.810	1.99	−5.98

The principal components σ'_ν, $\nu = \alpha, \beta, \gamma$, of the chemical shift tensor were determined from ^{19}F NMR spectra of NF_3 trapped in β-quinol clathrates at temperatures around 4.2 K (NF_3 molecules become oriented under these conditions). Values in ppm are $\sigma'_\alpha = -60 \pm 30$, $\sigma'_\beta = 260 \pm 40$, $\sigma'_\gamma = -200 \pm 30$. The α axis is in the plane of the fluorine triangle, and the β axis is along an N–F bond. The chemical shift tensor is defined as traceless, i.e., the mean chemical shift $\bar{\sigma}' = \frac{1}{3}\Sigma\sigma'_\nu = 0$ [10].

The width of the ^{19}F NMR line in solid NF_3 has been measured as a function of temperature from 4.2 K up to the triple point at 66.37 K. These measurements, together with the temperature dependence of nuclear quadrupole resonance frequencies, were analyzed in terms of hindered rotations [11], see also p. 201.

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4.1.4.6.6 Magnetic Constants

Analysis of the high field (25301 G) Zeeman effect of the $J = 1 \leftarrow 0$ transition in the microwave spectrum gave the perpendicular component of the rotationally induced molecular splitting factor $g_\perp = -0.060 \pm 0.001$ nuclear magnetons and the magnetic susceptibility anisotropy $\chi_\parallel - \chi_\perp = (3.0 \pm 1.5) \times 10^{-6}\ \mathrm{erg \cdot G^{-2} \cdot mol^{-1}}$; the "$\parallel$" and "$\perp$" indices refer to the molecular C_3 axis.

Reference:

R. G. Stone, J. M. Pochan, W. H. Flygare (Inorg. Chem. **8** [1969] 2647/55).

4.1.4.6.7 Rotational Constants. Rotation-Vibration Constants. Centrifugal Distortion Constants

NF_3 is an oblate symmetric top with rotational constants $A=B>C$. Equilibrium and effective rotational constants, B_e and B_0, rotation-vibration constants, α_i^B with $i=1$ to 4, and centrifugal distortion constants, D_J and D_{JK}, are presented in Table 2, p. 190. Values are from rotational microwave, rotational IR, or vibrational IR spectra (denoted as rot. MW, rot. IR, vibr. IR in Table 2).

The rotational constant C for rotation about the figure axis has been calculated from the equilibrium or effective structure derived from B_e or B_0 of $^{14}NF_3$ and $^{15}NF_3$ as $C_e=5880\pm20$ MHz, $C_0=5844\pm20$ MHz [1]. Rotation-vibration constants pertinent to C from vibrational IR spectra are, in units of 10^{-4} cm^{-1}, $\alpha_1^C=8$ (evaluated from the spectrum of the ν_1 band presented in [5]) [7], $\alpha_2^C=4$ [8] and 6 [5], $\alpha_3^C=6\pm2$ [5] ($\alpha_3^C=7\pm1$ for $^{15}NF_3$ [6]), $\alpha_4^C=6$ [8], 4.5 [5], and 5.3 [9].

The large negative value of α_1^B is mainly due to a Coriolis interaction between ν_1 and ν_3 [1, 10].

Rotation-vibration constants and centrifugal distortion constants have been calculated from various sets of force constants [6, 10 to 18]. The constant D_K, which apparently has not been measured so far, is predicted to be 10.30 kHz [15] and 10.098 kHz [16] from accurate force fields capable of reproducing observed frequencies of $^{14}NF_3$, centrifugal distortion constants (D_J and D_{JK} from [2]; D_J from [3] appears to be in error, cf. footnote [b)] of Table 2, p. 190), Coriolis coupling constants [15, 16], and isotopic frequency shifts [15].

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Table 2

Rotational Constants, Rotation-Vibration Constants and Centrifugal Distortion Constants of NF_3.

molecule	unit	B_e	B_0	α_1^B	α_2^B	α_3^B	α_4^B	$10^3 \cdot D_J$	$10^3 \cdot D_{JK}$	spectrum[a]	Ref.
$^{14}NF_3$	MHz	10761.91 ±0.2	10681.02 ±0.01	−43.45 ±0.04	38.65 ±0.03	78.81 ±0.04	4.48 ±0.02	—	—	rot. MW	[1]
$^{14}NF_3$	MHz	—	10681.078 ±0.005	—	—	—	—	14.534 ±0.068	−22.694 ±0.096	rot. MW	[2]
$^{14}NF_3$	MHz	—	10680.45	—	—	—	—	9.5[b]	−22	rot. MW	[3]
$^{14}NF_3$	cm^{-1}	—	0.3562	—	—	—	—	4.5×10^{-4}	—	rot. IR	[4]
$^{14}NF_3$	cm^{-1}	—	0.356	−0.0014	0.0011	0.0025	0.00014[c]	5×10^{-4}	—	vibr. IR	[5]
$^{15}NF_3$	MHz	10710.63 ±0.2	10629.44 ±0.03	−38.41 ±0.07	40.14 ±0.05	75.67 ±0.05	4.64 ±0.05	—	—	rot. MW	[1]
$^{15}NF_3$	cm^{-1}	—	0.3541 ±0.0004	−0.00128 ±0.00002	—	0.0027 ±0.0003	—	—	—	vibr. IR	[6]

[a] For abbreviations, see p. 189. – [b] This value appears to be in error since it cannot be reproduced by any reasonable set of force constants [2]. – [c] Evaluated [7] from the spectrum of the ν_4 band presented in [5].

References p. 189.

4.1.4.6.8 Bond Distance. Bond Angle

Accurate rotational constants of $^{14}NF_3$ and $^{15}NF_3$ from microwave spectra were used to derive:

r(N–F) in Å	∢FNF	structure
$1.364_8 \pm 0.002$	102.37° ± 0.03°	equilibrium
$1.371_0 \pm 0.002$	102.17° ± 0.03°	effective

The effective structure is in almost perfect agreement with an earlier determination from microwave spectra, see "Fluor" Erg.-Bd. 1, 1959, p. 242.

Reference:

M. Otake, C. Matsumura, Y. Morino (J. Mol. Spectrosc. **28** [1968] 316/24).

4.1.4.6.9 Molecular Vibrations

Fundamental Frequencies. Harmonic Frequencies. Anharmonicity Constants

The six normal modes of the NF_3 molecule form two totally symmetrical vibrations, $\nu_1(a_1)$ and $\nu_2(a_1)$, and two doubly degenerate vibrations, $\nu_3(e)$ and $\nu_4(e)$. Force-field calculations, discussed on p. 194, show that to a good approximation the higher frequency mode in each of the two symmetry species is a bond stretch and the lower an angle deformation. Fundamental frequencies for various phases of NF_3 are compiled in Table 3, p. 192.

Harmonic frequencies ω_i and anharmonicity constants x_{ik} (i, k = 1 to 4, i ≤ k) and g_{33}, g_{34}, g_{44} (all in cm^{-1}; for definitions, see [15]) have been derived from fundamental and combination frequencies. The second set of values [16] refers to solution spectra in liquid Ar [11] and was evaluated by taking l-type resonance (see p. 200) into account:

ω_1	ω_2	ω_3	ω_4	Ref.
1052.5	663.9	928.6	498.3	[17]
1044.2	655.5	920.30	499.20	[16]

x_{11}	x_{12}	x_{13}	x_{14}	x_{22}	x_{23}	x_{24}	Ref.
−2.8	−3.5	−9.9	−2.3	−2.5	−6.5	−2.4	[17]
−2.69	−3.65	−8.03	−2.00	—	−6.37	−2.63	[16]
−3.0	−4.0	−10.0	−2.0	−1.0	−7.0	−3.0	[12]
—	−3.50	−9.9	−2.30	−2.22	−5.90	−2.50	[18]
−2.80	−3.50	−9.91	−2.32	−2.48	−6.46	−1.32	[19]

x_{33}	x_{34}	x_{44}	g_{33}	g_{34}	g_{44}	Ref.
−3.5	−1.5	−0.6	—	—	—	[17]
−4.13	−5.34	0.82	1.7	0.4	−1.96	[16]
—	—	—	—	—	—	[12]
—	—	—	—	—	—	[18]
—	—	−0.72	—	—	0.72	[19]

Table 3

Fundamental Frequencies of NF_3 in cm^{-1}.
Gas-phase values represent Q-branch maxima. Band origins are underlined. RT = room temperature, Ra = Raman spectrum.

molecule	T in K	phase; spectrum	ν_1	ν_2	ν_3	ν_4	Ref.
$^{14}NF_3$	RT	gas; IR	$\underline{1031.91}$	$\underline{647.16}$	$\underline{908.40}$	$\underline{492.62}$	[1]
$^{14}NF_3$	RT	gas; IR	1032	647	907	492	[2]
$^{14}NF_3$	RT	gas; IR	1032	642	906	492	[3]
$^{14}NF_3$	RT	gas; IR	1031	642	907	497	[4]
$^{14}NF_3$	RT	gas; IR	—	—	—	$\underline{493.51}$	[5]
$^{14}NF_3$	RT	gas; IR	—	—	—	$\underline{493.43}$	[6]
$^{14}NF_3$	RT	gas (3 atm); Ra	1031.5	646.1	908	494	[7]
$^{14}NF_3$	RT	gas ($\leq$1 atm); Ra	1032	647	—	—	[8]
$^{14}NF_3$	RT	gas (8 atm); Ra	1035	649	910	500	[9]
$^{14}NF_3$	RT	gas (2.5 atm); Ra	1033	646	911	495	[10]
$^{14}NF_3$	72	liquid; Ra	1031.5, 1025*)	645	927, 881*)	494	[7]
$^{14}NF_3$	77	liquid; Ra	1050	667	905	515	[4]
$^{14}NF_3$	90	NF_3 in liquid Ar; IR	1027.2	644.5	897.3	491.7	[11]
$^{14}NF_3$	~86	NF_3 in liquid Ar; IR	1026.96	644.75	897.12	491.62	[12]
$^{15}NF_3$	RT	gas; IR	$\underline{1008.93}$	644.84	$\underline{886.34}$	492.02	[13]
$^{15}NF_3$	RT	gas; IR	1009	—	886	—	[14]
$^{15}NF_3$	~86	NF_3 in liquid Ar; IR	—	—	876.87	—	[12]

*) The splitting is accounted for by a transition dipole – transition dipole interaction.

Coriolis Coupling Constants ζ_3, ζ_4

The values compiled below have been derived from ν_3 and ν_4 vibrational satellites in rotational microwave spectra [14], from line positions in vibration-rotation bands in the IR [1, 13], and from envelopes of pressure-broadened vibrational IR bands [2, 20]. For an earlier determination from IR band envelopes, see [21].

molecule	$^{14}NF_3$	$^{14}NF_3$	$^{14}NF_3$	$^{14}NF_3$	$^{15}NF_3$	$^{15}NF_3$
ζ_3	—	0.81	0.88*)	0.91	0.797*)	0.77
ζ_4	−0.895	−0.90	−0.97	−0.96	−0.888	—
Ref.	[14]	[1]	[20]	[2]	[14]	[13]

*) From ζ-sum rule, $\zeta_3 + \zeta_4 = (B/2C) - 1$ (B and C are rotational constants).

For Coriolis coupling constants calculated from approximate force fields, see [17, 22 to 24].

Vibrational Amplitudes

Root-mean-square amplitudes u(N–F) = 0.0487 Å [25, 26] and u(F···F) = 0.0589 Å [25], both at 298 K, have been calculated from force fields capable of reproducing rather accurately observed vibrational frequencies, Coriolis coupling constants, and centrifugal distortion constants. For calculations with approximate force fields, see [17, 22 to 24, 27 to 30].

Tunneling Through Inversion Barrier

Contrary to NH_3, no inversion between the two positions of the apical N atom with respect to the basal plane is observed for NF_3. From ab initio SCF and SCF-CI calculations [31 to 33, 56], the height of the barrier separating the pyramidal from the planar configuration is predicted to lie between 67 and 89 kcal/mol. By using a crude valence force field, the barrier height is calculated to be between 56 and 59 kcal/mol [55] (which replaces lower values calculated earlier [54]). An upper limit for the tunneling frequency of ≤ 0.03 Hz was estimated by correlation with NH_3 [34]. However, this calculation was performed using an obsolete value for the frequency of the totally symmetric bending mode ν_2 of NF_3.

Vibrational Relaxation

Ultrasonic absorption measurements in the temperature range 143 to 295 K were analyzed in terms of self-relaxation from the lowest-frequency mode of NF_3 (ν_4) to rotational and translational degrees of freedom [53].

Force Constants

The general valence force field of pyramidal XY_3-type molecules contains six independent constants. In internal coordinates, these are the stretching and bending force constants f_r and f_α, and four interaction constants: f_{rr} for two adjacent bends, $f_{r\alpha}$ and $f_{r\alpha'}$ for a stretch and an adjacent and a nonadjacent bend, and $f_{\alpha\alpha}$ for two bends. Besides the four fundamental frequencies, additional spectroscopic data such as isotopic frequency shifts, centrifugal distortion constants, and Coriolis coupling constants are required to fix a unique set of force constants. Various authors have performed such calculations, and the sets so obtained [13, 14, 25, 26, 35 to 38, 45] agree reasonably well. As a representative example, the symmetry and valence force constants, all in mdyn/Å, of Sawodny et al. [25] are presented below.

Symmetry force constants [25]:

F_{11}	F_{12}	F_{22}	F_{33}	F_{34}	F_{44}
6.13 ± 0.22	0.63 ± 0.04	1.29 ± 0.04	3.40 ± 0.10	-0.33 ± 0.04	0.90 ± 0.02

Valence force constants [25]:

f_r	f_α	f_{rr}	$f_{r\alpha}$	$f_{r\alpha'}$	$f_{\alpha\alpha}$
4.31 ± 0.14	1.03 ± 0.03	0.91 ± 0.11	0.32 ± 0.03	-0.01 ± 0.04	0.13 ± 0.02

There is a slight discrepancy between the values of Allan et al. [13] and Otake et al. [14] for the symmetry force constants of species a_1, F_{11}, F_{12}, and F_{22}, which these authors have fixed using ^{14}N-^{15}N isotopic frequency shifts. The values of [14] come close to those of [25, 35, 38], which were fixed by observed centrifugal distortion constants, but the agreement may be only fortuitous [13].

For the symmetry force constants of species e, F_{33}, F_{34}, and F_{44}, two solutions exist which exactly reproduce the two observed e-mode frequencies, isotopic frequency shifts, centrifugal distortion constants, and Coriolis coupling constants. They differ in the associated normal coordinates, i.e., either the higher frequency is predominantly a stretching mode and the lower a bending mode, or vice versa. The latter assignment is usually discarded in the literature (explicitly or tacitly) as physically unreasonable, but it has been pointed out that such an argument may not be necessarily correct [13, 37]. Infrared intensities, together with CNDO calculations of dipole derivatives [39], and ab initio calculations of force constants [40] have been used to select the physically correct force field. These criteria indicate the solution yielding ν(stretch) > ν(bend) to be correct [39, 40]. The N–F vibrational amplitude has also been shown to be useful for a proper choice of force constants [26, 37], but does not appear to have been measured up to now.

Sawodny et al. [25] have shown that a similar ambiguity exists for the a_1 symmetry force constants which have been fixed by observed centrifugal distortion constants. The physically unreasonable solution yielding ν(bend) > ν(stretch) for these modes appears [25] to have been unintentionally chosen by Levin and Abramowitz [2]. Their e symmetry force constants were likewise discarded [25] because they were based on rather inaccurate Coriolis coupling constants (the force field is rather sensitive to small changes of these constants) [25]. This then likely also disproves the force field presented in [20].

Numerous sets of general valence force constants have been calculated by various approximate methods using only the four fundamental (or harmonic) frequencies [17, 22, 23, 27, 28, 41 to 44].

The constants of a Urey-Bradley force field for NF_3 [46, 47] are either physically unreasonable or very badly reproduce observed frequencies if the repulsion constants F and F′ are subject to the Lennard-Jones condition $F' = -1/10\ F$ [46]. Better agreement between observed and calculated frequencies is obtained if a nonbonded interaction between the lone pair at nitrogen and the fluorine atoms is taken into account. However, the number of force constants to be determined may then rise to 8, and some of them have to be estimated merely by physical intuition [48, 49].

The cubic force field of pyramidal XY_3-type molecules contains 14 independent parameters. Usually, however, the number of spectroscopic constants dependent on the anharmonic force field, such as rotation-vibration constants, l-type doubling constants, or anharmonicity constants, is smaller than the number of parameters to be determined. Their number thus has to be reduced by introducing model potentials and imposing certain constraints. Some of the possible routes were presented by Morino et al. [50]. Cubic force constants for NF_3 pertinent to model potentials (mostly Morse potentials) have been calculated by several groups of workers [11, 12, 19, 51, 52]. Some of the principal quartic constants have been estimated as well [12, 51].

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4.1.4.6.10 Dissociation Energies

The bond dissociation energies D(F$_2$N–F), D(FN–F), and D(N–F) have been obtained from appearance potentials (AP) of fragment ions in mass spectra combined with ionization potentials (IP) of the neutral precursors, thermochemical values for atomization enthalpies (ΔH_{at}), and standard enthalpies of formation (ΔH_f°) of NF$_3$ and NF$_2$ [1 to 3]. They have also been obtained from thermochemical cycles alone [4, 5]. D(F$_2$N–F) was also directly determined from the equilibrium constant of the gas-phase reaction $NF_3 \rightleftharpoons NF_2 + F$ [6]. The values are compiled in Table 4.

Table 4
Bond Dissociation Energies of NF$_3$ in kcal/mol.
For symbols and notation, see text.

D(F$_2$N–F)	D(FN–F)	D(N–F)	method of determination	Ref.
58.1 ± 1.2 (T = 0 K)	79 ± 4 (T = 0 K)	60 ± 4 (T = 0 K)	D(F$_2$N–F) = AP(NF$_2^+$)[a] – IP(NF$_2$) D(FN–F) = AP(NF$^+$)[a] – IP(NF) – D(F$_2$N–F) D(N–F) = ΔH_{at}(NF$_2$) – D(FN–F)	[1]
57.2 ± 1.0 (T = 298 K)	—	—	ΔH for $NF_3(g) \rightarrow NF_2(g) + F(g)$ by 1st- and 2nd-law method	[6]
55.1 + 2 (T = 0 K)	79.5 ± 5	54.6 ± 5	D(F$_2$N–F) = AP(NF$_2^+$)[a] – IP(NF$_2$) D(FN–F) ≈ EA(F)[b] D(N–F) = ΔH_{at}(NF$_3$)[c] – D(F$_2$N–F) – D(FN–F)	[2]
61.1 ± 3 (T = 298 K)	70.6 ± 2.4 (T = 298 K)	70.6 ± 2.4 (T = 298 K)	D(F$_2$N–F) = $-\Delta H_f^\circ$(NF$_3$) + ΔH_f°(NF$_2$) + ΔH_f°(F) ΔH_f°(NF$_2$) = ½ [ΔH_f°(N$_2$F$_4$) + D(F$_2$N–NF$_2$)] D(FN–F) = D(N–F) = ½ [ΔH_{at}(NF$_3$) – D(F$_2$N–F)]	[4]
57.1 ± 2.5 (55.2)	71	71	D(F$_2$N–F) = $-\Delta H_f^\circ$(NF$_3$) + ΔH_f°(NF$_2$) + ΔH_f°(F) (D(F$_2$N–F) = AP(NF$_2^+$)[a] – IP(NF$_2$)) D(FN–F) = D(N–F) = ½ [ΔH_{at}(NF$_3$) – D(F$_2$N–F)]	[3]
59.1 ± 2 (T = 298 K)	—	—	D(F$_2$N–F) = $-\Delta H_f^\circ$(NF$_3$) + ΔH_f°(NF$_2$) + ΔH_f°(F)	[11]
73	62	62	D(F$_2$N–F)/ΔH_{at}(NF$_3$) = D(H$_2$N–H)/ΔH_{at}(NH$_3$) D(FN–F) = D(N–F) = ½ [ΔH_{at}(NF$_3$) – D(F$_2$N–F)]	[5], see also [9]

[a] AP observed in mass spectra of NF$_3$. – [b] Electron affinity of F. – [c] $\Delta H_{at,0}$(NF$_3$) = 189.3 kal/mol [2] appears to be too low (see p. 197).

Individual bond dissociation energies in Table 4 give values for the atomization enthalpy $\Delta H_{at}(NF_3) = 197$ [1, 5], 199 [3], and 201.3 kcal/mol [4]. These are reasonably close to $\Delta H^\circ_{at,0}(NF_3) = 197.8 \pm 4.7$, $\Delta H^\circ_{at,298}(NF_3) = 201.1 \pm 4.6$ kcal/mol obtainable from the well established enthalpies of formation of NF_3 [7], N [7], and F [8], via $\Delta H^\circ_{at}(NF_3) = -\Delta H^\circ_f(NF_3) + \Delta H^\circ_f(N) + 3\Delta H^\circ_f(F)$. Thus, the value $\Delta H_{at,0}(NF_3) = 189.3 \pm 1.0$ kcal/mol quoted in [2] appears to be too low. Contrary to a previous conjecture that, by analogy with NH_3, the first bond dissociation energy should be the largest [5, 9] and despite the relatively large uncertainties of individual bond dissociation energies, the order $D(F_2N{-}F) < D(FN{-}F)$ appears to be firmly established [1 to 4]. This order has been explained by the stronger tendency of NF_2 to form multiple bonds as compared to NF_3 [10].

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4.1.4.6.11 Proton Affinity. F^+ Affinity

A gas-phase proton affinity of NF_3, $A_p = 140.7 \pm 1$ kcal/mol, referred to $A_p(C_2H_4) = 162.6$ kcal/mol, was obtained from equilibrium constants of the reactions $N_2OH^+ + NF_3 \rightleftharpoons N_2O + NF_3H^+$ and $H_2Br^+ + NF_3 \rightleftharpoons HBr + NF_3H^+$ measured by high-pressure mass spectrometry at 400 K [1]. $A_p = 151 \pm 10$ kcal/mol was determined from observations of the course of ion-molecule reactions in the system NF_3–CH_4 and NF_3–HCl by ion cyclotron resonance [2], and $A_p = 148 \pm 5$ kcal/mol on the basis of proton transfer from HCO^+ to NF_3 and from NF_3H^+ to CH_3F [3]. A quantum chemical calculation by the MNDO method yielded a negative proton affinity (the calculated $\Delta H_f(NF_3H^+)$ value was too high) [4].

The gas-phase F^+ affinity, ΔH for $NF_3 + F^+ \rightarrow NF_4^+$, has been estimated from formation enthalpies of NF_4^+ salts and lattice enthalpies to be −202 kcal/mol [5].

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4.1.4.6.12 Quantum Chemical Calculations

A synopsis of ab initio calculations presenting the methods for computing wave functions and the derived molecular properties is given in Table 5. References for calculations with semiempirical methods are briefly given below. The abbreviations and symbols used are explained on p. 235.

Molecular properties calculated by the semiempirical CNDO, INDO, and related methods are: ε_i and E_i [13 to 19], EA [19], μ [14, 15, 20, 21], derivatives of μ [22, 23], $\sigma(^{14}N)$ [24 to 27], $\sigma(^{19}F)$ [28, 29], spin-spin coupling constant J(N-F) [30, 31], r(N–F), ∢FNF [15, 18, 21, 32, 33], inversion barrier [33], atomic charges and related quantities [13, 15, 17, 34], f and vibrational frequencies [35]. Molecular properties calculated by the X_α method are: E_i [40] and ε_i [36, 37, 41]. Molecular properties calculated by a modified Hückel method are: ε_i, μ [38] and J(N-F) [39].

Table 5

Ab Initio MO Calculations for NF_3.

basis set	$-E_T$ in a.u.	calculated molecular properties	Ref.
DZ GTO + bond functions	352.6318	r, ∢FNF, μ	[42]
DZ STO	352.6109	$-E_T = 352.4768$ a.u. for planar NF_3, CI [2]	[1, 2]
6-31G	352.52601	$-E_T = 352.39359$ a.u. for planar NF_3, r, ∢FNF	[43]
STO-3G; DZ	352.5241 (DZ)	μ, dipole moment derivatives	[3]
4-31G	352.062906	planar structure quoted optimum	[4]
GTO	352.01749	ε_i, μ, Θ, D, derivatives of electric potential	[5]
GTO	352.016568	$-E_T = 351.9091$ for planar NF_3, r, ∢FNF, μ	[6]
GTO	352.0162	r, ∢FNF	[7]
GTO	348.8349	E_i, μ, general valence force field	[8]
DZ GTO	—	r, ∢FNF, D	[9]
STO-3G	—	E_i, r, ∢FNF	[10]
3-21G	—	harmonic frequencies	[11]
STO-3G	—	r, ∢FNF, f	[12]

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4.1.4.6.13 Spectra

Rotational Microwave and Infrared Spectra

Rotational transitions obeying the selection rules for a symmetric top, $\Delta J = \pm 1$, $\Delta K = 0$, have been observed in microwave spectra for states $J \leq 5$ [1 to 7] (transition $J = 5 \leftarrow 4$, $K = 0 \leftarrow 0$ at 106803.68 MHz [3]) and for $9 \leq J \leq 13$ (transition $J = 13 \leftarrow 12$, $K = 0 \leftarrow 0$ at 277580.39 MHz) [3].

Hyperfine structure due to quadrupole coupling of the ^{14}N nucleus (see p. 187) has been observed for the transitions $J=1\leftarrow0$ [1, 4, 6] and $J=2\leftarrow1$ [7]. Stark modulation of a hyperfine structure component in the former transition was used to measure the molecular dipole moment [4]. Zeeman studies were carried out to determine magnetic constants [6]. Vibrational satellites (ν_1 to ν_4 and $2\nu_4$ of $^{14}NF_3$, ν_3, ν_4, and $\nu_2+\nu_4$ of $^{15}NF_3$) were observed as well [1, 3]. Rotational transitions between states with $14\leq J\leq64$ were recorded in the infrared at 10 to 46 cm^{-1} without resolution of the K structure [8].

Vibrational Infrared Spectra

For fundamental frequencies, see p. 191. For Raman spectra of the fundamentals in solid NF_3, see p. 202.

The observed combination bands in IR spectra extend to 3319 cm^{-1} for gaseous NF_3 [9] and to 3669 cm^{-1} for NF_3 in liquid Ar [10, 11]. The intensities of binary overtone and combination bands of gaseous NF_3 and its solution in liquid Ar were interpreted quantitatively by a model of anharmonic coupling between the fundamentals [12].

In the doubly degenerate vibrational states ν_3 and ν_4, an l-type resonance occurs which has attracted some attention. Its spectral consequences depend on how the vibrational angular momentum (quantum number l) adds to the rotational angular momentum of the rigid molecular frame to produce a total angular momentum with respect to the figure axis (quantum number K). The main spectral consequences are the following: (1) all rotational levels are shifted, although in general only slightly, due to an interaction connecting levels (K, l) with ($K\pm2$, $l\pm2$) ("q-type" interaction), and connecting levels (K, l) with ($K\pm1$, $l\mp2$) ("r-type" interaction); (2) levels with $K\cdot l=+1$ are split into a doublet by the "q-type" interaction; (3) l-type resonance greatly affects the line intensities of $\Delta K=\pm1$ subbands of a Q branch (see e.g., [13, 14]). The latter effect (3) is particularly obvious for the ν_3 and ν_4 states of NF_3 and served to determine the signs of the l-type doubling constants as $q_3<0$ [15] and $q_4>0$ [15 to 17]. (The sign convention is that used in [13].) Rotational microwave spectra in ν_3 and ν_4 excited states very accurately gave the absolute values of these constants, $q_3=\pm121.38$ MHz, $q_4=\pm51.41$ MHz (both for $^{14}NF_3$), but their signs remained indeterminate [2]. In the $2\nu_4$ overtone band, l-type resonance manifests itself quite differently; in particular, an intensity perturbation is less obvious than for the fundamental bands [18]. Analysis of the $\nu_2+\nu_4$ band confirmed $q_4>0$ [16].

Electronic Spectra

The vacuum UV spectrum of NF_3 below 200 nm shows a continuous absorption with no indication of resolved electronic transitions. The absorption coefficient increases in a regular way down to the first ionization limit at 96 nm (104170 cm^{-1}) [19]. Above 200 nm, the absorption cross section gradually approaches zero and in the region 260 to 2500 nm NF_3 is transparent [20].

The X-ray absorption spectra of nitrogen and fluorine in NF_3 in the vicinity of the K-absorption edges (414.1 eV for N, 694 eV for F, see p. 185) consist of a broad line which for both atoms lies about 7.5 eV below the K-ionization thresholds. This line is assigned as a transition to a bound state in a potential exerted on the outgoing photoelectrons by the electronegative fluorine atoms. In the K spectrum of nitrogen, three additional weak and sharp lines appear which are assigned as members of a Rydberg series. The situation resembles that found in the X-ray absorption spectrum of SF_6 (see "Schwefel" Erg.-Bd. B 2, 1978, pp. 166/7) [21].

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4.1.4.7 Crystallographic Properties

The crystal structure of NF_3 does not appear to have been determined so far. Early reports of a solid-solid phase transition, see "Fluor" Erg.-Bd. 1, 1959, p. 243, were confirmed by calorimetric measurements, indicating a discontinuous rise of entropy of 6.389 $cal \cdot mol^{-1} \cdot K^{-1}$ at 56.62 K [1]. The ^{19}F NMR linewidths decrease at temperatures above 35 K and pass continuously through the transition point [2]. They were interpreted in terms of hindered rotations about the molecular C_3 axis, which are observed even at low temperatures, and in terms of diffusional motions, which become particularly noticeable above the transition temperature [2, 3]. Similarly, ^{14}N quadrupole resonance spectra, which show a decrease of resonance frequencies and an increase of the asymmetry parameter starting at about 10 K and passing continuously through the transition point, also indicate diffusional motions. These experimental results complement the results obtained from a model of motional averaging of nuclear quadrupole interaction which took only torsional motions into account to give a reasonable fit to experimental data only up to ~35 K. Two torsional frequencies of 50.2 and 33.4 cm^{-1} were derived from the fit. They refer to rotations about the a- and b-principal axes of inertia of the molecule; rotation about the c axis (figure axis) does not influence the ^{14}N quadrupole resonance spectrum [2]. The linewidths and shapes of the ν_2 and ν_4 fundamental bands in the Raman spectrum of solid NF_3 at 62 K were also analyzed in terms of hindered rotations. Wave numbers of the NF_3 fundamentals in the solid state at 62 K are $\nu_1 = 1031.5$ and 1025, $\nu_2 = 645$, $\nu_3 = 930$ and 879.2, $\nu_4 = 494$ cm^{-1}. The splitting of ν_1 and ν_3 is the same as in the liquid at 72 K and is accounted for by a transition dipole – transition dipole interaction [4].

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4.1.4.8 Thermal Properties

pVT and pϱT Data. Equation of State

The pVT surface of NF_3 has been measured from 66 K to 500 K at pressures up to 50 MPa [1]. A 32-term modified Benedict-Webb-Rubin equation of state was fit to the experimental data. Comprehensive tabulations are available of pϱT data along the melting line, the liquid-vapor coexistence line, and along several isobars up to 50 MPa. The 32 coefficients of the equation of state were given with 10 significant figures [2]. This compilation appears to be superior to pVT data calculated from a 10-parameter Martin-Hou equation of state which had been established purely empirically because experimental pVT data for the single-phase region of NF_3 were not available at the time [3].

Melting Curve. Triple Point

The melting curve is represented by p (in MPa) $= A + B \cdot T^C$, with $A = -1.90939971 \times 10^2$, $B = 0.0813750194$, $C = 1.85$. The triple point parameters are given as $T_{tr} = 66.36$ K, $p_{tr} = 0.185425$ Pa, ϱ_{tr}(liquid) = 26.320, ϱ_{tr}(vapor) $= 0.33612 \times 10^{-8}$ mol/L [2]. The triple point temperature is in agreement with two direct observations, $T_{tr} = 66.46$ K [4], and $T_{tr} = 66.36$ K (mean of two measurements and converted to 0°C = 273.15 K) [5, 6].

Liquid and Vapor Densities. Vapor Pressure. Normal Boiling Point

The vapor and liquid density ϱ_l and ϱ_v and the vapor pressure p_v along the coexistence line have been represented by multi-term functions, comprising 7 adjustable parameters for ϱ_l, 13 for ϱ_v, and 9 for p_v (only 6 are defined for the latter by the general form of the vapor pressure equation presented in the orginal reference [2]). Some of the numerical values given between the triple point and the critical point in 5-K intervals in [2] are presented in the following table.

T in K	70	80	90	100
ϱ_l in g/cm^3	1.855	1.816	1.775	1.734
ϱ_v in g/cm^3	4.08×10^{-6}	4.29×10^{-6}	6.36×10^{-6}	6.661×10^{-5}
p_v in MPa	0.00000	2×10^{-5}	1.6×10^{-4}	9.5×10^{-4}

T in K	120	140	160	180
ϱ_l in g/cm^3	1.649	1.558	1.459	1.349
ϱ_v in g/cm^3	9.284×10^{-4}	4.743×10^{-3}	0.01568	0.04028
p_v in MPa	0.01275	0.07538	0.2730	0.7261

T in K	200	210	220	230
ϱ_l in g/cm^3	1.217	1.135	1.032	0.8632
ϱ_v in g/cm^3	0.08937	0.1308	0.1955	0.3236
p_v in MPa	1.578	2.203	2.995	3.991

Parts of the liquid-density curve [7] and of the vapor pressure curve [6, 7] were determined earlier. Various analytical expressions were used to fit the vapor pressure curve [3, 6, 7]. The normal boiling point in the vapor pressure curve presented in the table above is T_b = 144.1082 K [8]. Previously, T_b = 144.09 K [7] and 144.14 K [6] (both converted here to 0°C = 273.15 K) were derived. Only the boiling point temperature and critical constants taken from literature served as input parameters to determine the vapor pressure equation in [16].

Critical Constants T_c, p_c, ϱ_c

The following values were obtained by direct observation and/or extrapolations from vapor pressure curves or by other calculations without the source of data being clear in all cases:

T_c in K	234.0	233.89 ± 0.1	233.80 ± 0.1
p_c in MPa	4.4607	4.531 ± 0.02 (44.72 ± 0.2 atm)	4.531 ± 0.02 (44.72 ± 0.2 atm)
ϱ_c in mol/L	7.92 (0.5625 g/cm^3)	8.06	8.078
Ref.	[2]	[9]	[3, 7]

Sound Velocity

Values derived from pϱT data along the melting curve, the liquid-vapor coexistence line, and along several isobars up to 50 MPa are available [2].

Enthalpy and Entropy of Solid-Solid Transition, Fusion, and Vaporization

These quantities were measured calorimetrically to yield the following results [6] (the transition temperatures are converted here to 0°C = 273.15 K):

transition	solid-solid	solid-liquid	liquid-gas
T in K	56.51	66.36 (T_{tr})	144.14 (T_b)
ΔH in cal/mol	361.8	95.11	2769
ΔS in cal·mol^{-1}·K^{-1}	6.389	1.433	19.21

An identical value of ΔH at T_b was derived from a vapor pressure equation [7].

Heat Capacity C_p, C_v. Thermodynamic Functions

Values of C_p° and of entropy S°, enthalpy $H^\circ - H^\circ_{298}$, and Gibbs free energy $(G^\circ - H^\circ_{298})/T$ for the ideal gas at 1 atm have been repeatedly calculated [10 to 15] and are in accord. Those given below are from the 1982 Supplement of the JANAF Tables [10]; C_p°, S°, and $(G^\circ - H^\circ_{298})/T$ in cal·mol^{-1}·K^{-1}, $H^\circ - H^\circ_{298}$ in kcal/mol:

T in K	0	200	298	400	600	800
C_p°	0.000	10.224	12.756	14.785	17.072	18.158
S°	0.000	57.735	62.300	66.349	72.836	77.914
$-(G^\circ - H^\circ_{298})/T$	∞	63.387	62.300	62.828	65.130	67.715
$H^\circ - H^\circ_{298}$	−2.832	−1.131	0.000	1.409	4.624	8.159

T in K	1000	1500	2000	3000	4000	5000
C_p°	18.728	19.342	19.569	19.736	19.795	19.823
S°	82.034	89.767	95.366	103.339	109.026	113.447
$-(G^\circ - H_{298}^\circ)/T$	70.180	75.500	79.799	86.405	91.383	95.370
$H^\circ - H_{298}^\circ$	11.853	21.399	31.135	50.804	70.574	90.384

The calorimetric heat capacity of the solid increases from 3.077 $cal \cdot mol^{-1} \cdot K^{-1}$ at 15 K to 16.62 $cal \cdot mol^{-1} \cdot K^{-1}$ at 65 K. The discontinuity in the vicinity of the solid-solid transition point at 56.61 K gave the transition enthalpy listed above [6].

Calorimetric measurements of C_v of the real gas have been performed along several isochores above and along one below the critical isochore, and also for the coexisting gas and liquid. The results for the two-phase region are presented in **Fig. 4**. From C_v in the two-phase region, the heat capacity C_σ of the saturated liquid was evaluated [4]. Earlier measurements in the two-phase region up to the normal boiling point [6] gave C_σ values about 1% higher than these [4].

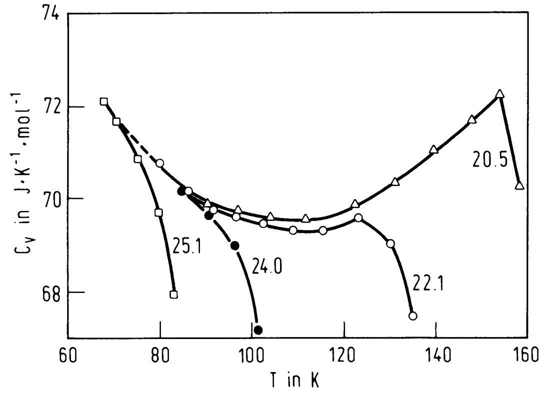

Fig. 4. Heat capacity C_v of NF_3 in the two-phase region for various densities in mol/L (from [4]).

Values of C_p, C_v, internal energy E, enthalpy H, and entropy S of the real gas are also available from calculations using reference values for the ideal gas and a modified Benedict-Webb-Rubin equation of state, the melting curve, vapor and liquid density curves, and the vapor pressure curve mentioned above. They are parameterized in the same way (along coexistence lines and isochores) as the pϱT data, see p. 202 [2]. In a similar manner, H and S were calculated earlier from a Martin-Hou equation of state, see p. 202 [3].

The calorimetrically determined entropies of the liquid at the triple point, of the liquid at the boiling point, and of the ideal gas (including a gas imperfection correction) at the boiling point are 22.055, 35.206, and 54.50 $cal \cdot mol^{-1} \cdot K^{-1}$, respectively [6].

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4.1.4.9 Transport Properties

Near room temperature, a thermal conductivity $\lambda = 0.180\ \mathrm{mW \cdot cm^{-1} \cdot K^{-1}}$ has been measured by the hot-wire method [1, 2]. This was used to evaluate a viscosity $\eta = 2 \times 10^{-4}$ P [1]. For λ and η up to 5000 K calculated from a Lennard-Jones potential with potential constants estimated from the molar volume at the boiling point and from the critical temperature, see [3].

A slight decrease of λ is observed when an electric field [1, 2, 4 to 7] or a magnetic field [4, 5, 7, 8] is applied to gaseous NF_3. The influence on η is quite similar [1, 8, 9]. This so-called electric or magnetic Senftleben-Beenakker effect (for a review, see [10]) depends on the ratios E/p or H/p, where E and H are the electric and magnetic field strength and p is the gas pressure. The relative changes $\Delta\lambda/\lambda$ and $\Delta\eta/\eta$ of the field-free quantities λ and η converge to saturation values in the limit of high E/p or H/p. One group of workers has found these values to be around -3×10^{-3} [1, 2, 4, 9], but other authors [5] have found them to be larger by a factor of ~3. The Senftleben-Beenakker effect on λ has also been observed in alternating fields [11 to 13] and at low gas pressures in the Knudsen-regime where transport properties are dominated by wall collisions [14].

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4.1.4.10 Electrical and Optical Properties

The dielectric strength of NF_3 is reported to be substantially higher than that of SF_6, that is, NF_3 can be exposed to higher electric field strengths than SF_6 before dielectric breakdown occurs [1].

For refractive indices of gaseous NF_3, see "Fluor" Erg.-Bd. 1, 1959, p. 243. Flow birefringence has been observed at $\lambda = 632.8$ nm (He–Ne laser) increasing linearly as a function of the gradient of stream velocity and independent of gas pressure between 10 and 50 Torr [2].

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4.1.4.11 Chemical Behavior

4.1.4.11.1 Thermolysis

The thermal decomposition of nitrogen trifluoride, according to the equilibrium $NF_3 + M \rightleftharpoons NF_2 + F + M$, followed by slower irreversible formation of permanent products, nitrogen and fluorine, has been investigated in several shock-wave studies [1 to 6]. The experiments were performed with mixtures of 0.25 to 10% NF_3 in Ar and cover the temperature range 1050 to 2400 K and the post-shock pressure range 0.1 to 6 atm (an exception was [2] with pressures up to 60 atm). The reaction kinetics were followed by measuring the UV absorption of NF_2 at 260 nm [3 to 6], the IR emission of NF_3 at 5.18 μm ($\nu_3 + \nu_1$) [2], or the density gradient [1]. The principal reaction under the conditions used was shown to be the reversible dissociation and the rate was found to be second-order overall [1, 3, 4, 6] or between first- and second-order overall [2]. Second-order rate expressions in Arrhenius form and rate coefficient values k at 1100 and 1400 K are given in the following table:

temperature range in K	log (A/cm^3·mol^{-1}·s^{-1})	E in kcal/mol	k in cm^3·mol^{-1}·s^{-1} 1100 K	 1400 K	Ref.
1050 to 1390	13.10 ± 0.02	30.1 ± 2.3	1.32×10^{7}*)	2.52×10^{8}*)	[4]
				4.75×10^{8}*)	[5]
1150 to 1530	16.61 ± 0.13	48.0 ± 0.8	1.18×10^{7}	1.30×10^{9}	[3]

temperature range in K	log (A/cm^3·mol^{-1}·s^{-1})	E in kcal/mol	k in cm^3·mol^{-1}·s^{-1} 1100 K	1400 K	Ref.
1330 to 2000	15.36	40.7	1.86×10^7	1.01×10^9	[1]
1461 to 2026	13.12 ± 0.06	25.7 ± 0.6	1.03×10^8	1.28×10^9	[6]
1000 to 2400	14.7	56.3	$3.26 \times 10^{3*)}$	$8.14 \times 10^{5*)}$	[2]

*) Value adopted from [3].

The results of [2] in the above table are some orders of magnitude below the values given by the other workers [1, 3 to 6] throughout the common temperature range. This discrepancy was the subject of discussions [1, 3] and comments [7, 8]. The thermal decomposition in the presence of Ar was also studied theoretically using an RRKM approach [9].

The temperature dependence of the equilibrium constant for $NF_3 \rightleftharpoons NF_2 + F$ was determined from a shock-wave experiment between 1150 and 1530 K [3] and recalculated later using more extensive NF_2 absorptivity measurements [10]. The results are represented by the equation $\ln K_p = 18.20 - 28900/T$ for T = 1129 to 1374 K. Values of K_p are 7.8×10^{-4} and 7.5×10^{-2} mol/L at 1129 K and at 1374 K [10].

For the pyrolysis of NF_3 to produce N_2F_4 and N_2F_2, see p. 300 and p. 387, respectively.

References:

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4.1.4.11.2 Radiolysis. Photolysis

During radiolysis of gaseous or liquid nitrogen trifluoride, not only the elements F_2 and N_2 form but also substances such as N_2F_2 and N_2F_4, which obviously result from recombination of radicals after the removal of F atoms from NF_3 molecules [1, 2]. cis-N_2F_2 could be identified after radiolysis with 30 MeV electrons. The following reaction is believed to take place: $8NF_3 \rightarrow 3N_2 + 11F_2 + \text{cis-}N_2F_2$ [1]. After irradiation of liquid NF_3 at 77 K with 3 MeV bremsstrahlung, cis-, trans-N_2F_2 and N_2F_4 were analyzed mass spectrometrically at 100 and 134 K. Likewise, mixtures of NF_3 and a number of inorganic compounds were investigated and many products tentatively identified [3]. N_2F_4 was also formed by irradiation of liquid NF_3 at 77 K with a ^{60}Co γ-source; the radiation-chemical yield was 0.4 to 0.5 molecule per 100 eV absorbed by NF_3 [4].

The decompostion of NF_3 (1 Torr) in a buffer gas (Xe or CO_2, 2 to 100 Torr) exposed to pulsed CO_2 laser radiation increases with pressure to a maximum at about 10 Torr. Dissociation decreases with additional pressure until at about 50 Torr, pressure dependence disappears and an equilibrium is established. It was supposed that at pressures up to about 20 Torr, NF_3 decomposes via dissociative electron attachment while at pressures above about 50 Torr thermal dissociation predominates [5, 6].

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4.1.4.11.3 Decomposition in Discharges

Nitrogen trifluoride decomposes into fluorine and nitrogen in a glow discharge tube [1 to 3]. Addition of fluorine retards the decomposition, whereas nitrogen and oxygen accelerate it [1]. The generation of excited fluorine atoms in discharges can be observed by their optical emission at 704 nm, the intensity of which is enhanced by adding helium. Excited F atoms may be formed by direct electron impact and resonant energy transfer from metastable excited He atoms according to the equations

$$NF_3 + e \rightarrow NF_2 + F^* + e \quad \text{and} \quad He(2^{1,3}S) + NF_3 \rightarrow He + NF_2 + F^* \text{ [4]}$$

More than 50% dissociation was observed in d.c. hollow cathode discharges in NF_3 for an initial pressure of 80 mTorr. F^- and F_2^- are formed directly by the discharge, with F^- being dominant [5]. The negative ion density (2.4×10^9 cm^{-3}) is one to two orders of magnitude larger than the electron density (5.8×10^8 cm^{-3}) [6].

Further information on discharges in diluted NF_3 yielding NF radicals is given on p. 264.

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4.1.4.11.4 Reactions with Electrons

Electron capture leads to the formation of negative ions (see also the preceding chapter). Electron impact under single-collision conditions in the ion source (10^{-5} Torr) produced F^-, NF^-, F_2^-, and NF_2^- with the relative abundances 1000.0:0.2:3.0:0.5 at electron energies of 70 eV (comparable results in [1, 2]) and 1000.0:0.0:5.0:1.2 at their respective resonance capture maxima [3]. Appearance potentials (AP), resonance maxima, dissociative capture cross sections for ion formation at their resonance maxima (σ_{max}), average kinetic energies for the ions ($\bar{\varepsilon}_i$), and formation processes for the negative ions are summarized [3] in the following table:

ion	AP in eV	res. max. in eV	σ_{max} in cm^2	$\bar{\varepsilon}_i$ at AP in kcal/mol	process
F^-	$0.6 \pm 0,2$	1.7 ± 0.1	6×10^{-17}	9.3 ± 0.9	$NF_3 + e \rightarrow F^- + NF_2$
F_2^-	0.9 ± 0.1	1.8 ± 0.1	3×10^{-19}	thermal	$NF_3 + e \rightarrow F_2^- + NF$
NF_2^-	0.9 ± 0.1	1.8 ± 0.1	3×10^{-20}	thermal	$NF_3 + e \rightarrow NF_2^- + F$

In a previous study [1], NF^- has been found to form with low or no kinetic energy in a dissociative capture process at zero electron energy, possibly by the process $NF_3 + e \rightarrow NF^- + 2F$. Its resonance maximum was at 2.8 eV. The cluster ion $NF_3 \cdot F^-$ was identified in electron swarm experiments with a mixture of 0.04% NF_3 in N_2 using a drift tube mass spectrometer system [13].

The attachment of electrons to NF_3 has been investigated in conjunction with noble gas fluoride lasers with NF_3 as the fluorine donor. Rate constants obtained for the dissociative attachment of thermal energy electrons to NF_3 are $(2.1 \pm 0.8) \times 10^{-11}$ and 2.4×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ measured with a flowing afterglow technique [4] and an electron resonance technique [5], respectively. The value of $(1.6 \pm 0.6) \times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ determined also in a flowing afterglow experiment [6] appears too high according to Nygaard et al. [7]. Other measurements extend over a larger mean-electron energy range. The rate constant calculated by Chantry [11] based on his experimental cross section shows a maximum value of 5.4×10^{-9} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at about 2 eV. Trainor and Jacob [8] found, at an average energy of 1 eV, the values (4 to 5) $\times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 300 K and (5 to 5.5) $\times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 500 K ($\leq 1\%$ NF_3 in N_2; results given only in a figure in the original). The results of electron swarm experiments performed with 0.01 to 0.1% NF_3 in N_2, He and Ar [13] or 0.5% NF_3 in He [7] as buffer gases are given in **Fig. 5**, p. 210, where a comparison is made with the other studies. Fig. 5 clearly demonstrates the large spread in attachment data. In the electron energy range of interest for noble gas fluoride lasers (>1 eV), the attachment rate constant appears to be $(6.5 \pm 1.5) \times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [13]. The attachment rate constant 1.5×10^{-9} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ was determined by Basov et al. [9]. Cross sections and rate constants calculated as function of various parameters such as gas pressure, NF_3 concentration, and electron energy are reported in [10].

Formation of positive ions. At an electron energy of 70 eV, NF_3 gives the following ions in its mass spectrum [12]:

m/e	14	19	33	34	52	53	71	72
ion	N^+	F^+	$^{14}NF^+$	$^{15}NF^+$	$^{14}NF_2^+$	$^{15}NF_2^+$	$^{14}NF_3^+$	$^{15}NF_3^+$
abundance	0.68	1.55	26.3	0.03	100	0.28	25.9	0.03

The appearance potientials of the ions are (in eV): 13.2 ± 0.2 [2, 14] for NF_3^+, 14.2 ± 0.3 [2], 14.2 to 14.6 [14], 14.6 [15] for NF_2^+, 17.9 ± 0.3 for NF^+, 22.2 ± 0.2 for N^+, and 25 ± 1 for F^+ [2].

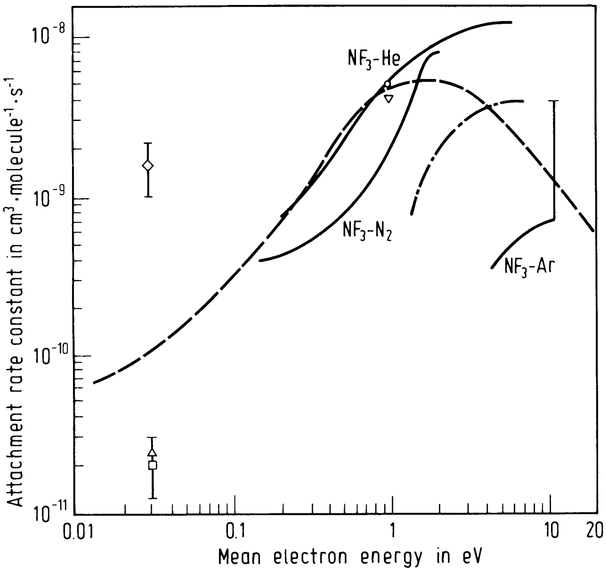

Fig. 5. Electron attachment rate constants for NF_3 as a function of the mean electron energy, from [13]. ———, Lakdawala and Moruzzi [13]; – – –, Chantry [11]; –·–·, Nygaard et al. [7]; △, Mothes et al. [5]; □, Sides and Tiernan [4]; ◇, Shaw and Jones [6]; ○ (500 K), ▽ (300 K), Trainor and Jacob [8].

The formation of highly excited, long-lived ($\geq 10^{-5}$ s) N and F atoms (Rydberg atoms) from NF_3 during dissociative excitation by electron impact is described in [16].

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4.1.4.11.5 Reactions with Elements

4.1.4.11.5.1 Reactions with Noble Gases

The reaction with excited atoms of the noble gases Ar, Kr, and Xe, generated, for instance, on passing the gases through a hollow cathode discharge, produces noble gas fluoride excimers, ZF*, which subsequently undergo radiative decay to the dissociative ground state

$$Z^* \ (Z = Ar, Kr, Xe) + NF_3 \rightarrow ZF^* + NF_2$$

$$ZF^* \rightarrow Z + F + h\nu$$

This transition between the upper (bound) state and the lower (free) state is the basis for high-power excimer lasers. In practice, the reactive process (reactive quenching) is accompanied by other quenching processes, e.g., Penning ionization or excitation transfer. Rate constants for the total quenching, k_Q, of excited noble gas atoms were measured in flowing-afterglow experiments (see e.g., [1 to 4]). The excimer emmission spectra identify the states of the ZF* product, and comparison of the relative emission intensities from the $Z^* + NF_3$ reaction to that of $Z^* + Cl_2$ as a reference reaction provided the rate constants, k_{ZF}, for excimer formation that lead to chemiluminescence. The branching fraction for excimer formation is then given by $\Gamma = k_{ZF}/k_Q$. The ZF formation rate constants and branching fractions at 300 K are as follows (uncertainties of the branching fractions were estimated to be of the order of 20% for XeF* formation and of 40% for the other Γ values [5]):

	$Ar(^3P_{2,0})$	$Kr(^3P_2)$	$Xe(^3P_2)$	$Xe(^3P_1)$
k_{ZF} in $10^{-11} cm^3 \cdot molecule^{-1} \cdot s^{-1}$	4.2	—	2.4	6.5
$\Gamma = k_{ZF}/k_Q$	0.30	0.57[a]	0.27[b]	—
Ref.	[1, 6, 7]	[1, 7, 8]	[5]	[5]

[a] This value is probably too large by a factor of two [5], since a systematic error seems to have affected the previous experiments [1, 7, 8]. – [b] This value replaces the previous result of $\Gamma = 1.1$ [1, 7, 8].

A computer simulation of the emission from $Kr(^3P_2) + NF_3 \rightarrow KrF^* + NF_2$ and $KrF^* \rightarrow Kr + F + h\nu$ indicates that about 40% of the available energy of reaction (58 kcal/mol) goes into vibrational energy of the KrF* product [7, 9].

The formation of the XeF^+ ion by the reaction $Xe^+(^2P_{1/2}) + NF_3 \rightarrow XeF^+ + NF_2$ was observed in an ionized Xe–NF_3 mixture using ion cyclotron resonance mass spectrometry. The rate constant was measured to be $(0.7 \pm 0.3) \times 10^{-10}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [10].

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4.1.4.11.5.2 Reactions with Hydrogen

Mixtures of nitrogen trifluoride and hydrogen are explosive when the concentration of NF_3 is within the range of 9.4 to 95 mol% [1]. However, it was observed by other workers that NF_3–H_2 mixtures in a Kel-F-coated Pyrex flask do not react below 100°C [2]. At higher temperatures, the behavior of NF_3–H_2 mixtures diluted with Ar ($\geq$94%) was investigated in shock-wave experiments. Below about 1000 K, NF_3–H_2 mixtures were inert for $\geq$2 ms while above about 1500 K, reaction occurred in $\leq$50 μs according to the overall equation

$$2NF_3 + 3H_2 \rightleftharpoons N_2 + 6HF$$

The formation of HF was followed by its 2.7 μm emission and the presence of the transient intermediate NH was identified by its chemiluminescent emission at 336 nm [3].

The system NF_3–H_2 shows high combustion temperatures, about 3500 K at 100 Torr for a 2:3 mixture [4]. NF_3–H_2 flames are blue-white at the top and straw-colored at the base. With excess NF_3, the flames are very bright. The emission spectra of the NF_3–H_2 flames are almost identical with those of the NH_3–F_2 flames [5]. The flame propagation rates in stoichiometric mixtures were measured to be 175 to 198 m/s between 17.5 and 180 Torr. Above 180 Torr the mixtures detonate. The order for the reaction $NF_3 + H_2$ in flames was found to be two and the effective activation energy and preexponential factor were determined as 56 ± 5 kcal/mol and 1.3×10^{19} $cm^3 \cdot mol^{-1} \cdot s^{-1}$, respectively. A chain mechanism was assumed [4].

The irradiation of NF_4BF_4 with a low-power CO_2 laser produces reactive species which initiate reactions in an NF_3–H_2 mixture. The products HF, NF, N_2, and CN (from impurities in NF_3) were identified by their IR and UV emissions [6]. Product distributions in the NF_3–H_2–He combustion system calculated for various reactant ratios at 1500 and 2000 K are listed in [7, 8].

The heat of reaction of nitrogen trifluoride and hydrogen to form nitrogen and hydrogen fluoride was measured in a calorimetric bomb as $\Delta H^\circ_{298} = -199.49 \pm 0.22$ kcal/mol referring to the equation

$$NF_3(g) + {}^3/_2H_2(g) \rightarrow {}^1/_2N_2(g) + 3HF\ (1\ \text{in}\ 123H_2O)\ [9]$$

A previously obtained value is -205.3 ± 3.2 kcal/mol for HF extrapolated to infinite dilution [10]. Referring to this basis for HF, the former value changes from -199.49 to -208.40 kcal/mol [9].

The reaction of nitrogen trifluoride and hydrogen atoms in a fast-flow system was studied by electron spin resonance and mass spectrometry. Between 475 and 600 K, the rate constant can be described as a function of temperature by the equation

$$k = (6.0 \pm 2.5) \times 10^{11} \cdot \exp(-13.2 \pm 0.6\ \text{kcal} \cdot \text{mol}^{-1}/RT)\ L \cdot mol^{-1} \cdot s^{-1}$$

The reaction produced HF and N_2 while simultaneously consuming H atoms and H_2. The overall reaction, a sum of exothermic elementary steps, was assumed to be

$$H + H_2 + NF_3 \rightarrow 3HF + {}^1/_2N_2,\ \Delta H = -217\ \text{kcal/mol}\ [11]$$

NF_3–$H_2(D_2)$ mixtures have gained importance in HF (DF) chemical lasers; for more details, see "Fluorine" Suppl. Vol. 3, 1982, p. 128ff.

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4.1.4.11.5.3 Reactions with Oxygen

A reaction of nitrogen trifluoride with oxygen does not occur up to 770° C [1].

An electric discharge through an equimolar mixture of nitrogen trifluoride and oxygen at 77 K leads to the formation of trifluoroamine oxide, F_3NO, with a maximum yield of 15% [2, 3]. Other products identified were O_2F_2 and NO_2 [3]. This reaction was recommended as a method of synthesizing F_3NO. At ambient temperatures, NO_2 was formed in a discharge and no FNO_2 was observed as expected [3]. The formation of the FOO radical was identified by ESR during the ^{60}Co γ-irradiation of a liquid mixture of NF_3 and O_2 at 77 K [4].

NF_3 reacts with O^- and O_2^- to form F^- and F_2^- with approximate fractional abundances of 0.85 and 0.15, respectively. The rate constants measured are $(3.7 \pm 1.1) \times 10^{-10}$ and $(2.4 \pm 0.7) \times 10^{-10}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for the reactions with O^- and O_2^-, respectively [5].

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4.1.4.11.5.4 Reactions with Halogens

The reaction of nitrogen trifluoride with fluorine in the presence of strong Lewis acids and an energy source such as heat, glow discharge, UV or γ radiation leads to the formation of NF_4^+ salts. This type of reaction is described on pp. 164/5. The formation of NF_4^+ was also suggested when mixtures of NF_3 and F_2 were radiolyzed at room temperature by fission fragments produced by neutron irradiation of enriched UF_4 [1].

Microwave discharge in a 1:1 mixture of nitrogen trifluoride and chlorine yielded ClF, N_2, and HF as principal products; smaller amounts of HCl, N_2F_2, and HClO were also formed [3].

An electric discharge through a mixture of nitrogen trifluoride and bromine at 77 K gave the bromine fluorides BrF_5 and BrF_3 as principal products. Bromodifluoroamine was not formed [2].

The reaction between metastable excited iodine atoms and NF_3 forming electronically excited iodine monofluoride IF* is thought to occur in discharge-excited Ar(He)–CF_3I–NF_3 gas mixtures and produces the upper energy level for the IF laser. The rate constant determined from the time decay of the blue-green IF fluorescence is $(2.6 \pm 0.5) \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 300 K [4, 5, 6]. However, this reaction step, $I^* + NF_3 \rightarrow IF^* + NF_2$, is doubted by [7] to take place in Ar–CF_3I–NF_3 mixtures (rather the direct process, $CF_3I + h\nu \rightarrow IF^* + CF_2$, is favored) while it probably occurs in I_2–NF_3 mixtures excited by ultraviolet radiation.

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4.1.4.11.5.5 Reactions with Sulfur, Boron, Carbon, Phosphorus, Arsenic, Antimony, and Bismuth

Nitrogen trifluoride passed into molten sulfur at 350 to 400°C reacts to give thiothionyl fluoride, SSF_2, and thiazyl fluoride, NSF, as main products and smaller amounts of SF_4, SF_6, and SO_2F_2. The composition of the product mixture depends on the depth of the molten sulfur layer and the contact time of the NF_3. Below 350°C, small amounts of $N_3S_3F_3$ are formed [1]. The combustion of sulfur with nitrogen fluoride in a nickel bomb proceeds according to the equation

$$S(c,rh) + 2NF_3(g) \rightarrow SF_6(g) + N_2(g)$$

The standard heat of reaction was measured calorimetrically as $\Delta H^\circ_{298.15} = -228.26 \pm 0.2$ kcal/g-atom of sulfur [2].

The combustion of crystalline boron in nitrogen trifluoride gives boron trifluoride according to the reaction

$$B(c) + NF_3(g) \rightarrow BF_3(g) + \tfrac{1}{2}N_2(g)$$

The standard heat of reaction measured in a bomb calorimeter is $\Delta H^\circ_{298.15} = -239.7 \pm 1.2$ kcal/g-atom of boron [3].

Nitrogen trifluoride reacts with activated charcoal at 150°C to give CF_4 and N_2 [4]. When nitrogen trifluoride is passed over petroleum coke in a fluidized bed at about 400°C, N_2F_4, CF_4, C_2F_6, and NO_x are formed [5]. For the preparation of N_2F_4 by this method, see p. 301.

After heating a mixture of red phosphorus and nitrogen trifluoride, $[F_3P(NPF_2)_2NPF_3]PF_6$ as well as $(NPF_2)_3$, PF_3, and PF_5 were identified [6].

The thermal reaction of nitrogen trifluoride with arsenic, antimony, or bismuth gives N_2F_4 [7] according to the equation (see p. 300)

$$n\,NF_3 + M \rightarrow {}^{n}\!/_{2}\,N_2F_4 + MF_n$$

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4.1.4.11.5.6 Reactions with Alkali and Alkaline Earth Metals

The flame reactions of alkali metal vapors (Li, Na, Cs) with nitrogen trifluoride between about 500 and 1000 K and at a few Torr show strong chemiluminescence. The emission results from electronically excited alkali metal atoms. Photon yields of up to 3% were measured. The excitation mechanism was assumed to involve the formation of an excited species and the transfer of energy from this species to the alkali metal atom (A) according to the simplified sequence [1, 2]:

$$A + NF_n \rightarrow AF(v) + NF_{n-1}$$

$$NF + NF \rightarrow N_2^* + 2F \qquad A + N_2^* \rightarrow A^* + N_2$$

Emissions from electronically excited CN molecules (and Li atoms) were observed in the ternary Li–NF_3–CCl_4 flame system [3]. No difference in the chemiluminescence was seen in the Na–NF_3–N_2O system compared to the Na–NF_3 system. However, in the Cs–NF_3 flame system, NO ($A^2\Sigma^+ \rightarrow X^2\Pi$) emission together with emission from the Cs atom were observed. The NO emission was probably caused by O_2 impurities in the gases [4].

The reaction

$$Ca + NF_3 \rightarrow CaF(X^2\Sigma^+, v) + NF_2$$

was studied in thermal crossed beam experiments using laser-induced fluorescence detection techniques. The largest fraction of the available exoergicity (67%) was found to be transformed into vibrational excitation of the CaF product with inverse population distribution of the vibrational states. Formation of $CaF(X^2\Sigma^+)$ was determined to be first order with respect to both the Ca atom and NF_3 molecule concentration [5]. The integral cross sections for the chemi-ionization reactions of Ca and Sr with NF_3

$$Ca, Sr + NF_3 \rightarrow CaF^+, SrF^+ + NF_2^-$$

were determined in molecular beam experiments at collision energies up to 4 eV (center-of-mass system). The results support the existence of a collision complex in which all degrees of freedom are activated [6].

Chemiluminescence spectra of BaF result from the flame reaction of barium vapor and nitrogen trifluoride. The highest photon yield measured was 50% at 2 Torr [7] whereas the corresponding quantity in the Mg + NF_3 reaction was 3×10^{-2}% at 100 Torr [8].

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4.1.4.11.5.7 Reactions with Other Metals

In contrast to previous reports (see "Fluor" Erg.-Bd. 1, 1959, p. 245), zinc powder does not react with NF_3 when rapidly heated in an NF_3 atmosphere (20°C per minute in a differential scanning calorimeter) until about 300°C. Successive heating of the same sample apparently passivates the surface so that no reaction takes place at 300°C [17].

Nitrogen trifluoride reacts with mercury in a flow system at 320 to 330°C to give HgF and N_2F_4, with a small amount of cis-N_2F_2 [1]. An electrical discharge produces N_2F_4, N_2F_2, mercury fluorides, and nitrogen at 1 to 4 Torr NF_3 and at about 200°C [2]. Both reactions have been recommended for laboratory scale preparation of N_2F_4; for more details, see p. 301. Chemiluminescence from HgF was observed in the reaction of metastable mercury atoms with NF_3

$$Hg(^3P_2) + NF_3 \rightarrow HgF(B \rightarrow X) + NF_2$$

The rate constant for HgF(B) formation, $k = 8.1 \times 10^{-11}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (corresponding to the cross section $\sigma = 23.3\ Å^2$), was measured using a flowing afterglow technique [3].

Aluminium powder rapidly heated in an NF_3 atmosphere (20°C per minute in a differential scanning calorimeter) appears to become passivated at 300 to 325°C [17]. Aluminium atoms in a large excess of Ar as a buffer gas mixed with NF_3 in a flow system produce a flame showing three colors: violet in the inner part, blue in the intermediate part, and green in the outer part and top of the flame. The emission spectrum extended from about 200 to 1060 nm and consisted of AlF, NF, and N_2 molecular bands and Al atomic lines (~90% of total yield). The maximum photon yield defined as the flux of photons emitted from the reaction zone divided by the flux of NF_3 flowing into the zone was 2% at 0.5 Torr. A mechanism was suggested for populating high lying levels of the metal atom by energy transfer from excited molecular nitrogen according to the following sequence of exoergic reactions [4 to 6]:

$$Al + NF_n \rightarrow AlF + NF_{n-1}\ (n = 3, 2, 1;\ \text{consecutive stripping of } NF_3)$$

$$N + NF \rightarrow N_2^* + F \qquad N_2^* + Al \rightarrow N_2 + Al^*$$

The kinetics of the reaction

$$Al+NF_3 \rightarrow AlF+NF_2$$

has been studied from 300 to 1000 K. The rate constants between 300 and 800 K are represented by the Arrhenius expression $k=(2.07 \pm 0.42) \times 10^{-10} \exp(-2990 \pm 95\ cal \cdot mol^{-1}/RT)\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$. Above 800 K, NF_3 decomposes significantly under the experimental conditions [7].

The reaction of samarium and NF_3 shows strong chemiluminescence. The emission results from excited SmF molecules and Sm atoms. The highest photon yield measured (for the definition, see the $Al+NF_3$ reaction) was 70% at 2.3 Torr. About 12% of the reaction exothermicity was converted into radiation [8].

The reaction of thin zirconium foils with NF_3 in combustion flash lamps

$$4NF_3+3Zr \rightarrow 3ZrF_4+2N_2$$

generates light with a color temperature of about 4500 K. This reaction leads to a higher color temperature than is possible by oxidation of zirconium (~3900 K) [9 to 11].

Relatively strong emission from lead atoms and very weak emission from PbF_4 molecules was observed in the reaction of Pb atoms with NF_3 in a flow system [6].

Both, powdered molybdenum and tungsten react with nitrogen trifluoride at 280°C to give the hexafluorides and small amounts of N_2F_4. The fluorination also involves the formation of a lower fluoride which could be identified as MoF_3 in the case of the $Mo+NF_3$ reaction [12]:

$$2Mo+6NF_3 \rightarrow 2MoF_3+3N_2F_4$$
$$2MoF_3+2NF_3 \rightarrow 2MoF_6+N_2$$
$$4MoF_3+3N_2F_4 \rightarrow 4MoF_6+3N_2$$

NF_3 (0.2 to 0.4 atm) is reduced by a molybdenum incandescant filament (350 to 400°C) yielding solid MoF_3 and MoF_5 as main products as well as gaseous MoF_6 and N_2. The reaction is thought to proceed according to the equation

$$5Mo+8NF_3 \rightarrow MoF_3+3MoF_5+MoF_6+4N_2\ [13]$$

Nickel, iron, and copper wires (diameter of 0.127 mm each) electrically heated in an NF_3 atmosphere ignite at the following temperatures (in °C):

metal	Ni	Fe	Cu
1 atm NF_3	1187	817	550
6.8 atm NF_3 ...	967	612	475

Nickel, copper, and silver as powdered samples rapidly heated in NF_3 (20°C per minute in a differential scanning calorimeter) appear to become passivated: nickel at about 330°C, copper at 270 to 340°C, and silver at 350°C [17].

Nitrogen trifluoride reacts with copper at 375°C in a flow reactor to give N_2F_4 according to the equation

$$2Cu+2NF_3 \rightarrow N_2F_4+2CuF\ [14]$$

For more details, see p. 300. Copper atoms in a large excess of argon mixed with NF_3 in a flow system produce a flame which is green at the bottom and blue at the top. The emission spectrum contains a variety of molecular bands belonging to CuF ($C,B,A \rightarrow X$) and lines of atomic Cu (12% of the total emission). The photon yield (for the definition, see the $Al+NF_3$ reaction) was measured to be 0.1% at 5 Torr. Population inversion was observed between some of the Cu-atom states, and this was explained by a mechanism similar to that in the $Al+NF_3$ reaction [6, 15, 16].

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4.1.4.11.6 Reactions with Inorganic Compounds

4.1.4.11.6.1 Reactions with Noble Gas Compounds

Nitrogen trifluoride is fluorinated by KrF_2 in the presence of Lewis acids such as BF_3, TiF_4, PF_5, SbF_5, or NbF_5 to give perfluoroammonium salts. The reaction can be carried out in liquid anhydrous HF [1, 2] or in the gas phase [2]. For more details, see p. 165.

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4.1.4.11.6.2 Reactions with Water and Hydroxide Solution

Nitrogen trifluoride is virtually inert to chemical attack by water at 133°C [1]. Another source [2] reports that 1.5% of NF_3 reacted according to the equation $NF_3 + 2H_2O \rightarrow 3HF + HNO_2$ when a mixture of 23 mL of H_2O and 0.40 g of NF_3 was heated to 100°C for 7 d. However, slow hydrolysis occurs at 100°C by aqueous hydroxide solution to give nitrite and fluoride while concentrated NaOH (12N) reacts only very slowly with NF_3 [1]. Nitrogen trifluoride is also hydrolyzed very slowly by aqueous ferric chloride solution at 100°C. $FeCl_3$ acts as a hydrolysis catalyst, forming NO and NO_3^-. Other transition-metal ions do not show this property as concluded from the total inertness of NF_3 to solutions of $CoCl_2$, $MnSO_4$, $NiSO_4$, or $CuSO_4$ at 100°C over periods up to 7 d [1].

A gaseous mixture of 740 Torr NF_3 and 15 Torr H_2O (2 mol%) could not be ignited when exposed to an electric discharge [3], in contrast to previous reports, see "Fluor" Erg.-Bd. 1, 1959, p. 244.

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4.1.4.11.6.3 Reactions with Nitrogen Compounds

Nitrogen trifluoride and ammonia do not react below 150°C. NH_4F and/or NH_4HF_2 are formed in a flow system at 350°C in the presence of N_2. In the absence of N_2, the reaction occurs at 550°C with complete consumption of NH_3 to give N_2F_4. The NF_3–NH_3 mixture is explosive at these temperatures [1]. The system NF_3–NH_3 shows combustion temperatures of about 3300 K at 70 Torr for a 1:1 mixture. The flame propagation rates in stoichiometric mixtures were measured to be 105 to 120 m/s between 22.5 and 190 Torr. The order of the $NF_3 + NH_3$ reaction in flames was two and the effective activation energy and preexponential factor were determined as 58 ± 5 kcal/mol and 1.76×10^{18} $cm^3 \cdot mol^{-1} \cdot s^{-1}$, respectively [2]. The heat of reaction was measured in a calorimetric bomb as $\Delta H^\circ_{298} = -259.5 \pm 1.0$ kcal/mol referring to the equation

$$NF_3(g) + 4\,NH_3(g) \rightarrow 3\,NH_4F(c) + N_2(g) \quad [3]$$

Calculated product distributions (HF and N_2) at 1500 and 2000 K of the NF_3–NH_3–He and NF_3–N_2H_4–He combustion systems for various reactant ratios are listed in [4].

A patent [5] disclosed the reaction between nitrogen trifluoride and nitric oxide at temperatures up to 950°C in a nickel tube to form tetrafluorohydrazine and nitrosyl fluoride (see p. 301)

$$NF_3 + NO \rightarrow \tfrac{1}{2}N_2F_4 + FNO$$

This reaction also occurs during irradiation with a CO_2 laser [6]. Thermodynamic data were calculated to be $\Delta H^\circ_{298} = -7.80$ and $\Delta G^\circ_{298} = -3.10$ kcal/mol. Calculated conversion factors of NF_3 for $0 \leq t(°C) \leq 500$ and $1 \leq p(atm) \leq 100$ indicate a favorable equilibrium situation at moderate temperatures for the products [11]. ^{60}Co γ-irradiation of a heterogeneous mixture of NF_3 and NO at 77 K produces FNO, F_2NNO, and N_2F_4 [7]. Only traces of FNO were formed when NO_2 or N_2O were passed with NF_3 through a nickel tube at temperatures up to 770°C [8]. The product distributions (N_2, O_2, F) in combustion of NF_3–NO and NF_3–N_2O mixtures at 1500 K [9] as well as the attainable F-atom concentrations at various temperatures (>1400 K) and ratios of reactants [4] have been calculated.

Nitrogen trifluoride is not attacked at 133°C by excess aqueous nitric acid (HNO_3) [10]. Calculated thermodynamic data for the unknown reaction $NF_3 + ClNO \rightarrow \tfrac{1}{2}N_2F_4 + FNO + \tfrac{1}{2}Cl_2$ are $\Delta H^\circ_{298} = 1.27$ and $\Delta G^\circ_{298} = 2.09$ kcal/mol [11].

References:

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[9] R. Roback, L. Lynds (AIAA Paper No. 74-1142 [1974] 1/6; C.A. **83** [1975] No. 200026).

[10] G. L. Hurst, S. I. Khayat (Advan. Chem. Ser. No. 54 [1966] 245/60).

[11] A. V. Pankratov (Zh. Fiz. Khim. **43** [1969] 403/7; Russ. J. Phys. Chem. **43** [1969] 216/9).

4.1.4.11.6.4 Reactions with Halogen Compounds

Nitrogen trifluoride is not attacked by pure HCl at 133°C, but a slow reaction occurs with aqueous HCl at this temperature. The products are dependent on the concentration of the acid: 0.5N HCl yields nitric oxide and nitric acid, whereas 4N HCl yields gaseous chlorine, nitrogen, and hydrogen fluoride. Nitrogen trifluoride also reacts readily with hot NaCl solution. The reactions with aqueous solutions of HBr (or NaBr) or HI (or NaI) occur more readily than with HCl and mainly produce NH_4^+, F^-, N_2, and Br_2 or I_2, respectively. The reaction mechanism apparently involves nucleophilic attack by the halide ion, and the reaction rate increases with nucleophilic strength in the order $ClO_4^- \ll Cl^- < Br^- < I^-$. Nitrogen trifluoride is stable in dilute $HClO_4$ at 133°C.

Reference:

G. L. Hurst, S. I. Khayat (Advan. Chem. Ser. No. 54 [1966] 245/60).

4.1.4.11.6.5 Reactions with Sulfur and Selenium Compounds

An NF_3–SO_2 (1:1) mixture reacts at 455°C in a nickel tube to give SOF_2 (60% yield) as well as NO and NO_2 according to the equations

$$NF_3 + SO_2 \rightarrow SOF_2 + FNO \text{ and } SO_2 + 2FNO \rightarrow SOF_2 + NO + NO_2$$

But, on heating to 440°C in a nickel autoclave, a 1:1 mixture produces mainly SO_2F_2, SF_6, and NO_2 while a 2:1 mixture yields SF_6 and NO_2 under the same conditions [1]:

$$2NF_3 + 3SO_2 \rightarrow 3SO_2F_2 + N_2$$

$$2NF_3 + SO_2 \rightarrow SF_6 + NO_2 + \tfrac{1}{2}N_2$$

The reaction $NF_3 + \frac{3}{2}SO_2 \rightarrow \frac{3}{2}SO_2F_2 + \frac{1}{2}N_2$, $\Delta H = -148.9$ kcal/mol

can also be initiated by CO_2-laser irradiation [2]. No association between NF_3 and SO_2 down to −130°C could be detected using infrared spectroscopy [3].

Nitrogen trifluoride reacts with sulfur trioxide at 520°C in a nickel tube to give SO_2F_2 (30%), SOF_2 (4%) as well as NO and NO_2, and a white solid consisting of $(NO)_2[S_2O_5F_4]$ (30%):

$$NF_3 + SO_3 \rightarrow SO_2F_2 + FNO$$
$$SO_2F_2 + SO_3 \rightarrow S_2O_5F_2$$
$$S_2O_5F_2 + 2\,FNO \rightarrow (NO)_2[S_2O_5F_4]$$

At higher pressures a 1:1 mixture gives SO_2F_2 and SF_6, whereas SF_6 is exclusively formed with excess NF_3 [1].

Nitrogen trifluoride is not attacked at 133°C by aqueous sulfuric acid [4].

On heating thionylfluoride, SOF_2, with nitrogen trifluoride in the ratio 1:1 in an autoclave at 440°C, the products are SO_2F_2 and SF_6 with the mass ratio 1:3, NO, and NO_2. SOF_4 is formed as an additional product when a 3:2 SOF_2–NF_3 mixture reacts at 400°C in the presence of CsF. The overall reaction is thought to occur according to the equations [5]:

$$6\,SOF_2 + 6\,NF_3 \rightarrow 3\,SOF_4 + 3\,SF_6 + NO + NO_2 + 2\,N_2$$
$$2\,SOF_4 \rightarrow SO_2F_2 + SF_6$$

Sulfuryl fluoride, SO_2F_2, and nitrogen trifluoride (1:1) heated at 450°C in the presence of CsF in an autoclave yield only traces of SF_6, NO, and NO_2 [5].

The reaction of thionyl chloride, $SOCl_2$, with excess nitrogen trifluoride at 360°C is

$$3\,SOCl_2 + 2\,NF_3 \rightarrow 3\,SOF_2 \text{ (80\% yield)} + 3\,Cl_2 + N_2$$

The amount of SOF_2 decreases with temperature: at 280°C, only traces of SOF_2 form [5].

Sulfuryl chloride, SO_2Cl_2, reacts with excess nitrogen trifluoride between 265 and 360°C to yield varying amounts of SO_2F_2, SO_2FCl, Cl_2, and N_2 according to the equations [5]:

$$3\,SO_2Cl_2 + 2\,NF_3 \rightarrow 3\,SO_2F_2 + 3\,Cl_2 + N_2$$
$$6\,SO_2Cl_2 + 2\,NF_3 \rightarrow 6\,SO_2FCl + 3\,Cl_2 + N_2$$

Nitrogen trifluoride hydrolyzes in aqueous thiosulfate solution giving sulfur, ammonium, and fluoride [4].

On passing nitrogen trifluoride at 350°C into liver of sulfur (mixture of K-polysulfide, K-sulfate, and K-thiosulfate), SF_6 and SO_2F_2 are formed as main products plus SF_4 and SOF_2. At 250°C, the products are NSF, SO_2F_2, SOF_2, and SSF_2 [6].

Selenium dioxide, SeO_2, reacts with nitrogen trifluoride (1:1) at 440°C in an autoclave to yield $SeOF_2$ (50% yield) as well as SeF_6, NO, and NO_2 [1].

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4.1.4.11.6.6 Reactions with Boron Compounds

Nitrogen trifluoride and diborane do not react at room temperature and pressures up to 8 atm (under these conditions, B_2H_6 and PF_3 give the adduct $F_3P \cdot BH_3$) [1]. At 145°C, yellow solids deposit in the reaction tube but no volatile products are produced [2]. NF_3–B_2H_6 mixtures are explosive when handled as liquids [1].

Passing nitrogen trifluoride at 615°C over B_2O_3 produces about a 90% yield of $NOBF_4$ (based on NF_3 reacted), plus NO, NO_2, and N_2O [3]:

$$B_2O_3 + 3\,NF_3 \rightarrow 2\,BF_3 + 3\,FNO$$

$$B_2O_3 + 6\,FNO \rightarrow 2\,BF_3 + 3\,NO + 3\,NO_2$$

$$BF_3 + FNO \rightarrow NOBF_4$$

Reactions of nitrogen trifluoride with boron trifluoride or trimethylboron may be initiated by the multiphoton absorption of infrared radiation from a CO_2 laser. A BF_3–NF_3–C_2H_4 (1:1:1) mixture produces BF_4^-, C_2H_2, HCN, and HF as the major products as identified by infrared spectra. For 1:1 and 2:1 mixtures of $B(CH_3)_3$ and NF_3, the gaseous products are C_2H_2, HCN, CH_4, HF, and a small amount of BF_3. In a 1:2 mixture, the products are C_2F_4, CF_4, C_2F_6, CF_3CN, CF_3H, HF, and BF_3 [4].

Vapor pressure measurements on the system NF_3–BF_3 at 158.95 K (triple point of HCl) show large deviations from Raoult's law, however, there is no evidence for acid-base association between the two components [5]. Very weak association resulting from small van der Waals forces was observed for NF_3 and BF_3 below 148 K and for NF_3 and BCl_3 below 173 K by means of infrared spectroscopy [6].

References:

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4.1.4.11.6.7 Reactions with Carbon Compounds

The reaction of an equimolar mixture of nitrogen trifluoride and carbon monoxide at 520°C in a nickel tube produces COF_2 (90 to 95% yield), CF_4, NO, and NO_2 [1]:

$$3\,CO + 2\,NF_3 \rightarrow 3\,COF_2 + N_2$$

$$COF_2 + NF_3 \rightarrow CF_4 + FNO$$

$$COF_2 + 2\,FNO \rightarrow CF_4 + NO + NO_2$$

The reaction has also been initiated at room temperature by irradiation with two CO_2 lasers. The main products identified are COF_2, CF_4, N_2, and O_2. A 100% conversion of CO can be reached [2, 3].

Reaction with carbon dioxide occurs at 825°C also yielding COF_2 (80% yield), CF_4, NO, and NO_2 [1]:

$$CO_2 + NF_3 \rightarrow COF_2 + FNO$$

$$CO_2 + 4\,FNO \rightarrow CF_4 + 2\,NO + 2\,NO_2$$

A stoichiometric mixture of both gases can not be ignited when exposed to an electric discharge [4].

Phosgene and nitrogen trifluoride (1:1 ratio) react at 400°C in a nickel tube to quantitatively produce COF_2 according to

$$3\,COCl_2 + 2\,NF_3 \rightarrow 3\,COF_2 + 3\,Cl_2 + N_2$$

At 310°C and with the educts in the ratio 2:1, COFCl and COF_2 (2:1), Cl_2, and N_2 are formed [5].

The reaction between nitrogen trifluoride and hydrogen cyanide at 350°C leads to the final products N_2F_4 and $(CN)_2$ [6]:

$$NF_3 + HCN \rightarrow HF + NF_2 + CN$$
$$NF_2 + NF_2 \rightarrow N_2F_4$$
$$CN + CN \rightarrow (CN)_2$$

Chlorine cyanide, ClCN, and excess nitrogen trifluoride at 450 to 500°C yield $(FCN)_3$, $F_3CN{=}NCF_3$, $F_3CN{=}CF_2$, and Cl_2. Above 520°C, the reaction occurs vigorously [7].

Sodium cyanide, NaCN, and nitrogen trifluoride in a nickel tube at 300 to 320°C give nearly completely $(CN)_2$:

$$2\,NF_3 + 6\,NaCN \rightarrow 3\,(CN)_2 + 6\,NaF + N_2$$

At 400°C, the main product is a highly polymerized solid containing the elements C, N, and F and the gaseous products are $(FCN)_3$, $(CN)_2$, $F_3CN{=}NCF_3$, CF_4, and C_nF_{2n+2} compounds for short reaction times, and exclusively $(FCN)_3$ and C–F compounds for long reaction times [7].

Product distributions in the combustion systems $CO{-}NF_3{-}He$, $CS_2{-}NF_3{-}He$, and $(CN)_2{-}NF_3{-}He$ calculated for various reactant ratios at 1500 and 2000 K are listed in [8].

References:

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4.1.4.11.6.8 Reactions with Silicon Compounds

The irradiation of a $SiH_4{-}NF_3$ gas mixture of 35 Torr with a CO_2 laser (929.02 cm^{-1}, 11 to 15 W/cm^2) produces a solid mixture of Si, Si_3N_4, $Si_3N_4O_n$, and K_2SiF_6 (NF_3 contained potassium as an impurity) as well as gaseous SiH_xF_{4-x} ($x = 0$ to 4) compounds. With excess NF_3 the intermediate radical SiF is formed in its electronically excited state $A^2\Sigma^+$ as deduced by its strong fluorescence [1].

On passing NF_3 over SiO_2 at 615°C, $(NO)_2SiF_6$ (about 90% yield), SiF_4, NO, and NO_2 are produced [2] according to

$$SiO_2 + 2\,NF_3 \rightarrow SiF_4 + 2\,FNO \rightarrow (NO)_2SiF_6$$
$$SiO_2 + 4\,FNO \rightarrow SiF_4 + 2\,NO + 2\,NO_2$$

References:

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4.1.4.11.6.9 Reactions with Phosphorus and Arsenic Compounds

On heating phosphorus pentoxide and NF_3 (1:1) in an autoclave to 480°C, POF_3, NO, and NO_2 are formed. With excess NF_3 a small amount of $NOPF_6$ forms [1]:

$$P_2O_5 + 2\,NF_3 \rightarrow 2\,POF_3 + NO + NO_2$$
$$POF_3 + NF_3 \rightarrow PF_5 + FNO \rightarrow NOPF_6$$

Triphosphorus pentanitride, P_3N_5, reacts with NF_3 to give the fluorocyclophosphazenes $(NPF_2)_3$ and $(NPF_2)_4$ in small amounts [2].

Ion cyclotron resonance spectroscopy has been used to observe fluorine atom and fluoride ion transfer from neutral NF_3 to PF_3^+ and PF_2^+, respectively, in PF_3–NF_3 mixtures according to the reactions $PF_3^+ + NF_3 \rightarrow PF_4^+ + NF_2$ and $PF_2^+ + NF_3 \rightarrow PF_3 + NF_2^+$ [3]. Product distributions in the combustion system PF_3–NF_3–He calculated for various reactant ratios at 1500 and 2000 K are listed in [4].

No association between PF_5 and NF_3 was observed down to −128°C using infrared spectroscopy [5].

Phosphorus oxide fluoride, POF_3, reacts with NF_3 (1:1 ratio) in an autoclave at 480°C to yield 80% $NOPF_6$ and a small amount of PF_5 [6].

An equimolar mixture of NF_3 and phosphorus oxide chloride, $POCl_3$, reacts quantitatively in an autoclave at 250°C according to the equation

$$2\,POCl_3 + 2\,NF_3 \rightarrow 2\,POF_3 + 3\,Cl_2 + N_2$$

A $POCl_3$–NF_3 mixture in the ratio 3:2 at 195°C gives POF_3, POF_2Cl, $POFCl_2$, and Cl_2 [6].

The reactions with tetraphosphorus trisulfide, P_4S_3, at 180 to 360°C and with tetraphosphorus decasulfide, P_4S_{10}, at 345 to 440°C in a nickel trap lead to product mixtures of varying composition. At temperatures of 180 to 215°C, $(NPF_2)_n$, $n = 3$ to 9, is formed in a 60% yield along with PF_3, PF_5, and N_2. At higher temperatures the amount of $(NPF_2)_n$ decreases and the yield of SPF_3 (up to 80%), SF_4, and SF_6 increases. Higher flow rates of NF_3 favor the production of $(NPF_2)_n$. Traces of POF_3, SO_2F_2, SOF_2, $S_2P_2F_4O$, $[F_3P(NPF_2)_2NPF_3]PF_6$, and $NOPF_6$ were also identified [7].

Calcium phosphide, Ca_3P_2, heated in a stream of NF_3 at 410 to 520°C gives PF_5, $(NPF_2)_n$ with $n = 3$ to 5, and $[F_3P(NPF_2)_2NPF_3]PF_6$ as the main products. By-products are POF_3, N_2O, NO, NO_2, and $NOPF_6$ [7].

Nickel phosphide, Ni_2P, reacts at 620°C to yield a mixture containing $NOPF_6$, NO, NO_2, FNO, and NiF_2 [7].

Triphenylphosphine and tris(dimethylamino)phosphine are fluorinated under mild conditions to give the phosphoranes $(C_6H_5)_3PF_2$ and $((CH_3)_2N)_3PF_2$, respectively [9].

The gas-phase reaction of NF_3 and the trifluoroarsonium ion, $HAsF_3^+$, was studied in an NF_3–AsF_3–CH_4 mixture by ion cyclotron resonance spectroscopy [8]. The reaction suggests a nucleophilic addition of the weak base NF_3 to the $HAsF_3^+$ ion (formed from AsF_3 and CH_4) followed by a unimolecular elimination of HF to yield an ion in which NF_3 is bound to the AsF_2^+ cation.

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4.1.4.11.6.10 Reactions with Metal Compounds

Oxides

Vanadium pentoxide heated in a stream of nitrogen trifluoride for 12 h at 400°C gives $NO[VOF_4]$ nearly quantitatively and small amounts of VOF_3, NO, and NO_2 [1]:

$$V_2O_5 + 3\,NF_3 \rightarrow 2\,VOF_3 + 3\,FNO$$
$$VOF_3 + FNO \rightarrow NO[VOF_4]$$
$$V_2O_5 + 6\,FNO \rightarrow 2\,VOF_3 + 3\,NO + 3\,NO_2$$

Only about 60% of chromium(III) oxide reacted with nitrogen trifluoride at 430°C to give CrF_3 and a relatively large amount of FNO (10% of the gaseous products), NO, and NO_2 [1]:

$$Cr_2O_3 + 3\,NF_3 \rightarrow 2\,CrF_3 + 3\,FNO$$
$$Cr_2O_3 + 6\,FNO \rightarrow 2\,CrF_3 + 3\,NO + 3\,NO_2$$

Nitrogen trifluoride and chromium(VI) oxide do not react up to 200°C, the decomposition temperature of the latter [1].

The reaction of molybdenum(VI) oxide and nitrogen trifluoride for 10 h at 430°C leads to an 80% yield of $NO[MoO_2F_3]$ plus MoO_2F_2, MoF_6, FNO, NO, and NO_2. The following processes were thought to occur [1]:

$$MoO_3 + NF_3 \rightarrow MoO_2F_2 + FNO$$
$$2\,MoO_2F_2 + 5\,FNO \rightarrow NO[MoO_2F_3] + MoF_6 + 2\,NO + 2\,NO_2$$

Under the same conditions, tungsten(VI) oxide gives $NO[WOF_5]$ in nearly quantitative yield [1]:

$$WO_3 + 2\,NF_3 \rightarrow WOF_4 + 2\,FNO$$
$$2\,WOF_4 + 3\,FNO \rightarrow NO[WOF_5] + WF_6 + NO + NO_2$$

Chlorides

Nitrogen trifluoride reacts with aluminium trichloride for 4 d at 80°C to give nitrogen and chlorine. Chlorine evolves rapidly at 135°C [2]. In CS_2, this reaction starts at 0°C [3].

Vanadium(III) chloride and nitrogen trifluoride react at 70°C to give solid $VCl_{1.5}F_{1.5}$ and the gaseous products N_2F_4 and NF_2Cl (traces):

$$4VCl_3 + 6NF_3 \rightarrow 4VCl_{1.5}F_{1.5} + 3N_2F_4 + 3Cl_2$$
$$N_2F_4 + Cl_2 \rightarrow 2NF_2Cl$$

Increasing the temperature to 300°C generates VF_3; the liberated Cl_2 reacts with VCl_3 to give VCl_4. Above 400°C, VF_5 as well as VCl_4, Cl_2, and traces of VF_3 are formed [1].

Chromium(III) chloride reacts with nitrogen trifluoride at 480°C to give a 60% yield of CrF_3 [1]:

$$2CrCl_3 + 2NF_3 \rightarrow 2CrF_3 + N_2 + 3Cl_2$$

Miscellanea

The reaction of vanadium nitride with nitrogen trifluoride at 400°C produces solid VF_3 and some gaseous N_2F_4 [1]:

$$3VN + 7NF_3 \rightarrow 3VF_3 + 3N_2F_4 + 2N_2$$

Molybdenum nitride is quantitatively converted into MoF_6 at 260°C where MoF_3 is an intermediate product [1]:

$$MoN + NF_3 \rightarrow MoF_3 + N_2$$
$$2MoN + 6NF_3 \rightarrow 2MoF_3 + 3N_2F_4 + N_2$$
$$2MoF_3 + 2NF_3 \rightarrow 2MoF_6 + N_2$$

Heating MoS_2 with nitrogen trifluoride at 280°C, generates the gaseous products MoF_6 (50% based on NF_3 reacted), SF_4, SF_6, and SNF (5%) [1].

Acidic or neutral ferrous sulfate solution at 60°C reduces NF_3 to ammonium

$$4H^+ + 6Fe^{2+} + NF_3 \rightarrow NH_4^+ + 3F^- + 6Fe^{3+}$$

In a typical experiment, 44% of the NF_3 (3 mmol NF_3, 20 mL 0.5N aqueous $FeSO_4$) was converted after 12 d [2].

References:

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4.1.4.11.7 Reactions with Organic Compounds

The flammability range of n-butane–NF_3 mixtures is from 1.5 to 75 mol% C_4H_{10}. The ranges of flammability for mixtures with methane, ethane, and propane can be anticipated to lie between that of hydrogen (5 to 90.6 mol%) and butane. Mixtures of NF_3 and 26 to 52 mol% C_2F_6 burn but do not explode when sparked [1].

Equimolar quantities of nitrogen trifluoride and ethane react at temperatures above 250°C to yield CF_4, CH_3CN, and HF. With a twofold excess of NF_3 the formation of CH_3CN is favored and no CF_4 is formed. Unstable intermediates such as $CH_3CH_2NF_2$, which decompose to form CH_3CN and HF, were suggested [2].

The CO_2-laser initiated reaction of nitrogen trifluoride with ethylene or 1,1-difluoroethylene, $C_2H_2F_2$, produces HF, CF_4, CF_3CN, CF_3H, C_2F_4, and C_2F_6 as products when a twofold excess of NF_3 is used. When a 1:1 NF_3–$C_2H_2F_2$ mixture is irradiated a small amount of HCN is additionally formed, while for a 1:1 NF_3–C_2H_4 mixture only HF, HCN, and traces of CF_4 and CF_3H are obtained [3].

The pyrolysis of a 1:1 mixture of nitrogen trifluoride and propylene at 300 to 320°C in a tube filled with petroleum coke gives acrylonitrile and HF [4]:

$$CH_3CH{=}CH_2 + NF_3 \rightarrow [CH_3CHFCH_2NF_2] \rightarrow CH_2{=}CHCN + 3HF$$

The reaction with perfluoropropylene, $CF_3CF{=}CF_2$, under flow conditions in a nickel tube has been studied over NaF at 520°C and over CsF at 320°C [5]. At 520°C, NF_3 reacts as a fluorinating agent to mainly give C_3F_8, $(CF_3)_2C{=}CF_2$, iso-C_4- to C_6-fluoroalkanes and fluoroalkane imines ($F_2C{=}NCF_3$, $CF_3CF{=}NCF_3$). At 320°C, only a very small amount of C_3F_8 is formed and it seems that the intermediate $(CF_3)_2CF$ radicals couple almost entirely with each other or with NF_2 radicals to form $(CF_3)_2CFCF(CF_3)_2$, $(CF_3)_2CFNF_2$, and $(CF_3)_2CNF$ as the major products.

Trifluoroacetonitrile and nitrogen trifluoride react at 515°C to give F_3CNF_2 (60%), CF_4 (15%), C_2F_6 (15%), and $(FCN)_3$ (10%) [12]. At 520°C and in the presence of CsF, the products identified were F_3CNF_2, $F_3CN{=}CF_2$, CF_4, $(FCN)_3$, and $(CF_3)_2NF$ with the relative mole ratio 2.2:1.3:1.9:1.4:1.0 [5].

Thermochemical calculations have been performed to determine the conditions that can be attained with various NF_3-fuel-diluent systems and the concentrations of chemical species (F, HF, CF_4, N_2) in the reaction products. The intention was the assessment of reactant systems that might replace the hydrogen-fluorine system in combustion-driven HF chemical lasers. Results are available for the NF_3–C_2H_2 system at 1500 K [6] and the combinations of NF_3 with C_2H_6, C_2H_2, C_6H_6, C_2F_6, C_2F_4, C_3F_6, C_4F_8, or C_6F_6 at 1500 and 2000 K [7]. The enthalpy of reaction of NF_3 and hexafluoroethane

$$\tfrac{2}{3}NF_3(g) + C_2F_6(g) \rightarrow 2CF_4(g) + \tfrac{1}{3}N_2(g)$$

was measured as $\Delta H_{298} = -103.9 \pm 1$ kcal/mol [8].

Alkyl radicals react with nitrogen trifluoride to give the corresponding alkylfluorides, RF, and/or difluoroaminoalkanes, RNF_2. The reactions have been carried out by photolyzing mixtures of NF_3 (2.7 to 135 Torr) and appropriate ketones (2 to 40 Torr) between 303 and 486 K [9]. With smaller radicals such as CH_3, CF_3, or C_2H_5 only the difluoroaminoalkanes form; however, with i-C_3H_7 and t-C_4H_9, both the difluoroaminoalkanes and alkyl fluorides are obtained.

Thermal reactions of nitrogen trifluoride with perfluoroalkylsulfur(VI) fluorides, R_FSF_5 and $R_FSF_4R_F'$, lead to the perfluoroalkylamines R_FNF_2 and $R_F'NF_2$ (R_F, R_F' are perfluoroalkyl groups). With $C_2F_5SF_5$ and excess NF_3 at about 520°C, a 30% yield of $C_2F_5NF_2$ was obtained. By-products were SF_4, SF_6, C_2F_6, and CF_4. Better yields result from N_2F_4 instead of NF_3 [10].

Nitrogen trifluoride reacts with methylmagnesium bromide at −80°C to give trimethylamine:

$$NF_3 + 3CH_3MgBr \rightarrow N(CH_3)_3 + 3MgBrF$$

The reaction with ethylmagnesium bromide is more complex: a brown solid precipitates which decomposes into NH_3 and $N(C_2H_5)_3$. The volatile phase contains a very small amount of trans-N_2F_2 [11].

At room temperature, polymers appear to be inert toward nitrogen trifluoride. Samples of polyethylene, polypropylene, polystyrene, or poly-α-methylstyrene exposed for 6 d to 5 atm of NF_3 at 135°C showed a mild surface reaction. After six weeks of exposure to 10 atm at 150°C, samples of neoprene, silicone rubber, Buna-N, butyl rubber, and ethylene propylene were noticeably deteriorated. Teflon, Tetrafluor, Viton, and Kel-F were not attacked under these conditions [1].

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4.1.4.12 Solubility

There are two studies on the very low solubility of nitrogen fluoride in water (10^{-5} to 10^{-6} mole fraction) carried out from 278 to 323 K [1] and from 298 to 318 K [2]. The agreement of the measured data is regarded as satisfactory over the common temperature range [2]. The following table lists some selected solubility data in form of Kuenen coefficients k, defined as the volume of gas in cm^3, corrected to 273.15 K and 760 Torr, which, at a partial pressure of 760 Torr, will dissolve in 1 g of solvent.

T in K	288.15	298.15	298.21	308.15	308.29	318.15	318.28
$k \cdot 10^3$	22.70 ±0.10	17.97 ±0.10	17.76 ±0.24	14.79 ±0.10	14.82 ±0.07	12.85 ±0.10	12.95 ±0.07
Ref.	[1]	[1]	[2]	[1]	[2]	[1]	[2]

The results of both studies were fitted by the method of least-squares to the equations

$$\log x_2 = 4596.4/T + 29.558 \cdot \log T - 93.404 \quad \text{for } T = 298 \text{ to } 318 \text{ K [2]}$$

$$\text{and } \log x_2 = 5785.95/T + 38.2556 \cdot \log T - 118.9122 \quad \text{for } T = 278 \text{ to } 323 \text{ K [1]}$$

where x_2 means the mole fraction of NF_3.

At 298.15 K, 3.5 [2] and 3.8 [1] kcal/mol for the enthalpy of solution and 34 [2] and 35 [1] $cal \cdot mol^{-1} \cdot K^{-1}$ for the entropy of solution were derived from the temperature dependence of the solubility data.

The solubility of NF_3 in anhydrous liquid hydrogen fluoride at three temperatures is shown in **Fig. 6**, from [3]. The slopes of the curves give Henry's law constants of 18400, 15000, and 4770 $Torr \cdot kg \cdot mol^{-1}$ at +19.8, −0.21, and −77.2°C, respectively. The lines at +19.8 and

−0.21°C give a heat of solution of −1533 cal/mol. The nonlinearity of the solubility curve at −77.2°C might be explained by hydrogen bonding between HF and NF_3, or more likely, interaction of NF_3 with itself.

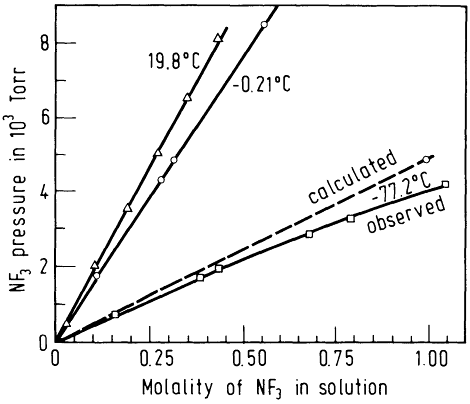

Fig. 6. Solubility of NF_3 in anhydrous liquid HF.

The solubility of NF_3 in the superacid system HSO_3F-SbF_5 (0.36 M)–SO_3 (1.06 M) at 20°C is less than 1 mL NF_3 gas per 100 mL of the solvent and, thus, of the same order as its solubility in water [4].

The miscibility of liquid NF_3 with some liquified gases at low temperatures has been investigated [5]. The temperatures at which the components mix homogeneously in equimolar amounts are as follows:

liquified gas	O_2	OF_2	Ar	O_3	$CClF_3$	CF_4
temperature in K	77	77	85	90	90	90

NF_3 and the following liquified gases form two separate layers on mixing: O_2F_2 at 130 K, ClF_3 and HF at 140 K, and ClF at 150 K [5]. NF_3 and HCl are partially miscible between about 0.1 and 0.9 mole fraction NF_3 at 158.95 K, the triple point of HCl [6].

References:

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4.1.4.13 Clathrates

With water, nitrogen trifluoride forms a clathrate hydrate when ice at −25 to −40°C is exposed to pressurized NF_3 (9 to 23 atm). Hydrate formation was found complete within 24 h by the fall of gas pressure. X-ray analysis indicated the clathrate hydrate to be of structure I, space group Pm3n. The dielectric behavior and the ^{19}F NMR spectrum of that hydrate as well of others containing tetrahydrofuran, p-dioxane, or sulfur hexafluoride as additional hosts, were analyzed to study the site distribution and motional dynamics of NF_3 [1]. A crystalline clathrate of NF_3 with β-quinol was grown from a saturated n-propanol solution under a gas pressure of 60 atm. The ^{19}F NMR spectrum of NF_3 in this clathrate served to determine the components of the chemical shift tensor, see p. 188 [2].

References:

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4.1.5 The NF_3^+ Ion

CAS Registry Numbers: NF_3^+ *[54384-83-7]*, $^{14}NF_3^+$ *[37366-70-4]*, $^{15}NF_3^+$ *[67745-75-9]*

Occurrence

The NF_3^+ cation is formed by ionization of NF_3 and also as a radiolysis product of NF_4^+ salts [1, 2]. In addition, there is evidence from electron paramagnetic resonance for the formation of NF_3^+ as an intermediate in the synthesis of the salts NF_4AsF_6 and NF_4BF_4 by low-temperature UV photolysis of NF_3–F_2–AsF_5 and NF_3–F_2–BF_3 mixtures, respectively [3].

Structure. Bonding

Like its neutral parent molecule, the NF_3^+ ion is a regular pyramid with C_{3v} symmetry. A single vacancy $6a_1^{-1}$ in the doubly occupied highest molecular orbital $6a_1$ of neutral NF_3 gives the ground term $^2A_1$ [4]. Some excited states with orbital vacancies $5e^{-1}$, $1a_2^{-1}$, $4e^{-1}$, $5a_1^{-1}$, and $3e^{-1}$ are known from photoelectron spectra of NF_3, see p. 185.

Hyperfine structure constants were derived from EPR spectra (see below) and used to derive spin populations in atomic orbitals. This gave the following simplified hybrid-orbital picture of the bonding in NF_3^+: The unpaired electron mainly occupies a nonbonding N orbital which is mixed with a p_z orbital of fluorine. Its z axis is tilted away from the normal to the N–F bond toward the C_3 axis by 15°. The bonds are formed by hybridization of nitrogen s and p orbitals giving a hybrid orbital, which is between sp^2 and sp^3 [1, 4, 5]. Another set of hyperfine structure constants, derived from an earlier EPR spectrum, apparently led to a different bonding picture, but the arguments given [2] were somewhat unclear [6].

Bond Distance. Bond Angle

A bond angle of 113.9° is consistent [4] with the ratio of isotropic and anisotropic parts of the nitrogen hyperfine coupling constants [5]. Bond distances and angles from ab initio molecular orbital calculations [4, 6, 10, 11, 12] are in the range 1.253 [10] to 1.381 Å [6] and 114.4° [12] to 115.96° [6].

Molecular Vibrations

The first photoelectron band of NF_3 shows a progression in the ν_2 bending vibration with a spacing of ~565 cm^{-1}. At about the band maximum, the vibrational spacing appears to change to about one-half this value. This is taken as evidence for a conversion to a planar conformation after vibrational excitation of the cation has reached states above the inversion barrier separating the two possible pyramidal forms. The barrier height is then assumed to be ~0.75 eV, which is the separation between the band maximum and the onset of the band, i.e., the difference between the vertical and the adiabatic first ionization energy of NF_3 [7]. Ab initio molecular orbital calculations gave a barrier height of ≤0.53 eV (≤12.3 kcal/mol) [4, 10, 11, 12]. Inclusion of correlation effects raised the calculated barrier to about 14 to 17 kcal/mol [12].

Electron Paramagnetic Resonance (EPR)

The EPR spectrum of NF_3^+ has been measured both as a radiolysis product of NF_4^+ salts and as an intermediate in their formation [1, 2, 3]. NF_4^+ salts were γ-irradiated [1, 2], or mixtures of NF_3, F_2, and a Lewis acid (e.g., AsF_5) were UV-photolyzed at 77 K [1, 3]. The spectra proved to be rather complex due to the presence of both nitrogen and fluorine hyperfine structures (hfs) and anisotropies which were different at low and high temperatures [1, 2]. Final analysis [5] of a spectrum at 25 K [1] gave the following tensor components of the splitting factor g and hfs constants A(N) and A(F), in MHz, in the respective principal axis system:

$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}(N)$	$A_{\perp}(N)$	$A_x(F)$	$A_y(F)$	$A_z(F)$
2.001	2.002	324.3 ± 1.4	187.1 ± 5.0	340.0 ± 20	360.0 ± 20	880.0 ± 1

The "$\parallel$" and "$\perp$" indices refer to the molecular C_3 axis. The z axis in the fluorine hfs principal axis system is tilted from the normal to the N–F bond toward the C_3 axis by 15°. Evidence for this angle from EPR spectra alone is ambiguous in that only its size can be determined. The direction of tilting with respect to the C_3 axis, which could also be opposite, cannot be determined [5]. This ambiguity was, however, removed by ab initio calculations of spin densities [4]. The signs of the hfs constants remained indeterminate, but were thought to be positive for ^{14}N. Nitrogen hfs constants of ^{15}N were in the ratio of the nuclear magnetic moments, $A(^{15}N)/A(^{14}N) = 1.4029$ [1, 5].

Spectra at 240 K are indicative of a freely rotating NF_3^+ ion; thus, only effective values of the ^{19}F hfs constants, referred to the C_3 axis, can be deduced [1].

Dissociation

Dissociation of the NF_3^+ cation from its electronic states $X6a_1^{-1}$, $A5e^{-1}$, $B1a_2^{-1}$, $C4e^{-1}$, and $D5a_1^{-1}$ (−1 indicates a single vacancy in NF_3 molecular orbitals) has been studied as a function of its internal energy release by the photoelectron-photoion coincidence technique. The ion source was gaseous NF_3 ionized by monochromatic He I radiation. Dissociation into $NF_2^+ + F$ was a slow, statistical process for $NF_3^+(X)$ and $NF_3^+(C)$, but a rapid direct process for NF_3^+ in A and B states. In the dissociation of NF_3^+ B and C states, formation of the product ion NF_2^+ in its ground state probably competes with formation of excited NF_2^+, presumably in a triplet state. Dissociation of $NF_3^+(C)$ is accompanied also by formation of NF^+, which may be a primary product or may be formed by sequential dissociation through NF_2^+ [8]. Existing experimental evidence is insufficient to clearly distinguish between these two possibilities [9]. For $NF_3^+(D)$, a deexcitation to the C state prior to dissociation is likely [8].

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4.1.6 Nitrogen Difluoride, NF_2

Other names: Difluoroamino radical, difluoroamidogen

CAS Registry Number: *[3744-07-8]*

Review

The commonly used name, difluoroamino radical, is used in this text.

The NF_2 radical exists in thermal equilibrium with N_2F_4 at normal and elevated temperatures. At normal pressure and temperature, it contributes less than 1‰ to the mixture but above 200°C the equilibrium is almost completely on the NF_2 side. Many molecular and spectral properties have been determined. Because of the facile equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ many reactions of N_2F_4 can probably be ascribed to NF_2. They are described in connection with the reactions of N_2F_4.

4.1.6.1 Formation

Compounds containing the difluoroamino group, R–NF_2, may generally be a source of NF_2 radicals. But, the main source, and a very convenient one, is N_2F_4 because of the facile equilibrium $N_2F_4 \rightleftharpoons 2NF_2$. More details are given on pp. 326/31. Other compounds which dissociate into NF_2 radicals under appropriate conditions are, for instance, NHF_2 (see "Fluorine" Suppl. Vol. 5), NF_3 (p. 206ff.), $ClNF_2$ (p. 352), and $ONNF_2$ (see "Fluorine" Suppl. Vol. 5).

4.1.6.2 Molecular Properties and Spectra

4.1.6.2.1 Electronic Structure

Electronic Ground State

Experimental and theoretical studies agree that the NF_2 radical with six core and nineteen valence electrons belongs to point group C_{2v} and has an electronic ground state $^2B_1$.

Experimental Results. The multiplet patterns in the microwave (MW) spectrum of NF_2 [1] indicate that the wavefunction of the electronic ground state is antisymmetric to a twofold rotation about the symmetry axis (the b axis of the asymmetric top) and thus belongs to species B_1 or B_2 of point group C_{2v}. The hyperfine (hf) coupling constants for N and F, obtained from the MW spectrum, indicate that NF_2 is a π radical with the spin density mainly located on the N atom, and thus, the electronic ground state was identified as $^2B_1$ [1]. Empirical relationships between the π-electron spin densities on N or F, $\varrho^\pi(N)$ or $\varrho^\pi(F)$, and the isotropic hf coupling constants $a_{iso}(N)$ and $a_{iso}(F)$ were derived: $a_{iso}(N) \approx 50\varrho^\pi(N) + 50\varrho^\pi(F)$ and $a_{iso}(F) \approx 2000\varrho^\pi(F) - 250\varrho^\pi(N)$ (a_{iso} in MHz). They lead to $\varrho^\pi(N) \approx 0.8$ and $\varrho^\pi(F) \approx 0.2$. The facts that the largest component of the dipolar part of the hf coupling tensor on N is the out-of-plane component and that the tensor is nearly axially symmetric show that the unpaired electron mainly resides in the N2pπ orbital [1].

The out-of-plane components $b_{xx}(N)$ and $b_{xx}(F)$ obtained from the ESR spectrum of matrix isolated NF_2 radicals ($b_{xx} = a_{xx} - a_{iso}$) [2] have been converted into p-orbital unpaired spin densities on N or F by the relations ϱ^p(N or F) = b_{xx}(N or F)/b_{ref}(N or F), where b_{ref} is the anisotropic coupling factor for the free atom: values for $\varrho^p(N)$ between 0.80 and 1.0, for $\varrho^p(F)$ between 0.12 and 0.15 were obtained [3 to 6] using the different reference values reported in [7 to 9].

On the other hand, the isotropic hf coupling which is a consequence of spin polarization (e.g. [10]) gives an estimate of the small amount of s character in the orbital occupied by the unpaired electron. The s-orbital spin densities (squares of the contributions from N2s and F2s orbitals) can be obtained by the relations ϱ^s(N or F) = a_{iso}(N or F)/a_{ref}(N or F). The values $\varrho^s(N) = 0.029$, $\varrho^s(F) = 0.003$ [6] result from ESR data [2] and reference values reported in [9], $\varrho^s(N) = 0.03$, $\varrho^s(F) = 0.004$ [11], or $\varrho^s(N) = 0.028$ [12] from the respective ESR data [11, 12] and reference values calculated by using an estimated N2s [13] and a theoretical F2s electron density [14].

Theoretical Results. To solve the open-shell problem, various MO methods have been applied and, in some cases, compared with each other. Most commonly, the restricted Hartree-Fock formalism for the open-shell case (RHF) [15] and the unrestricted Hartree-Fock formalism before (UHF) [16] and after single spin annihilation (UHFASA) [17] have been used besides other methods, see [18 to 21] and footnote [c] of Table 6, p. 234.

A survey of the ab initio SCF-MO calculations for NF_2 [22 to 34] is in Table 6, p. 234. It gives the lowest values for the total molecular energy, E_T^{SCF}, of each study and the methods and basis sets used (for sake of completeness, the sixth column indicates all molecular properties calculated by use of the respective wavefunction).

Semiempirical calculations have been carried out by an unparameterized SCF-MO method with integral approximations [5], various versions of the CNDO [37 to 42] and INDO [6, 38, 43 to 45] methods, the MNDO [46, 47] and MINDO [48] methods, the extended Hückel method [3, 4, 49, 50] (presumably also [51]), a Pariser-Parr-Pople-type open-shell method [49] (presumably also [51]), and a simple MO approach [52]. Besides some other molecular properties, the charge distribution (atomic charges and/or overlap populations) [5, 38, 40, 41, 43, 49 to 51] and the spin density distribution (and thus, the hyperfine coupling constants, compare above and p. 241) [3 to 6, 46, 48] have been the subjects of many of these studies.

The ground state electron configuration is given as $(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(5a_1)^2(1b_1)^2(1a_2)^2(4b_2)^2(6a_1)^2(2b_1)^1$. Different energetical orderings were obtained for $3b_2$, $5a_1$, and $1b_1$: $3b_2 < 5a_1 < 1b_1$ [5, 22, 23, 34] and $5a_1 < 3b_2 < 1b_1$ [28, 52]. Separate calculations for the two spin sets with α and β spin gave $1b_1 < 5a_1 < 3b_2$ for the α-MOs and $5a_1 < 3b_2 < 1b_1$ for the β-MOs [26] as well as $3b_2 < 1b_1 < 5a_1$ (α) and $3b_2 < 5a_1 < 1b_1$ (β) [39].

The bonding in NF_2 was found to be similar to that in NF_3: the four lowest valence MOs, $3a_1$ to $3b_2$, are primarily σ bonding, while $1b_1$, $1a_2$, and $4b_2$ are nearly nonbonding π orbitals on F. The $5a_1 - 6a_1$ pair represents the F2pπ − N2pz interaction and the unpaired electron ($2b_1$) occupies primarily the nitrogen 2pπ(2px) orbital [5]. The existence of a significant amount of π bonding, which had been postulated from earlier semiempirical studies to explain the increased N–F bond strength in NF_2 as compared with NF_3 [49, 52, 53], could be refuted by considering the calculated σ- and π-overlap populations: Instead, the bonding is almost entirely attributable to σ overlap [5, 25], and the increased N–F bond strength in NF_2 is more likely a result of decreased lone-pair–lone-pair repulsions [5].

Table 6

NF_2. Ground State $^2B_1$: Ab Initio MO Calculations[a].

Experimental geometry: $r = 1.363$ Å, $\alpha = 102.5°$ [35] or $r = 1.37$ Å, $\alpha = 104.2°$ [36]. Total energy E_T^{SCF} in a.u.

$-E_T^{SCF}$	geometry[b]	method[c]	basis set	other method[c] and/or basis set	calculated molecular properties[d]	Ref.
253.263392	optd.	UHF	ext. GTO	UHFASA for hf	ε_i, pop., μ, hf, q, others	[22]
253.256818	optd.	RHF	ext. GTO			
253.2235	exp. [35]	RHF	ext. GTO	DZ GTO	ε_i, pop., μ, Θ, Ω, q, χ, σ, ΔH_{at}, others	[23]
253.15509	exp. [36]	UHFASA	DZ STO	RHF + CI; DZ STO-nG, DZ STO-nG + d functions, n = 1,6	hf	[24]
253.15234	exp. [36]	UHF	DZ STO			
253.15019	optd.	RHF	GTO (>DZ)	GTO (>DZ, other contraction), min. GTO	ε_i, pop., ΔH_{at}	[25]
253.0485	exp. [36]	UHF	DZ GTO	UHFASA for hf; min. STO, min. GTO, min. GTO for 2s, DZ GTO for 2p	ε_i, pop., μ, Θ, χ, σ, eqQ, q, hf, others	[26]
252.1497	exp. [36]	UHFASA	STO-3G		μ, Θ, χ, σ, eqQ, hf	[27]
252.1476	exp. [36]	UHF	STO-3G		hf	
252.0232	optd.	"Nesbet"	min. STO		g	[28]
252.0230	optd.	"Nesbet"	min. STO		hf	[29]
251.929219	exp. r [35], optd. α	UHF	min. GTO + 3s,3p, 3d functions	UHFASA for hf	pop., hf	[30]
249.7404	optd.	RHF	STO-3G	RHF at exp. geometry [35]		[31]
249.7326	optd.	"half-el."	STO-3G	"half-el." at exp. geometry [35]		
—	exp. [35]	RHF	DZ GTO	ext. GTO, DZ GTO + bond functions	ΔH_{at}	[32]
—	exp. [35]	UHF	DZ GTO	PUHF, PO, SECI	hf	[33]
—	optd.	OCBSE	STO-3G		μ	[34]

[a] The most commonly used abbreviations and symbols are given in Table 7, p. 235. – [b] exp. = experimental, optd. = optimized. – [c] UHFASA = UHF after single spin annihilation, i.e., annihilation of the contaminating quartet component [17], "Nesbet" = Nesbet's method of symmetry and equivalence restrictions [18], "half-el." = "half-electron" method, e.g. [19], OCBSE = orthogonality constrained basis set expansion method [20], PO = pseudo-orbital theory [21], PUHF = projected UHF (not indicated whether a full projection or a single projection (= ASA) was carried out), SE = single excitation. – [d] eqQ = quadrupole coupling constant, q = electric field gradient, g = electronic g factor, hf = hyperfine coupling constants and/or other spin properties, others = other one-electron properties or expectation values.

Table 7

Summary of Abbreviations and Symbols Used in Tables Concerning Quantum Chemical Calculations.

AO, MO	atomic, molecular orbital
STO, GTO	Slater-type, Gaussian-type orbital
min., ext., DZ	minimal, extended, double-zeta
SCF	self-consistent field method
CI	configuration interaction
STO-nG	Gaussian expansion of STO basis
RHF, UHF	restricted, unrestricted Hartree-Fock
CNDO	complete neglect of differential overlap
(M)(I)NDO	(modified) (intermediate) neglect of differential overlap
NDDO	neglect of diatomic differential overlap
pop.	population analysis
E_T	total energy
E(r)	potential energy function
r	internuclear distance
ε_i	orbital energy
E_i	ionization energy
ΔE	electronic excitation energy
f	force constants
ΔH_{at}	atomization energy
ΔH_f	enthalpy of formation
μ, Θ, Ω	dipole, quadrupole, octupole moment
χ	magnetic susceptibility
σ	magnetic shielding constant

Excited States

Valence States. The ultraviolet absorption band of NF_2 at about 260 nm (see pp. 257/9) has not been unambiguously interpreted. The observed long progression in the bending vibration of the excited state with a much lower frequency than in the ground state [54 to 57] indicates an increase in bond angle; considering Walsh's diagram for nonlinear AB_2 molecules [58], an assignment to one of the two lowest $^2A_1$ states (see below) has been proposed [54 to 56]. An absorption continuum peaking at 164 nm (ca. 7.6 eV) was thought to be due to some higher intravalence transition [59].

A few theoretical studies deal with the excited valence states of NF_2. The most detailed ab initio MO calculation [28] uses Nesbet's method of symmetry and equivalence restrictions [18], a minimum STO basis set and the ground state optimized geometry [29] for all excited states. It gives the total molecular energies for eleven excited states of $^2A_1$, $^2B_2$, and $^2A_2$ symmetry which arise from single excitations into the highest occupied orbital (HOMO) $2b_1$, from single excitations between $2b_1$ and the lowest unoccupied orbitals (LUMOs) $5b_2$ and $7a_1$, and from double and triple excitations into the HOMO and/or the LUMOs. Additional results stem from two other ab initio studies [25, 34] and a simple semiempirical MO calculation [52]. A semiempirical study (various CNDO versions + configuration interaction) [41] calculated the transition energies (ca. 38000 to 70000 cm^{-1}) and oscillator strengths of three electronic transitions but without characterizing the excited states.

Rydberg States. There are nine Rydberg orbitals with n = 3 leading to the formation of $NF_2^+(^1A_1)$. Eleven absorption bands between 140 and 126 nm (8.9 to 9.8 eV) were assigned to electronic and vibronic transitions into these Rydberg orbitals [59].

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4.1.6.2.2 Ionization Potentials E_i in eV

Data from Photoelectron Spectra (PES)

The HeI PES of NF_2 (from N_2F_4 at 80°C and 10^{-4} Torr) exhibits four bands; the following adiabatic and vertical ionization potentials (±0.02 eV) and assignments to several ionic states (with the aid of a ΔSCF-INDO calculation) are given [1, 2]. For comparison, the results from the so-called ΔINDO + FOCI calculation (FOCI = first-order configuration interaction) [3] and the results obtained by applying the many-body Rayleigh-Schrödinger perturbation theory (MBRSPT) of second order within the framework of the INDO method [4] are included:

E_i (ad) [1, 2]	11.62	14.60	—				—
E_i (vert) [1, 2]	12.10	14.60	16.38				ca. 17.6
assignment [1, 2]	$^1A_1$	$^3B_1$	$^1B_1$	$^3B_2$	$^3A_2$		
assignment [3, 4]	$^1A_1$	$^3B_1$	$^1B_1$	$^3B_2$	$^3A_2$	$^1A_2$	$^1B_2$
E_i (ΔINDO + FOCI) [3]	15.4	17.4	18.6	18.8	19.0	19.2	21.3
E_i (MBRSPT) [4]	12.53	14.8	15.44	18.80	16.58	16.38	20.11

The X-ray PES (MgKα radiation) of NF_2 (from N_2F_4 at 180 to 200°C) gave the following core electron binding energies (±0.5 eV): $E_i(N1s) = 414.4$ and 412.5 ($\Delta E_i = 1.934 \pm 0.041$ eV) and $E_i(F1s) = 695.3$ and 694.5 ($\Delta E_i = 0.720 \pm 0.008$ eV). The doublet splitting ΔE_i of the 1s hole states, interpreted by use of a multiplet-hole theory, is the consequence of parallel and antiparallel spin coupling between the remaining core electron and the unpaired valence electron [5].

Mass Spectrometric Data

The appearance of NF_2^+ ions in the mass spectrum of N_2F_4 is attributed to the two processes $N_2F_4 + e^- \rightarrow NF_2 + NF_2^+ + 2e^-$ (d) and $NF_2 + e^- \rightarrow NF_2^+ + 2e^-$ (i) according to the existence of an equilibrium $N_2F_4 \rightleftharpoons 2NF_2$. In the first case, the ionization potential $E_i(NF_2)$ is the difference between the appearance potential $AP^d(NF_2^+)$ and the dissociation energy $D(F_2N\text{–}NF_2)$; in the second case, $AP^i(NF_2^+)$ gives the first ionization potential directly. Thus, $E_i(NF_2) = AP^d(NF_2^+) - D(F_2N\text{–}NF_2) = 11.8$ [6] ($AP^d = 12.7 \pm 0.2$ eV [7], $D = 0.9$ eV [8]) and $E_i(NF_2) = AP^i(NF_2^+) = 11.8 \pm 0.2$ [9] (reinvestigation and reinterpretation of the results from [10]), 12.0 ± 0.2 [11], 11.79 ± 0.12 [12, 13], 11.76 ± 0.1 [14], 11.82 ± 0.06 [15].

The threshold energy of the photoionization process $NF_3 + h\nu \rightarrow NF_2^+ + F + e^-$, 14.12 ± 0.01 eV, yields the enthalpy of formation for NF_2^+ (cf. p. 261) and thus, $E_i(NF_2) = \Delta H^\circ_{f,0}(NF_2^+) - \Delta H^\circ_{f,0}(NF_2) = 11.73 \pm 0.09$ eV [16] (using $\Delta H^\circ_{f,298}(NF_2)$ due to [17] and the difference between $\Delta H^\circ_{f,0}$ and $\Delta H^\circ_{f,298}$ obtained from [18]).

Theoretical Work

Ab initio studies include RHF calculations for the open-shell case [19, 20] and UHF calculations [21, 22] all using large Gaussian basis sets: The eigenvalues ε_i for all core and valence MOs ($1a_1$ to $2b_1$) are given in [19, 22] and a diagram of the valence MO energies ($3a_1$ to $2b_1$) for opposite spins, $\varepsilon_i(\alpha)$ and $\varepsilon_i(\beta)$, is given in [21]. The first ionization potential is given as the difference between the total SCF energies of the cation and the radical, $E_i = \Delta E_T^{SCF}$ [20].

Semiempirical calculations for ε_i or ΔE_T^{SCF} were carried out by the SCF-MO method with integral approximations [23], by various versions of the CNDO [24 to 27] and INDO [1 to 4, 28] methods, by the MNDO method [29], by the extended Hückel and Pariser-Parr-Pople methods [30], and by a simple [31] MO method [32].

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4.1.6.2.3 **Electron Affinity** A in eV

Experimental values were derived from the appearance potentials of NF_2^- ions formed by the dissociative resonance electron-capture processes $NF_3 + e^- \rightarrow NF_2^- + F$ [1, 2] and $N_2F_4 + e^- \rightarrow NF_2^- + NF_2$ [3]: An appearance potential $AP(NF_2^-/NF_3) = 0.9 \pm 0.1$ eV gave $A = 1.68 \pm 0.21$ [1], and $AP(NF_2^-/NF_3) = 1.90 \pm 0.09$ eV (the resonance maximum was observed near this energy [1]) gave $A \geq 0.7 \pm 0.2$ [2]. From $AP(NF_2^-/N_2F_4) = 0.55 \pm 0.06$ eV, $A \geq 0.4 \pm 0.2$ was derived [3].

Theoretical values obtained by various versions of the CNDO method [4 to 6] and the Pariser-Parr-Pople method [7] vary between −0.89 and +6.28.

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4.1.6.2.4 Dipole Moment μ in D. Quadrupole Moment Θ. Octupole Moment Ω

The only experimental value, $\mu=(\pm)0.13_6\pm0.01$ (4.5×10^{-31} C·m), was obtained from the Stark effect on two components of the $1_{1,0}\leftarrow1_{0,1}$ multiplet in the microwave spectrum of NF_2 [1]. Presumably, the direction of the dipole moment was taken to be N^+F^-, because a "remarkable agreement" was noted [1] between a theoretical value of $\mu=-0.138$ [2] (see below) and the experimental value (negative sign means N^+F^-).

A few ab initio SCF-MO calculations showed that μ is very sensitive to changes in basis set. Minimal basis sets of Slater and of Gaussian lobe functions gave $\mu=+0.656$ [2, 3] and $+0.506$ [2], respectively, an STO-3G basis set gave $\mu=+0.49$ [4], whereas larger Gaussian lobe basis sets with partial (2p functions) and full double zeta accuracy gave $\mu=-0.143$ and -0.138, respectively [2]. Extended Gaussian basis sets (d functions on N and F) gave the N^+F^- direction, but overestimated the absolute value: $\mu=-0.564$ [5] and -0.393 [6].

Semiempirical CNDO [7 to 9], INDO [8, 10], and MNDO [11] calculations predicted moments between 0.0035 and 0.85 without elucidating the direction. However, the direction of the dipole moment was included in the results $\mu=-0.12$ (CNDO) and -0.38 (INDO) [12, 13].

Only theoretical quadrupole, Θ_{ii}, and octupole, Ω_{ii}, tensor elements ($i=x, y, z$) are available: Four sets of Θ_{ii} were calculated using different basis sets (see above) [2, 3]. By comparison with experimental results for the related molecules OF_2 and O_3 and Hartree-Fock results for NO_2, the values $\Theta_{xx}=1.6$, $\Theta_{yy}=-1.2$, and $\Theta_{zz}=-0.4$ (all in 10^{-26} esu·cm^2; $z=C_2$ axis, $x\perp$ molecular plane) obtained with the Gaussian basis set of double zeta accuracy were recommended to be most reliable [2]. In fair agreement are values calculated with an extended Gaussian basis set, $\Theta_{zz}=1.28$, $\Theta_{yy}=-1.38$, and $\Theta_{xx}=0.10$ ($x=C_2$ axis, $z\perp$ molecular plane) [5]. The latter study gave $\Omega_{xx}=1.59$, $\Omega_{yy}=-1.18$, and $\Omega_{zz}=-0.51$ (all in 10^{-34} esu·cm^3) [5].

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4.1.6.2.5 Nitrogen Nuclear Quadrupole Coupling Constant eqQ(N)

Analysis of the microwave spectrum of NF_2 (transitions involving rotational quantum numbers N=1 to 4) yielded the following components of the quadrupole coupling tensor $eq_{ii}Q(N)$, in MHz: $eq_{xx}Q(N)=-4.86$, $eq_{yy}Q(N)=+5.59$, and $eq_{zz}Q(N)=-0.73$ ($x\perp$ molecular plane, z = symmetry axis with positive direction from N to the Fs) [1]. Corresponding theoretical values, −2.95, +4.51, and −1.56 MHz (rounded), resulted from the components q_{ii} of the electric field gradient at N (ab initio UHF calculation using a large Gaussian basis set) and a nuclear quadrupole moment $Q(N) = 1.47 \times 10^{-26}$ esu·cm^2 [2]. For results from a minimum Slater-type orbital basis set, see [3]. For q_{ii} values obtained from ab initio MO calculations with large Gaussian basis sets, see also [4, 5].

References:

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4.1.6.2.6 Electronic g Factor. Hyperfine (hf) Coupling Constants

Experimental Results

The g factors and the majority of hf coupling constants come from ESR spectra (see p. 253) of NF_2 in the gaseous [1, 2] and liquid [2] states, in solution [3], molecular sieves [4], and inert gas matrices [5 to 8]. One set of ^{14}N and ^{19}F hf coupling constants was obtained from an analysis of the multiplets involving low rotational quantum numbers, N = 1 to 4, in the microwave spectrum of NF_2 at 333 to 343 K (see p. 252) [9].

ESR spectra of matrix-isolated NF_2 at liquid-helium temperature yielded the principal values g_{ii} (i = x, y, z) of the anisotropic g tensor and a_{ii} of the ^{14}N and ^{19}F hf coupling tensors (z = C_2 axis, x ⊥ molecular plane). The matrix spectra at higher temperatures (>30 K) and the spectra of gaseous, liquid, dissolved, and adsorbed NF_2 gave the isotropic values, $g_{iso} = \frac{1}{3}\Sigma g_{ii}$ and $a_{iso} = \frac{1}{3}\Sigma a_{ii}$, for a nearly or completely freely rotating NF_2 radical. The analysis of the microwave spectrum gave isotropic, a_{iso}, and anisotropic hf coupling constants, $b_{ii} = a_{ii} - a_{iso}$.

The experimental results are compiled in Table 8, pp. 242/3.

Theoretical Work

For the methods used, see footnote c) of Table 6, p. 234.

The g-tensor elements were calculated by a modified ab initio UHF method ("Nesbet") [11], by a semiempirical SCF-MO calculation (integral approximations) [12], and by a semiempirical procedure called the energy weighted maximum overlap model [13].

The constants $a_{iso}(N)$ and $a_{iso}(F)$ were obtained by a number of ab initio studies: UHF ("Nesbet") [14], UHF and UHFASA [15 to 19], comparison of the UHF, PUHF, PO, and SECI methods [20], RHF + CI [19], and some semiempirical calculations: MNDO [21], MINDO within UHF and UHFASA formalisms [22], and INDO (s-electron spin densities a_{iso}/a_{ref} only given, see p. 233) [23].

The b_{ii}'s were calculated by the ab initio UHF ("Nesbet") [14] and UHF and UHFASA [15, 16] methods. The largest component, b_{xx}, was obtained (but p-electron spin density b_{xx}/b_{ref} only given, see p. 233) from semiempirical MO (integral approximations) [12] and INDO [23] calculations and by the extended Hückel method [24, 25].

Table 8

NF_2 Radical: g Factor and Hyperfine Coupling Constants. Results from Electron Spin Resonance and Microwave Spectroscopy.

a_{ii} ($i = x, y, z$) and a_{iso} in G ($x \perp$ molecular plane, z = bisector of FNF angle).

method	sample	T in K	g_{xx}	g_{yy}	g_{zz}	g_{iso}
ESR	gas, p = 20 to 40 Torr	342 to 435	—	—	—	2.010
	liquid	298	—	—	—	2.006 ±0.001
	solution	~295	—	—	—	2.009
	molecular sieves	~295	—	—	—	2.009
	Ar matrix ($Ar:N_2F_4/NF_2 = 300$)	4.2	2.0022 ±0.0004	2.0059 ±0.0004		—
	Ar matrix ($Ar:N_2F_4/NF_2 = 1200$)	4.2	2.0022[a)] ±0.0004	2.0066[a)] ±0.0004	2.0051[a)] ±0.0004	—
	Ar, Kr matrices	~30	—	—	—	2.0053 ±0.0006
	Ne matrix	4	2.0011 ±0.0005	2.0079 ±0.0005	2.0042 ±0.0005	(2.0044)[b)]
	Ne matrix ($Ne:NF_2 = 3000$)	4.2	2.0019 ±0.0002	2.0086 ±0.0002	2.0050 ±0.0002	(2.0052)[b)]
	Ar matrix ($Ar:NF_2 = 2500$)	4.2	2.0022 ±0.0002	2.0085 ±0.0002	2.0051 ±0.0002	—
		≥30	—	—	—	2.0053
	Kr matrix	4.2	2.0022 ±0.0002	2.0085 ±0.0002	2.0051 ±0.0002	—
		≥30	—	—	—	2.0053
MW	gas, p = 80 to 800 Pa	333 to 343	—	—	—	—

[a)] $g_1 = 2.0022$, $g_2 = 2.0051$, $g_3 = 2.0066$ without orientations are given in [5]. – [b)] Calculated from g_{ii} or a_{ii}. – [c)] Values given in MHz [9]: $a_{iso}(N) = 46.57$, $b_{xx}(N) = 98.19$, $b_{yy}(N) = -47.72$, $b_{zz}(N) = -50.47$ (all

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$a_{xx}(N)$	$a_{yy}(N)$	$a_{zz}(N)$	$a_{iso}(N)$	$a_{xx}(F)$	$a_{yy}(F)$	$a_{zz}(F)$	$a_{iso}(F)$	Ref.
—	—	—	—	—	—	—	—	[1]
—	—	—	—	—	—	—	64 ±2	[2]
—	—	—	16	—	—	—	56	[3]
—	—	—	16	—	—	—	56	[4]
—	—	—	—	—	—	—	—	[5]
—	—	—	—	—	—	—	—	
—	—	—	17 ±2	—	—	—	60 ±2	
49 ±0.5	0 ±1.0	0 ±1.0	(16 ±1)[b]	212 ±2.0	−16.9 ±1.0	−16.9 ±1.0	(59 ±1)[b]	[7]
49.2 ±0.25	1.0 ±0.25	1.0 ±0.25	—	212.8 ±0.25	−16.6 ±0.25	−16.6 ±0.25	—	[8]
49.3 ±0.25	1.0 ±0.25	1.0 ±0.25	—	212.0 ±0.25	−16.5 ±0.25	−16.5 ±0.25	—	
—	—	—	17.1 ±0.25	—	—	—	60.2 ±0.25	
49.5 ±0.25	1.0 ±0.25	1.0 ±0.25	—	212.0 ±0.25	−16.5 ±0.25	−16.5 ±0.25	—	
—	—	—	17.3 ±0.3	—	—	—	60.6 ±0.3	
51.66[c] ±0.04	−0.41[c] ±0.04	−1.39[c] ±0.04	16.59[c] ±0.04	225.75[c] ±0.14	−27.52[c] ±0.14	−22.12[c] ±0.14	58.57[c] ±0.14	[9]

±0.1) and $a_{iso}(F) = 164.39$, $b_{xx}(F) = 468.22$, $b_{yy}(F) = -241.75$, $b_{zz}(F) = -226.48$ (±0.4) ($b_{ii} = a_{ii} - a_{iso}$); conversion into G units using the relation $1G = 2.80247\ g/g_e$ MHz, $g_e = 2.0023$ [10], and g factors [8].

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4.1.6.2.7 Diamagnetic Susceptibility χ^d in 10^{-6} erg·G^{-2}·mol^{-1}.
Diamagnetic Shielding σ^d in ppm

Only theoretical predictions from ab initio calculations are available. Recommended values for the average diamagnetic susceptibility, $\chi^d = -95.5$, and for the average diamagnetic shielding at nitrogen and fluorine, $\sigma^d(N) = 442.6$ and $\sigma^d(F) = 558.6$, resulted from UHF calculations with four basis sets of increasing magnitude [1] (STO-3G [1, 2] up to double zeta GTO [1]). An RHF study with an extended Gaussian basis set (double zeta GTO plus polarization functions) gave $\chi^d = -96.36$, $\sigma^d(N) = 445.3$, $\sigma^d(F) = 557.8$ (signs for χ and σ in [3] reversed) and the tensor elements χ_{ii}^d and σ_{ii}^d ($i = x, y, z$) [3].

References:

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4.1.6.2.8 Rotational and Spin-Rotation Coupling Constants.
Centrifugal Distortion Constants

The NF_2 radical is a slightly asymmetric (nearly prolate) top, $A > B \geq C$, with $\varkappa = -0.94$. The b axis coincides with the symmetry axis, and the c axis is perpendicular to the molecular plane. The coupling between the spin of the unpaired electron and the molecular rotation about the a, b, or c axis is accounted for by the spin-rotation constants $\varepsilon_{\alpha\alpha}$ ($\alpha = a, b, c$).

The rotational and spin-rotation constants for the ground state $X\,^2B_1$, $v = 0$ were obtained from analyses of the microwave (MW) spectrum [1] and of the highly resolved absorption lines (IR laser spectroscopy) of the ν_1 fundamental band [2]. Constants for the vibrationally excited states $v_1 = 1$ [2] and $v_3 = 1$ [3] were obtained from the IR laser spectra of the ν_1 and ν_3 fundamental bands, for the $v_1 = 1$ state also from the laser magnetic resonance (LMR) spectrum of the ν_1 band [4]. The results are compiled in Table 9, and details are given in the remarks below the table.

Table 9

$NF_2(X\,^2B_1)$. Rotational Constants A, B, C, and Spin-Rotation Coupling Constants $\varepsilon_{\alpha\alpha}$ for the Vibrational Ground State and the Excited States $v_1=1$ and $v_3=1$.
Uncertainties in the last digits are given in parentheses.

v	A in cm^{-1} [MHz]	B in cm^{-1} [MHz]	C in cm^{-1} [MHz]	ε_{aa} in MHz	ε_{bb} in MHz	ε_{cc} in MHz	method	remark	Ref.
v=0	[70496(2)]	[11872.24(20)]	[10136.46(20)]	−951.79(10)	−92.86(10)	4.49(10)	MW	a)	[1]
	2.35149(7)	0.396015(7)	0.338116(7)	—	—	—	MW	b)	[1,2]
	2.351353(477)	0.395987(82)	0.338086(75)	−968.4(764)	−98.9(240)	−2(23)	MW	c)	[2]
	2.351471(69)	0.396012(13)	0.338102(12)	−940.4(252)	−90.2(84)	6.0(86)	MW+IR	d)	[2]
$v_1=1$	2.354099(59)	0.393822(18)	0.337949(21)	−939.5(237)	−94.1(111)	9.9(123)			
	2.35448(36)	0.39481(102)	0.338020(30)	−943(93)	−128(75)	22(72)	LMR	e)	[4]
$v_3=1$	2.357539(58)	0.3940597(33)	0.3343841(39)	−918.11(129)	−90.33(45)	−8.57(552)	IR	f)	[3]

a) The rotational constants were obtained by a fit to 10 MW transitions with $N\leq13$; centrifugal distortion included. The spin-rotation constants come from least-squares analyses of the $1_{1,0}\leftarrow1_{0,1}$ and $3_{1,2}\leftarrow3_{0,3}$ multiplets [1].

b) Rotational constants of [1] converted into units of cm^{-1} ($c=2.997925\times10^{10}$ cm/s) for comparison with IR data [2].

c) Refitted by [2] to 18 MW transitions with $12\leq N\leq38$ and $2\leq K_a\leq8$ given by [1]; centrifugal distortion included.

d) Simultaneous fit for $v_1=0$ and 1 to 18 MW transitions [1] (weight 100) and 98 rotational-vibrational transitions in the ν_1 band measured with tunable diode lasers [2] (weight 1); centrifugal distortion included.

e) Fitted to 9 LMR transitions with $1\leq N\leq3$ of the ν_1 band using the ground state constants of [1] and assuming equal centrifugal distortion constants for the $v=0$ and $v_1=1$ states [4].

f) Fitted to ca. 240 rotational-vibrational transitions with $4\leq N\leq42$ of the ν_3 band (IR laser spectrum) [3] using the ground state constants obtained from the ν_1 band analysis [2]; centrifugal distortion included.

For the centrifugal distortion, different formulations, i.e., the Kivelson-Wilson formulation in terms of the parameters τ [5], and Watson's formulation in terms of the quartic constants Δ, δ [6], were chosen by the MW [1] and IR [2, 3] spectroscopists, respectively, which precludes a direct comparison (see, e.g., [7]). Analysis of the MW spectrum gave (in MHz): $\tau_{aaaa} = -7.75 \pm 0.2$, $\tau_{bbbb} = -0.081 \pm 0.02$, $\tau_{aabb} = 0.297 \pm 0.03$, and $\tau_{abab} = -0.126 \pm 0.06$ [1]. These parameters were used to derive fundamental vibrations [1, 8] and force constants [1] (see below); vice versa, vibrational and structural parameters of [9] gave τ values, however, in moderate agreement with the MW results [10]. The Watson parameters (in cm^{-1}), $\Delta_N = 4.71(10) \times 10^{-7}$, $\Delta_{NK} = -1.716(81) \times 10^{-6}$, $\Delta_K = 6.251(29) \times 10^{-5}$, $\delta_N = 1.006(78) \times 10^{-7}$, $\delta_K = 1.42(78) \times 10^{-6}$ for the vibrational ground state resulted from the simultaneous analysis of the MW and the IR (ν_1) spectra [2]. Analogous parameters for the excited states $\nu_1 = 1$ [2] and $\nu_3 = 1$ [3] were also given.

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4.1.6.2.9 Fundamental Vibrations. Coriolis Coupling Constants. Force Constants

Vibrational frequencies for the three fundamentals, the symmetric and antisymmetric stretching, $\nu_1(a_1)$ and $\nu_3(b_1)$, and the bending fundamental, $\nu_2(a_1)$, were measured by conventional IR spectroscopy in the gas phase [1] and in inert gas matrices at low temperatures [2, 3] and by conventional gas-phase Raman spectroscopy [4]. Very precise values for the origins of the ν_1 and ν_3 bands were obtained by high-resolution IR absorption using tunable diode lasers [5, 6] and by laser magnetic resonance (LMR) using a CO_2 laser [7] (LMR also applied by [8, 9]). The calculations of fundamental frequencies from the centrifugal distortion constants gave no satisfactory agreement with the experimental results for the stretching vibrations [10, 11]. The results for the electronic ground state obtained by the various methods are compiled in Table 10.

For an electronically excited state (presumably $^2A_1$) the vibrational structure of the UV absorption band at 260 nm suggests the bending fundamental is at 380 cm^{-1} [12] or 390 cm^{-1} [13] for gaseous NF_2 and at 408 cm^{-1} for NF_2 in an Ar matrix at 14 K [14].

Coriolis coupling is expected between the a_1 and b_1 symmetry modes, i.e., between ν_1 and ν_3 and between ν_2 and ν_3. By combining the centrifugal distortion constants ($\tau_{\alpha\beta\gamma\delta}$ [10]) and the observed vibrational frequencies (ν_1 [1], ν_2, ν_3 [2]), the coupling constants $\zeta_{13} = -0.7724$ and $\zeta_{23} = -0.6351$ were derived [10]. An approximate method [15] was applied to the inertial defects observed for the ν_1 [5] and ν_3 [6] bands and yielded $\zeta_{13} = 0.698 \pm 0.010$ and $|\zeta_{23}| > 0.7105$ ($\zeta_{23} = -0.7105$ for CF_2 [16] was adopted) [6]. Calculated from force fields were $|\zeta_{13}| = 0.564$, $|\zeta_{23}| = 0.826$ [17], and $\zeta_{13} = 0.637$, 0.589, $\zeta_{23} = -0.77$, -0.631 [18].

Table 10

$NF_2(X\ ^2B_1)$. Fundamental Vibrations (ν_i in cm^{-1}).

$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(b_1)$	method	Ref.
1074.3±0.1	—	~935	IR, gas, 448 K	[1]
1074	572	—	Raman, gas, 523 K	[4]
1069.6±0.5	573.4±1.0	930.7±0.5	IR, N_2 matrix, 20 K	[2]
1070	—	928, 933	IR, Ar matrix, 14 K, photolysis of $Ar:F_2+Ar:H^{15}N^{14}N_2$	[3]
1048[a)]	—	910, 913[a)]		
1074.9897(8)	—	942.48153(30)	IR (laser), gas, 373 to 423 K	[5, 6]
1074.9879(12)	—	—	LMR, gas, 333 to 343 K	[7]
—	—	944.19[b)]	LMR, gas, ca. 343 K	[8]
1003.7	575.9	1086.2	by means of centrifugal distortion constants from MW spectrum [10]	[10]
1001.7	580.9	1097.6		[11]

[a)] For $^{15}NF_2$. – [b)] Resonances for CO_2 laser lines at 1082.92 and 940.56 cm^{-1} were also observed by [9].

The three fundamentals of $^{14}NF_2$ [1, 2] and the symmetric stretching fundamental of $^{15}NF_2$ [3] were used to determine the four independent harmonic force constants [19, 20]. Using only the three fundamentals of $^{14}NF_2$ [1, 2], approximate methods, i.e., several versions of the L-matrix method [18, 21], simplification of the FG-matrix method [17], and a variation method [2], were employed to evaluate the symmetry force constants $F_{11}(a_1)$, $F_{22}(a_1)$, $F_{12}(a_1)$, and $F_{33}(b_1)$ [18, 21] or the valence force constants f_r (stretching), f_α (bending), and f_{rr}, $f_{r\alpha}$(interaction) [2, 17]. Under the assumption that the force constants for NF_2 do not differ appreciably from those of NF_3, the valence force constants were calculated for both molecules (ν_1, ν_3 for NF_2 [1], ν_1 to ν_4 for NF_3 [22]) by applying the Vol'kenshtein-El'yashevich-Stepanov method [23]. Valence and symmetry force constants were also derived from the centrifugal stretching constants [10]. Urey-Bradley force constants K, H, F (assumption $F'=0$) were calculated using ν_1, ν_2, ν_3 for NF_2 in a matrix [2], and the large nonbonded interaction (F = 4.51 mdyn/Å) was discussed [24]. Results from [2, 10, 17 to 20] are given in Table 11.

Table 11

NF_2. Symmetry Force Constants F_{ij} (i, j = 1, 2, 3) and Valence Force Constants f (all in mdyn/Å). $F_{11}=f_r+f_{rr}$, $F_{22}=f_\alpha$, $F_{12}=\sqrt{2}\ f_{r\alpha}$, $F_{33}=f_r-f_{rr}$.

f_r	f_α	$f_{r\alpha}$	f_{rr}	Ref.	F_{11}	F_{22}	F_{12}	F_{33}	Ref.	remark
4.83	1.08	0.30	1.22	[20]	6.05	1.08	0.42	(3.61)	[19]	a)
5.1 ±0.5	1.15 ±0.15	0.4 ±0.3	1.5 ±0.5	[2]	—	—	—	—		b)
5.136	1.103	0.335	0.182	[10]	5.318	1.103	0.473	4.95	[10]	c)
5.4204	0.2506	0.3257	1.8104	[17]	—	—	—	—		d)
—	—	—	—		5.34	0.981	0.213	4.83	[18]	e)

a) Exact solution using ν_1, ν_2, (ν_3) for $^{14}NF_2$ [2] (not stated whether the gas-phase frequency $\nu_1=1074\ cm^{-1}$ [1] (quoted in [2]) or the matrix frequency $\nu_1=1069\ cm^{-1}$ [2] was used) and ν_1 for $^{15}NF_2$ [3]. F_{33} is not given in [19]. – b) Using the gas-phase ν_1 [1] and matrix ν_2, ν_3 [2], allowed ranges for f_r, f_α, and $f_{r\alpha}$ were calculated as functions of f_{rr}, and the "best values" were chosen near the minimum of f_α with the further assumption that f_r in NF_2 is slightly larger than in OF_2. – c) The F_{ij} were derived from the centrifugal distortion constants (MW spectrum [10]) by the method of [28]. – d) Simplified FG-matrix method [29]; ν_i from [2]. – e) Wilson's L-matrix approximation method, i.e., $L_{12}=0$ approximation within FG-matrix formalism; ν_1 [1], ν_2, ν_3 [2].

A CNDO calculation gave $f_\alpha = 0.97$ mdyn/Å [25]. A modified INDO calculation [26] and a calculation based on a simple bond-charge model [27] gave unsatisfactory results.

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4.1.6.2.10 Internuclear Distance. Bond Angle. Mean Amplitudes of Vibration

A bent structure (C_{2v} symmetry), predicted by the Walsh rules [1], was obtained by experimental and theoretical studies (see also pp. 232/4).

Electron diffraction of gaseous NF_2 (N_2F_4 at 225°C and 5 Torr) gave the r_g geometry (internuclear distances r(N–F) and r(F···F) and bond angle α) [2, 3]. The microwave spectrum of NF_2 gas (N_2F_4 at 60 to 70°C) allowed the determination of the r_0 geometry, i.e., the geometry for the vibrational ground state, using the rotational constants, and the determination of the average geometry ⟨r⟩ using vibrational frequencies and centrifugal distortion constants [4]. Values for r and α are given in the following table.

experiment	geometry	r(N–F) in Å	r(F···F) in Å	α(FNF)
electron diffraction [2]	r_g	$1.363_1 \pm 0.008$	$2.126_6 \pm 0.016$	102.5° ± 0.9°
microwave spectrum [4]	r_0	1.3494	—	103°20′
	⟨r⟩	1.3528 ± 0.0001	—	103°11′ ± 2′

The earlier values r(N–F) = 1.37 Å (taken from NF_3) and α = 104.2° (consistent with the rotational structure of the ν_1 band in the IR spectrum of gaseous NF_2) [5] were often quoted and used for numerous calculations of NF_2 molecular properties (see Table 6, p. 234).

Ab initio SCF-MO calculations [6 to 12] usually give bond lengths between 1.35 and 1.36 Å (1.381, 1.445 Å [12]), and bond angles between 101° and 103° (104.7° [10]). An ab initio geometry optimization for NF_2 is mentioned, but no results are given in [13]. The semiempirical CNDO [14 to 16, 24], INDO [14, 15, 17], and MNDO [18] studies slightly underestimated the bond length (1.22 to 1.27 Å) and gave bond angles between 101.7° and 109.7°. A modified INDO calculation (SINDO) overestimated r(N–F) and underestimated α [19]. A simple steric model predicted α = 104.8° [20]. For two electronically excited states, increases in bond length and bond angle were predicted by two ab initio calculations: r(N–F) = 1.37 Å, α = 120° for the $^2A_1$ state arising from the $6a_1 \rightarrow 2b_1$ transition [7], and r(N–F) = 1.455 Å (1.572 Å), α = 148° (147.6°) (different basis set) for the $^2A_1$ state arising from the $2b_1 \rightarrow 7a_1$ transition [12].

For the mean amplitudes of vibration (in Å), an electron diffraction study gave u(N–F) = $0.053_6 \pm 0.005$ and u(F···F) = $0.064_7 \pm 0.011$ at 498 K [2]. Somewhat lower values were calculated by Cyvin's method for 298 K, u(N–F) = 0.0464, u(F···F) = 0.0542 [21], u(N–F) = 0.0492, u(F···F) = 0.0594 [22] and for 0 K, u(N–F) = 0.0477, u(F···F) = 0.0626 [22], both using the structural and vibrational data of [5, 23].

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4.1.6.2.11 **Bond Dissociation Energy** D(FN–F), **Atomization Energy** ΔH_{at}, in kcal/mol

D(FN–F) = 79 ± 4 [1] is the average of two values obtained from the appearance potentials of NF^+ in the mass spectra of N_2F_4/NF_2 [1] and NF_3 [2]: $AP(NF^+) = 15.32 \pm 0.08$ eV, attributed to the process $NF_2 + e^- \rightarrow NF^+ + F + 2e^-$, and $AP(NF^+) = E_i(NF) = 11.82 \pm 0.06$ eV, attributed to $NF + e^- \rightarrow NF^+ + 2e^-$, gave D(FN–F) = 80.7 ± 2 [2]; $AP(NF^+) = 17.64 \pm 0.08$ eV, attributed to $NF_3 + e^- \rightarrow NF^+ + 2F + 2e^-$, combined with $E_i(NF)$ (see above) and the (own) bond dissociation energy of NF_3 (57.6 ± 0.5 kcal/mol) gave D(FN–F) = 77 ± 6 [1].

D(FN–F) = 72.8 ± 2.3 was based on the difference of the appearance potentials of NF_2^+ in the mass spectrum of N_2F_4/NF_2, $AP(NF_2^+) = 12.70 \pm 0.1$ eV, attributed to $N_2F_4 + e^- \rightarrow NF_2 + NF_2^+ + 2e^-$, and $AP(NF_2^+) = 12.40 \pm 0.1$ eV, attributed to $N_2F_4 + e^- \rightarrow NF_2^+ + NF + F^- + e^-$ (this reaction was criticized by [2]), and on an electron affinity A(F) = 3.448 eV [3]; the correct value A(F) = 3.400 eV, see "Fluorine" Suppl. Vol. 2, 1980, p. 41, gives D(FN–F) = 71.7. D(FN–F) = 304 kJ/mol (72.7 kcal/mol), quoted in a review [4], was based on shock-wave experiments on NF_3 [5] which had given $D(F_2N–F)$ and on the formation enthalpies for NF_3, NF, and F.

D(FN–F) ≤ 83.7 ± 2.1 (3.63 ± 0.09 eV) results from the appearance potential of F^- in the mass spectrum of N_2F_4/NF_2, $AP(F^-) = 0.18 \pm 0.09$ eV, attributed to $NF_2 + e^- \rightarrow NF + F^-$, and A(F) = 3.45 eV [2]; the correct value A = 3.400 eV gives D(FN–F) ≤ 82.6.

D(FN–F) = 79.4 ± 10 at 0 K and 80.5 ± 10 at 298 K were estimated [6, p. 81] from $\Delta H_{f,0}(NF_2) = 10.1$, $\Delta H_{f,0}(NF) = 71 \pm 10$ [6, p. 132], and $\Delta H_{f,0}(F) = 18.5$ [6, p. 116] (ΔH_f in kcal/mol). The values 75 ± 5 at 0 K and 76 ± 5 at 298 K, based on the estimated D(FN–F) [6] and $D_{av}(N–F)$ values [7, 8] (see below), were recommended in another review [9].

For ΔH_{at} and the average bond energy $D_{av}(N{-}F) = \Delta H_{at}/2$ the following values have been derived:

ΔH_{at}	$D_{av}(N{-}F)$	T in K	Ref.	data used
138.4	69.2	0	[10]	ΔH_f of NF_2, N, and F
140.8	70.4	298	[11]	
141.0	70.5±1.6	298	[7, 12]	
142	71	not specified	[8]	$D_{av}(NF_3)$ and $D(F_2N{-}F)$
143.4	71.7		[4]	$D(FN{-}F)$ and $D(N{-}F)$

Theoretical work dealt with the total molecular binding energy (= ΔH_{at}). Three ab initio MO studies which used extended GTO basis sets greatly underestimated ΔH_{at} by factors ≥ 5 [13, 14] and 4 [15]. A semiempirical MO calculation (integral approximations) predicted ΔH_{at} about 1.4 and 1.9 times too large [16]. CNDO calculations resulted in $\Delta H_{at} = 137$ [17] and 145.6 [18], a modified INDO calculation in $\Delta H_{at} = 157.4$ [19], and an extended Hückel calculation in $\Delta H_{at} = 143.2$ [20].

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4.1.6.2.12 Microwave Spectrum

The MW spectrum of NF_2 (N_2F_4 at 50 to 100°C, 100 to 200 mTorr) was first observed in the 25- to 26-GHz region. Tentative assignments were given for two rotational transitions, each multiplet consisting of 18 lines [1, 2]. A detailed study [3] with N_2F_4 gas at 60 to 70°C and 10 to 800 Pa (133.3 Pa = 1 Torr) in various frequency ranges between 13.0 and 65.2 GHz resulted in about 350 lines and a complete assignment of 21 rotational transitions in the asymmetric top molecule, which is almost of the prolate symmetric type, see Table 12. The molecular rotation couples with the electron spin, $S = \frac{1}{2}$, the resultant fluorine spins, $I_{F_1} + I_{F_2} = 0$ (antisymmetric), or $I_{F_1} + I_{F_2} = 1$ (symmetric), and the nitrogen spin, $I_N = 1$. Multiplet patterns of transitions for the ground electronic state $^2B_1$ were expected to consist of two triplets corresponding to the combination of the antisymmetric spin state of fluorine with eo or oe rotational levels (e = even, o = odd), and two triplets of triplets corresponding to the combination of the symmetric spin state of fluorine with ee or oo rotational levels, see [3, figures 4 and 5]. These patterns were observed for higher rotational states with $N > 5$ where the selection rule $\Delta N = \Delta I = \Delta F = 0, \pm 1$ holds fairly well. For transitions involving lower values of N, a greater number of components appeared (up to more than 50 lines for the $2_{1,1} \leftarrow 2_{0,2}$ transition) which is a consequence of electron spin-nitrogen spin and electron spin-fluorine spin hyperfine couplings as well as nitrogen quadrupole coupling. The Stark effect was studied on two components of the $1_{1,0} \leftarrow 1_{0,1}$ multiplet to obtain the dipole moment [3].

Table 12
Microwave Spectrum of NF_2.
Multiplet center frequencies (in MHz) and assignments [3].

frequency	transition[a]
14339.5	$10_{2,8} \leftarrow 11_{1,11}$
14643.95	$1_{1,1} \leftarrow 2_{0,2}$
16684.0	$14_{2,12} \leftarrow 15_{1,15}$
17499.0	$27_{6,22} \leftarrow 28_{5,23}$
25666.5[b]	$25_{4,22} \leftarrow 24_{5,19}$
25748.0	$32_{7,26} \leftarrow 33_{6,27}$
25760.38[c]	$12_{3,9} \leftarrow 13_{2,12}$
27448.2	$8_{1,7} \leftarrow 7_{2,6}$
27752.8	$32_{7,25} \leftarrow 33_{6,28}$
28666.85	$5_{2,4} \leftarrow 6_{1,5}$
28843.2	$8_{2,6} \leftarrow 9_{1,9}$
33096.0	$37_{8,30} \leftarrow 38_{7,31}$
33202.90	$4_{0,4} \leftarrow 3_{1,3}$
33417.0	$21_{5,17} \leftarrow 22_{4,18}$
34195.3	$30_{5,25} \leftarrow 29_{6,24}$
60358.16	$1_{1,0} \leftarrow 1_{0,1}$
62019.5	$15_{4,11} \leftarrow 16_{3,14}$
62132.24	$2_{1,1} \leftarrow 2_{0,2}$
62450.08	$10_{3,7} \leftarrow 11_{2,10}$
64813.0	$20_{5,15} \leftarrow 21_{4,18}$
64863.96	$3_{1,2} \leftarrow 3_{0,3}$

[a] $N'_{K'_a,K'_c} \leftarrow N''_{K''_a,K''_c}$. K_a and K_c are the quantum numbers K for the limiting cases of the prolate and oblate symmetric top, respectively. – [b] First observed and tentatively assigned to $8_{1,7} \leftarrow 7_{2,6}$ [1]. – [c] First observed and tentatively assigned to $12_{3,9} \leftarrow 13_{2,12}$ [1].

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4.1.6.2.13 Electron Spin Resonance Spectrum

When the coupling of the electronic spin with the nuclear spins of the two equivalent F atoms and the N atom is considered, and the coupling of electronic and rotational angular momentum is neglected, then the ESR spectrum of the free radical is expected to consist of a 1:2:1 triplet (^{19}F-hf coupling), each component being split further into a 1:1:1 triplet (^{14}N-hf coupling). The inner triplet corresponds to the NF_2 spin state in which the two ^{19}F spins are antiparallel, i.e., $m_I(2F) = 0$, the two outer triplets are due to the parallel, i.e., $m_I(2F) = \pm 1$, spin states.

For gaseous NF_2, only a single broad line was observed with linewidths of 104 G at T = 342 to 435 K and p = 20 to 40 Torr [1] and of 150 G at T = 298 K and a calculated vapor pressure of 13 atm [2].

The liquid-phase spectrum of NF_2 in N_2F_4 at 298 K exhibits the 1:2:1 triplet (hfs: 64 ± 2G), the ^{14}N splitting remaining unresolved even after 1:1 dilution with CF_2Cl_2 [2].

The completely resolved spectrum of the free radical, a triplet of triplets, could be recorded at room temperature for NF_2/N_2F_4 equilibrium mixtures dissolved in perfluoro-2,3-dimethylhexane, in 2,2-dichloro-3-chloroperfluorobutane and in various Kel-F oils [3] and, even with better resolution, for NF_2 introduced into molecular sieves with effective pore diameters of 5 to 9 Å [4].

The ESR spectra of NF_2 radicals trapped in inert matrices at low temperatures show asymmetries which are characteristic of anisotropies in the g and hf coupling tensors. The amount of anisotropy depends on the degree of orientation of the radical, i.e., whether or not the radical is free to rotate, which in turn depends on temperature, matrix material, and matrix-to-radical ratio. Measurements were carried out at 4 to ≥30 K with noble gas matrices, Ne [8, 9], Ar [5, 6, 9], Kr [6, 7, 9], and also with CCl_4 [6] and N_2 [9] matrices.

The spectra of NF_2 in Ar matrices at 4.2 K were compared for two different mole ratios of matrix-to-radical precursor, M/R = 300 and 1200 (deposition of room-temperature equilibrium mixtures of N_2F_4/NF_2 and matrix gas onto a liquid helium cooled sapphire rod). The M/R = 300 sample gave an approximately axially symmetric g tensor indicating nearly free rotation of the NF_2 radical about an axis perpendicular to the molecular plane (x axis, see below). The more diluted sample (M/R = 1200) unexpectedly exhibited the spectrum of a randomly oriented radical with three different principal values for the g tensor; this may be due to a stronger crystalline field effect. The spectrum of NF_2 in Kr at 4.2 K (M/R = 300) indicated freer rotation than in Ar with M/R = 300. At about 30 K the completely resolved isotropic triplet set of triplets of an almost freely rotating NF_2 radical was observed in the Ar and Kr matrices [6, 7]. With CCl_4 as the matrix material, somewhat distorted spectra were observed at 4.2 to 30 K [6].

The spectrum of randomly oriented NF_2 at 4 K could be interpreted in terms of an anisotropic g tensor and axially symmetric ^{14}N- and ^{19}F-hf tensors. Oriented samples of NF_2 in Ne were prepared by preheating NF_2 to about 300 K before deposition (M/R ratio not given), and the x axis (⊥ molecular plane) was identified [8].

An improved degree of orientation was achieved by use of a large gradient between the temperature of the initial radical-matrix mixture ($Ne/NF_2 = 3000$, $Ar/NF_2 = 2500$, Kr/NF_2 not given) and the final temperature at the time of deposition and by use of a uniformly controlled rate of sample spray. In Ar and Kr better orientation was observed than in the "softer" Ne matrix. Anisotropic g tensors and axially symmetric ^{14}N- and ^{19}F-hf tensors were obtained at 4.2 K. As the sample was warmed to 30 K rotation was observed about the x axis followed by rotation about the x and the C_2 axes; above 30 K almost free rotation was indicated by the nine-line spectra giving isotropic g factors and isotropic hf coupling constants. The ESR spectrum of NF_2 in an N_2 matrix (M/R = 2000) at 4.2 K was not informative [9].

The earlier observation of some hfs with ±16 G (believed to be $a_{iso}(N)$) and weak, broad, and asymmetric lines at ±47 G in the spectrum of NF_2 in Ar at 4.2 K [5], presumably can be identified with $a_{xx}(F)$ and $a_{xx}(N)$, see Table 8, pp. 242/3.

The ESR parameters (i.e., g factors and hf coupling constants) of NF_2 in the gaseous and liquid states, in solutions, molecular sieves, and inert gas matrices are given, along with the results from microwave spectroscopy, in Table 8, pp. 242/3.

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4.1.6.2.14 Raman Spectrum

Two intense sharp and strongly polarized bands at 1074 and 572 cm^{-1} in the Raman spectrum of gaseous N_2F_4 at 250°C (Kr^+ laser excitation at 647.1 nm), which are absent in the room temperature spectrum, were assigned to the symmetric stretching (ν_1) and bending (ν_2) fundamentals of NF_2, respectively.

Reference:

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4.1.6.2.15 Infrared Absorption

Conventional IR Spectroscopy

The earliest IR spectra of gaseous NF_2 were obtained by simply heating gaseous N_2F_4 in the IR cell (to increase the proportion of NF_2 in the $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium) [1, 2] or by a differential pressure technique using a low-pressure N_2F_4 sample at temperatures up to 110°C and a reference sample of high-pressure N_2F_4 at room temperature [2 to 4]. Absorption bands were recorded between 1100 and 900 cm^{-1} and assigned to the two stretching fundamentals ν_1 and ν_3 of NF_2 [1, 2]. At 175°C the ν_1 band at 1074 cm^{-1} exhibited a well-resolved rotational structure characteristic of a perpendicular band of a near-prolate symmetric rotor [1]. No explanation was offered for the strong band at 730 cm^{-1} recorded by the differential pressure technique [2 to 4].

IR absorption was also used to study matrix-isolated NF_2 radicals. For the first time, all three fundamentals were observed in an N_2 matrix at 20 K for NF_2 radicals produced by condensation of N_2–N_2F_4 mixtures at various temperatures and pressures [5]. With Ar or CO matrices at 14 K the stretching fundamentals were recorded of NF_2 produced by photolysis of Ar–NF_3 or CO–NF_3 samples [6] and of $^{14}NF_2$ and $^{15}NF_2$ produced by photolysis of Ar–F_2 and Ar–HN_3 or Ar–F_2 and Ar–$H^{15}N^{14}N_2$ samples [7].

High-Resolution IR Laser Spectroscopy

By using tunable diode lasers in the 9 and 11 μm regions, the ν_1 [8] and ν_3 bands [9] of gaseous NF_2 (N_2F_4 heated to ca. 100 to 150°C) were measured at Doppler limited resolution (preliminary studies [10, 11]).

For the ν_1 band about 300 absorption lines were recorded between 1020 and 1145 cm^{-1}. The spectrum resembles, particularly in the Q branches with high K_a quantum numbers (see p. 252), a perpendicular band of a prolate symmetric top, i.e., the selection rules $\Delta N = 0, \pm 1$, ΔK_a ($\approx \Delta K$) $= \pm 1$ are effective. The absorption lines could be assigned to a number of ^PQ_K, ^RQ_K, ^RR_K, and ^PP_K branches with N up to 28, 34, 38, and 28, respectively (for the band center, see p. 247). The electron spin-rotation interaction causes doublet splitting of almost each component. The asymmetry doubling is obvious in some ^PQ_K transitions with $K < 5$; it increases with decreasing K and increasing N. Effects of hyperfine coupling could be detected as line broadenings or partly resolved splittings in the transitions with low N, but these effects were not included in the analysis [8].

For the ν_3 band about 270 absorption lines were recorded between 920 and 967 cm^{-1}. The ν_3 band is an a-type band of a near-prolate asymmetric rotor, and at large K_a it should resemble the parallel band of a prolate symmetric top, i.e., $\Delta N = 0, \pm 1$, ΔK_a ($\approx \Delta K$) $= 0$. In the ν_3 band the symmetric top characteristics are not as obvious as in the ν_1 band, however, a number of ^QP_K and ^QQ_K branches with N up to 28 and ^QR_K branches with N up to 42 could be identified (for the band center, see p. 247). The assignment was supported by the results from a Fourier transform spectrum of NF_2 at 890 to 980 cm^{-1}. The spin-rotation splitting is relatively small and unresolved in transitions with low K_a values. The asymmetry splitting is apparent in lines with low K_a and high N values, which was demonstrated with the $^QQ_5$ (N = 19 to 21) branch [9].

The molecular parameters, i.e., rotational and centrifugal distortion constants, spin-rotation and Coriolis coupling constants, obtained from the diode laser spectra, are given on pp. 245/6.

Diode laser studies are planned for the ν_2 bending mode of NF_2 [9].

Laser Magnetic Resonance (LMR)

The fact that many of the lines in the ν_1 and ν_3 bands of NF_2 have close or exact coincidences with CO_2 laser lines, enables NF_2 to be studied by LMR.

The ν_1 and ν_3 band lines of NF_2 were tuned into resonance with the R(26) ($00^01 \leftarrow 02^00$) and P(24) ($00^01 \leftarrow 10^00$) lines of CO_2, respectively, using weak magnetic fields (H up to 450 G) [12, 13].

For strong magnetic fields where the Zeeman splittings become greater than the intervals between neighboring rotational levels and thus Zeeman level crossings occur, LMR spectra could nonetheless be observed. Their origin was ascribed to a new type of Zeeman-tuning mechanism due to the avoidance of crossings between Zeeman levels which are labeled by the same $M_J = M_N + M_S$ number and belong to a pair of rotational levels ($\Delta K_a = 0$, $\Delta N = \pm 1$), connected by spin-rotation interaction. This effect was first studied and discussed for ClO_2 (see e.g., [14 to 16]). The ν_1 band region of NF_2 (N_2F_4 at 60 to 70°C and ca. 0.8 Torr) was studied in magnetic fields up to 20 kG. Eight CO_2 laser lines in the 9.4 μm band were brought into coincidence with seven rotational-vibrational transitions of NF_2, two of them are asymmetry doublets. The results are given in Table 13, p. 256, [17]. The asymmetry components of the $^PQ_2(2)$ ($v_1 = 1 \leftarrow 0$) transition, i.e., the spectrum around 15 kG due to $2_{1,2} \leftarrow 2_{2,1}$ ($v_1 = 1 \leftarrow 0$) and the spectrum around 16 kG due to $2_{1,1} \leftarrow 2_{2,0}$ ($v_1 = 1 \leftarrow 0$) were observed with the $^{12}C^{16}O_2$ R(6) line at 1069.0141 cm^{-1}. The Zeeman tuning diagrams are given and the tuning mechanism is demonstrated. In the first case, crossings are avoided between the $1_{1,0}$ ($M_S = +0.5$) and $2_{1,2}$($M_S = -0.5$) levels of the excited vibrational state at about 14.6 kG, in the second case between $1_{1,1}$ and $2_{1,1}$ of the excited vibrational state at about 17.0 kG. Hyperfine structures due to both the nitrogen spin and the fluorine spin complicate the spectra. (Some misprints concerning level labeling in the text and in the figures are disturbing.) The analysis of the LMR spectrum yielded the zero-field wavenumbers of the observed transitions (see Table 13) and the origin of the ν_1 band (see p. 247) as well as rotational and spin-rotation constants for the excited vibrational state (see p. 245) [17].

Table 13

NF_2. Laser Magnetic Resonance Spectra for the ν_1 Band.

Observed LMR transitions, assignments, and zero-field wavenumbers of the observed transitions [17].

laser line wavenumber in cm^{-1}	origin	resonant field in G*)	assignment		zero-field transition in cm^{-1}
			M_J	$N'_{K'_a,K'_c} \leftarrow N''_{K''_a,K''_c}$	
1067.3589	$^{12}C^{18}O_2$ P(22)	17025	1/2	$1_{1,0} \leftarrow 2_{2,1}$	1067.5981
		17175	3/2		
1068.9425	$^{12}C^{18}O_2$ P(20)	14512	3/2	$2_{1,2} \leftarrow 2_{2,1}$	1068.9509
		15085	1/2	$2_{1,1} \leftarrow 2_{2,0}$	1069.1194
		15289	3/2		
1069.0141	$^{12}C^{16}O_2$ R(6)	15230	1/2	$2_{1,2} \leftarrow 2_{2,1}$	see above
		15425	3/2		
		15860	1/2	$2_{1,1} \leftarrow 2_{2,0}$	see above
		16065	3/2		
1071.8837	$^{12}C^{16}O_2$ R(10)	11544	−1/2	$1_{0,1} \leftarrow 2_{1,2}$	1071.6210
		11661	1/2		
1073.2785	$^{12}C^{16}O_2$ R(12)	17781	3/2	$1_{0,1} \leftarrow 1_{1,0}$	1072.9735
1074.6465	$^{12}C^{16}O_2$ R(14)	13872	−1/2	$2_{1,2} \leftarrow 3_{0,3}$	1074.6915
		13987	1/2		
		14098	3/2		
1077.3025	$^{12}C^{16}O_2$ R(18)	11326	3/2	$1_{1,0} \leftarrow 1_{0,1}$	1077.0030
1081.0874	$^{12}C^{16}O_2$ R(24)	14042	1/2	$2_{2,1} \leftarrow 2_{1,2}$	1081.0379
		14262	3/2		
		14658	1/2	$2_{2,0} \leftarrow 2_{1,1}$	1080.8654
		14864	3/2		

*) Center field of the hyperfine components.

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4.1.6.2.16 Ultraviolet Absorption

The 260 nm Band

A poorly structured band, with λ_{max} = 260.2 nm and a half width of 20 nm, was observed for the first time in the absorption spectrum of N_2F_4 gas at about 290 to 350 K and attributed to the NF_2 radical (because of a resemblance to NO_2 bands) [1]. At higher resolution vibrational structure became apparent (but rotational structure seemed to be completely hidden by a continuous background or destroyed by predissociation of the radical). A progression of at least eight diffuse bands between 247.3 and 264.9 nm, with an average vibrational spacing of $\Delta\nu_{av}$ = 380 cm^{-1}, was observed at room temperature and 400 to 700 Torr [2], and a progression of 14 diffuse bands between 237.7 and 270.3 nm with $\Delta\nu_{av}$ = 390 cm^{-1} at 20 to 100°C and 5 to 200 Torr (studied up to 750°C) [3]. The vibrational spacing was attributed to the bending fundamental in the excited electronic state, which was supposed to be one of the two lowest $^2A_1$ states (compare p. 235) [2, 3]. For NF_2 in Ar matrices, produced by photolysis of NF_3 in Ar at 14 K, the absorption spectrum exhibits a red shift of about 150 cm^{-1} (as compared with the gas-phase spectrum) and consists of a progression of seven bands between 247.8 to 263.8 nm with $\Delta\nu_{av}$ = 408 cm^{-1} [4].

Measuring the UV absorption of NF_2 at 260 nm became an established method of determining NF_2 concentrations. The dissociation of N_2F_4 and formation of NF_2 (see pp. 326/31) or the kinetics of reactions involving NF_2 radicals can be followed by monitoring the absorption intensity at 260 nm.

The extinction coefficient at 260 nm has been measured repeatedly; the results, however, are unsatisfactory, except possibly those of [5, 6] (and thus [1]) who obtained comparable ε values by two different methods. For some years, many authors [7 to 12] fortuitously (?) measured ε values of about 540 to 600 $L\cdot mol^{-1}\cdot cm^{-1}$. The values were thought to be in good or reasonable agreement with those initially measured [1]. However, the original values were later clarified [13] to be decadic extinction coefficients, that is, $\varkappa = \log_{10}(I_0/I) \cdot l^{-1} \cdot [NF_2]^{-1}$ (thus $\varepsilon = \varkappa \cdot \ln 10$), in response to greater scrutiny [5].

Published extinction coefficients ε are listed in Table 14 and details concerning the method of measurement and the derivation of the data are given in the "remarks" following the table.

Table 14

NF_2. Extinction Coefficients at 260 nm.

$\varepsilon = \ln(I_0/I) \cdot l^{-1} \cdot [NF_2]^{-1}$, I_0 and I = incident and transmitted light intensities, l = path length.

ε in $L \cdot mol^{-1} \cdot cm^{-1}$	T in K	method of measurement	remark	Ref.
1089	298	spectrophotometry of $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium	a)	[1, 5]
1070	298		b)	[5]
580 ± 40	323 to 373		c)	[7]
241 ± 12	295.5		d)	[17]
1344.5 − 0.4659 T	1140 to 1500	shock heating of N_2F_4–Ar (and N_2F_4–N_2 [10, 11]) mixtures	e)	[5]
1236.7 − 0.3933 T	1000 to 1500		f)	[6]
1470.2 − 0.6150 T	500 to 800		g)	[6]
615 ± 25	>600		h)	[8]
603	800 to 1400		i)	[9]
537 ± 10	360 to 570		j)	[10, 11]

a) $\varkappa = \varepsilon/\ln 10 = 550$ at 323 K and 565 at 298 K (see text above) were based on the experimentally determined equilibrium constants for $N_2F_4 \rightleftharpoons 2NF_2$ [1]. A recalculation using JANAF [14] equilibrium constants gave $\varkappa = 473$ at 298 K and thus $\varepsilon = 1089$ [5].

b) Two measurements at 121 and 400 Torr gave (using JANAF [14] equilibrium constants) $\varepsilon = 1057$ and 1082, respectively, and thus, the average value $\varepsilon = 1070$. These values compare favorably with $\varepsilon = 1206$ for 298 K obtained by a linear extrapolation of shock-tube data (see e)) [5].

c) Equilibrium constants were adopted from [8, 9, 15, 19].

d) p = 15 to 1720 Torr. Equilibrium constants from [18].

e), f), g) Mixtures of 0.25% N_2F_4 and 99.75% Ar, T = 500 to 1500 K. Least-squares fits of the experimental points ε(T) to straight lines. e) Measurements and fit for 1140 to 1500 K [5]. f) Measurements at 1000 to 1280 K [6] and 1140 to 1500 K [5] and simultaneous fit [6]. g) Measurements at 500 to 800 K; relation assumed to hold also for the range 375 to 462 K (where N_2F_4 is not completely dissociated) [6].

h) Mixtures of 0.1% N_2F_4 and 99.9% Ar. Mean value of ε. Results from 14 experiments (no precise temperature data given) were found to be temperature independent [8].

i) Mixtures of 1% N_2F_4 and 99% Ar. A slight temperature dependence of ε was found. $\varepsilon = 603$ is the average for the reported temperature range [9].

j) Mixtures of 1% N_2F_4 and 99% Ar (T = 358 to 701 K) or 99% N_2 (T = 398 to 571 K). ε was found independent of temperature between 360 and 570 K [10, 11].

The discrepant ε values obtained from the shock-tube experiments [9 to 11], as compared to other reported ε values [1, 5], can be attributed to the higher NF_2 concentrations used thus nullifying Beer's law [5]. Just this effect has been demonstrated for still higher concentrations (1, 2, and 5% N_2F_4 in Ar) and temperatures between 527 and 935 K for which the apparent extinction coefficient decreased to 230 [12].

The use of broad band interference filters at 260 nm [15, 16] or 257 nm [20] (instead of a monochromator) for the wavelength selection also violated the conditions for the application of Beer's law and resulted in very low extinction coefficients: Shock heating of 1:103 (mole ratio) N_2F_4–Ar mixtures [15] (experiments with 1:103, 1:206, and 2:104 mixtures [16]) at 554 to 738 K resulted in $\varepsilon = 276$ to 317 $L \cdot mol^{-1} \cdot cm^{-1}$ (equilibrium NF_2 concentrations obtained from $(\partial p/\partial T)_v$ data [1]); a mean value of $\varepsilon = 325 \pm 10$ $L \cdot mol^{-1} \cdot cm^{-1}$ resulted from measurements at 353 to 376 K for which $\ln(I_0/I) < 0.30$ [15]. A spectrophotometric study of the thermal dissociation of N_2F_4 in a low-pressure flow system gave an effective absorption cross section $\sigma = 5.13 \times 10^{-23}$ m^2/molecule at 293 K which corresponds to $\varepsilon = 309$ $L \cdot mol^{-1} \cdot cm^{-1}$ ($\varepsilon = \sigma \cdot 10$ L, L = Avogadro number) [20]. It may be noted that there must be some error in figure 2 in [20], i.e., [NF_2] vs. percentage absorption (I/I_0), because the given absorption cross section cannot be obtained therefrom as was claimed [20].

Far UV Absorption at $\lambda < 170$ nm

With N_2F_4 gas at a low pressure of 50 Pa (ca. 0.4 Torr) and T = 450 K, an absorption spectrum could be observed in the Schumann region. A continuum peaking at 164 nm with $\varepsilon = 57 \pm 5$ $atm^{-1} \cdot cm^{-1}$ was assigned to some intravalence transition. For eleven diffuse bands between 140 and 126 nm the following wavelengths and extinction coefficients (at 273 K) were reported (ε derived by using equilibrium constants from [1, 14]):

λ in nm	139.30	136.84	135.50	134.79	133.57	132.32
ε in $atm^{-1} \cdot cm^{-1}$ ...	17.5±2	115±10	ca. 7	75±10	32±5	35±5
λ in nm	130.97	129.76	128.50	127.63	ca. 126.1	
ε in $atm^{-1} \cdot cm^{-1}$ ...	ca. 15	ca. 20	ca. 45	ca. 30	ca. 10	

Considering the ionization potential of NF_2 (see pp. 237/8) these bands were generally assigned as the first members of Rydberg series (i.e., n = 3) leading to NF_2^+ ($^1A_1$), specific assignments, however, were not attempted [21].

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4.1.6.3 Thermal Properties

Heat of Formation

$\Delta H^{\circ}_{f,298}(NF_2, g) = 7.8 \pm 1.0$ kcal/mol was obtained from a reanalysis of the equilibrium constant and the thermochemistry of the reaction $NF_3(g) \rightleftharpoons NF_2(g) + F(g)$ [1]. Based upon heat of formation and dissociation data for N_2F_4 the following $\Delta H^{\circ}_{f,298}(NF_2, g)$ values in kcal/mol were evaluated: 8.9 ± 2.5 [2], 8.5 ± 2 [3], 9.8 ± 2.1 [4], 9.5 ± 2.5 [5], and 10.1 ± 2.0 [6]. $\Delta H^{\circ}_{f,298}(NF_2, g) \approx$ 8.8 kcal/mol was deduced from the translational energy of F^- at the appearance potential (F^- formed by the dissociative resonance capture process $NF_3 + e^- \rightarrow F^- + NF_2$ [7]).

Heat Capacity C_p. Thermodynamic Functions

Heat capacities and thermodynamic functions for NF_2 as an ideal gas have been calculated by standard methods using the gas-phase value $\nu_1 = 1074$ cm^{-1} [8] and/or the matrix values $\nu_1 = 1069.6$, $\nu_2 = 573.4$, and $\nu_3 = 930.7$ cm^{-1} [9] for the fundamental frequencies: C°_p, $-(G^{\circ} - H^{\circ}_0)/T$, S°, and $(H^{\circ} - H^{\circ}_0)/T$ at T = 273.15, 298.15, 300, 400, ···, 1400, 1500, 2000, 2500, and 3000 K are given by [9] (ν_1 [8], ν_2, ν_3 [9]), and C°_p, $H^{\circ} - H^{\circ}_0$, S°, and $-(G^{\circ} - H^{\circ}_0)$ at T = 0 to 6000 K (100 K intervals) and 298.15 K by [10] (ν_1, ν_2, ν_3 [9]). From the JANAF tables [6], containing C°_p, entropy S°, Gibbs free-energy function $-(G^{\circ} - H^{\circ}_{298})/T$, all in cal·mol^{-1}·K^{-1}, and enthalpy $H^{\circ} - H^{\circ}_{298}$ in kcal/mol at T = 0 to 6000 K (100 K intervals), the following values are selected ($\nu_1 = 1074$, $\nu_2 = 573$, $\nu_3 = 931$ cm^{-1} used):

T in K	0	100	200	298	400	600	800
C°_p	0.000	7.985	8.677	9.801	10.851	12.159	12.820
S°	0.000	50.345	56.044	59.715	62.748	67.425	71.024
$-(G^{\circ} - H^{\circ}_{298})/T$	∞	67.667	60.574	59.715	60.113	61.809	63.680
$H^{\circ} - H^{\circ}_{298}$	−2.528	−1.732	−0.906	0.000	1.054	3.370	5.875

T in K	1000	1500	2000	3000	4000	5000	6000
C°_p	13.177	13.568	13.714	13.822	13.861	13.879	13.889
S°	73.927	79.358	83.284	88.870	92.852	95.947	98.479
$-(G^{\circ} - H^{\circ}_{298})/T$	65.449	69.237	72.281	76.941	80.445	83.247	85.581
$H^{\circ} - H^{\circ}_{298}$	8.478	15.182	22.008	35.787	49.631	63.502	77.368

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4.1.7 The NF_2^+ Ion

CAS Registry Number: *[31685-31-1]*

NF_2^+ was observed in the mass spectra of N_2F_4 (see p. 337), NF_3 (see p. 209), and other compounds containing the NF_2 group (see e.g., [1]). Photoionization of the NF_2 radical produced NF_2^+ in its ground state and lowest electronically excited states [2, 3].

A recommended value for the heat of formation, $\Delta H^\circ_{f,298} = 284$ kcal/mol [1], is based on the mass spectra of N_2F_4 [4, 5] and NF_3 [4 to 6]. $\Delta H^\circ_{f,0} = 279.7 \pm 0.5$ kcal/mol (12.13 ± 0.02 eV) [7] results from the threshold energy, 14.12 ± 0.01 eV, for the photoionization process $NF_3 + h\nu \rightarrow NF_2^+ + F + e^-$ combined with $\Delta H^\circ_{f,0}(NF_3) = -30.38 \pm 0.02$ kcal/mol [7] and too low a value $\Delta H^\circ_{f,0}(F) = 15.45 \pm 0.35$ kcal/mol [8]. A theoretical result (MNDO approximation) is $\Delta H^\circ_{f,298} = 264.3$ kcal/mol [9].

Information on the electronic structure came from the photoelectron spectrum of NF_2 [2, 3] and from theoretical studies: ab initio SCF–MO + CI [10], INDO + CI [11], many-body perturbation theory within INDO approximation [12], CNDO [2, 3], and extended Hückel (presumably) [13]. The ground state of NF_2^+ (C_{2v} symmetry, see below) is $^1A_1$, the corresponding electron configuration $\cdots(1a_2)^2\,(4b_2)^2\,(6a_1)^2$ (unpaired electron of the NF_2 radical removed, see p. 233). The lowest excited states arising from the configuration $\cdots(1a_2)^2\,(4b_2)^2\,(6a_1)^1\,(2b_1)^1$ are $^3B_1$ and $^1B_1$, which, according to the photoelectron spectrum of NF_2, lie 2.5 and 4.3 eV above the ionic ground state. Theory predicted energy differences of 1.43 and 3.25 eV [10], 2.0 and 3.2 eV [11], 2.27 and 2.91 eV [12], 2.9 and 3.9 eV [3]. Excitations $4b_2 \rightarrow 2b_1$ and $1a_2 \rightarrow 2b_1$ give the higher excited triplet-singlet pairs $^3B_1$, $^1B_1$ and $^3A_2$, $^1A_2$, respectively [11, 12]. Charge distributions were calculated for the states $^1A_1$ [10, 13] and $^{3,1}B_1$ [10].

The geometry of NF_2^+ has not been determined by experiment. However, a geometry optimization with respect to the bond angle ($r(N\text{–}F) = 1.363$ Å of NF_2 assumed) gave bent structures for the lowest three states with $\sphericalangle FNF^+ = 105°$ ($^1A_1$), 122° ($^3B_1$), and 120° ($^1B_1$) [10].

Vibrational structure in the first two photoelectron bands of NF_2 gave a stretching fundamental of 1250 cm^{-1} for the ground state and a stretching or bending fundamental of 520 cm^{-1} for the lowest triplet state [2, 3].

A dissociation energy, $D^\circ_0(FN^+\text{–}F) = 3.8$ eV (ca. 88 kcal/mol), was estimated from isoelectronic sequences [14]. An atomization energy, $\Delta H_{at} = 153.1$ kcal/mol (apparently for the products $N^+ + 2F$) was obtained from a CNDO calculation [15].

References:

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4.1.8 The NF_2^- Ion

CAS Registry Number: *[37366-64-6]*

Gaseous NF_2^- was generated by dissociative electron capture from N_2F_4 [1], NF_3 [2], and NHF_2 [3]. In the negative-ion mass spectrum of N_2F_4 (70 eV electrons) the abundance of NF_2^- was 5.1 relative to 100 for F^- [1], in the spectrum of NF_3 the abundance of NF_2^- (relative to 1000 for F^-) was 0.5 for 70 eV electrons and 1.2 at its resonance capture maximum of 1.8 ± 0.1 eV [2].

The existence of NF_2^- as a kinetically independent ion in aqueous solutions of NHF_2, i.e., equilibrium dissociation $NHF_2 \rightleftharpoons H^+ + NF_2^-$, was supposed earlier, but disproved later, see "Fluorine" Suppl. Vol. 5.

The heat of formation, $\Delta H^\circ_{f,298} = -29.5 \pm 7.5$ kcal/mol [2], was obtained from the electron affinity of NF_2 and the heat of formation of NF_2 (8.9 ± 2.5 kcal/mol [4]). A theoretical value (MNDO) is -43.6 kcal/mol [5].

The proton affinity, $A_p = 360.0$ kcal/mol, was determined from studies of the proton transfer equilibria $NHF_2 + A^- \rightleftharpoons HA + NF_2^-$ by ion-cyclotron resonance with one of the following reference bases, $A^- = HO^-$, $HCOO^-$, CH_3COO^-, F_2CHCOO^-, CF_3COO^-, Cl^-, or F^- (experiments with ca. 80 other anions). Theoretical values are $A_p = 352.3$ kcal/mol (ab initio MO, STO-3G basis) and 374.9 kcal/mol (CNDO) [3].

An energy-optimized geometry with $r(N\text{–}F) = 1.495 \pm 0.002$ Å and $\sphericalangle FNF^- = 99.4^\circ \pm 0.45^\circ$ was obtained from an ab initio MO calculation using a Gaussian basis set including d functions, and with $r(N\text{–}F) = 1.525 \pm 0.15$ Å and $\sphericalangle FNF^- = 99.1^\circ \pm 0.45^\circ$ using the same basis set but without d functions. The corresponding total molecular SCF energies are $E_T^{SCF} = -252.8006$ and -252.7892 a.u. [6]. MNDO results for the geometry are r(N–F) = 1.308 Å and ∢FNF⁻ = 107.6° [5].

The charge distribution, calculated semiempirically (presumably by the extended Hückel method), is given in [7].

The atomization energy was calculated (CNDO) to be $\Delta H_{at} = 116.1$ kcal/mol (apparently for the products $N + F + F^-$) [8].

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4.1.9 Nitrogen Monofluoride, NF

Other names: Fluoronitrene, fluoroazene, fluoroimidogen

CAS Registry Number: *[13967-06-1]*

4.1.9.1 Formation

4.1.9.1.1 Gaseous NF

4.1.9.1.1.1 General

The thermal or photochemical decomposition of gaseous NF_2 was presumed to generate NF (cf. pp. 331/3).

The free NF radical produced in two low-lying excited electronic states by various gas-phase reactions is observed by the green and near-IR emission spectra which correspond to the $b\,^1\Sigma^+ \rightarrow X\,^3\Sigma^-$ and $a\,^1\Delta \rightarrow X\,^3\Sigma^-$ transitions (cf. pp. 272 and 285/7). These two lowest singlet states, $a\,^1\Delta$ and $b\,^1\Sigma^+$, are metastable; transitions to the triplet ground state are partially forbidden permitting long radiative lifetimes τ for both states. Therefore, recent interest in the chemistry of the $a\,^1\Delta$ and $b\,^1\Sigma^+$ states of NF arose from the possibility of realizing an electronic transition chemical laser operating in the visible at 529 nm (b → X) and in the near-IR at 874 nm (a → X). Much work has been invested in the development of a chemical NF laser, however, lasing has not yet been demonstrated (see e.g., [1 to 5]). Another possibility has aroused interest, that is, the rapid and efficient conversion of the energy stored in excited NF into laser light. Excited NF should then serve as a chemical pump for species probably more amenable to lasing, for example, Bi atoms [5 to 8], BiF molecules [9], or IF molecules [10]. However, results from these tests are not yet encouraging.

For references, see p. 269.

4.1.9.1.1.2 Reactions Forming NF in Specific Electronic States

In the following, the radical in its X $^3\Sigma^-$, a $^1\Delta$, and b $^1\Sigma^+$ state is occasionally abbreviated as NF(X), NF(a), and NF(b). The symbol "†" denotes vibrational excitation. The radical in another excited state, c $^1\Pi$, was recently formed from the dissociative charge-transfer reaction of He^+ with NF_3 [51].

$Ar + NF_3$, $Ar + N_2F_4$, $Xe + N_2F_4$

The first definitive identification of NF(b) and NF(a) came from the analysis of the green [11, 12] and near-IR [11, 13] emissions. These spectra were observed in the afterglow when a dilute solution of NF_3 in Ar was passed through a microwave discharge. NF(b) was also observed in slow-flowing diluted mixtures of NF_3 or N_2F_4 in Ar excited by pulsed Tesla-type discharges; the radicals were believed to be generated by dissociative energy transfer between metastable $Ar(^3P_{0,2})$ atoms and NF_3 or N_2F_4 [14]. A similar flowing afterglow source of NF(b) and very small amounts of NF(a) is the reaction of metastable $Ar(^3P_{0,2})$, generated by a hollow-cathode discharge in flowing Ar, with NF_2 radicals obtained from the thermal dissociation of N_2F_4 [15]. Analogously, the reaction of $Xe(^3P_2)$ with NF_2 gave significant amounts of NF(b) [16].

$NF_2 + H$

The reaction of H (or D) atoms with NF_2 has usually been used as a source for predominantly NF(a) and thus as a basis for various studies of NF(a) properties. For the $NF_2 + H$ reaction the following reaction channels are expected [17]:

$$NF_2(^2B_1) + H(^2S) \xrightarrow{k_X} NF(X\,^3\Sigma^-) + HF(v) \qquad \text{(1a)}$$

$$\Delta H_0^\circ = -66\ \text{kcal/mol, thus } v \leq 6$$

$$\xrightarrow{k_a} NF(a\,^1\Delta) + HF(v) \qquad \text{(1b)}$$

$$\Delta H_0^\circ = -34\ \text{kcal/mol, thus } v \leq 3$$

$$\xrightarrow{k_b} NF(b\,^1\Sigma^+) + HF(v) \qquad \text{(1c)}$$

$$\Delta H_0^\circ = -13\ \text{kcal/mol, thus } v \leq 1$$

The rate constant for the overall reaction is $k_1 = k_X + k_a + k_b$.

For the determination of k_1, the intensity of the infrared chemiluminescence from HF ($v \geq 1$) was monitored as a function of the reagent flow at 300 K in a fast-flow, low-concentration, flowing afterglow apparatus. Comparison of the HF(v) emission intensity to that of HCl(v) from the $H + Cl_2$ reaction yielded the rate constant 3.8×10^{-12} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for the formation of HF($v \geq 1$) (based on $k = 2.06 \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for $H + Cl_2$). The value had to be increased by a factor of about 3 to allow for HF($v = 0$) formation, thus $k_1^{300\,K} \approx 1.3 \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (uncertainty ±50%) [17]. By measuring the decay of the hydrogen atomic resonance fluorescence under pseudo-first-order conditions (mean ratio $[NF_2]_0/[H]_0 = 11.3$) at T = 298, 421, 471, and 550 K, the rate constant $k_1^{298\,K} = (1.5 \pm 0.2) \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ and an Arrhenius expression for T = 298 to 550 K, $k_1 = (1.9 \pm 0.5) \times 10^{-11} \exp[-(30 \pm 50)/T]$, were obtained [18].

An unpublished result from a reactive flow analysis [19] was quoted as $k_1^{298\,K} \approx 2 \times 10^{13}$ cm$^3 \cdot$ mol$^{-1} \cdot$ s^{-1} (0.3×10^{-11} cm$^3 \cdot$ molecule$^{-1} \cdot$ s^{-1}) [20, 21].

NF(a $^1\Delta$). One hypothesis supposed an initial formation of NF(X) and subsequent collisional excitation to NF(a) or NF(b) by some unknown species [22]. Later, the rapid H + NF_2 (or D + NF_2) reaction was proposed to lead mainly, if not exclusively, to NF(a) radicals according to reaction (1b) [23]. Considering the Wigner-Witmer spin conservation rules [24], process (1b) must be an addition-elimination reaction probably proceeding through a singlet-state intermediate, $NHF_2(^1A)$. Direct abstraction is expected for process (1a), that is, attack of the H atom on one of the F atoms [21, 23].

The production of NF(a) with a branching ratio ≥ 0.9 was demonstrated by two independent methods: (A) Atomic resonance-fluorescence was used in a discharge flow system to study the concentration profiles of ground state $N(^4S°)$ and excited state $N(^2D°)$, $N(^2P°)$ atoms which had been produced by the possible secondary reactions (cf. p. 293):

$$H(^2S) + NF(X\,^3\Sigma^-) \rightarrow HF(X\,^1\Sigma^+) + N(^4S°) \qquad (2a)$$

$$H(^2S) + NF(a\,^1\Delta) \rightarrow HF(X\,^1\Sigma^+) + N(^2D°, ^2P°) \qquad (2b)$$

$$H(^2S) + NF(b\,^1\Sigma^+) \rightarrow HF(X\,^1\Sigma^+) + N(^2P°) \qquad (2c)$$

Large amounts of $N(^2D°)$, minor amounts of $N(^2P°)$ ($[N(^2P°)]/[N(^2D°)] \approx 0.1$), and negligible amounts of $N(^4S°)$ were found at short reaction times (<8 ms) indicating that NF(a) is initially the major product in reaction (1) [25, 26]. (B) A branching ratio of $k_X : k_a : k_b = 0.07 : 0.91 : 0.02$ (estimate for NF(X) very uncertain, probably overestimated) was derived [17] from the intensity ratio of b→X to a→X emissions and from the intensity ratio of HF(v = 4→3) to HF(v<4, Δv = 1) emissions observed in the fast flow reaction (the presence of HF (v = 4) indicated direct formation of NF(X), see reactions (1a) and (1b)) and by using radiative lifetimes (see pp. 286, 287) of 5.6 s for NF(a) [17] and 0.2 s for NF(b) [22]; the latter value, however, is too large by a factor of about 10 according to more recent results [14, 15].

In the course of studies toward the development of an electronic transition chemical NF laser, that is, production of high densities of electronically excited NF radicals, scale-up studies of NF(a) in a subsonic laser device [20, 27] and in a combustor-driven flow facility [2, 3] succeeded in steady-state densities of about 10^{14} molecules/cm^3 and thus in an increase by a factor of 10^4 over earlier flow-tube studies [28]. Scaling to even larger concentrations of about 6×10^{15} molecules/cm^3 was demonstrated in a supersonic flow [29]. For a reasonable laser gain, however, densities on the order of 10^{17} molecules/cm^3 would be required because of the long radiative lifetime of NF(a) [2, p. 109]. This estimate, however, was based on $\tau(a\,^1\Delta) \approx 0.7$ s which is smaller than the more recent value by a factor of 8 (cf. p. 287).

NF(b $^1\Sigma^+$). The formation of NF(b) was attributed to a rapid near-resonant vibrational-to-electronic (V–E) energy transfer process:

$$HF(v \geq 2) + NF(a\,^1\Delta) \xrightarrow{k_3} HF(v-2) + NF(b\,^1\Sigma^+) + \Delta E \qquad (3)$$

The energy difference of about 0.92 eV between b $^1\Sigma^+$ and a $^1\Delta$ (cf. p. 272) is close to certain Δv = 2 transitions in $HF^\dagger$. For example, the resonance defects are $\Delta E = -309.09$ cm^{-1} for v = 2, and -30.44 cm^{-1} for v = 3, assuming the NFs to be in their vibrational ground levels [23] (but see [17, 26] and pp. 285, 286). The occurrence of reaction (3) was supported by the observed concentration dependence of NF(b) and NF(a) on the concentration of $HF^\dagger$ and by the observation that the b→X emission practically disappeared when H was replaced by D in reaction (1). The very much lower probability of V–E transfer between $DF^\dagger$ and NF(a) is a consequence of the lower fundamental frequency of DF resulting in large resonance defects, e.g., $\Delta E \approx 1000$ and 730 cm^{-1} for Δv = 3 transitions in DF(v = 3) and DF(v = 4), respectively [23].

An electronic-to-electronic (E–E) energy transfer process

$$O_2(a\,^1\Delta_g) + NF(a\,^1\Delta) \xrightarrow{k_4} O_2(X\,^3\Sigma_g^-) + NF(b\,^1\Sigma^+) \qquad (4)$$

was believed to cause NF(a) to NF(b) conversion and thus b → X emission when a stream of $O_2(a\,^1\Delta_g)$ was introduced into the $D + NF_2$ reacting mixture. Estimates for the rate constants for reactions (3) and (4) (based, however, on $\tau(b\,^1\Sigma^+) = 0.2$ s, cf. p. 265) resulted in $k_3 \approx 10^{11}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (10^{-13} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) and $k_4 = 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (10^{-14} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) [23]; $k_4 = 9 \times 10^{11}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (1×10^{-12} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) [30].

Alternatively, the direct formation of NF(b) according to reaction (1c) was inferred [17] from the observed independence of the (b → X)/(a → X) intensity ratio on the NF_2 concentration. Computer simulations of NF(b) and NF(a) formation from the $H + NF_2$ reaction showed a strong dependence of this intensity ratio on NF_2 concentration for collisional formation of NF(b), but independence of NF_2 concentration for direct formation. Moreover, the calculations showed that even if the V–E transfer rate constant was gas kinetic, the amount of NF(b) would be insignificant because of the very small concentration of $HF(v \geq 2)$ obtained under the experimental conditions chosen [17].

Increased NF(b) densities were achieved by NF(a) → NF(b) conversion in E–E transfer processes. When $O_2(a\,^1\Delta_g)$ molecules and ground state iodine atoms (produced by the $D + HI$ reaction in the reaction zone of $H + NF_2$) were simultaneously present and when the $O_2\,(a\,^1\Delta_g)$ concentration was chosen such that the increase of NF(b) due to reaction (4) was insignificant, then the large increase in NF(b) density was attributed to the rapid near-resonant E–E transfer process

$$I(^2P^\circ_{1/2}) + NF(a\,^1\Delta) \xrightarrow{k_5} I(^2P^\circ_{3/2}) + NF(b\,^1\Sigma^+) + 110\ cm^{-1} \qquad (5)$$

with an approximately gas-kinetic rate constant $k_5 \approx 10^{15}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (the excited iodine atoms resulted from the rapid E–E transfer process $I(^2P^\circ_{3/2}) + O_2(a\,^1\Delta_g) \rightarrow I(^2P^\circ_{1/2}) + O_2(X\,^3\Sigma_g^-)$) [30]. By raising about 33% of the ground state iodine atoms to the excited state by intracavity iodine laser pumping, it was possible to convert about 33% of NF(a) into NF(b) and to maintain it in this state throughout the duration of the pumping iodine laser pulse. The achieved NF(b) population of 5.6×10^{-10} mol/cm^3 represented a 30-fold increase over the previously reported (see [30]) steady-state concentrations [31] (for preliminary results, see [32]).

$NF(X\,^3\Sigma^-)$. The ground state NF(X) radicals produced according to reaction (1a) with a very small initial population [17] (cf. p. 265) could not be detected either by microwave Zeeman spectroscopy (EPR) [33] or laser magnetic resonance (LMR) [34]. This is consistent with the prediction that NF(X) is more reactive than NF(a) [21]. It is remarkable that the IR laser absorption spectrum in the region of the fundamental vibration band of NF(X) could be recorded [35] by applying higher pumping speeds to the $H + NF_2$ reactive flow, which means shorter reaction times than in earlier studies [36] dealing with the fundamental band of NF(a).

The quenching of NF(a) and NF(b) to give NF(X) is covered in Section 4.1.9.2.9.

$NF_2 + CH_3$

The reaction of NF_2 and CH_3 (addition of CH_4 to the Ar–NF_3 discharge) resulted in a → X and b → X chemiluminescence both with intensities of 0.4 relative to those observed in the $NF_2 + H$ reaction. The formation of NF(a) was attributed to an addition-elimination reaction involving an excited intermediate (compare p. 265)

$$CH_3 + NF_2(^2B_1) \rightarrow CH_3NF_2(^1A) \rightarrow CH_3F^\dagger + NF(a\,^1\Delta) \qquad (6)$$

whereas the formation of NF(b) was ascribed to energy pooling of NF(a) with $HF(v \geq 2)$ according to reaction (3) (free F atoms produced in the NF_3 discharge react with CH_4 to give $HF^\dagger$ and CH_3). The lower yields of the NFs, as compared with the $H + NF_2$ reaction, are obviously due to a second reaction channel for the dissociation of the excited intermediate, that is, $CH_3NF_2 \rightarrow HCN + 2HF$ [23].

$NF_2 + O$, $NF_2 + N$

Chemiluminescence due to NF(b) and NF(a) was observed when NF_2 was introduced into a flow tube through which a stream of ground state $O(^3P^\circ)$ or $N(^4S^\circ)$ atoms in Ar carrier gas from a MW discharge was passed [22]. Kinetic investigations of the $NF_2 + O$ (cf. p. 348) and $NF_2 + N$ (cf. p. 349) reactions were carried out by monitoring the decrease of the O or N concentrations by atomic resonance absorption and atomic resonance fluorescence in a discharge-flow system at 298 K under pseudo-first-order conditions. At initial concentration ratios $[NF_2]_0/[O]_0 \geq 30$, resonance fluorescence yielded a rate constant $k_7^{298\,K} = (1.8 \pm 0.9) \times 10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ which was ascribed to the reaction channel

$$NF_2 + O \xrightarrow{k_7} NF + OF \tag{7}$$

Resonance absorption yielded a similar value, but of lower accuracy (agreement within a factor of 2 of the fluorescence result) [18].

For initial ratios $[NF_2]_0/[N]_0 > 10$, resonance fluorescence yielded $k_8^{298\,K} = (4.6 \pm 0.3) \times 10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ [25] attributed to the reaction channel

$$NF_2 + N \xrightarrow{k_8} 2NF \tag{8}$$

A value of lower accuracy, $k_8^{298\,K} = (3.0 \pm 1.2) \times 10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$, was obtained from the resonance absorption for $[NF_2]_0/[N]_0 = 15$ [18].

No distinction was made between NF(a), NF(b), or NF(X) in reactions (7) and (8).

$F + HN_3$

Chemiluminescence due to NF(a) and NF(b) was observed in a flow tube when small amounts of HN_3 were allowed to react with F atoms [5, 37 to 39]. The results suggested that a very rapid H abstraction from HN_3 was followed first by the reaction of N_3 with F to give NF(a),

$$F + HN_3 \xrightarrow{k_9} HF(v \leq 5) + N_3;\ \Delta H^\circ = -54\ kcal/mol\ for\ v = 0 \tag{9}$$

$$F + N_3 \xrightarrow{k_{10}} NF(a\,^1\Delta) + N_2;\ \Delta H^\circ = -55 \pm 8\ kcal/mol \tag{10}$$

and then by a V–E transfer process between NF(a) and $HF^\dagger$ to give NF(b) (reaction (3), p. 265). No evidence for a direct production of NF(b) analogous to reaction (10) could be found [37, 38]. The postulated reactions (9) and (10) were supported by the observation of $HF^\dagger$ overtone emissions from vibrational levels with v = 5, 4, and 3 [37, 38], by the observation of the characteristic UV absorption spectrum of the azide radical [39], and by the fact that the yield of NF(a) (measured from the time decay of the $a \rightarrow X$ emission) is near unity in the low-density limit [5, 39]. For low F atom concentrations the $b \rightarrow X$ and $HF^\dagger$ emissions exhibited a similar temporal behavior. The $a \rightarrow X$ and $b \rightarrow X$ intensities measured as a function of the HN_3 amount (pseudo-first-order conditions $[F]_0 \gg [HN_3]_0$) clearly indicated a second-order process for NF(b) formation: over more than 5 orders of magnitude in the NF(b) concentration, the NF(b) concentration varied quadratically with the NF(a) concentration, which in turn was linear with the HN_3 concentration at low HN_3 concentration and deviated from linearity with increasing HN_3 concentration [37, 38]. Arguments based on the quenching experiments with CO_2 (an efficient $HF^\dagger$ quencher) [37, 38] were rejected later, because the same effects could be observed when CO_2 was replaced by SF_6 which does not significantly quench $HF^\dagger$ [5, 39]. Finally, experiments with DN_3 instead of HN_3 precluded the direct formation of NF(b) (cf. p. 265) [5].

The rate constant for reaction (10) was estimated from the risetime of the $a \rightarrow X$ emission assuming $k_9 \gg k_{10}$, that is, the separability of processes (9) and (10). Then $k_{10} = (\tau_{rise} \cdot [F])^{-1}$ (where

$[F] \gg [HN_3]$) is valid, hence $k_{10} \approx 10^{12}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ ($2 \times 10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$) [37]. $k_9 \geq 1 \times 10^{-11}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ was later determined [40]. A second reaction mechanism was proposed involving a long-lived FHN_3 intermediate which dissociates into NHF and N_2 rather than HF and N_3 [41]. The NHF fragment, which was expected to decompose into $HF^†$ and N, however, was ruled out as a potential source of NF(a) [40] (cf. [42] and p. 269).

In order to study the possibility of using reactions (9) and (10) as a source for a chemical NF or NF–Bi laser, scale tests of the $F + HN_3$ and $F + DN_3$ reactions were carried out; scaling to densities required for an efficient laser gain was not feasible. The yield of NF(a) falls off rapidly with increasing initial HN_3 concentration. Because of $k_9 \gg k_{10}$, significant N_3 concentrations are certainly available. However, N_3 can undergo very rapid second-order side reactions, for example, self-annihilation or decay collisions with the parent HN_3 [5] (see also [39]).

It was pointed out that in none of the experiments was any evidence obtained suggesting direct population of ground state NF(X) [5]. However, two bands in the He I photoelectron spectrum of NF produced by the $F + HN_3$ reaction were recorded (see p. 276) and attributed to the ionization of NF(X) [43].

$F(F_2) + NH_3 + O_2$

The green luminescence due to NF(b→X), $v = 0 \rightarrow 0$, $0 \rightarrow 1$, $1 \rightarrow 1$, was observed when singlet molecular oxygen $O_2(a\ ^1\Delta_g)$ was added to the reacting mixture of NH_3–He and F atoms in a low-pressure flow tube. The intensity was found to depend strongly on the concentration ratio $[NH_3]_0/[F]_0$. At a fixed F concentration the intensity increased steadily with the NH_3 concentration and reached a maximum at $[NH_3]_0/[F]_0 \approx 1/3$ to $1/2$, then decreased rapidly with further increase in NH_3 concentration. For $[NH_3]_0 \geq [F]_0$ the emission disappeared completely. For NH_3 and F concentrations fixed at their optimum ratio, the intensity was found to increase linearly with the O_2(a) concentration. The intensity decay (after ca. 10 to 30 ms) obeyed first-order kinetics; the decay rate was independent of the O_2(a) concentration in the tested range of concentrations. Complete extinction could be obtained by allowing small amounts of CO_2 (an efficient $HF^†$ quencher) to flow into the reacting mixture. No visible emission was observed in the absence of O_2(a). The following scheme for generation and excitation of NF was inferred from the experimental results [44, 45]:

$$F + NH_3 \rightarrow NH_2 + HF(v \leq 2),\ \Delta H°(v=0) = -109 \pm 8\ kJ/mol \qquad (11)$$

$$F + NH_2 \rightarrow NH + HF(v \leq 4),\ \Delta H°(v=0) = -167 \pm 21\ kJ/mol \qquad (12)$$

$$F + NH \rightarrow NF(X\ ^3\Sigma^-) + H,\ \Delta H° = 13 \pm 54\ kJ/mol \qquad (13)$$

$$NF(X\ ^3\Sigma^-) + HF(v \geq 3) \rightarrow NF(a\ ^1\Delta) + HF(v-3)\ \text{or} \qquad (14)$$

$$F_2 + NH \rightarrow NF(a\ ^1\Delta) + HF,\ \Delta H° = -397 \pm 54\ kJ/mol \qquad (15)$$

and (compare p. 266)

$$NF(a\ ^1\Delta) + O_2(a\ ^1\Delta_g) \rightarrow NF(b\ ^1\Sigma^+) + O_2(X\ ^3\Sigma_g^-),\ \Delta H° = -8 \pm 33\ kJ/mol \qquad (4)$$

The experimental evidence was not sufficient to decide whether reactions (13) and (14) or reaction (15), or an alternate two-step process $F + NH \rightarrow N + HF$ and $N + F_2 \rightarrow NF + F$ was responsible for the NF(a) formation. The quenching experiments with CO_2, however, suggested that $HF^†$ might be involved [44, 45].

In a repetition of earlier experiments [44, 45], using, however, reactant concentrations that were approximately 20 to 30 times higher, both the a→X and b→X emissions were observed along with NH(b→X) and the $HF^†$ second-overtone bands [46]. The b→X emission intensity versus time exhibited an initial rise, then a fall after 1.8 ms and a second rise at approximately 4 ms with a long decay. This provided evidence for two reaction mechanisms of NF(b) excitation such as energy pooling with $HF(v \geq 2)$ (see reaction (3), p. 265) for the initial rise and the slower transfer process between $O_2(a)$ and NF(a) (reaction (4), see above) for the second rise. The a→X emission was observed after quenching the $HF^†$ overtone emission (same spectral region as a→X emission) by CO_2, but only in the presence of $O_2(a)$. The result, however, does not rule out the formation of NF(a) by $HF^†$ according to reaction (14). The NF(b) yield from the $F+NH_3+O_2(a)$ reaction was found to be less than 0.1% of the initial NH_3 concentration [46].

In consideration of these recent results [44 to 46], an earlier observation [47] of weak b→X luminescence (in addition to strong NH(A→X) luminescence) in the reaction of NH_3 with F atoms (from discharges in CF_4 or F_2–Ar) presumably was due to the presence of O_2 impurities, the existence of which has been admitted at least for F_2 [47].

$F+N_2$

Addition of a small quantity of N_2 into a MW discharge through CF_4 resulted in NF(a) and presumably NF(X) formation, since b→X emission occurred upon addition of HF($v \geq 3$). The b→X emission and the vibrational-rotational population in $HF^†$ could be interpreted in terms of V–E processes between NF(a) and HF(v = 2 and 3) (see reaction (3), p. 265) and between NF(X) and HF(v = 3) (reaction analogous to (3) involving $\Delta v = 3$) [48].

NF_3+Al

In the chemiluminescent flame from the reaction of Al vapor with excess NF_3, the a→X and b→X emissions were observed and attributed to the exoergic reactions [49]:

$$NF_3 + Al \rightarrow NF_2 + AlF + 4.4\ eV \tag{16}$$

$$NF_2 + Al \rightarrow NF + AlF + 3.6\ eV \tag{17}$$

F+HNF

The observation of $HF^†$ (v up to 5) in the reaction of F atoms with HNCO, although $v \leq 2$ is only allowed for F + HNCO → HF + NCO, suggested a second reaction channel, F + HNCO → HNF + CO and formation of NF [42] (cf. p. 268) according to (only IR luminescence of HF studied):

$$F + HNF \rightarrow NF(X\,^3\Sigma^-) + HF(v \leq 5) \tag{18a}$$

$$\rightarrow NF(a\,^1\Delta) + HF(v \leq 2) \tag{18b}$$

$$\rightarrow NF(b\,^1\Sigma^+) + HF(v = 0) \tag{18c}$$

$N+O_2F$

The observation of the $N_2(B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+)$ emission in the reaction of O_2F with active nitrogen was attributed to the formation of NF(a) or NF(b) intermediates,

$$N + O_2F \rightarrow NF^* + O_2,\ \Delta H \approx -60\ kcal/mol \tag{19}$$

and N_2 production by means of $N + NF(a\ or\ b) \rightarrow N_2^* + F$ [50].

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4.1.9.1.2 Matrix-Isolated NF

The formation of NF in inert matrices at low temperatures was proved by the appearance of IR bands at about 1115 and 1095 cm^{-1} attributed to the fundamental vibrations of ^{14}NF and ^{15}NF, respectively (cf. p. 284).

Flash photolysis of NF_2 in Ar or Kr matrices at 4 K (heating of the gaseous mixtures N_2F_4–Ar or N_2F_4–Kr to ca. 150°C prior to deposition) was monitored by noting the disappearance of the NF_2 bands and the growth of the NF and one of the NF_3 bands, which suggested the reactions $NF_2 \xrightarrow{h\nu} NF + F$ and $F + NF_2 \rightarrow NF_3$ (summarized as $2NF_2 \xrightarrow{h\nu} NF + NF_3$) [1]. NF formation was observed after photolysis of Ar–FN_3 (also Ar–$F^{15}N^{14}N_2$) at 4 K ($FN_3 \xrightarrow{h\nu} NF + N_2$) [2, 3], photolysis of samples of Ar–F_2 and Ar–HN_3 (also Ar–$H^{15}N^{14}N_2$ and Ar–DN_3) at 14 K ($F + HN_3 \rightarrow HF + N_3$ and $N_3 \xrightarrow{h\nu} N_2 + N$, $F + N \rightarrow NF$ or less likely $N_3 + F \rightarrow FN_3$, $FN_3 \xrightarrow{h\nu} NF + N_2$) [4], and photolysis of Ar–NF_3 at 14 K [5].

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4.1.9.1.3 NF in Solution

Reactions of nucleophiles with difluoroamine or certain precursors have been rationalized by mechanisms involving NF as a reactive species. Thus, NF has been postulated as a reactive intermediate in the basic hydrolysis of NHF_2; for more details, see "Fluorine" Suppl. Vol. 5. Another example is the reaction of a nucleophile with an α-difluoroamino carbonyl compound. The feasibility of this type of reaction was illustrated in a paper [1] on the reaction of aqueous hydroxide with N,N-difluorourea at low temperatures according to

$$F_2NCONH_2 + OH^- \rightarrow H_2NCOOH + NF_2^-$$
$$NF_2^- \rightarrow NF + F^-$$

In a similar manner NF was thought to be generated by the reaction of N,N-difluoroisopropyl carbamate with potassium t-butoxide

$$F_2NCO_2\text{-i-}C_3H_7 + {}^{-}OC(CH_3)_3 \rightarrow (CH_3)_3COCO_2\text{-i-}C_3H_7 + NF_2^-$$
$$NF_2^- \rightarrow NF + F^-$$

This system can also be employed in nonaqueous solutions [2, 3].

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4.1.9.2 Molecular Properties and Spectra

4.1.9.2.1 Electronic Structure. Internuclear Distance

Lowest Energy Electron Configuration

According to MO theory, the lowest energy electron configuration of the four core and twelve valence electrons is (in contrast to the isoelectronic O_2 molecule, cf. [1, pp. 343/6]) $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^2$.

The MOs 1σ to 4σ correlate with the F1s, N1s, F2s, and N2s AOs, 5σ is the N2pσ–F2pσ bonding orbital, and 1π and 2π are the bonding and antibonding combinations of N2pπ and F2pπ (see e.g., [2]). This configuration gives rise to the ground state $X\,^3\Sigma^-$ and two excited metastable states $a\,^1\Delta$ and $b\,^1\Sigma^+$.

Experimental Results. The analogues of the red and infrared atmospheric oxygen bands [1, pp. 278/9] were discovered in the emission spectrum of NF produced and excited by a discharge through Ar–NF_3. The green emission at 529 nm was identified with the "forbidden" $b\,^1\Sigma^+ \rightarrow X\,^3\Sigma^-$ transition [3, 4], the near-IR emission at 874 nm with the "forbidden" $a\,^1\Delta \rightarrow X\,^3\Sigma^-$ transition [3, 5]. Rotational analyses gave the term values $T_0(=\nu_{00}) = 18905.20\ cm^{-1}$ (2.34 eV) and $T_e = 18877\ cm^{-1}$ for the $b\,^1\Sigma^+$ state and $T_0 = 11435.16\ cm^{-1}$ (1.42 eV) for the $a\,^1\Delta$ state ($T = 12003.60\ cm^{-1}$ [6, p. 454] is the energy of the v = 0 level of $a\,^1\Delta$ relative to the minimum of the $X\,^3\Sigma^-$ state potential curve).

The original values for the internuclear distances, $r_e(X\,^3\Sigma^-) = 1.3173$ Å, $r_e(b\,^1\Sigma^+) = 1.3001$ Å [4], and $r_0(a\,^1\Delta) = 1.3082$ Å [5] were revised (based on an improved value for the Planck constant) to give

$$r_e(X\,^3\Sigma^-) = 1.3169_8\ \text{Å},\ r_e(b\,^1\Sigma^+) = 1.2998_3\ \text{Å, and}\ r_0(a\,^1\Delta) = 1.3079\ \text{Å}\ [6,\ p.\ 454].$$

Theoretical Results. A survey of ab initio SCF–MO (restricted Hartree-Fock) and configuration interaction (CI) calculations for NF in the three lowest states $X\,^3\Sigma^-$, $a\,^1\Delta$, and $b\,^1\Sigma^+$ is presented in Table 15, p. 273. It contains the total molecular energies E_T and the corresponding (calculated or experimental) bond lengths r, and, for sake of completeness, a listing of other molecular data obtained from the respective wavefunctions.

In addition to the results given in Table 15, bond lengths for $NF(X\,^3\Sigma^-)$ were calculated with various basis sets (STO-3G, 3-21G, 6-31G*) using the restricted and unrestricted Hartree-Fock procedures (RHF and UHF) and Møller-Plesset perturbation theory at second and third order (MP2 and MP3) (r_e between 1.30 and 1.39 Å) [26] and with the 6-31G* basis set using UHF, CI, MP2, and MP3 methods (r_e between 1.30 and 1.33 Å) [27]. Geometry optimizations were carried out for $NF(X\,^3\Sigma^-)$(RHF, 4-31G basis) [28] and for $NF(X\,^3\Sigma^-,\ a\,^1\Delta,\ b\,^1\Sigma^+)$ (large CI calculations, no details) [29].

Table 15

NF(X $^3\Sigma^-$, a $^1\Delta$, b $^1\Sigma^+$). Ab Initio Calculations[a].

Total experimental energy of NF(X $^3\Sigma^-$): $E_{exp}=-154.5404$ a.u. [7]. Total correlation energy of NF(X $^3\Sigma^-$) (estimated): $E_{corr}=-0.606$ a.u. [8]. Experimental internuclear distances: r_e(X $^3\Sigma^-$) = 1.3173 Å [4], r_0(a $^1\Delta$) = 1.3082 Å [5], r_e(b $^1\Sigma^+$) = 1.3001 Å [4]. E_T in a.u., r_e in Å.

$-E_T$(X $^3\Sigma^-$) r_e	$-E_T$(a $^1\Delta$) r_e	$-E_T$(b $^1\Sigma^+$) r_e	method[b]	basis set	calculated molecular parameters[c]	Ref.
154.18472 1.3145	154.1362 1.315	154.0986 1.300	MRD CI	ext. GTO	E(r), $\varepsilon_i(2\pi)$, μ, ω_e, D	[36]
154.20337 1.316	154.1534 1.314	154.1176 1.301	"full" CI (estimated)			
154.1390			MRD CI + "full" CI estimate	ext. GTO	ΔH for F+HNF→HF+NF	[9]
153.81109			SCF			
1.341			SCF			
153.83526 r_e(exp)	153.76887 r_0(exp)	153.70791 r_e(exp)	SCF	ext. STO	ε_i, μ, Θ, A, other expectation values charges [10]	[7]
153.83520 1.30			SCF	ext. STO	ε_i, μ, Θ, E(r), ω_e, $\omega_e x_e$, B_e, α_e	[11]
153.8311 r_e(exp)	153.7649 r_0(exp)	153.7024 r_e(exp)	SCF	ext. STO	ε_i charge density [13], force constants [14], transformation of wavefunction into the momentum space representation [15]	[12]
153.8201 1.2911			SCF	6-311G*	μ, ω_e	[16]
153.7828 1.3646			SCF	6-311G		
153.58257	153.50879		SCF	4-31G		[17]
151.73353	151.65639			STO-3G		
1.324	1.342			STO-3G		
153.29375 1.382	153.2270 1.369	153.1983 1.378	SCF+CI	min. STO	E(r), ω_e, $\omega_e x_e$, B_e, α_e, D_e, D_0 transformation of wavefunction into the momentum space representation [19]	[18]
153.2928 1.381	153.2268 1.367	153.1968 1.367	SCF+CI	min. STO	E(r), ω_e, $\omega_e x_e$, B_e, α_e	[20, 21]
153.2046 1.296[e]	153.1138[d] 1.296[e]		SCF	min. STO	E(r), $\varepsilon_i(2\pi, 1\pi)$	[22, 23]

Table 15 (continued)

$-E_T(X\,^3\Sigma^-)$ r_e	$-E_T(a\,^1\Delta)$ r_e	$-E_T(b\,^1\Sigma^+)$ r_e	method[b)]	basis set	calculated molecular parameters[c)]	Ref.
— r_e(exp)			SCF+ perturbation theory	ext. STO	spin-spin interaction, singlet-triplet transition energies [24], matrix element of electronic angular momentum [25]	[24, 25]

[a)] The most commonly used abbreviations and symbols are given in Table 7, p. 235. – [b)] MRD CI = multi-reference double-excitation CI, "full" CI = CI without configuration selection. – [c)] ΔH = reaction enthalpy, A = electron affinity, ω_e, $\omega_e x_e$, B_e, α_e = vibrational and rotational constants, D = dissociation energy. – [d)] Publications [22] and [23] give identical results; the excited state, however, is labeled a $^1\Delta$ in [22] and b $^1\Sigma^+$ in [23], the latter obviously in view of the discovery of the b→X emission spectrum, see "note added in proof" in [23]. – [e)] Calculated E_T minima at 2.44 a.u. (=1.291 Å) for X $^3\Sigma^-$ and 2.43 a.u. (=1.286 Å) for a $^1\Delta$ or b $^1\Sigma^+$.

The few semiempirical studies dealt with the molecular correlation energy of NF (X $^3\Sigma^-$, b $^1\Sigma^+$) (effective-pair correlation method) [30], the bond lengths of NF(X $^3\Sigma^-$, a $^1\Delta$) (MNDO approximation) [31], the bond lengths of "singlet" and "triplet" NF (CNDO, INDO) [32], the valence MO energies of NF(X $^3\Sigma^-$) (CNDO) [33], and the populations in "singlet" and "triplet" NF (CNDO, INDO) [34] and NF(X $^3\Sigma^-$) (extended Hückel method) [35].

Excited Configurations

An excited state $\cdots(1\pi)^4(5\sigma)^1(2\pi)^3\ ^1\Pi$ was recently detected by its radiative decay to b $^1\Sigma^+$, occurring between 440 and 570 nm [40].

No other reliable experimental results on states corresponding to excited configurations of NF are available. An emission system observed in the Ar–NF_3 discharge at 334.4 nm and tentatively attributed to NF($^3\Pi$) [37] was reassigned as the NH(A $^3\Pi \rightarrow$ X $^3\Sigma^-$) system [38]. The assignment of two absorption systems observed between 120 and 180 nm upon flash photolysis of N_2F_4 to Rydberg transitions in NF is very tentative [39].

A number of unobserved excited states were studied by ab initio methods [21, 24, 29, 36].

The lowest excited electron configurations correspond to the following states (see [1, pp. 336/7], [36]):

$\cdots(1\pi)^4(5\sigma)^1(2\pi)^3$	$^{1,3}\Pi$
$\cdots(1\pi)^4(5\sigma)^2(2\pi)^1(6\sigma)^1$	$^{1,3}\Pi$
$\cdots(1\pi)^3(5\sigma)^2(2\pi)^3$	$^{1,3}\Sigma^-$, $^{1,3}\Delta$, $^{1,3}\Sigma^+$

The $^3\Pi$, $^1\Pi(5\sigma\rightarrow 2\pi)$, and $^1\Pi(2\pi\rightarrow 6\sigma)$ states were found to be repulsive; vertical excitation energies from X $^3\Sigma^-$ obtained by MRD CI (and extrapolation for "full" CI) are ΔE = 7.22 (7.14), 9.48(9.35), and 9.63(9.39) eV, respectively [36]. Single configuration SCF calculations for $^3\Pi$ and $^1\Pi(5\sigma\rightarrow 2\pi)$ gave $\Delta E \approx 29000$ and 40000 cm^{-1} (3.6 and 5.0 eV) [24].

The lowest bound $^3\Pi$ $(2\sigma\rightarrow 6\sigma)$ state was obtained by MRD CI ("full" CI) at T_e = 5.39(5.04) eV with r_e = 2.11(2.09) Å and ΔE = 7.82(7.69) eV [36].

Results for the six states arising from the $\cdots(1\pi)^3(5\sigma)^2(2\pi)^3$ configuration are contradictory. The states $^3\Sigma^-$, $^1\Sigma^-$, $^3\Delta$, and $^3\Sigma^+$ (obviously the analogues of the four lowest "ungerade" states of O_2, cf. [6, pp. 494/8]) were found to be bound by two CI calculations: T_e = 43554, 45167, 45570, and 45973 cm^{-1} (5.40, 5.60, 5.65, and 5.70 eV) at r_e=1.6700, 1.6414, 1.6594, and 1.6629 Å, respectively (large CI, no details) [29] and T_0 = 43719, 44824, 45328, and 45495 cm^{-1} (5.42, 5.56, 5.62, and 5.64 eV) at r_e=1.853, 1.783, 1.803, and 1.812 Å, respectively (valence CI, minimum STO basis) [21]. The MRD CI calculation (extended GTO basis) predicted a bound $^3\Sigma^-$ state, T_e=5.10(5.04) eV, T_0=5.06(5.00) eV at r_e=2.125(2.087) Å, ΔE=9.64(9.49) eV ("full" CI extrapolation in parentheses), but repulsive $^1\Sigma^-$, $^3\Delta$, and $^3\Sigma^+$ states, ΔE=8.87(8.83), 8.99(8.87), and 9.24(8.98) eV, respectively [36]. A bound $^1\Sigma^+$ state was found at T_0 = 47598 cm^{-1} (5.90 eV) with r_e=1.945 Å [21], $T_e\approx$6.5 eV with $r_e\approx$1.7 Å [29, figure 6], and $T_e\approx$6.3 eV with $r_e\approx$2.1 Å [36, figure 9]. The remaining $^1\Delta$ state is repulsive [21, 29, 36], ΔE=10.47(10.35) eV [36], ≈9.5 eV [21, figure 1].

Further repulsive states $^{1,3,5}\Sigma^-$, $^{1,3}\Sigma^+$, $^{1,3}\Delta(\cdots(1\pi)^4(5\sigma)^1(2\pi)^2(6\sigma)^1)$, $^{1,3,5}\Pi$, $^{1,3}\Phi(\cdots(1\pi)^3(5\sigma)^2(2\pi)^2(6\sigma)^1)$, and $^{1,3}\Sigma^+$, $^{1,3}\Sigma^-$, $^{1,3}\Delta(\cdots(1\pi)^3(5\sigma)^2(2\pi)^1(6\sigma)^2)$ were obtained by a recent MRD CI calculation [36], and (without giving the electron configurations) $^1\Sigma^+$, $^3\Sigma^-$, $^1\Delta$ [21] and $^{1,3}\Sigma^+$, $^{1,3}\Sigma^-$, $^{1,3}\Delta$ [29] by earlier CI studies.

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4.1.9.2.2 Ionization Potentials. Electron Affinity

Adiabatic and vertical **ionization potentials** $E_i(ad) = 12.26 \pm 0.01$ eV and $E_i(vert) = 12.63 \pm 0.01$ eV corresponding to $NF(X\,^3\Sigma^-) \rightarrow NF^+(^2\Pi)$, and $E_i(ad) = 10.84 \pm 0.01$ eV and $E_i(vert) = 11.21 \pm 0.01$ eV corresponding to $NF(a\,^1\Delta) \rightarrow NF^+(^2\Pi)$, were derived from the He I photoelectron spectrum obtained from the $F + HN_3$ reaction (cf. pp. 267/8). The spectrum exhibited two bands in the region 9.0 to 14.0 eV with clearly resolved vibrational structure. The separation of the two adiabatic ionization potentials, 1.42 ± 0.01 eV, compares well with the separation of the zeroth vibrational levels in the $X\,^3\Sigma^-$ and $a\,^1\Delta$ states of NF, 1.418 eV, observed in the $a\,^1\Delta \rightarrow X\,^3\Sigma^-$ emission spectrum (cf. pp. 286/7). The vibrational structure showed only one vibrational mode of the positive ion to be present in each band, indicating that the same ionic state is involved in both ionization processes. Consistent with the ionization from the antibonding 2π orbital is the fact that the observed vibrational frequency, $\omega_e = 1520 \pm 40\ cm^{-1}$, in the ionic state is greater than those in the $X\,^3\Sigma^-$ and $a\,^1\Delta$ states of NF (cf. p. 279) [1].

Electron impact values for the first $E_i(vert)$ stem from the mass spectra of NF_3 [2] and NF_2 [3 to 5]: The appearance potential of NF^+, $AP = 17.9 \pm 0.3$ eV attributed to the process $NF_3 \rightarrow NF^+ + 2F + e^-$, and estimated bond strengths $D(NF_2{-}F)$ and $D(NF{-}F)$ gave $E_i = 12.0$ eV [2]. The appearance potentials of NF^+, $AP = 11.86$ eV attributed to $NF_2 \rightarrow NF^+ + F^-$ and $AP = 15.46$ eV attributed to $NF_2 \rightarrow NF^+ + F + e^-$, along with the electron affinity of F and $D(NF{-}F)$ resulted in an average value of $E_i = 12.24 \pm 0.2$ eV [4]. An earlier estimate, $E_i \leq 12.4 \pm 0.3$ eV, was derived in the same way from $AP = 11.8 \pm 0.2$ and 15.5 ± 0.2 eV [3]. The mean value $E_i = 13.1 \pm 0.2$ eV was recommended [6], based on the appearance potentials of NF^+ from NF_3 [2, 3], NF_2, and cis-N_2F_2 [3] and appropriate ΔH_f° values. Contrary to the above interpretations of the observed APs, $AP(NF^+) = 11.82 \pm 0.06$ eV was directly attributed to the ionization of NF (pyrolysis of N_2F_4 or NF_2 at 470 K) and the value $E_i = 11.8 \pm 0.2$ eV was recommended [5]. This, however, appears to be disproved by the photoelectron spectrum of the $F + HN_3$ reaction.

An interpolation procedure for XF molecules with X = Li to F predicted $E_i \approx 12.9$ eV [7].

Theoretical values for E_i were obtained from the differences of the calculated total molecular energies of NF^+ and NF (ΔSCF method; occasionally including correlation energy corrections) [1, 6, 8, 17] or from the molecular orbital energies (Koopmans' theorem) [6, 9 to 12]. Ab initio ΔSCF values (double zeta GTO basis plus d functions; $r_e(NF^+) = r_e(NF)$ assumed) are E_i(vert) = 13.44, 15.51, and 16.23 eV for the ionization of the 2π, 5σ, and 1π orbitals in NF($X\,^3\Sigma^-$) (resulting in the ionic states NF^+($X\,^2\Pi$, $^4\Sigma^-$, and $^4\Pi$)) and E_i(vert) = 11.63, 16.76, and 17.47 eV for the corresponding ionizations in NF($a\,^1\Delta$) (resulting in NF^+($X\,^2\Pi$, $^2\Delta$, and $^2\Phi$)). The first ionization potentials of NF($X\,^3\Sigma^-$) and NF($a\,^1\Delta$) increase to E_i(vert) = 13.52 and 11.71 eV, respectively [1], based on an estimated correlation energy change on ionization, NF($X\,^3\Sigma^-$) → NF^+($X\,^2\Pi$), of 0.08 eV [6, 9]. Ab initio Δ(SCF + CI) values (minimum STO basis; optimized r_e's for NF and NF^+) are E_i(ad) = 9.7, 12.0, and 13.2 eV for the ionization of the 2π, 1π, and 5σ orbitals in NF($X\,^3\Sigma^-$) [8] (5σ ionization results in a $^4\Sigma^-$ state, not $^4\Sigma^+$ as reported [8]). For the first E_i of NF($X\,^3\Sigma^-$), E_i(vert) = 13.2 ± 0.3 eV (ΔSCF including the correlation energy correction; extended STO basis approaching Hartree-Fock limit; $r_e(NF^+) = r_e(NF)$) [6] and E_i(vert) = 12.36 eV (Δ(SCF + CI); extended GTO basis; optimized r_e's for NF($X\,^3\Sigma^-$) and NF^+($^2\Pi$)) [17] were calculated.

Orbital energies ε_i for all seven MOs 1σ to 2π of NF($X\,^3\Sigma^-$) [6, 9, 10], NF($a\,^1\Delta$), and/or NF($b\,^1\Sigma^+$) [6, 10] result from ab initio MO calculations using extended STO basis sets. For ε_i of 1π and 2π of NF($X\,^3\Sigma^-$) a minimum STO basis was used [11, 12]. From $\varepsilon_i(2\pi)$ [11, 12] and a semiempirical estimate for the correlation energy correction, E_i = 11.42 eV followed for the first E_i of NF($X\,^3\Sigma^-$) [13]. A CNDO value is $-\varepsilon_i(2\pi)$ = 11.63 eV [14]. $E_i = D(NF) - D(NF^+) + E_i(N)$ = 14.20 eV was derived from CNDO calculated dissociation energies D of NF and NF^+ [15].

For the **electron affinity** of NF only theoretical values are available. From the total molecular energies of ground state NF and NF^- (same r_e assumed) and the corresponding correlation energy difference A = 0.6 ± 0.5 eV (14 ± 12 kcal/mol) [6] and later A = −0.1 eV [9] were calculated. Semiempirical values A = −0.12 eV for NF($X\,^3\Sigma^-$) and A = +0.96 eV for NF($a\,^1\Delta$) are the differences of the corresponding ΔH_f° values of NF and NF^- (MNDO approximation) [16], and A = 2.64 eV for NF($X\,^3\Sigma^-$) is the difference of the dissociation energies of NF^- and NF (CNDO approximation) augmented by the experimental electron affinity of F [15].

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4.1.9.2.3 Dipole Moment μ. Quadrupole Moment Θ

$\mu(a\ ^1\Delta) = (\pm)0.37 \pm 0.06$ D was obtained from a study of the Stark effect in the EPR spectrum of NF in the J = 2 rotational level of the first excited state a $^1\Delta$; the search for ground state NF(X $^3\Sigma^-$) by EPR was unsuccessful [1]. For Θ no experimental results are available.

Ab initio SCF-MO values (extended STO basis sets) at the respective experimental bond lengths are $\mu(X\ ^3\Sigma^-) = -0.41$ D, $\mu(a\ ^1\Delta) = -0.17$ D (with the negative end of the dipole at F) and $\mu(b\ ^1\Sigma^+) = +0.08$ D [2], $\mu(X\ ^3\Sigma^-) = -0.167$ a.u. (−0.424 D), $\mu(b\ ^1\Sigma^+) = -0.021$ a.u. (−0.053 D) [3]; for the calculated Hartree-Fock minimum of $r_e = 1.30$ Å, $\mu(X\ ^3\Sigma^-) = -0.323$ D was obtained [4]. A large-scale CI calculation (extended GTO basis) gave $\mu(X\ ^3\Sigma^-) = -0.081$ D and $\mu(a\ ^1\Delta) = +0.22$ D at the optimized bond lengths $r_e(X\ ^3\Sigma^-) = 1.3145$ Å and $r_e(a\ ^1\Delta) = 1.315$ Å [8].

The triple split valence Gaussian basis sets 6-331G and 6-311G* gave $\mu(X\ ^3\Sigma^-) = 0.855$ and 0.291 D, respectively, at the calculated bond lengths (see Table 15, p. 273). A comparison with some other diatomic molecules, for which experimental dipole moments are known, indicated the 6-311G* values to be more reliable [5]. Semiempirical values are (no discussion on the sign of μ; presumably N^+F^-) $\mu(X\ ^3\Sigma^-) = 0.441$ D at r_e(exp) (CNDO) [6], $\mu(X\ ^3\Sigma^-) = 0.16$ D (INDO), and μ("singlet NF") = 0.26 D (INDO), 0.01 D (CNDO), all at $r_e = 1.35$ Å [7].

The ab initio calculated quadrupole moments are (in 10^{-26} esu·cm^2): $\Theta(X\ ^3\Sigma^-) = -0.75$, $\Theta(a\ ^1\Delta) = -0.68$, and $\Theta(b\ ^1\Sigma^+) = -0.62$ (experimental r_e's) [2], $\Theta(X\ ^3\Sigma^-) = -0.80$ (optimized r_e) [4] (measured from the center of mass of the molecule).

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4.1.9.2.4 Vibrational and Rotational Constants. Potential Energy Functions

Experimental Results. The experimental spectroscopic constants for NF(X$^3\Sigma^-$, a$^1\Delta$, b$^1\Sigma^+$, c$^1\Pi$) are given in Table 16, p. 279, along with some explanatory comments regarding the methods of derivation.

The spectroscopic constants for NF(X $^3\Sigma^-$) and NF(b $^1\Sigma^+$) of [1] were used for the calculation of some type of Rydberg-Klein-Rees potential energy curves, that is, ground state energy values for v″ = 0, 2, 4, 6 (568.4 to 7039.1 cm^{-1}), and excited state energy values for v′ = 0, 2, 4 (596.6 to 5213.7 cm^{-1}) as well as the corresponding classical turning points r_{min} and r_{max} [9]. The "experimental" potential energy curves for NF (X $^3\Sigma^-$), NF(a $^1\Delta$), and NF(b $^1\Sigma^+$), see Fig. 7, p. 280, given without any further comment [10], were obviously based on earlier spectroscopic data [1, 2].

Table 16
NF($X\,^3\Sigma^-$, $a\,^1\Delta$, $b\,^1\Sigma^+$, $c\,^1\Pi$). Experimental Vibrational and Rotational Constants (all in cm^{-1}).

state	$T_e(T_0=\nu_{00})$	$\omega_e(\Delta G_{1/2})$	ω_ex_e	$B_e(B_0)$	$10^2\cdot\alpha_e$	$10^6\cdot D_e(D_0)$	$10^7\cdot\beta_e$	remark	Ref.
$X\,^3\Sigma^-$	0	1141.37	8.99	1.2056_8	1.492	(5.39)		a)	[1,3]
				$(1.1980_0$ $\pm 0.0003)$		(4.6)		b)	[2]
		(1123.2788 ±0.0030)		1.205679 ±0.000160	1.4889 ±0.0160	5.6 ±0.8	1.7	c)	[5]
$a\,^1\Delta$	(11435.16) [12003.60]			(1.2225 ±0.0003)		(4.5 ±0.3)		b)	[2,3]
		1184	8.5					d)	[4]
		1182.95 (1165.952 ±0.001)		1.22991 ±0.00007	1.447 ±0.001	5.2 ±0.1	0.51 ±0.37	e)	[6]
$b\,^1\Sigma^+$	18877.05 (18905.20)	1197.49	8.64	1.2377_0	1.448	(5.28)		a)	[1,3]
$c\,^1\Pi$	(41698±3)	(568±3)						f)	[18]

a) Rotational analysis of the 0–0, 1–1, 2–2, 0–1, and 1–2 bands of the $b\,^1\Sigma^+ \rightarrow X\,^3\Sigma^-$ emission spectrum at 529 nm. The ground state rotational levels were fitted to the Schlapp expressions (see [7, p. 223]), which consider the effects of spin-rotation and spin-spin interaction in addition to the effects of rotation including centrifugal distortion. The energy levels of the excited state were fitted in the usual way by the constants B and D. The values given for the centrifugal distortion are averages for v = 0 and 1. The spin-rotation and spin-spin interaction constants are $\gamma = -0.0048$ cm^{-1} and $\lambda = 1.21 \pm 0.02$ cm^{-1} [1]. $\lambda = 1.215$ cm^{-1} (no error limit given) comes from the analysis of the $a\,^1\Delta \rightarrow X\,^3\Sigma^-$ emission spectrum (see remark c)) [2].

b) Rotational analysis of the 0–0 band of the $a\,^1\Delta \rightarrow X\,^3\Sigma^-$ emission spectrum at 874 nm (for details, see remark a)) [2]. The term value in brackets is explained on p. 272.

c) Rotational analysis of the high-resolution IR-laser absorption spectrum in the region of the fundamental vibration band of NF($X\,^3\Sigma^-$) at 1090 to 1150 cm^{-1}. For the rotational levels (including centrifugal distortion, spin-rotation and spin-spin interaction) extensions [8] of the Schlapp formulas were used. Constants γ_v and λ_v for v = 0 and 1 are $\gamma_0 = -0.00465(60)$ cm^{-1}, $\gamma_1 = -0.00457(60)$ cm^{-1}, and $\lambda_1 = 1.2111(20)$ cm^{-1} with λ_0 fixed at 1.215 cm^{-1} (see remark a)) [5].

d) Derived from the wavelengths of the 0–0, 1–1, and 2–2 bands of the $a\,^1\Delta \rightarrow X\,^3\Sigma^-$ emission spectrum [4] using ground state constants [1].

e) Rotational analysis of the high-resolution IR-laser absorption spectrum in the region of the fundamental vibration band of NF($a\,^1\Delta$) at 1114 to 1207 cm^{-1} [6]. $\Delta G_{1/2}$ is the band center ν_0 and $\omega_e = \nu_0 + 2\omega_ex_e$ was obtained by using the anharmonicity correction $\omega_ex_e = 8.5$ cm^{-1} of [4].

f) Derived from the $c\,^1\Pi \rightarrow b\,^1\Sigma^+$ emission spectrum at 440 to 570 nm [18].

Theoretical Results. Generally, the ab initio ω_e values for the states X, a, and b are larger (up to 220 cm^{-1}) than the experimental values [11 to 14, 16], except $\omega_e(X\,^3\Sigma^-)$ [15] and $\omega_e(a\,^1\Delta)$ [10]. For the ground state, $\omega_e = 1151.8$ cm^{-1}, calculated by the MRD CI method (extended GTO basis) and extrapolated to $\omega_e = 1138.5\ \text{cm}^{-1}$ for a "full" CI calculation agrees best with experiment [16]. The $\omega_e x_e$ values are also slightly larger than the experimental results [12 to 14] except those of [11] which are too large by a factor of about 2. The rotational constants B_e were reproduced within $+0.02$ and $-0.2\ \text{cm}^{-1}$, and the interaction constants α_e within -0.01 and $+0.005\ \text{cm}^{-1}$ [10 to 14].

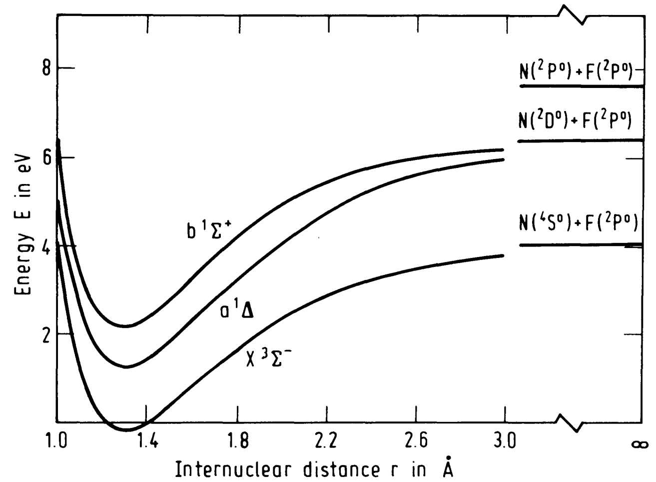

Fig. 7. Potential energy curves of NF in the ground state $X\,^3\Sigma^-$ and lowest excited states $a\,^1\Delta$ and $b\,^1\Sigma^+$. The zero energy is set at the ground vibrational level ($v=0$) of $NF(X\,^3\Sigma^-)$.

Calculated potential energy curves were depicted for the three lowest states [10, 11, 13, 14, 16].

Three CI calculations dealt with the potential curves for a number of unknown excited states (cf. pp. 274/5) [10, 14, 16].

For the lowest bound $^3\Pi$ state (correlating with $N(^2D^o)+F(^2P^o)$) the potential curve gave $\omega_e = 372$ (MRD CI) or $520\ \text{cm}^{-1}$ ("full" CI). Corresponding values for the lowest bound $^3\Sigma^-$ state ($N(^2D^o)+F(^2P^o)$) are $\omega_e = 458$ or $520\ \text{cm}^{-1}$. The potential curve for the bound $^1\Sigma^+$ state ($N(^2P^o)+F(^2P^o)$) was given [16]. In calculations [10, 14] which predicted bound $^3\Sigma^-$, $^1\Sigma^-$, $^3\Delta$, $^3\Sigma^+$ states ($N(^2D^o)+F(^2P^o)$) and gave nearly identical term values and similar bond lengths, satisfactory agreement, however, was not achieved for the spectroscopic constants (in cm^{-1}): $\omega_e = 432$ to 494, $\omega_e x_e \approx 22$ to 36, $B_e \approx 0.61$ to 0.66, $10^2 \cdot \alpha_e \approx 2.2$ to 3.2 [14], $\omega_e \approx 790$ to 1050, $\omega_e x_e \approx 52$ to 89, $B_e \approx 0.75$ to 0.78, and $10^2 \cdot \alpha_e \approx 0.9$ to 3.0 [10]. For $^1\Sigma^+$: $\omega_e = 513$, $\omega_e x_e = 28.3$, $B_e = 0.551$, and $10^2 \cdot \alpha_e = 0.565\ \text{cm}^{-1}$ [14].

Potential curves for a great number of repulsive states, correlating with $N(^4S^o)+F(^2P^o)$, $N(^2D^o)+F(^2P^o)$, and $N(^2P^o)+F(^2P^o)$, were calculated and depicted [10, 14, 16].

The spin-spin interaction constant λ for the ground state $X\,^3\Sigma^-$ and its contributions λ_{ss} due to first-order dipolar spin-spin interaction and λ_{so} due to second-order spin-orbit interaction (interaction between $X\,^3\Sigma^-$ and states $b\,^1\Sigma^+$, $^{1,3}\Pi$ ($\sigma\pi^3$ configuration) considered) were obtained from an ab initio perturbation calculation (extended STO basis): $\lambda_{ss} = 0.985\ \text{cm}^{-1}$, $\lambda_{so} = 0.296\ \text{cm}^{-1}$ (λ_{so} ($b\,^1\Sigma^+$) $= 0.305\ \text{cm}^{-1}$, $\lambda_{so}(^3\Pi) = 0.030\ \text{cm}^{-1}$, $\lambda_{so}(^1\Pi) = -0.039\ \text{cm}^{-1}$). Thus $\lambda = 1.281\ \text{cm}^{-1}$ is in good agreement with the experimental value (see Table 16, remark a), p. 279) [17].

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4.1.9.2.5 Dissociation Energy D

The dissociation energy of NF has only been estimated from spectroscopic or thermochemical data and from a few quantum chemical calculations.

$D_0^\circ = 3.5 \pm 0.3$ eV (81 kcal/mol), derived by [1] and adopted by [2], is the average of two similar values arrived at by independent methods. The first, $D_0^\circ = 3.6 \pm 0.3$ eV (28810 cm^{-1}) came from a linear Birge-Sponer extrapolation of the ground state spectroscopic data ($v'' = 0$ to 2) [3] (extrapolation modified according to [4]; without modification: $D_0^\circ = 4.4$ eV [5]). The second, $D_0^\circ = 77.5 \pm 5.5$ kcal/mol (3.4 ± 0.2 eV) was based on the relationship $D_0^\circ(XF)/\Delta H_{at}^\circ(XF_2) = 0.56 \pm 0.04$, which holds for the fluorides of B, C, and O, and was adopted for N, and using the atomization energy $\Delta H_{at}^\circ(NF_2) = 138.4$ kcal/mol (see p. 251).

$D_0^\circ = 71.4$ kcal/mol (3.1 eV) in the JANAF Tables [6] is the average of $D_0^\circ = 72.4$ kcal/mol estimated from isoelectronic series [7] and $D_0^\circ = 70.4$ kcal/mol which is one half of $\Delta H_{at}(NF_2) = 140.8$ kcal/mol (cf. p. 251).

$D_0^\circ = 71 \pm 10$, $D_{298}^\circ = 72 \pm 10$ kcal/mol, recommended by [8], are based on $D_0^\circ = 71$ kcal/mol which is the estimated average bond strength in NF_2 and N_2F_4 [9] and on the error limit given by [10] ($D_0^\circ = 60 \pm 10$, $D_{298}^\circ = 61$ kcal/mol were estimated from the mean N–H and N–F bond energies in NH_3 and NF_3, and from $D_0^\circ(NH)$ [10]; but the method was considered unreliable, see [5]).

$D_{298} = 295$ kJ/mol (70.5 kcal/mol) was quoted [11] within a consistent scheme of bond energies based on $\Delta H_f(NF_3)$ and $\Delta H_f(NF_2)$ [12].

$D_0 = 54.6 \pm 5$ kcal/mol was derived from a mass spectrometric study of NF_3 photoionization but using too low a value for $\Delta H_f(F)$ [13].

$D_e = 4.48$ eV (≈ 36000 cm^{-1}) was estimated [14] by approximating the RKR potential curve for NF($X\,^3\Sigma^-$) calculated from the spectroscopic constants [3] by a five-parameter Hulburt-Hirschfelder potential function [15].

D_e(NF, a $^1\Delta$) = 4.6 ± 0.3 eV was estimated from the a $^1\Delta \leftrightarrow X\,^3\Sigma^-$, $v = 0 \leftrightarrow 0$ separation of 1.42 eV [16] and D_e(NF, $X\,^3\Sigma^-$) = 3.6 ± 0.3 eV (from D_0° of [1]) on the assumption that NF($X\,^3\Sigma^-$) dissociates into N($^4S^\circ$) and F($^2P^\circ$) and NF(a $^1\Delta$) into N($^2D^\circ$) and F($^2P^\circ$) [17].

Theoretical Values. The Hartree-Fock binding energy (ab initio SCF wavefunction near HF limit) is $D_{HF} = 0.025$ (+0.01, −0.00) a.u. = 0.7(+0.3, −0.0) eV. Allowing for correlation effects, $D = D_{HF} + \text{MECE} = 3.6(+0.4, -0.2)$ eV = 0.131 a.u. was derived with the molecular extra correlation energy MECE = 0.106 a.u. obtained from calculated atomic correlation energies for N and F and an estimated NF correlation energy of −0.608 ± 0.01 a.u. (interpolated from CF, OF, and F_2) [1]. (A semiempirical estimate for the correlation energy combined with the above Hartree-Fock value [1] resulted in D = 61.8 kcal/mol (2.7 eV) only [18].)

An ab initio MRD CI calculation (see p. 274) for the ground state with an extended GTO basis gave $D_e = 2.94$ eV; $D_e = 3.03$ and $D_0 = 2.96$ eV (expected error ≤ 0.2 eV) are the extrapolated values which might be obtained from a "full" CI calculation, that is, without configuration selection [19]. Ab initio CI calculations with a minimum STO basis for the ground state $X\,^3\Sigma^-$ and the excited states a $^1\Delta$ and b $^1\Sigma^+$ resulted in $D_e(D_0)$ = 18424(17791), 30420(29758), and 24111(23435) cm^{-1}, respectively, (≙ 2.28(2.21), 3.77(3.69), and 2.99(2.90) eV) [20].

A CNDO study gave D = 81.8 kcal/mol [21], an extended Hückel calculation D = 74.2 kcal/mol [22], and a simple semiempirical MO approximation D = 69.9 kcal/mol [23] (≙ 3.54, 3.22, and 3.03 eV, respectively).

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4.1.9.2.6 Electron Paramagnetic Resonance

The EPR spectrum of NF in its lowest excited state a $^1\Delta$ (for production, see p. 265) was studied at a microwave frequency of 9328.50 MHz [1, 2]. Twenty-four lines observed at magnetic fields of 9441.50 to 10510.28 G were identified with the four $\Delta M_J = +1$ transitions, $M_J'' = -2, -1, 0, 1$, between the magnetic sublevels of the $J = 2$ rotational level. Each ΔM_J transition exhibited hyperfine structure due to $\Delta M_I = 0$ transitions. The large fluorine ($I = \frac{1}{2}$) hf splitting divided the spectrum into two groups of twelve lines, below ($M_I(^{19}F) = +\frac{1}{2}$) and above ($M_I(^{19}F) = -\frac{1}{2}$) 10011 G. The small nitrogen ($I = 1$) hf interaction caused the triplet splitting ($M_I(^{14}N) = -1, 0, +1$) of each ΔM_J, $M_I(^{19}F) = \pm\frac{1}{2}$ component [1, 2]. The spectrum was analyzed by allowing for the effects of rotation (constant B_0), hf interactions due to the nuclear spins (hf constants $a(^{19}F)$ and $a(^{14}N)$) and the nitrogen nuclear quadrupole moment (quadrupole coupling constant eq_NQ_N), and Zeeman interaction (nuclear rotational g factor g_r, effective orbital g factor g_L). The hf interaction constants were $a(^{19}F) = +758.06 \pm 0.23$ MHz, $a(^{14}N) = +109.92 \pm 0.14$ MHz, and $eq_NQ_N = +4.10 \pm 0.23$ MHz. The values of B_0, g_L, and g_r are closely related, but the observation of a single rotational level cannot determine g_r; thus $B_0 = (1.2229 + 3.66\, g_r) \pm 0.0005$ cm^{-1} and $g_L = (1.00005 + 0.5\, g_r) \pm 0.0003$. The g factors become $g_L = 1.0000 \pm 0.0003$ and $g_r = (-1 \pm 1.5) \cdot 10^{-4}$ [2] by adopting the optical value $B_0 = 1.2225 \pm 0.0003$ cm^{-1} [3].

Observation of the EPR spectrum in a Stark cavity yielded the dipole moment of NF(a $^1\Delta$) (see p. 278) [2].

The EPR spectrum of ground state NF(X $^3\Sigma^-$) could not be obtained [2] contrary to the conclusions drawn in the preliminary studies [1] (see also [4, p. 206]).

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4.1.9.2.7 Vibrational and Rotational Spectra

Gaseous NF. The fundamental vibration-rotation bands of the free NF radical in its ground state X $^3\Sigma^-$ and lowest excited state a $^1\Delta$ were measured at high resolution using a tunable diode laser spectrometer [1, 2]. For the ground state X $^3\Sigma^-$, which is an example of Hund's case (b) coupling scheme (see [3, pp. 221/4]), fifty-one lines in two ranges, 1092.5848 to 1113.5288 cm^{-1} and 1130.2597 to 1147.6508 cm^{-1}, could be identified as P-branch ($N = 4$ to 12) and R-branch ($N = 2$ to 8, 10) transitions, respectively. Each P- and R-branch transition exhibits a triplet splitting due to $\Delta J = \Delta N$ transitions between the three substates, $J = N + 1, N, N - 1$, of each rotational level (transitions with $\Delta J \neq \Delta N$ were not detected). No Q branch is permitted by the selection rules for Hund's case (b). The wavenumbers were fitted to the expressions for the rotational energies [4], which include the effects of rotation plus centrifugal distortion and the spin-spin and spin-rotation interactions. The analysis yielded the value for the band center and other spectroscopic constants (see p. 279) [1]. For the lowest excited state a $^1\Delta$ which belongs to Hund's case (a) coupling scheme (see [3, pp. 219/21]) thirty-one lines, between 1114.6787 and 1153.4357 cm^{-1}, 1164.9085 and 1165.8636 cm^{-1}, and 1180.0127 and 1206.7666 cm^{-1}, were identified with the P-branch ($J = 5, 6, 9, 10$ to 19), Q-branch ($J = 2$ to 6, 8), and R-branch ($J = 5$ to 11, 14 to 18) transitions, respectively. The analysis which included only the effects of rotation and centrifugal distortion yielded the band center and other spectroscopic constants (see p. 279). Several of the lower J components in all three branches showed resolved hyperfine structure due to ^{19}F and partially resolved hfs due to ^{14}N. In the case of the ^{19}F hfs, good agreement with the EPR results for NF(a $^1\Delta$) (see p. 283) was obtained [2].

The pure rotational transition $J = 7 \rightarrow 8$ in the a $^1\Delta$, $v = 0$ state was detected by far-IR laser magnetic resonance using the 513 μm laser line in formic acid (19.49305 cm^{-1}) and magnetic fields up to 1.9 T. With the electric vector of the laser perpendicular to the magnetic field five transitions with $\Delta M_J = -1$, $M_J'' = 1$ to 5 were observed, with the electric vector parallel to the magnetic field three transitions with $\Delta M_J = 0$, $M_J = 5$ to 7. In both polarizations, each M_J transition is resolved into a doublet of triplets due to the hyperfine interaction with the $^{19}F(I = 1/2)$ and $^{14}N(I = 1)$ nuclei. A higher resolution scan of the $M_J = 6$ parallel transition exhibited a nitrogen hfs of 7.9 ± 0.2 mT and a fluorine hfs of 60.8 mT which are comparable to the EPR results (see p. 283). Small asymmetries in the triplet and doublet spacings were attributed to quadrupole and second-order magnetic hyperfine effects [5].

Matrix-Isolated NF. The fundamental vibration band of NF (obviously in its ground state if compared with the gas-phase results) was identified with the absorption bands observed upon photolysis of NF_2, FN_3, $F_2 + HN_3$, or NF_3 in inert gas matrices:

sample	T in K	ν in cm^{-1}	Ref.
Ar–NF_2, Kr–NF_2	4	1115	[6]
Ar–FN_3($F^{15}N^{14}N_2$)	4	1115 (^{14}NF), 1094 (^{15}NF)	[7, 8]
Ar–F_2 + Ar–HN_3(DN_3)	14	1112, 1116, 1122	[9]
Ar–F_2 + Ar–$H^{15}N^{14}N_2$	14	1112, 1116 (^{14}NF), 1091, 1095, 1101 (^{15}NF)	
Ar–NF_3	14	1115	[10]

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4.1.9.2.8 Electronic Spectra

Since the discovery and first analysis of two NF emission systems excited by microwave discharges through Ar–NF_3 mixtures [1 to 3], the formation and the decay of excited NF radicals could be demonstrated and studied in detail in various other systems by observing the green ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) and near-IR ($a^1\Delta \rightarrow X^3\Sigma^-$) chemiluminescence (cf. Sections 4.1.9.1.1 and 4.1.9.2.9). Recently, seven red-degraded emission bands were observed in the region 440 to 570 nm from the dissociative charge-transfer reaction of He^+ with NF_3. They were assigned as $c\ ^1\Pi\ (v'=0,1) \rightarrow b\ ^1\Sigma^+\ (v''=1 \text{ to } 4)$ by analogy with the PF molecule [28]. Attempts to observe an electronic absorption spectrum in the near-UV, visible, and near-IR were unsuccessful [4, 5].

Visible Emission. The $b\ ^1\Sigma^+ \rightarrow X\ ^3\Sigma^-$ System

The green glow observed [1, 3] downstream from an Ar–NF_3 discharge consisted of five bands with heads at 5288, 5272, 5255, 5622, and 5598 Å and relative intensities of 100:10:1:10:1. The emissions turned out to be the 0→0, 1→1, 2→2, 0→1, and 1→2 ($v' \rightarrow v''$) components of the "forbidden" $^1\Sigma^+ \rightarrow {}^3\Sigma^-$ transition in NF, made possible by spin-orbit interaction. The rotational structure is that expected from the dipole selection rules ($+ \leftrightarrow -$, $\Delta J = 0, \pm 1$) for a transition between a $^1\Sigma^+$ state (J = N) and a $^3\Sigma^-$ state (Hund's case (b), J = N, N ± 1), cf. [6], [7, pp. 275/7]. Both the 0→0 and 0→1 bands consisted of three branches of a Q form ($\Delta N = 0$), namely, ^QQ (N″ = 1 to 4, 12 to 15 and N″ = 9, 16 to 24), ^QP (N″ = 1 to 32 and N″ = 2 to 30), and ^QR (same N″ as ^QP), one branch of S form ($\Delta N = +2$), ^SR (N″ = 0 to 24 and N″ = 1 to 27), and one of O form ($\Delta N = -2$), ^OP (N″ = 2 to 24 and N″ = 3 to 28). The 1→1 band exhibited the branches ^SR (N″ = 3 to 5, 7 to 13, 15, 17), ^OP (N″ = 7, 15 to 17, 19 to 21) and ^QR, ^QP (N″ = 3 to 8, 10 to 15, 17, 18, 20 to 27); the ^QQ branch was too weak to be observed. In the $^3\Sigma^-$ ground state the F_1 and F_3 levels (J = N ± 1) lie close together and somewhat below the F_2 level (J = N) (cf. [7, pp. 222/3]). Thus, the $^QP(N)$ and $^QR(N)$ lines due to spin-rotation and spin-spin interactions were resolved only for N″ > 19. For the weak 2→2 and 1→2 bands the unresolved ^QP and ^QR branches with N″ = 4 to 6, 8 to 10, 13 to 17 and N″ = 4 to 9, 11 to 13, respectively, could be recognized [1] (for molecular constants, see pp. 272, 279).

The spectroscopic constants [1] and Morse potential functions for both states were used to calculate the Franck-Condon factors [8, 9] and r-centroids [9, 10] for the observed and a number of unobserved $v' \rightarrow v''$ transitions in the b→X system.

The two unidentified bands at 528.7 and 527.2 nm (intensity ratio ca. 3:1) observed in NH_3–F_2 and N_2F_4–H_2 flames [5] are probably the 0→0 and 1→1 bands of the NF b→X system [1].

In the spectrum emitted from the H + NF_2 reaction at short reaction times (< 5 ms), the predominant 0→0 band and the weaker 1→1, 2→2, 3→3, and 4→4 bands were observed with partially resolved rotational structure (Q heads and clearly outstanding $^OP(N)$ and $^SR(N)$ branches). The relative intensities in this $\Delta v = 0$ sequence indicated a nonthermal vibrational distribution (298 K), which, however, relaxed rapidly in the flow tube, giving only weak 1→1 and 1→0 emission (in addition to 0→0) after about 30 ms [11]. A vibrational distribution of 0.95:0.04:0.01:0.003 for the v′ = 0 to 3 levels of $b\ ^1\Sigma^+$ was derived from the intensity ratios (peak heights) of the $\Delta v = 0$, v = 0 to 3 bands recorded after a reaction time of about 0.2 ms [12].

The spectrum observed (at low resolution) in the mixing region of NF_2 and metastable $Ar^*(^3P_{0,2})$ atoms exhibited the $\Delta v = -1$ sequence with v′ = 0 to 7 at about 570 to 540 nm, the $\Delta v = 0$ sequence with v′ = 0 to 6 at about 530 to 510 nm, and a weak band corresponding to the $\Delta v = 1$ sequence around 490 nm. Intensities and calculated Franck-Condon factors indicated a vibrational distribution of approximately 100:18:11:8:5:4:3:2 for the v′ = 0 to 7 levels. In the flowing afterglow (at ca. 5 cm downstream from the reaction zone; flow velocity ca. 16 m/s) only NF($b\ ^1\Sigma^+$, v′ = 0 to 2) with very low v′ = 2 population could be observed [13].

Radiative Lifetime τ_{rad}. Transition Moment. The decay of the intensity from NF(b $^1\Sigma^+$, v' = 0), excited by a pulsed Tesla-type discharge in slowly flowing, dilute NF_3–Ar mixtures, was measured at NF_3 concentrations of 2.5×10^{10} to 1.2×10^{13} molecules/cm^3, Ar pressures of 5 to 26.0 Torr, and Ar flow rates of 3.1×10^{-5} to 4.3×10^{-4} mol/s. The measured first-order decay was analyzed according to $k=\tau_{rad}^{-1}+k_{NF_3}[NF_3]+k_{Ar}[Ar]$, where k_{NF_3} and k_{Ar} are the quenching rate coefficients (see pp. 288/9). Data taken with $[NF_3]<3\times10^{12}$ molecules/cm^3, for which the effect of NF_3 quenching was within the scatter of data, gave $\tau_{rad}=22.6\pm1.7$ ms. For a less extensive set of experiments using N_2F_4 as the NF(b $^1\Sigma^+$, v' = 0) precursor, $\tau_{rad}=19\pm6$ ms was obtained [8]. Flow tube experiments [14] in the same laboratory were quoted to have resulted in $\tau_{rad}=28\pm8$ ms [8]. The emission decay for NF(b $^1\Sigma^+$, v' = 0) excited in the reaction of NF_2 with metastable Ar*($^3P_{0,2}$) was analyzed by considering the quenching by collisions with the wall of the flow tube in addition to the quenching by NF_2 and Ar and radiative decay. An upper limit was derived for τ_{rad}^{-1} (i.e., for zero quenching by the wall) of about 57 s^{-1} using $[NF_2]\approx$ (2 to 7) $\times10^{13}$ molecules/cm^3 and $p_{Ar}=0.5$ to 2.5 Torr; thus $\tau_{rad}\geq17$ ms [13]. Earlier experiments with NF(b $^1\Sigma^+$) obtained from the N + NF_2 and H + NF_2 reactions, but with less precisely known compositions of the flows, yielded $\tau_{rad}=160$ ms [15] and $\tau_{rad}=15\pm7$ ms [16, 17], respectively. The agreement of the latter value with more recent results [8, 14] was viewed as somewhat fortuitous [8].

The square of the electronic transition moment $|R_e|^2$, which is related to the radiative lifetime and the Franck-Condon factor $q_{v'v''}$ by $\tau_{rad}^{-1}=(64\pi^4/3h)\cdot|R_e|^2\cdot\sum_{v''}q_{v'v''}\cdot\nu_{v'v''}^3$ (variation of $|R_e|^2$ with r-centroid or vibrational level neglected; $\nu_{v'v''}$ = wavenumbers of the vibrational transitions) was calculated to be $|R_e|^2=(2.1_0\pm0.1_6)\times10^{-5}$ D^2 [8]. An ab initio calculation (extended STO basis), which considered also contributions from the transitions $^3\Pi$–X $^3\Sigma^-$ (unobserved) and $^1\Pi$–b $^1\Sigma^+$ (detected recently [28]) ($\cdots(1\pi)^4(5\sigma)^1(2\pi)^3\ {}^{1,3}\Pi$), resulted in $\mu_0=-0.00083$ a.u. $\triangleq-0.0021$ D and $\mu_1=0.0040$ a.u. $\triangleq0.0010$ D for the parallel (μ_0) and perpendicular (μ_1) transition moments (Watson's [18] definition) [19].

Near-IR Emission. The a $^1\Delta\rightarrow$ X $^3\Sigma^-$ System

A weak emission system in the near-IR at 866 to 881 nm could be detected [2, 3] in the afterglow of an Ar–NF_3 discharge. The first positive bands of N_2, which partly overlapped the NF bands, had to be eliminated from the spectrum (for technical details, see [2]). The NF spectrum consisted of a single band with its head near 874.2 nm, which was identified as the 0 → 0 band of the "forbidden" a $^1\Delta\rightarrow$ X $^3\Sigma^-$ transition. The rotational structure is that expected from the selection rules ($+\leftrightarrow-$, $\Delta J=0, \pm1$) for a transition between a $^1\Delta$ state (Hund's case (a), J = N with Λ-type doubling) and the $^3\Sigma^-$ ground state (see above) as has been discussed [7, pp. 226/7, 278/9], [20]: The 0 → 0 band exhibited two branches of a Q form ($\Delta N=0$), ^QQ (N" = 3 to 36) and unresolved $^QR+{}^QP$ (N" = 6 to 20), one branch of an S form ($\Delta N=+2$), ^SR (N" = 0 to 19) and one branch of an O form ($\Delta N=-2$), ^OP (N" = 6 to 19). Additionally, as a consequence of the Λ-type doubling in the a $^1\Delta$ state, two branches appeared of a P form ($\Delta N=-1$), ^PQ (N" = 3 to 27), ^PP (N" = 3 to 24) and two of an R form ($\Delta N=+1$), ^RQ, ^RR (N" = 1 to 36). The Λ-type splitting, however, was not resolved [2].

The a → X system was also observed in the H + NF_2 reaction. To prevent overlap by the vibration-rotation bands of HF($\Delta v=3$) and the B → A system of N_2, excess NF_2 and high flow velocities were chosen. A short reaction time of about 0.2 ms enabled the detection of the 1 → 1 and 2 → 2 bands at 870.9 and 867.6 nm in addition to the 0 → 0 band at 874.2 nm (rotational structure not resolved). The intensity ratios (peak areas) of this $\Delta v=0$ sequence indicated a vibrational distribution of 0.73 : 0.19 : 0.08 for the v' = 0, 1, and 2 levels of the a $^1\Delta$ state [12]. For reaction times greater than or equal to 5 ms, vibrational relaxation precluded the observation of the initially excited vibrational levels. The 0 → 0 band was observed with partially resolved rotational structure in the 880 to 865 nm range: ^{S}R, ^{R}Q, ^{R}R, ^{P}P, ^{P}Q, ^{O}P branches and mostly overlapped central ^{Q}Q, ^{Q}R, ^{Q}P branches [11].

Radiative Lifetime τ_{rad}. By comparing the NF(a→X) emission intensity from $H + NF_2 \rightarrow HF + NF$ (cf. p. 264) with the HF(v = 3→0) emission intensity from $H + ClF \rightarrow HF + Cl$ and using for the latter reaction the known rate constant, branching ratio, and vibrational distributions in HF, $\tau_{rad} = 5.6 \pm 0.6$ s was measured for the a $^1\Delta$ state [12]. This is in (fortuitous?) agreement with $\tau_{rad} \approx 5$ s, obtained earlier from less precise flow studies [16], but revises the value $\tau_{rad} = 0.7$ s derived (presumably later) by the same team [21, 22], see [23, p. 2].

UV Emission and Absorption

An emission system observed in the Ar–NF_3 discharge at 334.4 nm and attributed to NF($^3\Pi \rightarrow X\,^3\Sigma^-$) [24] was reassigned as the NH(A $^3\Pi \rightarrow X\,^3\Sigma^-$) system [17].

The assignment of two absorption band systems observed between 330 and 420 nm upon flash photolysis of 20:2:1 Ar–NF_3–COS mixtures to NF (or SF, or SF_2) is very tentative [25].

In the far UV, a transient absorption spectrum was observed between 120 and 180 nm upon flash-photolysis of NF_2 (N_2F_4 at 450 K) and tentatively attributed to Rydberg transitions in NF. Positions (in nm) and qualitative intensities of the diffuse absorption bands were: 120.26(m), 128.19(vw), 135.46(s), 136.22(m), 139.72(s), 145.2 ± 0.6(vw), 147.62(m), 150.95(vw), 162.0 ± 1.5(w), and 178.22(w). The bands at 136.22 and 139.72 nm were relatively short lived ($\tau_{rad} \approx 40\ \mu s$), those at 135.46, 147.62 and possibly that at 162.0 nm were found to be longer lived ($\tau_{rad} \approx 300\ \mu s$). This indicated that at least two states of NF were involved; the short- and long-lived bands, respectively, were attributed to either NF(a $^1\Delta$) and NF(X $^3\Sigma^-$) or NF(b $^1\Sigma^+$) and NF(a $^1\Delta$) [26]. The latter interpretation was (also tentatively) accepted [27].

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4.1.9.2.9 Quenching of Electronically Excited NF

NF(b $^1\Sigma^+$)

Quenching of NF(b) by various reagents was studied [1] in the flowing afterglow of the Ar($^3P_{0,2}$) + NF_2 reaction by measuring the decay of the NF(b→X) emission intensity I(b→X) which is proportional to the concentration of NF(b). The decay of NF(b) was assumed to consist of radiative decay, wall deactivation, and quenching by the Ar carrier gas, by the NF_2 precursor, and by the added reagents Q:

$$-d[NF(b)]/dt = \{\tau_{rad}^{-1} + k_w + k_{Ar}[Ar] + k_{NF_2}[NF_2] + k_Q[Q]\} \cdot [NF(b)]$$

Since the concentration of NF(b) was small compared to that of Ar, NF_2, and Q, pseudo-first-order kinetics were followed, and integration of the rate law gave $-\ln[NF(b)]/[NF(b)]_0 = k_{total} \cdot t$, where the pseudo-first-order decay constant k_{total} stands for the sum given in braces. For experiments without added reagents, no evidence for quenching by Ar, no obvious dependence of k_{total} on the concentration of NF_2, and a small deactivation probability ($\leq 10^{-3}$) for wall collisions (i.e., k_w small and independent of [NF(b)]) were found. Then, with added reagents Q, the slope of the ln I(b→X) versus Q concentration plot gave the quenching rate constant k_Q directly, see Table 17, p. 289. Generally, the concentration of Q was approximately 10^{13} to 10^{14} molecules/cm^3, and the intensity was measured at a fixed point in the flow tube corresponding to a reaction time of about 22 ms. Experiments with Q = Cl_2, Br_2, and CH_3Cl were also done using a movable detector along the flow tube. Plots of k_{total} versus the concentration of Cl_2 or Br_2 clearly demonstrated linearity for [Q] $\approx (5 \text{ to } 30) \times 10^{11}$ molecules/cm^3. For most molecular reagents the quenching mechanism was supposed to occur by way of an E-V transfer, except for Cl_2, Br_2, and O_2, which have low-energy electronic states and thus are appropriate for E-E transfer. For a number of reagents, H_2S, HBr, C_2H_4, C_2H_2, H_2, D_2, and perhaps NO, the NF(b) decay did not follow well-behaved first-order kinetics; for some cases the development of a wall quenching rate was strongly suspected to be dependent on the concentration of Q (i.e., k_w is no longer small and constant) [1].

In a study of the radiative decay of NF(b) generated in the Ar($^3P_{0,2}$) + NF_3 reaction, the quenching rate constants for Ar and NF_3 were measured [2]. The value for k_{NF_3} was larger by a factor of about 300 than that found later [1]. The discrepancy was attributed to impurities [2] in the NF_3 gas.

Quenching of NF(b) by HF, H_2, and H in the afterglow of the H + NF_2 reaction [3] and quenching of NF(b) by N_2 in the afterglow of the N + NF_2 reaction [4] were studied and the respective k_Q's obtained.

The short-lived ultraviolet absorption bands having NF(b) (or NF(a), cf. p. 287) in the lower state were removed by collisions with N_2, O_2, or NF_2 at 450 K. Upper limits for k_{N_2} and k_{O_2} and an approximate value for k_{NF_2} were thereby derived [5] (assignment to NF(b) also in [6]).

Quenching rate constants [1 to 5] are compiled in Table 17, p. 289.

Table 17
NF(b $^1\Sigma^+$). Quenching Rate Constants k_Q in 10^{-14} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 300 K. Results are from [1] if no other reference is given.

reagent	k_Q	reagent	k_Q	reagent	k_Q
HCl	30.2 ± 4.5	CF_3Br	1.2 ± 0.3	NF_2	≤ 0.5 ± 0.3
HF	97 ± 15	CF_4	0.6 ± 0.3		ca. 500 [5]b)
	ca. 170 [3]a)	C_3H_6	15.7 ± 6.5	N_2F_4	0.4 ± 0.2
NH_3	8.9 ± 1.5	O_2	3.8 ± 0.6	NF_3	0.6 ± 0.3
CH_4	22.1 ± 3.3		< 100 [5]b)		180 ± 70 [2]c)
CH_3F	20.7 ± 3.1	CO	1.5 ± 0.3	N_2	< 0.2
CH_3Cl	23.6 ± 3.5	NO	ca. 5 ± 2c)		0.02 ± 0.005 [4]
$CHCl_3$	6.4 ± 1.7	CO_2	0.53 ± 0.41		< 0.1 [5]b)
CH_3Br	17.9 ± 2.7	N_2O	0.33 ± 0.08	Ar	< 0.001 [2]
CH_3I	35.9 ± 5.4	Cl_2	2100 ± 300	H	ca. 500 [3]a), d)
CH_2Br_2	25.9 ± 5.2	Br_2	6000 ± 800	H_2	< 7 [3]a)
CF_3NO	11.6 ± 1.7				

a) k_Q (in $cm^3 \cdot mol^{-1} \cdot s^{-1}$) $= 1 \times 10^{12}$ for HF, 3×10^{12} for H, $< 4 \times 10^{10}$ for H_2 in [3]. – b) T = 450 K; attribution to NF(b) very tentative. – c) See text on p. 288. – d) For the H + NF reaction, see pp. 293/4.

A near-resonant E–E transfer between NF(b) (generated in the F + HN_3 reaction) and ground state IF (formed rapidly upon adding I_2 or CF_3I into the flow tube), that is, NF(b $^1\Sigma^+$) + IF(X $^1\Sigma^+$) → NF(X $^3\Sigma^-$) + IF(B $^3\Pi(0^+)$) − 49 cm^{-1}, was found to occur at a near gas kinetic rate. From the ratio of the IF(B → X) and NF(b → X) intensities plotted versus the partial pressures of the added I_2 or CF_3I, a lower limit was derived for the rate constant, $k_{IF} \geq 1.8 \times 10^6$ $Torr^{-1} \cdot s^{-1}$ [7].

NF(a $^1\Delta$)

For the quenching of the NF(a → X) emission in the afterglow of the H + NF_2 reaction by H_2, HF, NF, or NF_2, overall first-order rate constants (see above) were found to be in the range 75 to 150 s^{-1} (298 K). The radiative loss ($\tau_{rad}^{-1} \approx 0.18$ s^{-1}, see p. 287) is thus very small compared to the loss by collisional quenching [8]. Upper limits for the rate constants at 298 K, $k_{HF} < 1 \times 10^{11}$ and $k_{D_2} < 4 \times 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (1.7×10^{-13} and 7×10^{-14} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) were derived from flow studies [3].

The removal of the long-lived ultraviolet absorption bands having NF(a) (or NF(X), cf. p. 287) in the lower state by collisions with N_2, O_2, or NF_2 at 450 K occurred with rate constants $k_{N_2} < 10^{-16}$, $k_{O_2} < 10^{-13}$, or $k_{NF_2} \approx 2 \times 10^{-13}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, respectively, [5] (assignment to NF(a) also in [6]).

A near-resonant E–E transfer between NF(a) (generated in the D + NF_2 reaction) and ground state Bi atoms occurred when the NF(a) radicals were mixed into a stream of Bi vapor and Ar carrier gas. Atomic fluorescence due to the Bi($^2D^\circ_{3/2} \rightarrow {}^4S^\circ_{3/2}$) transition at 875.8 nm appeared in addition to the NF(a → X) emission suggesting the process NF(a $^1\Delta$) + Bi($^4S^\circ_{3/2}$) → NF(X $^3\Sigma^-$) + Bi($^2D^\circ_{3/2}$) + 16 cm^{-1}. The rate constant at 298 K, $k_{Bi} = 0.98 \times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, corresponding to a transfer cross section of about 200 $Å^2$, was derived from the time dependence of the Bi and NF emission intensities, assuming a radiative lifetime of about 1s for NF(a) (but see

p. 287) [9]. This large k_{Bi} could be rationalized by a theoretical model based on the crossings of the NF(a) + Bi($^4S^\circ$) and NF(X) + Bi($^2D^\circ$) potential curves at large interparticle distances [10]. k_{Bi} was revised by using the corrected $\tau_{rad}=5.6$ s [11] for NF(a) to give $k_{Bi}=1.75\times10^{-10}$ cm^3 · molecule^{-1} · s^{-1} [12]. A curve-crossing model assuming a charge-transfer state Bi$^+$NF$^-$, originally proposed [13], but later discarded by the same authors [10], led to a smaller transfer cross section corresponding to $k_{Bi}=1.4\times10^{-10}$ cm^3 · molecule^{-1} · s^{-1} [12].

In supersonic streams of NF(a) and Bi atoms population densities of Bi($^2D^\circ$), which are about 1% of those of NF(a), were demonstrated [14].

In addition to the NF(a→X) and Bi($^2D^\circ \rightarrow {}^4S^\circ$) emissions in the near-IR, a blue emission system centered around 450 nm was observed in a subsonic flow containing NF(a) radicals (from H + NF$_2$) and Bi atoms (metal vapor or gaseous trimethylbismuthine) which was identified as the BiF(A0$^+$ → X0$^+$) emission system. The processes, assumed to produce the excited BiF molecules, are the reaction of NF(a) with Bi($^2D^\circ$) to give ground state BiF(X0$^+$) (cf. p. 294) followed by a two-step process

$$NF(a\,^1\Delta) + BiF(X0^+) \xrightarrow{k_{BiF(X)}} NF(X\,^3\Sigma^-) + BiF(b\,^1\Sigma^+,\ v=4) + 80\ cm^{-1}$$

$$NF(a\,^1\Delta) + BiF(b\,^1\Sigma^+,\ v=0) \xrightarrow{k_{BiF(b)}} NF(X\,^3\Sigma^-) + BiF(A0^+,\ v=0) - 94\ cm^{-1}$$

The rate constants were estimated using the charge-transfer model [13] which suggested $k_{BiF(X)} \approx k_{Bi}$ and $k_{BiF(b)} = 1.65 \cdot k_{BiF(X)} \cdot \exp(-90\ cm^{-1}/kT) \approx k_{BiF(X)}$ at 300 K; thus, $k_{BiF(X)} \approx k_{BiF(b)} \approx 1.8 \times 10^{-10}$ cm^3 · molecule^{-1} · s^{-1} [12].

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4.1.9.3 Heat of Formation ΔH_f. Equilibrium Constants. Heat Capacity and Thermodynamic Functions

The following table lists ΔH_f° values derived from the dissociation energy D (both in kcal/mol); $\Delta H^\circ_{f,298}(N) \approx 113$ kcal/mol and $\Delta H^\circ_{f,298}(F) \approx 19$ kcal/mol were used (except [8], where too low a value, $\Delta H^\circ_{f,0}(F) = 15.45$ kcal/mol, was used (cf. "Fluorine" Suppl. Vol. 2, 1980, pp. 67/8). The remarks refer to the D values.

$\Delta H^\circ_{f,0}$	$\Delta H^\circ_{f,298}$	D_0	D_{298}	remark	Ref.
51 ± 7 (2.2 ± 0.3 eV)	—	81 (3.5 ± 0.3 eV)	—	a)	[1]
59.5 ± 8	59.5 ± 8	71.4	—	a)	[2]
—	61.4 ± 2.7	—	70.6 ± 2.4	b)	[3]
—	61.4 ± 4.2	—	70.5 ± 1.6	b)	[4]
—	61.4	—	70.5	a)	[5]
65.9345	65.9439	65.0000	65.9389	c)	[6]
71.0 ± 10	71.0(± 10)	60 ± 10	61 ± 10	a)	[7]
74 ± 5	—	54.6 ± 5	—	a)	[8]

a) See p. 281. – b) Average bond energy in NF_2. – c) D_0 assumed, based on average bond energy 66.4 ± 0.8 kcal/mol in NF_3 at 298 K [16].

Tabulations of $\Delta H^\circ_{f,T}$ [2, 6] and $\Delta G^\circ_{f,T}$ [2] at $T = 0$ to 6000 K (100 K intervals) were reported. The calculations were based on estimated spectroscopic constants and neglected electronic contributions from excited states (see below).

A semiempirical calculation resulted in $\Delta H^\circ_{f,298} = 31.6$ kcal/mol (MNDO approximation) for the formation of ground state $NF(X\,^3\Sigma^-)$ [9, 10] and $\Delta H^\circ_{f,298} = 56.3$ kcal/mol [9], 56.4 kcal/mol [10] for the formation of excited $NF(a\,^1\Delta)$ (MNDO + CI; without CI: 68.7 kcal/mol [10]).

Prior to the spectroscopic detection of gaseous NF, equilibrium constants for $N_2 + F_2 \rightleftharpoons 2NF$ and $N + F \rightleftharpoons NF$, heat capacity, and thermodynamic functions had been calculated and tabulated for $T = 0$ to 6000 K at 100 K intervals using partition functions which were based on estimated molecular constants [2, 6]. One set [6] of assumed values (in cm^{-1}) was: $\omega_e = 990$, $\omega_e x_e = 10.5$ $(= \omega_e^2/4D(NF))$, $D_e = 5.61 \times 10^{-6}$ $(= 4B_e^3/\omega_e^2)$, $\alpha_e = 0.016$ (Pekeris relation, cf. [11, p. 108]), and $B_e = 1.112$ from $r_e(NF_3) = 1.371$ Å which is accidentally equal to $r_e(NF)$. The results given in the JANAF Tables [2] (derived in 1960 to 1965) were based on $\omega_e = 1115$ cm^{-1}, the IR absorption band observed upon photolysis of FN_3 in an Ar matrix and attributed to NF [12], and on estimated values (in cm^{-1}) of $\omega_e x_e = 12.175$ (separation of vibrational levels assumed to be proportional to the vibrational quantum number), $\alpha_e = 0.0120$ (Pekeris relation), and $B_e = 0.923$ from $r_e = 1.51$ Å estimated by using the Guggenheimer relation [13] for single bonded molecules. Both evaluations [2, 6] did not include any contributions from electronically excited states in the partition functions. In the absence of better results, the following values may serve provisionally. Selected values from [6]:

T in K	100	298.15	500	1000
log K_p for $N_2 + F_2 \rightleftharpoons 2NF$	−143.2285	−47.4628	−27.9432	−13.4973
log (K_p/atm^{-1}) for $N + F \rightleftharpoons NF$	138.3565	43.2122	23.6325	9.0323
C°_p in cal·mol^{-1}·K^{-1}	6.9583	7.3828	8.0780	8.7691
S° in cal·mol^{-1}·K^{-1}	43.3923	51.1036	55.0969	60.9627
$H^\circ - H^\circ_0$ in kcal/mol	0.6946	2.1003	3.6656	7.9165
$-(G^\circ - H^\circ_0)$ in kcal/mol	3.6446	13.1361	23.8829	53.0462

Selected values from [2]:

T in K	100	298	500	1000
log K_p for $N_2+F_2 \rightleftharpoons 2NF$	−129.091	−42.669	−25.060	−12.035
C_p° in $cal \cdot mol^{-1} \cdot K^{-1}$	6.957	7.253	7.913	8.674
S° in $cal \cdot mol^{-1} \cdot K^{-1}$	43.760	51.427	55.339	61.113
$-(G^\circ - H^\circ_{298})/T$ in $cal \cdot mol^{-1} \cdot K^{-1}$	57.713	51.427	52.273	55.393
$H^\circ - H^\circ_{298}$ in kcal/mol	−1.395	0.000	1.533	5.720

The spectroscopic data for the three lowest electronic states of NF [14, pp. 454/5] were used to give polynomial expansions of the partition function Q and the equilibrium constant K_p (for $NF \rightleftharpoons N+F$) for the temperature range T = 1000 to 9000 K (astrophysical interest): $\log Q = a_0 + a_1 \cdot \log \Theta + a_2 \cdot (\log\Theta)^2 + a_3 \cdot (\log\Theta)^3$ with $\Theta = 5040/T$ and $a_0 = 4.5511$, $a_1 = -2.0680$, $a_2 = 0.5972$, $a_3 = -0.1613$; $\log K_p = b_0 + b_1 \cdot \log\Theta + b_2 \cdot (\log\Theta)^2 - \Theta \cdot D(NF)$ with p in Pa, $b_0 = 10.8509$, $b_1 = 0.5611$, $b_2 = -0.4198$, and D(NF) = 3.5 eV [15]. Thus for T = 1000 K, $\log K_p = -20.281$ and −25.275 corresponding to K_p in Pa and atm, respectively (cf. above).

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4.1.9.4 Chemical Behavior

4.1.9.4.1 Gaseous NF

NF + NF

Analysis of the decay (NF_2, NF) and growth (N_2, F) curves obtained from the mass spectrum of shock-heated NF_2 (2200 to 3000 K) at t = 0 to 150 μs indicated rapid bimolecular reaction of the NF radicals

$$NF + NF \xrightarrow{k_1} N_2 + 2F \quad (1)$$

with $k_1 \approx 4 \times 10^{-11}$ cm^3·molecule^{-1}·s^{-1} (2.5×10^{13} cm^3·mol^{-1}·s^{-1}) at 2500 K. An excited N_2F_2 molecule (excitation energy ≈ 100 kcal/mol) was assumed to be an intermediate [1].

Mass spectrometric detection of atomic fluorine in the reaction zone of the $N + NF_2$ reaction was assumed to be consistent with the removal of NF by reaction (1) [2]. The rapid reaction (1) constituted the predominant decay channel for NF radicals formed in the $H + NF_2$ reaction. $k_1 = (7.0 \pm 3.5) \times 10^{-11}$ cm^3·molecule^{-1}·s^{-1} at 298 K was derived by a computer model of the reaction scheme for the overall $H + NF_2$ system (containing excess H_2) and by fitting of the $H(^2S)$ atom and $N(^4S^\circ)$ atom profiles obtained from atomic resonance absorption in the vacuum UV. Reaction (1) was assumed to proceed by way of a weakly bound N–N–F species which collisionally dissociates into N_2 and F; the alternative reaction channel $2NF \rightarrow N + NF_2$ was ruled out [3]. No distinction was made between ground- and excited-state NFs. In view of the relatively high molecular concentrations used, fast electronic quenching of the initially (and predominantly) formed $NF(a\,^1\Delta)$ was assumed to occur. Reaction (1) was attributed to two ground-state $NF(X\,^3\Sigma^-)$ radicals; no evidence for rapid NF(a) + NF(a) or NF(a) + NF(X) reactions was found [3, 4].

All possible combinations of ground- and excited-state NF radicals, which are consistent with the potential energy functions for the various electronic states of N_2 and NF and consistent with the rules of spin and orbital angular momentum conservation were discussed. The corresponding reaction enthalpies estimated on the basis of D(N–F) = 70 kcal/mol are given in the following table (the processes that form molecular fluorine (ΔH in parentheses) are improbable because near four-center encounters are necessary) [5]:

reaction		ΔH_{300} in kcal/mol
$NF(X\,^3\Sigma^-) + NF(X\,^3\Sigma^-) \rightarrow N_2(X\,^1\Sigma_g^+) + 2F(F_2)$	(1)	−81 (−119)
$NF(a\,^1\Delta) + NF(a\,^1\Delta) \rightarrow N_2(a'\,^1\Sigma_u^-) + 2F(F_2)$	(2)	+46 (+8)
$NF(b\,^1\Sigma^+) + NF(b\,^1\Sigma^+) \rightarrow N_2(a'\,^1\Sigma_u^-) + 2F(F_2)$	(3)	+3 (−35)
$NF(X\,^3\Sigma^-) + NF(a\,^1\Delta) \rightarrow N_2(B\,^3\Pi_g) + 2F(F_2)$	(4)	+17 (−21)
$NF(X\,^3\Sigma^-) + NF(b\,^1\Sigma^+) \rightarrow N_2(B\,^3\Pi_g) + 2F(F_2)$	(5)	−5 (−43)
$NF(a\,^1\Delta) + NF(b\,^1\Sigma^+) \rightarrow N_2(a'\,^1\Sigma_u^-) + 2F(F_2)$	(6)	+24 (−14)
$NF(X\,^3\Sigma^-) + NF(X\,^3\Sigma^-) \rightarrow N(^4S^\circ) + NF_2(^2B_1)$	(7)	+4
$NF(X\,^3\Sigma^-) + NF(a\,^1\Delta) \rightarrow N(^2D^\circ) + NF_2(^2B_1)$	(8)	+26
$NF(b\,^1\Sigma^+) + NF(b\,^1\Sigma^+) \rightarrow N(^2D^\circ) + NF_2(^2B_1)$	(9)	+4

On the basis of scaling experiments with NF(a) [6], the rate constants for reactions (2) and (6) were estimated to be $k_2 \approx k_6 \leq 10^{12}$ cm^3·mol^{-1}·s^{-1} (1.7×10^{-12} cm^3·molecule^{-1}·s^{-1}) [5].

NF + H

Computer modelling of the $H(^2S)$ and $N(^4S^\circ)$ atom profiles observed in the $H + NF_2$ reaction by atomic resonance absorption (cf. above) resulted in $k_{10} = (2.5 \pm 0.5) \times 10^{-13}$ cm^3·molecule^{-1}·s^{-1} at 298 K for the reaction

$$NF + H \xrightarrow{k_{10}} N + HF \qquad (10)$$

where no distinction was made between ground- and excited-state NF (the $N(^4S^\circ)$ atoms arose either directly from reaction (10a) (below) or by decay of metastable $N(^2D^\circ)$ atoms produced by reaction (10b)) [3]. The state selective reactions, consistent with the correlation rules for spin and orbital angular momentum

$$NF(X\,^3\Sigma^-) + H(^2S) \rightarrow N(^4S^\circ) + HF(X\,^1\Sigma^+) \qquad (10a)$$

$$NF(a\,^1\Delta) + H(^2S) \rightarrow N(^2D^\circ) + HF(X\,^1\Sigma^+) \qquad (10b)$$

were studied by measuring the $N(^4S°)$, $N(^2D°)$, and $N(^2P°)$ concentration profiles using atomic resonance fluorescence in the vacuum UV. (The small concentrations of $N(^2P°)$ atoms might be formed from reactions (10a), (10b), or from the reaction of $H(^2S)$ with $NF(b\,^1\Sigma^+)$ if some relaxation of the correlation rule for the orbital angular momentum was allowed for.) Computer modelling of the overall $H+NF_2$ reaction and fit of the $N(^4S°)$ and $N(^2D°)$ concentration profiles resulted in rate constants (all in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) $k_{10a}=3\times10^{-13}$ and $k_{10b}=9\times10^{-13}$. The bimolecular reaction (2) was assumed to be important and to occur with a rate constant $k_2=k_1=7\times10^{-11}$ (as derived for NF(X) [3]). $k_{10a}=1.5\times10^{-13}$ and $k_{10b}=4.5\times10^{-13}$ if k_2 is set equal to zero [7].

NF + N

The intense yellow emission of the nitrogen first positive system $N_2(B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+)$ (for a review of the N_2 spectra, see [8]), following the $H+NF_2$ reaction, arises [4] (suggested also by [9]) from the reaction of the metastable $N(^2D°)$ atoms (due to reaction (10b)) and the initially formed NF(a) radicals according to

$$NF(a\,^1\Delta)+N(^2D°)\xrightarrow{k_{11}}N_2(B\,^3\Pi_g)+F \qquad (11)$$

rather than by the recombination of two ground-state $N(^4S°)$ atoms [2]. This interpretation [4] was based on the following observations: (1) The vibrational distribution in the $N_2(B\rightarrow A)$ system did not show the anomaly which exhibited the Lewis-Rayleigh afterglow spectrum resulting from $N(^4S°)$ recombinations; (2) the time evolution of the $N_2(B\rightarrow A)$ emission followed qualitatively those of the $NF(a\rightarrow X)$ emission and the $N(^2D°)$ resonance fluorescence, but did not follow the time evolution of the $N(^4S°)$ profile; and (3) the intensity of the $N_2(B\rightarrow A)$ emission (a measure of $[N_2(B)]$) varied linearly with $[NF(a)]\cdot[N(^2D°)]$. The observation of the Lyman-Birge-Hopfield $a\,^1\Pi_g \rightarrow X\,^1\Sigma_g^+$ emission system of N_2 in the $H+NF_2$ reaction under the same conditions as those favoring the $N_2(B\rightarrow A)$ emission, and the observation of weak bands of the forbidden $a'\,^1\Sigma_u^- \rightarrow X\,^1\Sigma_g^+$ system of N_2 was attributed to the formation of the metastable $N_2(a'\,^1\Sigma_u^-)$ state by a reaction analogous to (11) and subsequent collisional curve crossing to give $N_2(a\,^1\Pi_g)$ [4].

The first positive bands of N_2 were also observed in the emission from the $F+HN_3$ reaction. Again, the intensity distribution was indicative of the occurrence of reaction (11) rather than $N(^4S°)$ recombinations [10].

NF + Bi

The appearance of the blue-green $BiF(A0^+ \rightarrow X0^+)$ emission system in a stream containing NF(a) radicals and Bi atoms was explained by

$$NF(a\,^1\Delta)+Bi(^2D°)\xrightarrow{k_{12}}BiF(X0^+)+N(^4S°) \qquad (12)$$

with $k_{12}=2.3\times10^{-11}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (at room temperature) and subsequent quenching of NF(a) by BiF(X) to give NF(X) and BiF(A) (see p. 290) [11].

NF as Reactive Intermediate

NF is suggested as a reactive intermediate in several gas-phase reactions of nitrogen fluorides. Especially, when N_2F_2, the dimer of NF, is formed an NF intermediate is frequently postulated. Reactions of this type, such as photolysis of tetrafluorohydrazine or reaction of elemental fluorine with sodium azide, are dealt with in Sections 4.1.12.6 and 4.1.14.2.

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4.1.9.4.2 NF in Solution

The preparation of N_2F_2 in solution by basic hydrolysis of N,N-difluorourea [1] or from N,N-difluoroisopropyl carbamate and potassium t-butoxide [2] (see also p. 387) presumably occurs by dimerization of intermediate NF.

The main reaction path by which NF, generated by the basic hydrolysis of NHF_2, reacts with organic C–H, O–H, or S–H compounds is via hydrogen abstraction. Thus, N-hydroxy-2,2,6,6-tetramethyl-4-piperidone is converted into the corresponding nitroxide. Small amounts of biphenyl were isolated from benzene, and thiophenol gave a 100% yield of diphenyl disulfide (see "Fluorine" Suppl. Vol. 5) [3].

NF was proposed as the actual deaminating species in the deamination reactions of NHF_2 (see "Fluorine" Suppl. Vol. 5) or F_2NCO_2-i-C_3H_7 with primary and some secondary amines [4, 5]. The following mechanism was postulated [5]:

$$RNH_2 + NHF_2 \rightarrow R\overset{+}{N}H_3 + NF_2^- \qquad NF_2^- \rightarrow NF + F^-$$

$$RNH_2 + NF \rightarrow R\overset{+}{N}H_2\overset{-}{N}F \rightarrow RNHNHF \xrightarrow{-HF} R\text{–}N\text{=}N\text{–}H \rightarrow RH + N_2$$

R = n-butyl, sec-butyl, t-butyl, cyclopropyl, cyclopropylmethyl, or phenyl.

The reactions of NHF_2 [5] or F_2NCO_2-i-C_3H_7 [4] with dibenzylamine, which yield bibenzyl, demonstrate the potential synthetic value of NF as a means of producing carbon-carbon bonds [4].

Nitrogenation reactions of some secondary amines were observed with NHF_2 [6] or F_2NCO_2-i-C_3H_7 [4]; NF was assumed to be the nitrogenating agent. Thus, the conversion of diallylamine into N-allylpyrazoline by NHF_2 [6] and the conversion of pyrrolidine into 2,3,4,5-tetrahydropyridazine [4] by F_2NCO_2-i-C_3H_7 was observed.

NF acts as fluorinating agent in the reactions of F_2NCO_2-i-C_3H_7 with $(C_6H_5)_3X$ (X = P, As) yielding $(C_6H_5)_3XF_2$ [4].

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4.1.10 The NF^+ and NF^- Ions

CAS Registry Numbers: NF^+ *[33146-36-0]*, NF^- *[33088-90-3]*

NF^+

The photoelectron spectrum recorded for the $F+HN_3$ reaction was attributed to the ionization of NF from both its ground ($X\,^3\Sigma^-$) and first excited ($a\,^1\Delta$) state to ground state $NF^+(^2\Pi_r)$ [1].

The heat of formation was obtained from mass spectrometric data for NF_3, NF_2, and N_2F_2 and auxiliary thermochemical data. Combining the threshold energy for the photoionization process $NF_3+h\nu \rightarrow NF^+ + 2F + e^-$, $\Delta H = 17.54 \pm 0.02$ eV [2], $\Delta H^\circ_{f,0}(NF_3)$, and the revised $\Delta H^\circ_{f,0}(F)$ value [3] yields $\Delta H^\circ_{f,0}(NF^+) = \Delta H + \Delta H^\circ_{f,0}(NF_3) - 2 \cdot \Delta H^\circ_{f,0}(F) = 337.7 \pm 0.8$ kcal/mol [4]. This revises the original value, 343.1 ± 0.7 kcal/mol [2], which was based on too low a $\Delta H^\circ_f(F)$ value (cf. "Fluorine" Suppl. Vol. 2, 1980, pp. 67/8). The appearance potentials of NF^+ from NF_3, $AP = 17.9 \pm 0.3$ eV ($NF_3 \rightarrow NF^+ + 2F + e^-$) [5], from NF_2, $AP = 11.8 \pm 0.2$ eV ($NF_2 \rightarrow NF^+ + F^-$) and 15.5 ± 0.2 eV ($NF_2 \rightarrow NF^+ + F + e^-$), and from cis- and trans-N_2F_2, $AP = 16.9 \pm 0.2$ and 17.0 ± 0.2 eV ($N_2F_2 \rightarrow NF^+ + NF + e^-$) [6] together with thermochemical data [7] ($\Delta H^\circ_f(NF)$ presumably from [6]), led to $\Delta H^\circ_{f,298} = 345$, 347, 349, 349 and 355 kcal/mol. $\Delta H^\circ_{f,298} = 349$ kcal/mol was recommended (a value of 337 kcal/mol based on $AP = 15.0 \pm 0.2$ eV for $NF_2 \rightarrow NF^+ + F + e^-$ [8] was discarded) [9].

The electronic structure has been the subject of a few quantum chemical ab initio studies [1, 10 to 20], see Table 18. Accordingly, the ground state $X\,^2\Pi_r$ is represented by the electron configuration (cf. p. 272) $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^1$ [10 to 16]. Both the dissociation limits, $N(^4S^\circ) + F^+(^3P)$ [15] and $N^+(^3P) + F(^2P^\circ)$ [10] were obtained, the latter was also assumed [1].

Table 18
$NF^+(X\,^2\Pi_r)$ and $NF^-(X\,^2\Pi_i)$. Ab Initio SCF-MO and CI Calculations.
Estimated total correlation energy for NF^+: $E_{corr} = -0.605$ a.u. [11], -0.557 a.u. [21].

$-E_T$ in a.u.	r_e in Å	method$^{a)}$	basis set$^{a)}$	calculated molecular parameters$^{a)}$	Ref.
NF^+					
153.75$^{b)}$	ca. 1.1$^{b)}$	MRD CI	ext. GTO	E(r)	[10]
153.35837	$r_{opt}(NF) = 1.30$	SCF	ext. STO		[11]
153.35376	$r_{exp}(NF) = 1.317$	SCF	ext. STO	ε_i, μ, Θ, other expectation values charges [17]	[12]
153.3449	$r_{exp}(NF)$	SCF	ext. STO	ε_i charge density [18], force constants [19]	[13]
153.32049	r_{opt} (STO-3G)	SCF	4-31G		[14]
153.07991	1.252	SCF	STO-3G	r_e	

Table 18 (continued)

$-E_T$ in a.u.	r_e in Å	method[a]	basis set[a]	calculated molecular parameters[a]	Ref.
152.9375	1.340	SCF+CI	min. STO	E(r), r_e, ω_e, $\omega_e x_e$, B_e, α_e, D_e, D_0 for X $^2\Pi_r$ and excited states a $^4\Pi$, b $^4\Sigma^-$, E(r) for five higher states transformation of the wave function into the momentum space representation [20]	[15]
152.8214	1.217	SCF	min. STO	E(r), r_e, first ε_i for X $^2\Pi_r$ and a $^4\Pi$	[16]
—	$r_{exp}(NF) = 1.317$	SCF	ext. STO	X $^2\Pi$, $^4\Sigma^-$, $^4\Pi$, $^2\Delta$, $^2\Phi$ states relative to X $^3\Sigma^-$, a $^1\Delta$ of NF	[1]
NF^-					
153.76775	$r_{exp}(NF)$	SCF	ext. STO	ε_i, μ, Θ charges [17]	[12]
153.76393	$r_{opt}(NF) = 1.30$	SCF	ext. STO		[11]
153.7443	$r_{exp}(NF)$	SCF	ext. STO	ε_i charge density [18], force constants [19]	[13]
153.0271	1.473	SCF+CI	min. STO	E(r), r_e, ω_e, $\omega_e x_e$, B_e, α_e	[28]

[a] For abbreviations and symbols, see Table 7, p. 235 and footnotes [b] and [c] of Table 15, p. 274. – [b] Read from the potential curve [10, figure 9].

Among the various excited states arising from 1π or $5\sigma \rightarrow 2\pi$ excitations (cf. [22, p. 337]) the lowest a $^4\Pi$ and b $^4\Sigma^-$ (in [15]: b $^4\Sigma^+$; but $\cdots(1\pi)^4(5\sigma)^1(2\pi)^2$ configuration gives $^4\Sigma^-$) were calculated (CI study) to lie at $T_e = 2.253$ and 3.475 eV above X $^2\Pi_r$ (11.938 and 13.160 eV above X $^3\Sigma^-$ of NF) and to dissociate into N($^4S°$) and F^+(^3P); the theoretical potential curves were depicted [15] for five higher bound states separating into N^+(^3P) and F($^2P°$), A $^2\Pi$, B $^2\Pi$ and $^4\Sigma^+$, $^4\Sigma^-$, $^4\Delta$ (possibly due to $\cdots(1\pi)^3(5\sigma)^2(2\pi)^2$ and $\cdots(1\pi)^3(5\sigma)^1(2\pi)^3$, respectively, cf. [22, p. 337]). SCF calculations were carried out for the states $^4\Sigma^-$, $^4\Pi$ and $^2\Delta$, $^2\Phi$ corresponding to the 5σ, 1π ionizations in NF(X $^3\Sigma^-$) and NF(a $^1\Delta$), respectively (cf. p. 277) [1].

The spectroscopic constants, $r_e = 1.180 \pm 0.006$ Å, $\omega_e = 1520 \pm 40$ cm^{-1}, and $\omega_e x_e = 10 \pm 6$ cm^{-1} for the ground state, were derived from the vibrational structure of the two photoelectron bands attributed to NF(X $^3\Sigma^-$), NF(a $^1\Delta$) $\rightarrow$ NF^+(X $^2\Pi_r$) ionizations [1]. Theoretical values for the ground state and two excited states result from ab initio calculations [14 to 16], see Table 18. Theoretical potential energy curves are given for X $^2\Pi_r$ [10, 15], a $^4\Pi$, and b $^4\Sigma^-$ [15].

The dissociation energy is given as $D_e = 5.8 \pm 0.3$ eV ($= D_e$(NF, X $^3\Sigma^-$)$-E_i$(NF, X $^3\Sigma^-$)$+E_i$(N)) for the dissociation of NF^+(X $^2\Pi_r$) into N^+(^3P) and F($^2P°$) [1]. Estimates are: $D_0 = 4.8$ eV (interpolation of isoelectronic curves) [23], D = 5.2 eV (from "literature data") [24] (both $NF^+ \rightarrow N^+ + F$), $D_e = 5.43$, $D_0 = 5.35$ eV (CI calculation, $NF^+ \rightarrow N + F^+$) [15], and D = 3.88 eV (CNDO calculation, apparently $NF^+ \rightarrow N^+ + F$) [25].

For the ion-molecule exchange reaction, $^{14}NF^+ + {}^{15}N_2 \rightarrow {}^{15}NF^+ + {}^{14}N^{15}N$, $k \leq 10^{-12}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (probably at 298 K) was derived from mass spectrometric studies [26].

From the mass spectrometric study of the reaction of NF^+ with O_2, only the dissociation of NF^+, but not the alternative reaction channels, $NF^+ + O_2 \rightarrow NO^+ + FO + 2.8$ eV and $NF^+ +$

$O_2 \rightarrow NO^+ + F + O - 0.5$ eV, could be detected in the kinetic energy range investigated [24]. From a study of Xe–NF_3 mixtures by ion cyclotron resonance mass spectrometry, rate constants (at 20 to 25°C) for the reactions of NF^+ with Xe and NF_3 were derived: $NF^+ + Xe \rightarrow NF + Xe^+$, $k = (1.0 \pm 0.5) \times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, and $NF^+ + NF_3 \rightarrow NF_2^+ + NF_2$, $k = (0.55 \pm 0.15) \times 10^{-9}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$. The corresponding reaction enthalpies calculated from thermochemical data are $\Delta H = 1.5 \pm 8.0$ and -19.7 ± 2.3 kcal/mol, respectively [4].

NF^-

Electron impact ($E \leq 50$ eV) on NF_3 ($p = 5 \times 10^{-6}$ Torr) gave NF^- in addition to F^- and F_2^-; for $E = 50$ eV, the relative abundances were $F^- : F_2^- : NF^- = 1000 : 5.0 : 0.7$. The ionization efficiency curve of NF^- exhibited two appearance potentials indicating two processes for NF^- formation: The dissociative capture process $NF_3 + e^- \rightarrow NF^- + 2F$ forming NF^- with little or no kinetic energy occurred at zero electron energy, the ion-pair process $NF_3 + e^- \rightarrow NF^- + F^+ + F + e^-$ presumably corresponded to the appearance potential at 23.0 eV [27].

For the electronic ground state $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^3$ $X\,^2\Pi_i$, four ab initio calculations have been published [11 to 13, 28], see Table 18, p. 297. The Hartree-Fock calculations were performed at the experimental [12, 13] or optimized [11] bond length of NF($X\,^3\Sigma^-$). The CI calculation, using only a minimum STO basis, gave $r_e = 1.473$ Å and vibrational and rotational constants (in cm^{-1}) $\omega_e = 1117$, $\omega_e x_e = 5.3$, $B_e = 0.964$, and $\alpha_e = 0.789$; the increase of r_e as compared with NF is due to the extra antibonding 2π electron [28]. A semiempirical estimate (MNDO approximation) resulted in $r_e = 1.268$ Å for NF^- as compared with $r_e = 1.220$ Å for NF [29].

A semiempirical estimate (CNDO approximation) for the dissociation energy gave D = 63.0 kcal/mol (2.73 eV; apparently for $NF^- \rightarrow N + F^-$) [25].

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4.1.11 The $N_2F_5^+$ Ion

CAS Registry Number: *[59229-54-8]*

Attempts to obtain the $N_2F_5^+$ ion were unsuccessful. The synthetic and spectroscopic evidence for the formation of $N_2F_5^+(CF_3)_3CO^-$ in the reaction of $(CF_3)_3COF$ with N_2F_4 in a Pyrex vessel, as claimed by [1], was critically reviewed: five arguments showed that the product was most likely $NO_2^+SiF_6^-$ [2]. Analogously, the photolytic reactions of N_2F_4–F_2–BF_3 mixtures in glass below −100°C gave $NF_4^+BF_4^-$ and $NO^+BF_4^-$ or $NO_2^+BF_4^-$ [2] and not $N_2F_5^+BF_4^-$ as claimed by [3].

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4.1.12 Dinitrogen Tetrafluoride, N_2F_4

Other name: Tetrafluorohydrazine

CAS Registry Number: *[10036-47-2]*

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Review

The commonly used name, tetrafluorohydrazine, is used in this text.

Tetrafluorohydrazine first synthesized in the late 1950s is a toxic, colorless gas of musty odor which liquefies at −73°C and solidifies at −163°C. The most characteristic chemical property of N_2F_4 is its easy dissociation into two difluoroamino radicals. At 300°C, N_2F_4 is almost completely dissociated. Many reactions of the very reactive N_2F_4 can be explained by its facile cleavage into NF_2 radicals and their relative stability.

4.1.12.1 Preparation. Formation

There are two basic approaches available for the preparation of N_2F_4. They are the abstraction of a fluorine atom from nitrogen trifluoride by different fluorine acceptors and the oxidation of difluoroamine. The first method was employed in the original preparation of N_2F_4. The oxidation of NHF_2 produces N_2F_4 of high purity, thereby avoiding the difficulties in the purification of the crude product present in other preparative methods.

4.1.12.1.1 From Nitrogen Trifluoride

N_2F_4 was first prepared by thermal reaction of NF_3 with various fluoride acceptors such as Cu, As, Sb, Bi, or stainless steel [1, 2]. Thus, N_2F_4 was produced in 62 to 71% yield based on NF_3 consumed (42 to 62% conversion) in a Cu-packed flow reactor at 375°C with a residence time of 13 min [1, 2]. Oxygen or nitrogen oxides are added to the NF_3 to reduce the induction period of the reaction and residence time in the Cu-packed reactor [3]. Although Cu is the most effective in producing N_2F_4 the reaction is erratic and often leads to complete reduction of NF_3 to nitrogen and the metal fluoride [15]. The conversion to N_2F_4 by passing NF_3 through hot fluidized carbon according to

$$4\,NF_3 + C \rightarrow 2\,N_2F_4 + CF_4$$

is easier to control. Yields of 75% at 75% conversion of the NF_3 were obtained with petroleum coke of 80 to 200 mesh, at $400 \pm 10°C$ and contact times < 5 s. The disadvantage of this method is that one of the principal impurities, hexafluoroethane, is difficult to separate because its volatility is quite close to that of N_2F_4. The process was conducted in a pilot plant [4 to 6]. Alternatively, mercury either in an electric discharge [7, 8] or at 320 to 330°C [9, 10] may be used as fluorine acceptor. The electric discharge reaction is performed in a Pyrex vacuum system. The conversion is very low, between 6 and 16% for a single pass through the discharge tube. The products are N_2F_4, N_2F_2, Hg-fluorides, and N_2. The highest N_2F_4 yield of 67% was obtained under the following conditions: NF_3 pressure 3 Torr, NF_3 flow rate 95 cm³/mm, discharge voltage 4400, temperature 200 to 210°C. The unreacted NF_3 was separated from N_2F_4 and N_2F_2 by fractional distillation from a −186°C to a −196°C trap. N_2F_4 was separated from cis- and trans-N_2F_2 by gas adsorption chromatography on silica gel at −40°C [7, 8]. Sixty percent of the NF_3 that reacted with Hg in a flow system at 320 to 330°C was converted into N_2F_4 plus a small amount of cis-N_2F_2, provided the reagents were absolutely dry and free of impurities, especially oxygen-bearing substances [9, 10].

Mixtures of NF_3 and NO reacted to give N_2F_4 and FNO

$$2\,NF_3 + 2\,NO \rightarrow N_2F_4 + 2\,FNO$$

in essentially quantitative yields when the two reactants were heated in a Ni flow tube to 607°C for 0.25 s. The FNO was scrubbed from the product gases with chilled 2N NaOH solution [11]. To eliminate or reduce explosion hazards in reacting mixtures containing NF_3, a diluent gas such as Ar may be added to maintain the NF_3 concentration below 9.4 mol% [12].

N_2F_4 besides cis- and trans-N_2F_2, N_2, and F_2 were identified after exposure of NF_3 to large doses of 3-MeV bremsstrahlung at 77 K [13]. The radiation-chemical yield G for the formation of N_2F_4 by ^{60}Co γ-irradiation (dosage up to 50 Mrad, dose rate 7.1 Mrad/h) of NF_3 at 77 K was determined to be 0.4 to 0.5 molecule/100 eV in the absence of fluorine acceptors [14]. $G(N_2F_4) = 0.1$ molecule/100 eV was found on irradiation of a liquid NF_3 layer of about 5 mm thickness with 800-keV electrons at 77 K (absorbed dose 1600 Mrad) [16].

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4.1.12.1.2 From Difluoroamine or Precursors

NHF_2, frequently prepared by hydrolysis of fluorinated urea, may be either readily disproportionated in the presence of catalysts according to

$$5\,NHF_2 \rightarrow 2\,N_2F_4 + NH_4F + HF$$

or converted into N_2F_4 by an appropriate oxidizer. Effective catalysts are stainless steel, copper, urea, solid residues from distillation of fluorinated urea, and LiH. Thus, for example, 14.5 cm^3 of NHF_2 was converted into N_2F_4 (5.5 cm^3) on holding 24.6 cm^3 NHF_2 and 21 mg urea at 0°C for 68 h in a 7 mL high pressure ampule. The yield was 95% according to the above equation. In stainless steel ampules N_2F_4 was obtained in 59% yield [1 to 4].

The oxidation of NHF_2 by Cl_2 at room temperature produces a mixture of N_2F_4 and $NClF_2$; the former predominates at $Cl_2:NHF_2$ molar ratios below about 2:1. An equimolar ratio produces N_2F_4 almost exclusively. Mixing and the use of a solvent favor the production of $NClF_2$ [5 to 7]. A 2:2:1 mixture of F_3NO, $NClF_2$, and N_2F_4 was obtained on reacting NHF_2 with ClF_3O between −116 and −37°C [8].

N_2F_4 was produced in almost quantitative yield (based on NHF_2) when NHF_2 was bubbled through a NaOCl solution at pH 11 to 12. $NClF_2$ was formed besides N_2F_4 at lower pH and was the main product at pH 6 [9]. A substantially quantitative conversion into N_2F_4 was achieved when gaseous NHF_2 was rapidly forced by a stream of inert gas (N_2, Ar, or He) through a 0.1 M $FeCl_3$ solution which was 0.05 M in H_2SO_4 at 25°C. The products collected in a liquid-nitrogen trap consisted of 97% N_2F_4, 3% N_2O, and traces of H_2O and NHF_2 [10]. The rate of oxidation by Fe^{3+} decreases rapidly with decreasing pH favoring NF_2^- rather than undissociated NHF_2 as the species being oxidized [17]. An alkaline solution, however, can not be used since metal hydroxides frequently precipitate if metallic salts are employed as catalysts and since basic hydrolysis of NHF_2 increases. Other salts like $KMnO_4$, chromic salts, chromates, and ceric salts could also be used for oxidation, but ferric salts are preferred on the basis of cost [10].

The anodic oxidation of NHF_2 on a Pt electrode was irreversible, pH dependent, and kinetically controlled. The NF_2 radical, the primary product of the electron transfer involving the one-electron oxidation of difluoroamine, rapidly combines to form N_2F_4 if no other radicals are present [16]. Thus, the electrolysis of 50 mL of a solution approximately 0.1 M in NHF_2 and 0.5 M in $NaClO_4$ to which $HClO_4$ was added to attain a final pH of 2.3 with 0.6 A for 2 h gave about a 70% yield of N_2F_4. Small amounts of NO and N_2O were probably formed on hydrolysis of NHF_2 or N_2F_4 [16].

Since NHF_2 is highly explosive it is desirable to prepare it in situ, that is, to combine the hydrolysis of N,N-difluorourea and the oxidation of NHF_2 according to

$$2\,H_2NCONF_2 + 2\,Fe^{3+} + 2\,H_2O \xrightarrow{H^+} N_2F_4 + 2\,CO_2 + 2\,NH_4^+ + 2\,Fe^{2+}$$

The reaction was carried out with $NH_4Fe(SO_4)_2 \cdot 12H_2O$ as oxidant at 500 Torr and 75°C [11, 12]. According to another patent the N,N-difluorourea is treated with basic NaOCl solution in tetrahydrofuran at 60°C. The N_2F_4 was collected at −156°C [13]. N_2F_4 was also prepared by oxidation of N,N-difluorocarbamate with CrO_3, $NH_4Fe(SO_4)_2 \cdot 12H_2O$, K_2CrO_4, $NaClO_3$, $KMnO_4$, or $FeCl_3$ in aqueous solution of pH 7 or lower at 5°C. The CO_2 is scrubbed from the product gases with alkali (Ascarite) leaving essentially pure N_2F_4 [14]. Other starting materials used were the phosphorylamide derivatives $OP(NH_2)RR'$, where R and R′ may be NH_2, alkyl, aryl, alkyloxy, or aryloxy groups. They were fluorinated by F_2 in a H_2O–CH_3OH mixture at −35°C and the fluorinated products were either directly oxidized with $NH_4Fe(SO_4)_2$ solution at 90°C and pH 2 or were first hydrolyzed with concentrated H_2SO_4 followed by oxidation of the evolved NHF_2 [15].

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4.1.12.1.3 Miscellaneous Methods

N_2F_4 may be obtained besides NF_3 from the elements by contacting fluorine with a nitrogen plasma at about 3500°C and quenching the gas stream with liquid nitrogen. The $F_2:N_2$ molar ratios were between 0.4 and 1. The main product was NF_3 at higher molar ratios [1].

The vapor-phase reaction of F_2 with NH_3 in a Cu-packed reactor in the presence of excess NH_3 ($NH_3:F_2$ molar ratios 1.5 to 2) led to the formation of N_2F_4 (yields up to 11% based on F_2) besides NF_3, N_2F_2, and NHF_2. NF_3 and NH_4F were the reaction products in the presence of excess F_2 [2 to 4]. The direct fluorination of some substituted ammonia compounds like $NaNH_2$, sulfamide, biuret, or urea in the presence of metal fluorides (NaF, LiF, $NaHF_2$) at 0 to 100°C yielded N_2F_4 as well as NF_3 and trans-N_2F_2 [5]. The electrofluorination of N_2H_4, aminoguanidine or semicarbazide produced N_2F_4 at best in minute amounts [6].

The introduction of CF_4 or SF_6 into a nitrogen plasma with subsequent quenching of the gas stream from about 3500 K to room temperature yielded small quantities of N_2F_4 besides NF_3, CF_3NF_2, C_2F_6, and trace quantities of N_2F_2 (cis and trans) and C_2F_4 [7].

Chlorodifluoroamine, $NClF_2$, reacted rapidly with Hg at room temperature to form N_2F_4 and Hg_2Cl_2 [8, 9]. $NClF_2$ was nearly quantitatively converted into N_2F_4 on reaction with dimethylamine in diethyl ether at −80°C. Lower yields of N_2F_4 were obtained with dimethylamine in dimethyl ether or with sodium methoxide, both at 25°C [9]. N_2F_4 formed besides other products on reacting $NClF_2$ with aqueous KI, NO, or LiH [10].

In the presence of fluoride ion acceptors like HF, BF_3, AlF_3, or PF_5, the electrolysis of $NH_4F \cdot HF$ between 4 and 20 V, at 75 to 150°C, using a Ni anode led to the formation of N_2F_4 besides the main product NF_3, plus N_2F_2, N_2, and N-oxides [11].

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4.1.12.1.4 Purification

N_2F_4, which has been prepared from NF_3, usually contains NF_3, CF_4, N_2O, NO, SiF_4, and N_2F_2 as impurities. Fractionation of the crude product from a −160°C slush bath (isopentane), removed NF_3, CF_4, and NO almost entirely, N_2O, SiF_4, and N_2F_2 were removed by gas chromatography on a silica gel column [1], see also [2, 3].

N_2F_4, which has been prepared by passing NF_3 through fluidized carbon, contains varying amounts of CF_4, C_2F_6, and NF_3. Because its volatility is quite close to that of N_2F_4, C_2F_6 cannot be readily removed, but its inertness usually renders complete removal unneccessary [4, 5]. To separate N_2F_4 from a mixture including NF_3, CF_4, and C_2F_6, the mixture is fed into the middle of a packed column through which a solvent ($CHCl_3$) trickles down preferentially dissolving N_2F_4.

By repeated cycling substantially pure N_2F_4 was obtained. The efficiency of the separation was increased by differential heating of the column, multiple columns in series, and the use of an upward inert gas sweep [6].

N_2F_4 prepared from difluorourea or difluorocarbamate is generally contaminated with CO_2, which is removed with alkali, for example, with Ascarite [7].

N_2F_4 and $NClF_2$ were separated by partition chromatography from a column packed with solid polychlorotrifluoroethylene and polychlorotrifluoroethylene oil as the stationary liquid phase [8].

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4.1.12.1.5 Heat of Formation

$\Delta H^\circ_{f,298} = -5.3 \pm 1.4$ kcal/mol was obtained from revised values of the heat of dissociation of N_2F_4 (20.9 ± 0.4 kcal/mol) and the heat of formation of NF_2 (7.8 ± 1.0 kcal/mol) [1]. This value differs from $\Delta H^\circ_{f,298} = -2.0 \pm 2.5$ kcal/mol, which was determined by measuring the heat of reaction of N_2F_4 (only about 94% pure) with NH_3 [2]. The latter value appears in the JANAF Tables [3]. $\Delta H^\circ_{f,298} = -5$ kcal/mol was derived [4] from $\Delta H^\circ_{f,298}(NF_3, g) = -31.75$ kcal/mol [4] and Armstrong's [2] values of heats of reaction for NF_3 and N_2F_4 with NH_3. Semiempirical MO calculations (MNDO) gave $\Delta H^\circ = -18.3$ kcal/mol [5].

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4.1.12.2 Toxicity, Handling, and Uses

N_2F_4 causes respiratory distress and is highly toxic [1]. Exposure to 10000 ppm N_2F_4 for 25 or more min was lethal to rats [2], see also [3]. If N_2F_4 did not decompose prior to inhalation, lethal concentrations caused oxidation of up to 65% of the hemoglobin to methemoglobin. Decomposed N_2F_4 was approximately as lethal, however, with only moderate formation of methemoglobin [2, 3]. The 50% lethal concentration (LC_{50}) of the gas injected intraperitoneally is about 0.5 mmol/kg, with limited methemoglobinemia. The significance of decomposition products in the overall toxicity of N_2F_4 was discussed [2].

Mixtures of N_2F_4 with air, combustible vapors, or organic substances are potentially explosive and must be handled with caution [1, 4]. Liquid N_2F_4 was tested from 195 to 213 K (~10^3 Torr) and was found to be nondetonable [5]. Pyrex, Kel-F, Teflon, polyethylene, or stainless steel are normally suitable for working with N_2F_4, but nickel or Monel are recommended at high temperatures [1, 6, 12].

N_2F_4 was produced in commercial quantities in the early 1960s for expected use as a high-energy oxidizer for propellants in rocketry [7, 8]. Currently, N_2F_4 is not of commercial interest and is only produced in small quantities [7]. N_2F_4 is of interest in the preparation of compounds containing N–F bonds, especially in the synthesis of organic difluoroamines. It is also an efficient polymerization initiator [11].

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4.1.12.3 Molecular Properties and Spectra

4.1.12.3.1 Molecular Structure

The molecular structure of N_2F_4 in the gaseous, liquid, and solid phases has been investigated by a variety of experimental techniques; the structure of the free molecule has also been the subject of a few theoretical studies (MO calculations). After considerable discussion, the presence of two $F_2N–NF_2$ rotamers, a trans form of C_{2h} symmetry and a gauche form of C_2 symmetry, in the gaseous and condensed states appears to be established, see **Fig. 8**. These two rotamers have identical bond lengths and nearly identical bond angles; the dihedral angle Θ of the gauche rotamer, i.e., the amount of rotation of one NF_2 group relative to the other starting from the cis position, lies between 60° and 70° ($\Theta = 180°$ for the trans rotamer). But the energy difference between the two rotamers, which appears to be very small (≤ 1 kcal/mol), could not be accurately obtained. Some experiments indicate a slightly more stable trans form. Some theoretical studies predict the energy minimum for the gauche form, others for the trans form.

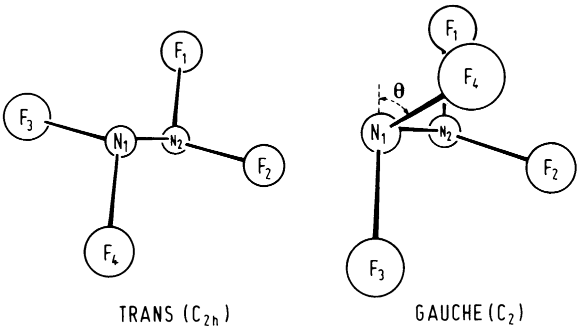

Fig. 8. Conformations of N_2F_4 (from [16]).

Experimental Results

The first experimental results from the microwave spectrum were consistent with the hydrazine-like (C_2) structure, and adopting the N–N and N–F bond lengths of N_2H_4 and NF_3, 1.47 and 1.37 Å, respectively, the angles $\sphericalangle FNF = 108°$, $\sphericalangle FNN = 104°$ and $\Theta = 65°$ (all $\pm 3°$) were derived. It was estimated that at 200 K this gauche form of N_2F_4 was present in at least 10% in a mixture possibly containing the trans form which cannot be detected by the MW technique, and that the internal rotation of the NF_2 groups is probably hindered by a barrier >3 kcal/mol [1]. The initial Raman spectrum of gaseous N_2F_4 [2] and the initial IR spectra of gaseous [3 to 7] and solid N_2F_4 [6 to 8] were interpreted only in terms of the gauche form [2, 5 to 7, 9, 10]. A gas-phase electron diffraction study [11] seemed to rule out the presence of substantial amounts of the trans form, although earlier electron diffraction data [12] had been interpreted only in terms of the trans form.

The first experimental evidence for the coexistence of both conformations in approximately equal amounts came from the ^{19}F NMR of N_2F_4 in various nonpolar solvents between -130 and $-180°C$. The five-line spectrum could be reasonably assigned by allocating one sharp, intense line to the four equivalent F nuclei in trans-N_2F_4 and the remaining four lines, an AB quartet, to the d,l-pair of gauche rotamers ($\Theta \approx \pm 65°$) (see Fig. 10, p. 313). The trans rotamer was found to be slightly lower in energy, $\Delta E(\text{trans}-\text{gauche}) \approx -100$ to -200 cal/mol, and an estimated rotational barrier of 4 to 7 kcal/mol was consistent with the observed change from very slow conversion (between the two conformations) to very rapid conversion over the small temperature range from -155 to $-130°C$ [13] (for a reinvestigation of the ^{19}F NMR under higher resolution and confirmation of the results, see [14]).

Finally, the presence of the two rotamers in all phases of N_2F_4 could be proved by (1) reinvestigation of the electron diffraction and (2) detailed spectroscopic studies:

(1) A gas-phase electron diffraction pattern obtained at an unknown temperature (somewhere between 150 and 250 K) could be best accounted for by assuming a trans : gauche ratio of $(53 \pm 3)\% : (47 \pm 3)\%$, which indicates that the trans rotamer is more stable by about 300 to 500 cal/mol [15, 16]. On the other hand, a subsequent electron diffraction study at 25°C [17, 18] suggested a ratio of $(71.2 \pm 8.1)\% : (28.8 \pm 7.7)\%$, which gives an energy difference between 650 and 1250 cal/mol (a rotational barrier of several kcal/mol is in accord with those observed amplitudes which are affected by the torsional motion). However, it is not clear which result is more nearly correct, or whether the discrepancies are significant [18]. The structural results (bond lengths, angles, and root-mean-square amplitudes of vibration) from these two recent electron diffraction studies [16, 18] are given in Table 19. Mean amplitudes of vibration at $T = 0$ and 298 K for the gauche rotamer were also calculated [19] using MW [1] and IR [5] data.

(2) Extensive and careful analyses of Raman and IR spectra of gaseous, liquid, and solid N_2F_4 have been carried out [20 to 26]. Comparison of Raman and IR band positions showed – in spite of considerable discrepancies in the assignments of the fundamental vibrations (compare pp. 316/8) – that the mutual exclusion principle was operative for a number of bands. These therefore belong to the centrosymmetric trans rotamer; the sufficient number of remaining bands were attributed to the gauche rotamer [20 to 24]. The IR band contours [21] and the polarization properties of the Raman fundamentals [22 to 24] suggest an equilibrium mixture of both isomers which differ very little in energy. An accurate determination of the energy difference ΔE(trans – gauche) was not possible from the Raman spectra of gaseous and solid N_2F_4 because the changes in relative intensities were extremely small over the temperature range from ca. 298 to 18 K; thus, the isolation of one isomer in the solid does not appear to be possible [24]. The Raman spectra of gaseous N_2F_4 at 22 and 250°C, however, tend to support the electron diffraction and NMR results of a slightly more stable trans form. At the higher temperature, the intensities of the bands at 1010 and 600 cm^{-1} assigned to N–F and N–N stretching modes of trans-N_2F_4 [22, 23] appear to decrease relative to the corresponding bands of gauche-N_2F_4 [22, 23] at 1036, 1025 and 588 cm^{-1} [25] (however, different assignments exist for most of these bands, see Table 21, p. 318). For N_2F_4 in liquid Ar between 95 and 134 K, the relative integrated IR intensities of the stretching modes indicate an increase in the number of trans rotamers at lower temperatures; ΔE(trans – gauche) = –(250 ± 50) cal/mol was estimated from a logarithmic plot of the intensity ratio vs. T^{-1} [26].

Table 19

N_2F_4. Electron Diffraction Data.

Bond lengths r (in Å), bond angles ∢ and dihedral angle Θ (in °), mean amplitudes of vibration u (in Å), trans : gauche ratio (in %), and energy difference ΔE(trans – gauche) (in cal/mol).

	150 to 250 K		298 K	
	trans (C_{2h})	gauche (C_2)	trans (C_{2h})	gauche (C_2)
r(N–N)	1.489 ± 0.004		1.492 ± 0.007	
r(N–F)	1.375 ± 0.004		1.372 ± 0.002	
∢FNF	102.9 ± 1.0	105.1 ± 1.5	103.1 ± 0.6[b]	
∢F_1NN[a]	100.6 ± 0.6	100.1 ± 1.5	101.4 ± 0.4[b]	
∢F_2NN[a]	100.6 ± 0.6	104.3 ± 1.0		
Θ	180.0	67.1 ± 1.0	180.0	64.2 ± 3.7
u(N–N)	0.044 ± 0.004		0.048 ± 0.005	
u(N–F)	0.045 ± 0.003		0.044 ± 0.002	
u($F_1 \cdots F_2$)[c]	0.053 ± 0.004		0.064 ± 0.004	
trans : gauche	(53 ± 3) : (47 ± 3)		(71.2 ± 8.1) : (28.8 ± 7.7)	
ΔE(trans – gauche)	–300 to –500		–950 ± 300	
Ref.	[16]		[17, 18]	

[a] See Fig. 8, p. 307. – [b] Weighted averages for trans and gauche form. – [c] Amplitudes for the remaining nonbonded F···F and N···F pairs are also given [16 to 18].

The zero-point energy difference ΔE_0°(trans – gauche) was derived [27] from the changes of enthalpy ΔH_0°(trans) and ΔH_0°(gauche) calculated for the partial equilibria trans-$N_2F_4 \rightleftharpoons 2NF_2$ and gauche-$N_2F_4 \rightleftharpoons 2NF_2$ (compare p. 319). Experimental equilibrium constants for the overall process [28 to 30], structural data [16, 18], and vibrational frequencies [22] for N_2F_4 were used.

Values for ΔE_0°(trans − gauche) are between −1.98 and 0.26 kcal/mol depending on the combination of the various equilibrium and structural data. ΔE_0°(trans − gauche) = −0.57 kcal/mol obtained by combining the data of [16] and [29] was considered to be the best value. The corresponding enthalpy and entropy changes and equilibrium constants for trans-$N_2F_4 \rightleftharpoons$ gauche-N_2F_4, calculated for T = 100 to 1000 K, indicate that at 287 K there are equal amounts of both rotamers [27].

Quantum Chemical Results

Prior to the first preparation of N_2F_4, a nonplanar structure had been predicted (38 valence electrons) by applying the isoelectronic principle to molecules of type X_2YYX_2 with 34, 36, or 38 valence electrons [31]. A number of semiempirical MO studies, CNDO [32 to 34], INDO [35, 36], MNDO [37], MINDO [38], SCF–IO (semiempirical SCF including overlap) and extended Hückel [32], calculated the gauche conformation with a dihedral angle Θ between 65° and 90° to be most stable; energy differences ΔE(trans − gauche) (in kcal/mol) of 0.25 [33], 0.49 [34], 1.3 [37], and 3.9, 7.7, and 39.4 [32] were obtained.

According to a qualitative discussion on N_2H_4 and N_2F_4 based on the so-called molecular orbital-valence bond theory, the N_2F_4 molecule tends to adopt the trans form rather than the gauche form (of N_2H_4) [39].

An ab initio MO calculation of the total energy as a function of Θ from 0° to 360° (GTO basis for (N/F) of (7s3p/7s3p) contracted to [2s1p/2s1p], experimental bond lengths and bond angles [11]) predicted two stable forms at Θ = 64° or 296° and Θ = 180°, with the trans form being more

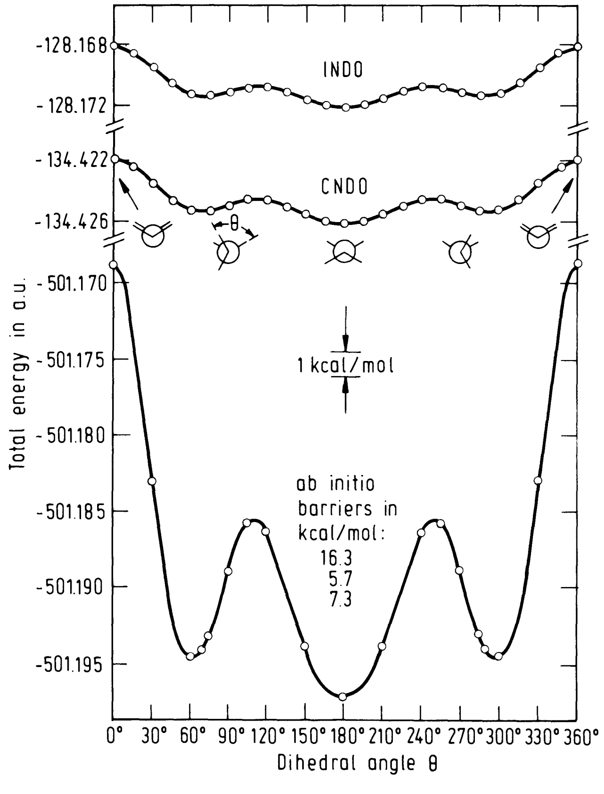

Fig. 9. Calculated energy barrier curves for N_2F_4 (from [40]).

stable by about 1.5 kcal/mol. The rotational barriers (maxima at $\Theta \approx 110°$ or 250°) are 7.3 and 5.7 kcal/mol relative to the trans and gauche positions, respectively, and the cis barrier (maximum at $\Theta = 0°$ or 360°) is 16.3 kcal/mol relative to the gauche position. By comparison, barrier curves calculated by the CNDO and INDO methods qualitatively reflect the ab initio curves but significantly underestimate the rotational barriers, see **Fig. 9**, p. 309 [40]. A geometry-optimized structure for N_2F_4 was obtained by an ab initio MO calculation (4-31G basis), but only N–N and N–F bond lengths are given [41].

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4.1.12.3.2 Electronic Structure. Dipole Moment

Prior to systematic studies of N_2F_4, the structure and the electron distribution of X_2Y_4 molecules (including N_2F_4) were discussed in terms of bond order and electronegativity [1] and by a Hückel MO formalism which considered σ- and/or π-electron delocalization [2].

The charge distribution in N_2F_4 has been derived by various semiempirical methods: charges on N and F by CNDO calculations [3, 4], charges on N and F and F–N and N–N overlap populations by an ab initio [13] and an extended Hückel calculation [5], and overlap populations by an SCF–IO (= semiempirical SCF including overlap [6]) calculation [7]. The gross atomic and overlap populations obtained by an ab initio SCF–MO calculation and the CNDO and INDO atomic charges are given as functions of the dihedral angle, $\Theta = 0°$ to $180°$ [8].

The bond indices obtained from CNDO calculations were given as functions of the dihedral angle [8], and were correlated with the corresponding bond energies and bond lengths [9].

The dipole moment $\mu \approx 0.26$ D of gauche-N_2F_4 ($\mu = 0$ for trans-N_2F_4) was obtained from measurements of the Stark effect in the microwave spectrum of gaseous N_2F_4 [10]. Theoretical values are $\mu = 0.23$ D (CNDO) [3] and $\mu \approx 0.4$ D (SCF–IO) [7, 11]. The sign of μ is unknown.

An N–F bonding moment of 1.29 or 1.81 D ($N^+–F^-$) was deduced [12] from $\mu = +0.26$ D or $\mu = -0.26$ D, respectively, and from the geometry in [10].

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4.1.12.3.3 Ionization Potentials. Electron Affinity

The first ionization potential obtained by electron impact mass spectrometry was $E_i = 12.04 \pm 0.10$ eV [1, 2] or 12.0 ± 0.1 eV [3]. The HeI photoelectron (PE) spectrum of N_2F_4 yields six vertical ionization potentials at 12.84, 13.74, 14.45, 16.2, 17.46, and 18.7 eV (no assignment) [4].

The core electron binding energies obtained from the X-ray PE spectrum (MgKα radiation) are $E_i(N1s) = 412.3$ eV [5], 412.5 ± 0.5 eV [6] (from shifts measured relative to N_2 with $E_i(1s) = 409.9$ eV) and $E_i(F1s) = 694.1 \pm 0.5$ and 694.6 ± 0.5 eV (shifts relative to CH_3F, $E_i(1s)$ not given); the splitting of the F1s line was believed to be due to inequivalent fluorines in N_2F_4 [6].

Theoretical values for the first E_i obtained from semiempirical MO calculations are 10.37 eV (CNDO) [7], 14.44 eV (CNDO) [8], 12.06 eV (MINDO) [9], and 13.02 and 12.61 eV for gauche- and trans-N_2F_4, respectively, (MNDO) [10]. Shifts (relative to N_2) $\Delta E_i(N1s) = 2.5$ to 3.2 eV were calculated semiempirically by the SCC(self-consistent charge)–MO method [11].

The electron affinity $A = 0.96$ eV was obtained by a CNDO calculation [8].

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4.1.12.3.4 Nuclear Magnetic Resonance

Experimental Results

^{19}F NMR. A single NMR band with $\delta \approx 134$ ppm downfield from CF_3COOH (correction of the erroneous value, $\delta = 75$ ppm, given in [1]) [2], or $\delta = 59.8$ ppm downfield from CCl_3F [3] was reported (neither temperature nor solvent data given). In a mixture of NF_2NO and N_2F_4 (presumably at room temperature; obviously 40.055-MHz spectrum) a resonance at 5484 Hz downfield from CF_3COOH was attributed to N_2F_4, which corresponds to $\delta = 136.9$ ppm with respect to CF_3COOH (or $\delta = 58.4$ ppm with respect to CCl_3F; $\delta = -78.5$ ppm for CF_3COOH upfield from CCl_3F [22]). The observed shift, however, is not the exact value for pure N_2F_4 due to the presence of the paramagnetic impurity NO [4].

For N_2F_4 dissolved in perfluoro-2,3-dimethylhexane at room temperature, the triplet structure due to the coupling of the equivalent F nuclei to the N nucleus within an NF_2 group was observed: the resonances (40.055-MHz spectrum) were at 5559, 5436, and 5325 Hz ($\delta \approx 138.8$, 135.7, and 132.9 ppm) downfield from CF_3COOH (or $\delta = 60.3$, 57.2, and 54.4 ppm downfield from CCl_3F); the spin-spin coupling constant is thus $J(^{19}F\text{-}^{14}N) \approx 117$ Hz [5]. The latter was converted to $J(^{19}F\text{-}^{15}N) \approx 164$ Hz for comparison with theoretical values (see below) [6]. Upon cooling, the triplet structure gradually faded due to increasing relaxation of the ^{14}N nuclei through a quadrupole mechanism. However, in suitable solvents (NF_3, CF_4) additional structure began to appear at about −130°C, and a five-line spectrum was present at −155°C which did not change on further cooling to −180°C. The 40-MHz spectrum of N_2F_4 in NF_3 at −155°C consisted of a strong line at $\delta = 60.4$ ppm (within a quartet at $\delta = 65.2$, 53.2, 44.0, and 31.9 ppm) downfield from CCl_3F. The 12.8-MHz spectrum of N_2F_4 in N_2F_2 at −155°C shows the strong line at $\delta = 60.5$ ppm (and a quartet at 88.0, 50.9, 47.4, and 9.5 ppm). These spectra constitute decisive evidence for the coexistence of the two N_2F_4 rotamers (compare pp. 306/8). The strong single line was attributed to the four equivalent F nuclei in trans-N_2F_4 and the quartet to the AA′BB′ ($F_aF_{a'}F_bF_{b'}$) spin system of the two gauche rotamers which constitute a d,l pair (see **Fig. 10**). The downfield pair of lines in the quartet were assigned to the "external" nuclei, F_a, $F_{a'}$, and the upfield pair to the "internal", F_b, $F_{b'}$, because the latter are shielded to a greater extent by the greater number of near-neighbor F atoms. In the trans rotamer the shielding of the four equivalent F nuclei is similar to that of F_a and $F_{a'}$ in the gauche rotamer. The area ratio of the trans and gauche spectra is about 1:1 independent of temperature (−145 to −180°C), which indicates nearly equal populations of the two rotamers [7]. Much improved resolution (factor ≈12) was achieved in the 40-MHz spectrum by using mixed solvents with NF_2NO and NO as chief constituents. Fine structure in the NMR lines of the gauche rotamer was revealed and satisfactorily interpreted in terms of the AA′BB′ approximation. The parameters for gauche-N_2F_4 are (errors ≤ 0.2 Hz): chemical shift between the two pairs F_a, $F_{a'}$ and F_b, $F_{b'}$ $\delta = 688.6$ Hz, spin-spin coupling constants $J(F_a\text{-}F_b) = \pm 489.6$ Hz, $J(F_a\text{-}F_{b'}) = J(F_{a'}\text{-}F_b) = \mp 13.4$ Hz, $J(F_a\text{-}F_{a'}) = \mp 58.8$ Hz, and $J(F_b\text{-}F_{b'}) = \pm 109.0$ Hz [8].

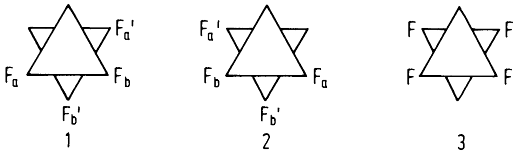

Fig. 10. Conformations of N_2F_4. 1, 2 = gauche, 3 = trans.

^{14}N NMR. The $^{19}F\text{-}^{14}N$ double resonance spectrum of N_2F_4 (neither temperature nor solvent data given) exhibits a chemical shift of $\delta = -39.8$ ppm upfield from NF_3 (in a field for which the resonance frequency of ^{19}F in NF_3 is 40.0 MHz) [3]; this corresponds to $\delta = -47.8$ ppm with respect to the NO_3^- reference [9]. From the ^{14}N NMR of neat liquid N_2F_4 at −110°C, $\delta = -(35 \pm 5)$ ppm was measured using the NO_3^- as a reference in a 4.5 M solution of NH_4NO_3 in aqueous HCl [9].

Theoretical Results

Spin-Spin Coupling Constants. $J(^{14}N\text{-}^{19}F) = -99.92$ Hz (−99.93 Hz in [11]), $J(^{14}N\text{-}N\text{-}^{19}F) = +11.26$ Hz for the gauche rotamer and $J(^{14}N\text{-}^{19}F) = -100.58$ Hz, $J(^{14}N\text{-}N\text{-}^{19}F) = +8.84$ Hz for the trans rotamer [12] follow from a semiempirical SCF calculation (method described in [10]). $J(^{19}F\text{-}^{15}N) = 190.697$ or 86.855 Hz (for cis-N_2F_4) follow from INDO calculations including two perturbation approaches [6].

^{14}N Nuclear Shielding and Chemical Shift. A few calculations of the total shielding constant $\sigma = \sigma^p + \sigma^d = ⅓(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, of the para- and diamagnetic contributions, σ^p and σ^d, and of the tensor elements, σ_{xx}, σ_{yy}, σ_{zz}, were performed. Approximate perturbed Hartree-Fock theory within the framework of the INDO method gives $\sigma^p = -243$ ppm (for gauche-N_2F_4) which gives $\delta = -43$ ppm with respect to the NO_3^- standard ($\sigma^p = -286$ ppm calculated) [13]. The use of gauge-dependent atomic orbitals within the CNDO/S (= CNDO + CI) approximation results in $\sigma = 34.03$ ppm corresponding to $\delta = -50.94$ ppm with respect to NO_3^-; the paramagnetic tensor elements are $\sigma^p_{xx} = -363.88$, $\sigma^p_{yy} = -182.93$, $\sigma^p_{zz} = -315.47$ ppm (for a planar $F_2N–NF_2$ molecule in the (xz) plane with the z axis in the N–N direction), their anisotropy $\Delta\sigma^p = \sigma^p_{yy} - ½(\sigma^p_{xx} + \sigma^p_{zz})$ is 156.74 ppm [14].

The local diamagnetic term σ^d_{loc}, i.e., shielding restricted only to the electrons of the N atom, and the difference $\Delta\sigma^d_{loc}$ with respect to N_2 were calculated semiempirically for small N-containing molecules including N_2F_4 using Pople's model [15] and the atom-dipole model [16]: for N_2F_4, $\sigma^d_{loc} \approx 320$ to 355 ppm, $\Delta\sigma^d_{loc} \approx -2.30$ to -4.30 ppm [17], $\sigma^d_{loc} \approx 321$ to 323 ppm, $\Delta\sigma^d_{loc} \approx -1.1$ to -3.2 ppm [18]. The theoretical results were compared with the experimental values obtained from $\Delta\sigma^d_{loc} = -0.652 \cdot \Delta E_i(N1s)$, where $\Delta E_i(N1s)$ in eV is the chemical shift in the core electron binding energy measured by X-ray photoelectron spectroscopy (XPS): $\Delta\sigma^d_{loc} = -1.70$ ppm [17] using XPS data of [19], $\Delta\sigma^d_{loc} = -1.63$ ppm [18] using XPS data of [19, 20]. For a discussion of the reliability of the theoretical methods for calculating nitrogen shielding constants, see [21].

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4.1.12.3.5 Rotational Constants. Moments of Inertia. Microwave Spectrum

The trans rotamer of N_2F_4 is an asymmetric top ($\varkappa \approx -0.006$), its axis of intermediate moment of inertia is the C_2 axis. The gauche rotamer approximates a prolate symmetric top ($\varkappa \approx -0.73$) with the C_2 axis as the axis of highest moment of inertia. Rotational constants A, B, C and moments of inertia I_A, I_B, I_C obtained from the microwave spectrum and from electron diffraction structural data are given in Table 20.

Table 20

N_2F_4. Rotational Constants A, B, C and Moments of Inertia I_A, I_B, I_C.

	gauche-N_2F_4				trans-N_2F_4
A in MHz (cm^{-1})	5576.21	5576.184	—	(0.186)	(0.178)
B in MHz (cm^{-1})	3189.35	3189.400	—	(0.106)	(0.127)
C in MHz (cm^{-1})	2812.95	2813.171	—	(0.094)	(0.077)
$\varkappa = (2B-A-C)/(A-C)$	−0.72757	—	—	—	−0.0058
I_A in amu·Å^2	90.68	—	91.9	—	—
I_B in amu·Å^2	158.6	—	161.8	—	—
I_C in amu·Å^2	179.8	—	177.4	—	—
remark	a)	b)	c)	d)	e)
Ref.	[1]	[4]	[2]	[5]	[5]

a) Twenty-five lines with J up to 21 were recorded in the microwave spectrum between 19000 and 33000 MHz. The rotational constants result from the analysis of ten $\Delta J = 1$ transitions with $J \leq 4$, however, with neglect of centrifugal distortion [1]. Conversion of A, B, and C into moments of inertia for comparison with electron diffraction values [2].

b) Distortion-free constants from analysis of the MW results [1]. The observed spectrum was fitted to the Watson relation [3] containing five quartic centrifugal distortion constants (in MHz): $d_J = -13.89 \times 10^{-3}$, $d_{WJ} = 4.7984 \times 10^{-6}$, $d_K = -208.72 \times 10^{-3}$, $d_{WK} = 81.164 \times 10^{-6}$, and $d_{JK} = -256.63 \times 10^{-3}$ [4].

c) Calculated from electron diffraction data, which, however, indicated only the gauche conformation [2].

d) MW values in cm^{-1} for comparison with the values for trans-N_2F_4 [5].

e) Calculated [5] from electron diffraction data which assumed only the trans form [6].

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4.1.12.3.6 Molecular Vibrations. Raman and IR Spectra. Force Constants

For each N_2F_4 conformer, twelve fundamental vibrations are expected which are distributed among the symmetry species of point groups C_{2h} and C_2. They obey the selection rules and exhibit the polarization properties in the Raman spectrum and the types of band contours in the IR spectrum as follows:

trans-N_2F_4 (C_{2h}): $4A_g$ (Ra, p) + $3A_u$ (IR, c) + $2B_g$ (Ra, dp) + $3B_u$ (IR, a, c)

gauche-N_2F_4(C_2): 7A (Ra, p; IR, c) + 5B (Ra, dp; IR, a, c)

p = polarized, dp = depolarized; a-, b-, c-type transition = change of dipole moment in the direction of the axis of least, intermediate (= C_2 axis of trans-N_2F_4), and highest (= C_2 axis of gauche-N_2F_4) moment of inertia, respectively.

The interpretation of the vibrational spectra has been the subject of considerable discussion. A consistent assignment, however, of the fundamental vibrations to the observed Raman and IR bands has not yet been attained, see Table 21, p. 318.

The earliest IR spectra ($8<\lambda<16$ μm) recorded after the first preparation [1 to 3] and purification [4] of N_2F_4 gas showed a very strong and complex band between 9.5 and 11 μm (≈1050 to 900 cm^{-1}) with the maximum at 10.4 μm, a strong broad band around 13.5 μm (≈740 cm^{-1}) [1, 2, 4] and a moderate increase of absorption from 15 to 16 μm [3]. The early vibrational analyses of the IR spectrum of the solid (77 K) between 300 and 4000 cm^{-1} [5], the Raman spectrum of the gas between 300 and 1100 cm^{-1} [6, 7], the IR spectrum of the gas between 75 and 4000 cm^{-1} [8], and the IR spectrum of the gas and the solid between 400 and 4000 cm^{-1} [9 to 11] were carried out on the assumption that N_2F_4 belongs to point group C_2 ([9 to 11] gave a temperature range of −110 to −150°C for the solid which is obviously incorrect [12, 13, 15] since N_2F_4 melts at or even below ca. −162°C, see p. 324). However, very discrepant assignments for the fundamental vibrations were obtained [6 to 11]. All these assignments had to be completely revised when it became evident that the vibrational spectra could only be correctly interpreted if an equilibrium mixture of gauche and trans conformers of N_2F_4 was taken into account (compare pp. 306/8) and when more careful analyses of better resolved spectra had been carried out.

The Raman spectrum of liquid N_2F_4 (−80 to −150°C) was measured between 100 and 4000 cm^{-1}, and the IR spectra of the gas (ca. 25°C) and the solid (−180°C) between 33 and 600 cm^{-1} [12, 13]. Considering also the IR spectra ($\nu>600$ cm^{-1}) for gaseous [8] and solid [9] N_2F_4, a number of frequencies were mutually exclusive in the Raman and IR spectra suggesting – supported by the polarization properties of the Raman bands – a vibrational assignment for both trans- and gauche-N_2F_4.These assignments for the symmetric NF_2 stretching and the N–N stretching vibrations have been used to interpret the temperature dependence of the corresponding Raman intensities between 22 and 250°C [14] (cf. p. 308).

A different assignment of the fundamental vibrations was reached [15] after comparing the IR spectra of the liquid (−120°C) and the solid (−175°C) recorded between 400 and 1100 cm^{-1} with the results of [12, 13] and earlier Raman [6] and IR [5, 8, 9] studies. The gas-phase IR spectrum (20°C, −70°C) was measured and reanalyzed between 20 and 4000 cm^{-1} [16]. The IR band contours were compared with those calculated for a-, b-, and c-type transitions in both gauche- and trans-N_2F_4 using MW [17] and electron diffraction [18] structural data, respectively. The vibrational assignment of [16] (based on the IR band contours and on the Raman depolarization ratios of [12, 13]) differs considerably from the earlier assignments of [12, 13] and [15] particularly for some of the NF_2 stretching, twisting, and scissoring modes. However, for some of the bands, Raman p or dp values conflicted with IR band contours [16]. It was also noted [19] that it was difficult in some cases to distinguish clearly between a- and c-type contours.

Another quite different assignment was proposed on the basis of Raman data (wavenumbers, intensities, and depolarization ratios) for the gas (25°C) and the solid (18 K) [19]. Again the most striking differences (in comparison with [16]) can be noted for the NF_2 stretching and bending modes of gauche-N_2F_4. As far as the ordering of bending modes is concerned, $\nu_{wag} > \nu_{sciss} > \nu_{twist}$ was chosen in [16], whereas [19] generally prefer (except for the ungerade modes ν_6 and ν_{12} of trans-N_2F_4) $\nu_{wag} > \nu_{twist} > \nu_{sciss}$. Curiously, both [16 and 19] refer to [20] which, however, neither definitely gives one of these sequences nor deals with N- and F-containing molecules (studies on N_2H_4 and P_2Cl_4 were also cited in [16]). A summary of the relevant interpretations of the vibrational spectra of both N_2F_4 conformers [12, 13, 15, 19] has been presented [19]. Unfortunately, the tables contain a number of errors, for example, the reversed numbering for ν_5 and ν_6 and for ν_{11} and ν_{12}, the scissoring and twisting modes of gauche-N_2F_4, used by [15, 16] was overlooked. A more recent low-temperature IR study of N_2F_4 gas (153 K, 0.65 Torr) and N_2F_4 solutions in liquid Ar and N_2 (77 to 140 K) in the 400 to 3300 cm^{-1} region appears to confirm – for wavenumbers above 467 cm^{-1} and except for an exchange of ν_5(trans) and ν_8(gauche) – the assignment in [19]. On this basis a great number of overtones and combination bands up to 1450 cm^{-1} for the gas and up to 2037.5 cm^{-1} for the solutions were identified [21].

The various assignments for the fundamental vibrations [12, 13, 15, 16, 19, 21] are summarized in Table 21, p. 318.

Rough intensity measurements from the MW spectrum placed the torsional vibration about the N–N bond between 100 and 150 cm^{-1} [17].

The integrated intensities of the IR bands at 466, 517, 539, 587, 738, and 900 to 1000 cm^{-1} of gaseous N_2F_4 (room temperature) were used to derive electrooptical parameters, i.e., dipole moment derivatives with respect to the corresponding normal coordinate (fundamental frequencies of [12] were obviously adopted) [22].

Symmetry force constants were calculated [23], however, using MW structural data [17] and obsolete fundamental frequencies [8].

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Table 21

N_2F_4. Fundamental Vibrations of the Trans and Gauche Conformations.

Wavenumbers ν_i in cm^{-1}; g = gas, l = liquid, s = solid, sol = solution; Ra = Raman spectrum; ϱ = depolarization ratio, p = polarized, dp = depolarized, a, b, c = type of IR band contour.

			vibration	Ra(l) [12]	ϱ [12]	IR(g) [8,12]	IR(s) [9,12]	Ra(l) [12]	IR(l) [15]	Ra(l) [12]	IR(g) [16]	Ra(g) [19]	Ra(s) [19]	IR(g) [8,12,16]	IR(sol) [21]
trans-$N_2F_4(C_{2h})$	A_g	ν_1	NF_2 sym. stretch	1010	0.40 p			1036		1036		1039 (p)	1038		
		ν_2	NF_2 wag	719	0.70 p			600		719		719 (p)	723		
		ν_3	N-N stretch	600	0.46 p			719		600		601 (p)	602		
		ν_4	NF_2 scissors	354	0.74 p			494		354		354 (p)	359		
	A_u	ν_5	NF_2 antisym. stretch			998	994		993		946 (b)			962	948.5
		ν_6	NF_2 twist			464	465		250 (g) [8]		252 (b)			252	
		ν_7	F_2N-NF_2 torsion			131	128		96 (g) [8]		131 (g) [8]			131	
	B_g	ν_8	NF_2 antisym. stretch	867	$^6/_7$ dp			867		867		873 (dp)	873		
		ν_9	NF_2 twist	494	$^6/_7$ dp			300		423		494 (dp)	498		
	B_u	ν_{10}	NF_2 sym. stretch			946	942		944		999 (c)			999	992.5
		ν_{11}	NF_2 wag			542	538		539		541 (a)			542	540.3
		ν_{12}	NF_2 scissors			254	257		466		466 (a)			467	467.5
gauche-$N_2F_4(C_2)$	A	ν_1	NF_2 sym. stretch	1036	0.33 p	1031	1033	1025	1021	1010	1009 (c)	1027 (p)	1026	1023	1020.5
		ν_2	NF_2 antisym. stretch	1025	0.40 p	1023	1022	1010	1005	923	934 (c)	1012 (p)	1011	1010	1006.5
		ν_3	NF_2 wag	733	0.72 p	737	735	588	735	733	740 (c)	733 (p)	736	737	734.8
		ν_4	N-N stretch	588	0.51 p	586	588	733	589	588	590 (c)	587 (p)	590	590	589.8
		ν_5	NF_2 twist	423	$^6/_7$ dp	—	—	354	—	284	284 (c)	423 (p)	430	—	—
		ν_6	NF_2 scissors	300	0.79 p?	295	301	—	—	300	300 (c)	298 (p)	304	300	—
		ν_7	F_2N-NF_2 torsion	122	?	116	122	122	122 (g) [8]	122	123 (c)	115 (p?)	—	116	—
	B	ν_8	NF_2 sym. stretch	960	?	959	960	960	961	1025	1016 (b)	946 (dp)	922	946	965.0
		ν_9	NF_2 antisym. stretch	923	0.81 dp?	933	920	923	920	960	962 (b)	931 (dp)	922	934	925.5
		ν_{10}	NF_2 wag	515	$^6/_7$ dp	519	517	515	518	515	518 (a)	494 (dp)	515	518	519.3
		ν_{11}	NF_2 twist	284	$^6/_7$ dp	284	286	284	283 (g) [8]	242	242 (b)	288 (dp)	288	284	—
		ν_{12}	NF_2 scissors	242	?	242	248	423	—	494	—	242 (?)	—	242	—
			assignment	Durig, Clark [12]				Koster, Miller [15]		Oskam et al. [16]		Durig, MacNamee [19]			Shchepkin et al. [21]

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4.1.12.3.7 Dissociation Energy D(F_2N–NF_2). Average N–F Bond Strength D_{av}(N–F). Heat of Atomization ΔH_{at}

D(F_2N–NF_2). The appearance potentials (AP) of NF_2^+ from N_2F_4 and NF_2 [1 to 5] and the activation energies of thermal dissociation of N_2F_4 [6, 7] were used for the determination of D, as well as various studies of the equilibrium $N_2F_4 \rightleftharpoons 2NF_2$ in the temperature range from 243 to 523 K: (1) mass spectrometry [8, 9], (2) pressure variation with temperature at constant volume [10 to 12], (3) temperature dependence of the ESR spectrum of NF_2 [13, 14], and (4) spectrophotometric methods based on the temperature dependence of the UV absorption (260 nm) [10, 11, 15] and the IR absorption [16] of NF_2. Dissociation energies of 21.6±3.2 [5] and 19.4±3.9 kcal/mol [3, 4] were obtained from appearance potential measurements. Single data derived from equilibrium and kinetics studies are given on pp. 326/31.

Apart from two early results [1, 2] that later were refuted [8 to 10, 20], dissociation energies between 18.6 and 21.7 kcal/mol were obtained. In the JANAF tables [17], the results of [9 to 11, 13, 14] have been reanalyzed by the third-law method, those of [9] also by the second-law method, yielding values of 21.79 to 22.87 kcal/mol at 298 K and a recommended value of $D_{298} = 22.26$ kcal/mol is given [17]. However, the JANAF values for heat capacity and entropy of N_2F_4 used for the third-law analysis were calculated only from fundamental vibrational frequencies for the gauche isomer, causing the third-law values of D_{298} to be too high, as demonstrated by [15]. Numerous other discussions, reviews, or tabular compilations which deal with the properties of N_2F_4 and/or the $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium give adopted or recommended dissociation energies for N_2F_4 [18 to 33]. D values of ca. 20 to 21 kcal/mol [18 to 30] were obtained from analyses of the early experimental results, mostly those of [9 to 11, 13, 14]. Two more recent reviews [31, 32] only summarize experimental results without recommending a certain value. $D_{298} = 22.3$ kcal/mol derived from "selected thermodynamic data" and given without any reference by [33] is presumably a rounded JANAF value (see above).

The enthalpy changes ΔH_0°(trans) and ΔH_0°(gauche) for the partial processes trans-$N_2F_4 \rightarrow 2NF_2$ and gauche-$N_2F_4 \rightarrow 2NF_2$ were calculated using the experimental overall equilibrium data [9, 11, 12], structural data [34, 35], and vibrational frequencies [36] for N_2F_4. Among the six sets of values obtained by the various combinations of equilibrium and structural data for N_2F_4, the values ΔH_0°(trans) = 20.33 and ΔH_0°(gauche) = 19.76 kcal/mol obtained by combining the data of [12] and [34] were considered to be most reliable. The corresponding ΔH°_T values were calculated for T=100, 200, ..., 1000 K; ΔH°_{300}(trans) = 21.36, ΔH°_{300}(gauche) = 20.56, and for the overall process ΔH°_{300} = 20.95 kcal/mol [37].

Results from quantum chemical calculations are: D = 12.5 kcal/mol at 298 K from an ab initio SCF-MO calculation with a Gaussian basis set [38], and 21.5, 22.6, and 22.5 kcal/mol at 298.15 K for the dissociation of trans- and gauche-N_2F_4 and for the overall process, respectively, from a CNDO/2 calculation (values also for T = 373.15, 423.15, and 523.1 K) [39].

D_{av}(N-F). The average bond strength in NF_2 (cf. p. 251) was accepted for N_2F_4: D_{av}(N-F) = 70.5 ± 1.6 kcal/mol [8, 9] or 71 kcal/mol [20].

ΔH_{at}. A value of $\Delta H_{at} \approx 302 \pm 10$ kcal/mol is estimated from the D(F_2N-NF_2) and the D_{av}(N-F) values given above.

$\Delta H_{at,0}$ = 297.4 kcal/mol for trans-N_2F_4 and 296.8 kcal/mol for gauche-N_2F_4 were derived by [39] using $\Delta H_{at,0}$ of NF_2 from JANAF [40] and the D_0 values of [37]. Values of 314.2 [41] and 316.5 [42] kcal/mol were presumably based on the older D(F_2N-NF_2) values of [1] and/or [2] and estimated average bond strengths in NF_2.

Theoretical values from CNDO calculations are (in kcal/mol): 320.9 for trans-N_2F_4 [41], 327.5 for both conformers [2], and 294.6 for trans- and 295.7 for gauche-N_2F_4 [39]. An estimation of bond energies [43] gave 308 kcal/mol (from D(F_2N-NF_2) = 32 and D_{av}(N-F) = 69 kcal/mol) [44].

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4.1.12.3.8 Microwave Spectrum. Raman Spectrum. Infrared Absorption

Data of the microwave spectrum are given in Section 4.1.12.3.5, p. 315.

The Raman spectrum and the conventional IR absorption spectrum are dealt with in Section 4.1.12.3.6, pp. 316/9.

4.1.12.3.9 IR Laser Spectroscopy with CO_2 Laser

The N_2F_4 molecule has a high density of absorption lines around 10 μm (the region of NF_2 stretching fundamentals, see p. 318) which are in resonance with CO_2 laser radiation. This fact was used to study laser-driven chemical reactions of N_2F_4, especially the kinetics of the thermal dissociation $N_2F_4 \rightarrow 2NF_2$ (see Section 4.1.12.6.2.1, pp. 326/31). Conversely, the absorption of CO_2 laser radiation and the saturation of N_2F_4 by CO_2 laser radiation have been used to solve various technical problems concerning the CO_2 laser, such as Q-switching, mode-locking, or prevention of parasitic oscillations and gain standoff, see [1] and references therein.

The absorption of CO_2 laser radiation by gaseous N_2F_4 was studied between 225 and 425 K from 1 to 100 Torr [1] and at room temperature (presumably) from ~0.1 to 2.5 Torr (also N_2F_4–Ar mixtures) [2]. The absorption of matrix isolated N_2F_4 (Ar, N_2, NO matrices) was studied presumably at about 25 to 30 K [3].

Laser-induced IR fluorescence was studied in three spectral ranges 1400 to 2500 cm^{-1}, 1100 to 1330, and 670 to 830 cm^{-1}, after excitation with the P(20) line (944.2 cm^{-1}) of CO_2 [5] (see also [2, 4]). The fluorescence risetimes were found to be shorter than the time between the molecular collisions. The fluorescence from 1400 to 2500 cm^{-1} thus indicated multiphoton absorption via direct coupling between laser radiation and molecular absorption. The fluorescence signals from states which lie below the energy of one absorbed CO_2 laser quantum (670 to 830 cm^{-1}) and from states which lie between one and two directly pumped levels (1100 to 1330 cm^{-1}) were attributed to rapid intramolecular relaxation between directly pumped and other vibrational states [5].

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4.1.12.3.10 Visible and Ultraviolet Spectra

Gas. The gas is colorless. Attempts to detect an absorption in the red region (100°C, 1 atm) were unsuccessful. The strong UV absorption band at 260 nm is due to the equilibrium concentration of NF_2 radicals (see pp. 257/9); heating and cooling the gas cause reversible enhancement and diminution of the absorbance at 260 nm [1]. A continuous absorption on the short-wavelength end of the absorption band was attributed to N_2F_4 [2, 3]. The extinction coefficient increases from 0.5 $L \cdot mol^{-1} \cdot cm^{-1}$ at 240 nm to 22.2 $L \cdot mol^{-1} \cdot cm^{-1}$ at 215 nm [3]. (See also [8].)

Liquid. N_2F_4 is a clear, colorless liquid below −73°C [4, 5] and at about −160°C [6]. A light to dark blue, originally attributed to impurities, was shown to be a function of the concentration of NF_2 radicals in the gas prior to condensation: samples condensed from the cold gas (−30°C) at relatively high pressures were colorless, but samples condensed from the gas at elevated temperatures and low pressures appeared blue-black; the depth of the color paralleled the expected NF_2 concentration in the gas phase provided the condensation was carried out rapidly with liquid nitrogen. The fact that no absorption spectrum could be detected in the red for gaseous N_2F_4, suggested that association in the condensed phase is responsible for the color [1].

The UV absorption band at 260 nm is absent in liquid N_2F_4 at −97°C; a weak continuum with ε increasing from 0.012 $L \cdot mol^{-1} \cdot cm^{-1}$ at 275 nm to 0.301 $L \cdot mol^{-1} \cdot cm^{-1}$ at 240 nm was reported [7].

Solid. At 77 K, N_2F_4 is a white solid [6].

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4.1.12.4 Crystal Structure

Without giving experimental details, the following was stated by Colburn: "The crystal structure is cubic, $a_0 = 24.95$ Å, space group O_h^7–Fd3m, characterized by a three-dimensional network with mutually connected intra-crystalline voids accessible through openings 13 Å in diameter (pore diameter). The void volume is 51 vol%."

Reference:

C. B. Colburn, Rohm & Haas Co. (U.S. 3220799 [1958/65]; C.A. **64** [1966] 6158).

4.1.12.5 Thermal Properties

Density ϱ in g/cm^3

For gaseous N_2F_4 at 21°C and 1 atm, $\varrho_g = 0.00444$ was reported [1, 2].

For liquid N_2F_4 at its boiling point, $\varrho_l = 1.65$ (−73°C) [1, 4, 5], 1.397 (−73°C) [6], 1.454 (−74.2°C) [7] were measured. At −100 and −97°C, the densities of liquid N_2F_4 were reported as 1.5 [6] and 1.54 [3], respectively. The temperature dependence of ϱ_l between −150 and +30°C (T≈123 to 303 K) is given by $\varrho_l = 2.20509 - 3.77531 \times 10^{-3}\,T$ [7].

Vapor Pressure

The vapor pressure of N_2F_4 as a function of absolute temperature T can be expressed by $\log p = -A/T + B$, p in Torr; the experimental parameters A and B are as follows (the values in parentheses were calculated from the critical conditions as given in [8, 9]):

A in K	B	T in K[a]	Ref.
692	6.33	"low temperatures" [11]	[4, 10, 11]
811	6.9634	not given	[13]
820.75	7.0051	111.65[b] to 198.95[c]	[7, 8]
862.9	7.2163	118.15 to 203.15	[12]
861.57	7.1950	198.95[c] to 309.35[d]	[8]
867.62	7.1950		[7]
(875)	(7.27)		[14]

[a] Original Celsius degrees converted taking 0°C≙273.15 K. – [b] Melting point (compare below). – [c] Boiling point. – [d] Critical point.

The data of [8] approach those of [13] in the temperature range between the melting point and the boiling point and those of [12] between the boiling point and the critical point; therefore, the differing results of [10, 11] were considered to be incorrect [8].

Equation of State

The parameters a and b in the van der Waals equation were calculated from the critical temperature T_c and the critical pressure p_c (see below) by means of the formulas $a = 27\,R^2 \cdot T^2/64p_c$ and $b = R \cdot T_c/8p_c$ (R = gas constant). Thus, $a = 7.4300 \times 10^6$ atm·cm^6·mol^{-2} and $b = 86.712$ cm^3/mol [9].

Melting Temperature t_m. Boiling Temperature t_b

$t_m = -164.5$°C according to [15], about −162°C according to [13, 16] without giving any experimental details. Melting point measurements according to the "method described in Brauer's Handbook [17]" gave $t_m = -161.5 \pm 0.5$°C [7, 8]. A melting range from −165.8 to −165.1°C was observed with a platinum resistance thermometer and was tentatively explained by the existence of two solid phases, i.e., gauche-N_2F_4 and trans-N_2F_4 [18].

The triple point was reported to be −168°C (no details) [1, 4, 5] (wrong citation in [2]).

For the boiling point, extrapolations of the vapor pressure data to 1 atm yielded $t_b = -73$°C [1, 4, 5, 10], -74 ± 1°C [13], −74.1°C [12], and -74.2 ± 0.1°C [8].

Critical Constants t_c, p_c, V_c

The critical temperature t_c measured by the Caignard de la Tour tube method is 36°C [4, 10, 11]; extrapolation of the vapor pressure data supposedly gave $p_c = 20$ atm [11] or 77 atm (?) [4, 10] (the respective vapor pressure equation (see above) actually yields $p_c = 16.2$ atm at 36°C). Experimental values for both t_c and p_c are: $t_c = 36.2 \pm 0.1$°C and $p_c = 36.6 \pm 0.8$ atm, thus $V_c = 181$ cm³/mol [7, 8]; from the vapor pressure equation for t = −74.2 to 36°C, a similar value of $p_c = 33.8$ atm was calculated [8]. Without any comment, $t_c = 37.5$°C and $p_c = 54$ atm are reported in [13]. The t_c value quoted by [19] is erroneous.

Heat of Evaporation ΔH_v

$\Delta H_v = 3.750$ [7, 8] and 3.170 [4, 10, 11] kcal/mol were obtained from the vapor pressure measurements. The second value was also quoted by [13]. The value quoted by [19] is erroneous.

Heat Capacity. Thermodynamic Functions

Heat capacity C_p°, entropy S°, and the Gibbs free-energy function $-(G^\circ - H_{298}^\circ)/T$ for the temperature range 298 to 1000 K have been calculated for both gauche- and trans-N_2F_4 [20] using the fundamental frequencies of [21] and structural data of [22], see Table 22. Values for 298 K, $C_p^\circ = 19.06$ cal·mol⁻¹·K⁻¹ and $S^\circ = 71.66$ cal·mol⁻¹·K⁻¹ are given by [15].

Table 22

N_2F_4(g). Heat Capacity C_p°, Entropy S°, and Gibbs Free-Energy Function $-(G^\circ - H_{298}^\circ)/T$ (all in cal·mol⁻¹·K⁻¹) [20].

	gauche-N_2F_4(g)			trans-N_2F_4(g)		
T in K	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$	C_p°	S°	$-(G^\circ - H_{298}^\circ)/T$
298	21.096	75.245	75.245	20.438	73.814	73.814
300	21.162	75.376	75.246	20.510	73.940	73.814
400	24.173	81.903	76.115	23.773	80.318	74.663
500	26.217	87.531	77.848	25.955	85.873	76.361
600	27.598	92.441	79.880	27.415	90.743	78.361
700	28.550	96.771	81.990	28.415	95.049	80.443
800	29.223	100.630	84.084	29.120	98.892	82.513
900	29.713	104.102	86.119	29.632	102.353	84.530
1000	30.079	107.252	88.077	30.013	105.495	86.471

The values for C_p°, S°, $-(G^\circ - H^\circ_{298})/T$ and $H^\circ - H^\circ_{298}$ at $T = 0$ to 6000 K listed in the JANAF Tables [23] were calculated by assuming that only a gauche isomer of N_2F_4 existed and by using the fundamental frequencies given by [24]; the assignment of [24], however, has been disproved (see pp. 316/8). For the same reason, the results for S°_{298} and ΔG° at $T = 298$ to 1000 K [25] based on the fundamental frequencies of [26] must be rejected.

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4.1.12.6 Chemical Behavior

4.1.12.6.1 General Remarks

An outstanding feature of N_2F_4 is its weak N–N bond that leads to facile cleavage yielding two NF_2 radicals. Thus, the chemical behavior of N_2F_4 is primarily governed by that of NF_2, especially at temperatures above about 200°C. Following the review of Lawless and Smith [1], five general types of reactions of N_2F_4/NF_2 can be discerned: (1) reactions of NF_2 radicals, (2) photochemical reactions of excited NF_2^*, (3) reactions of N_2F_4 as a fluorinating agent, (4) reactions of N_2F_4 as a reducing agent, and (5) F^- abstraction from N_2F_4 by strong F^- acceptors such as SbF_5. Type (1) reactions can be subdivided into (a) addition to unsaturated bonds (the best examples involve olefins), (b) radical combination (for example, with H or F atoms or with SF_5), and (c) abstraction of a labile H or other atom (examples are NHF_2 formation reactions from AsH_3 or RSH). Photochemical reactions of NF_2 are characterized by NF_2 dissociation into NF and F upon UV irradiation. Consecutive reactions of both fragments lead to characteristic NF_3 and N_2F_2 side products. Type (3) and (4) reactions cannot be subsumed under common mechanisms and are not very well defined. Type (5) reactions are remarkable because they are the only ones where the N–N bond is left intact. Ruff [2] classified the N_2F_4 reactions according to types (1a) to (1c) and (5). Colburn [3] reviews NF_2 radical reactions of type (1b), (1c), and (2). Examples from (1a) to (1c) and possible NF_2 redox reactions are treated by Freeman [4]. An early subdivision of N_2F_4 reactions included two types: addition of NF_2 and fluorination [5].

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4.1.12.6.2 Thermal Decomposition

4.1.12.6.2.1 The $N_2F_4 \rightleftharpoons 2NF_2$ Equilibrium

Gas Phase

Thermodynamic Data. Facile dissociation of gaseous tetrafluorohydrazine into two difluoroamino radicals at temperatures between 20 and 250°C provoked a number of studies of that equilibrium. Reaction enthalpies, ΔH, that have been derived from experimental data by second-law analysis are given below:

ΔH in kcal/mol	temperature range in K	experimental method, remarks	Ref.
19.85 ± 0.5	373 to 423	pressure variation with temperature at constant volume	[1]
20.5 ± 0.15	423 to 523	same as above	[2]
19.3 ± 1.0*)	342 to 435	temperature dependence of NF_2 ESR signal intensity and degrees of dissociation taken from [1]	[3]

ΔH in kcal/mol	temperature range in K	experimental method, remarks	Ref.
18.6 ± 1.4	~345 to ~415	temperature dependence of NF_2 IR absorption (at 1104 cm^{-1}) and degrees of dissociation taken from [1]	[4]
21.7*)	~295 to ~345	temperature-dependent NF_2 UV absorbance; preliminary note: ΔH = 19.2 kcal/mol [5]	[1]
20.9 ± 0.4*)	375 to 462	temperature-dependent NF_2 UV absorbance behind incident shock waves; temperature-dependent extinction coefficients extrapolated from higher temperatures	[6]
21.5 ± 1.6	333 to 451	temperature dependence of NF_2^+ and $N_2F_4^+$ ion currents in mass spectrum	[7]

*) At 298 K.

Internal energy changes ΔU, which are the primary result of the analysis of ESR, IR, and UV data, are lower than ΔH by $RT \approx 0.6$ kcal/mol at room temperature [3 to 6]. Heats of dissociation (from [1, 5, 7]) were reanalyzed in the JANAF Tables [8] by third-law methods, see p. 319 where further reviews are compiled. The result of a second-law analysis of the temperature-dependent 260-nm NF_2 absorption was preferred over that from a third-law analysis ($\Delta H^\circ_{298} = 21.05 \pm 0.10$ kcal/mol). The latter value depended on the unknown distribution of trans- and gauche-N_2F_4 conformers; a 1:1 mixture was assumed [6]. An ab initio MO calculation with a Gaussian basis set predicted $\Delta U^\circ_0 = 11.9$ kcal/mol and $\Delta H^\circ_{298} = 12.5$ kcal/mol [11]. Data derived from appearance potentials are mentioned on p. 319.

The enthalpy change ΔH for the overall process was later split to account for the two partial processes, trans-$N_2F_4 \rightleftharpoons 2NF_2$ (ΔH(trans)) and gauche-$N_2F_4 \rightleftharpoons 2NF_2$ (ΔH(gauche)). Experimental ΔH values, geometries, and vibrational frequencies [9] or molecular constants obtained from a semiempirical MO (CNDO) calculation [10] provided the basis. Thermodynamic functions were calculated within the harmonic oscillator-rigid rotator approximation. Third-law values that were considered to contain the best choice of experimental parameters were as follows (all in kcal/mol): ΔH°_T(trans) = 20.33 (0 K), 21.36 (300 K), 21.20 (400 K), 20.95 (500 K); ΔH°_T(gauche) = 19.76 (0 K), 20.56 (300 K), 20.35 (400 K), 20.09 (500 K) [9] (further data were calculated for the 100 to 1000 K interval). CNDO based enthalpy changes, $\Delta H^\circ_{298.15}$(trans) = 21.54 kcal/mol and $\Delta H^\circ_{298.15}$(gauche) = 22.60 kcal/mol [10] (further data for 373.15, 423.15, and 523.1 K were given) were slightly larger than those derived from experiments. For instance, $\Delta H^\circ_{298.15} = 22.51$ kcal/mol was calculated for the overall process [10], whereas the experimental value was 21.70 kcal/mol [1].

An average change in entropy for $N_2F_4 \rightarrow 2NF_2$ in the range 295 to 345 K was derived from the temperature-dependent UV absorbance, ΔS = 45 $cal \cdot mol^{-1} \cdot K^{-1}$ [1]. From $(\partial p/\partial T)_V$ measurements an average value of ~40 $cal \cdot mol^{-1} \cdot K^{-1}$ (range 373 to 423 K) was obtained [1]. Further experimental ΔS data may be derived from temperature-dependent equilibrium constants given below. Values calculated by statistical thermodynamics were quoted as 45.477 and 46.138 $cal \cdot mol^{-1} \cdot K^{-1}$ at 25 and 127°C, respectively [12] (input data?). With the assumptions mentioned above for the splitting of ΔH, reaction entropies have also been split into contributions for dissociation of trans- and gauche-N_2F_4 [9, 10]. ΔS°(trans) = 45.52 (300 K), ΔS°(gauche) = 42.75 (300 K), and ΔS°(overall) = 42.72 (300 K) (all data in $cal \cdot mol^{-1} \cdot K^{-1}$) are taken from the compilation for the 100 to 1000 K range [9]. With molecular constants derived from MO calculations the following data at 298.15 K have been obtained (in $cal \cdot mol^{-1} \cdot K^{-1}$): $\Delta S°(trans) = 43.90$, $\Delta S°(gauche) = 42.82$, and $\Delta S°(overall) = 42.32$ [10]. The latter value may be compared to 43.08 $cal \cdot mol^{-1} \cdot K^{-1}$ that emerged from a reanalysis [10] of earlier experimental data [1].

Values of the function $-\Delta(G_T^\circ - H_{298}^\circ)/T$ for temperatures between 375 and 462 K, for example, 42.794 $cal \cdot mol^{-1} \cdot K^{-1}$ at 375 K and 42.689 $cal \cdot mol^{-1} \cdot K^{-1}$ at 462 K, rely on the assumption that a 1:1 mixture of trans- and gauche-N_2F_4 dissociates into NF_2 radicals [6].

A change in Gibbs free energy of 8.26 kcal/mol at 298 K was derived [6] from an early equilibrium constant [1]. Second- and third-law values for ΔH_{298}° as obtained from the temperature-dependent NF_2 UV absorption and entropy changes calculated for a 1:1 mixture of N_2F_4 conformers led to $\Delta G_{298}^\circ = 8.13 \pm 0.4$ kcal/mol (2nd law) and $\Delta G_{298}^\circ = 8.28 \pm 0.10$ kcal/mol (3rd law) [6]. The value of 7.45 kcal/mol (misprinted in original text [12]) was refuted [6] because its consequence was an unrealistically low NF_2 extinction coefficient at 260 nm.

An equilibrium constant of 8.8×10^{-7} atm at 25°C was derived from the pressure-dependent NF_2 UV absorption. The N_2F_4 pressures varied between about 25 and about 800 Torr [1]. A more recent measurement at lower pressures between 2.5×10^{-3} and 4×10^{-2} Torr confirmed the earlier value, $K_p = (7.0 \pm 1.1) \times 10^{-4}$ Torr ($(9.2 \pm 1.4) \times 10^{-7}$ atm) at 300 K [16]. Values of 2.4×10^{-6} [1] (misquoted in [16]) and 1.3×10^{-6} atm [2] at 300 K were extrapolated from early $(\partial p/\partial T)_V$ measurements at higher temperatures and pressures. The ratio of the termolecular NF_2 recombination rate constant and bimolecular N_2F_4 dissociation rate constant (both measured at 298 K in Ar) yielded an equilibrium constant of $(4 \pm 1) \times 10^{13}$ molecule/cm^3 in fair agreement with directly measured [1] and calculated [8] values.

Measurements of the pressure variation with temperature resulted in temperature-dependent equilibrium constants. The equations read for K_p measured in atm: (1) $\log K_p = -4239/T + 8.519$ [1] (the coefficients are the average of individual data in the 368 to 423 K range [1], see e.g., [13]) and (2) $\log K_p = -4492/T + 9.1032$ (range 423 to 523 K) [2]. Equilibrium fugacity constants between 100 and 150°C were tabulated [1]; for example, $K_f = 1.23 \times 10^{-3}$ at 100°C and $K_f = 2.95 \times 10^{-2}$ at 150°C. Two studies report that equation (1) best describes the $N_2F_4 \rightleftharpoons 2NF_2$ equilibrium measured at shock temperatures between 350 K and 450 K [15] or 489 K [14]. For convenience, equilibrium constants were calculated in mol/L concentration units, (1) $\log K_c = (-19100\ cal \cdot mol^{-1}/2.303\ RT) + 6.67$ [14, 15]. The individual coefficients that were given by Johnson and Colburn [1] were later criticized as being still concentration dependent [12]. A revised equation, (3) $\log K_p = -4590/T + 10.15$ [12], which relies on an average ΔH_{298}° value taken from the literature and on ΔS calculated by statistical thermodynamics, gives, however, equilibrium constants that are higher than those from all other sources (e.g., factor 6 to 8 as compared to equation (2), between 300 and 600 K). In more recent shock tube studies individual equilibrium constants have been measured between 375 and 462 K, for example, $\ln K_p = -6.665$ (375 K), -1.318 (462 K) [6]. These values are in excellent agreement with those predicted by equation (2). Overall equilibrium constants, calculated by statistical thermodynamics and by use of experimental molecular constants, for example, $\log K_p = -5.925$, -2.129, and $+0.117$ at 300, 400, and 500 K, respectively [9], are also close to those from equation (2).

Constants calculated for dissociation of trans- and gauche-N_2F_4 amount to $\log K_p(trans) = -5.611$, -1.732, $+0.572$ and $\log K_p(gauche) = -5.637$, -1.907, and $+0.305$ at 300, 400, and 500 K, respectively [9] (further data for the 100 to 1000 K range are tabulated [9]). Constants at 298.15 K, $\log K_p(overall) = -7.251$, $\log K_p(trans) = -6.1937$, $\log K_p(gauche) = -7.2106$ [10] (see also data for 373.15, 423.15, and 523.1 K), which were calculated from CNDO based molecular parameters, predicted less dissociation than was expected from experiment.

The degree of N_2F_4 dissociation as a function of temperature and pressure was calculated by use of equilibrium constants from equation (1) [3, 13]. For instance, the degree of dissociation at 25°C increased from 0.004 to 0.12 when the pressure was lowered from 1 to 10^{-3} atm. At 150°C the respective values amounted to 0.9 and 0.94 [13]. Data equivalent to equilibrium constants from equation (3) were also published [12].

Kinetic Data. The kinetics of N_2F_4 dissociation have been studied in most cases by monitoring the NF_2 UV absorption at 260 nm behind incident shock waves [14, 15, 17 to 19]. Only a few data have been obtained by observation of the NF_2 laser magnetic resonance signal after N_2F_4 had been allowed to stream into a low-pressure cuvette with passivated quartz walls [16].

Second- and pseudo-first-order rate constants for N_2F_4 dissociation in inert gases M are compiled below:

M	temperature range in K	pressure range in atm	rate constant ($R = 1.9865\ cal \cdot K^{-1} \cdot mol^{-1}$)	Ref.
He	372 to 423	—	$k(He)/k(Ar) = 1.2 \pm 0.1$; k(Ar) from 1st entry for M = Ar	[15]
Ar	350 to 456	0.58 to 2.7	$k = 1.5 \times 10^{15} T^{0.5} \exp(-15200/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$	[15]
Ar	390 to 500	0.8 to 1.2	$k = 10^{17.37} \exp(-16700/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$	[17]
Ar	360 to 410	0.6 to 6	$k/[Ar] = 10^{13.47 \pm 0.43} \exp[-(17100 \pm 700)/RT]\ s^{-1}$	[18]
Ar	350 to 550	0.26 to 1.05	$k/[Ar] = 10^{12.9} \exp(-15500/RT)\ s^{-1}$	[19]
Ar	351 to 489	1 to 9.4	$k/[Ar] = 10^{15.37} \exp(-19800/RT)\ s^{-1}$	[14]
N_2	344 to 407	0.6 to 6	$k/[N_2] = 10^{14.98 \pm 0.42} \exp[-(19400 \pm 700)/RT]\ s^{-1}$	[18]
N_2	351 to 403	0.69 to 12	$k/[N_2] = 1.15 \times 10^{15} \exp(-19800/RT)\ s^{-1}$	[14]
NF_2	300	—	$k(NF_2) < 5\ k(N_2F_4)$; see next entry	[16]
N_2F_4	300	$(3.3\ to\ 53) \times 10^{-6}$	$k = (6.4 \pm 0.2) \times 10^5\ cm^3 \cdot mol^{-1} \cdot s^{-1}$	[16]
N_2F_4	~360 to 400	—	$k(N_2F_4)/k(Ar) = 1.8 \pm 0.2$; see 1st entry for M = Ar	[15]
SF_6	~350 to 370	—	$k(SF_6)/k(Ar) = 1.7 \pm 0.2$; see 1st entry for M = Ar	[15]

Bimolecular rate constants measured in Ar below 2 atm [14, 15, 18] were combined in a single Arrhenius representation, $k(Ar) = 10^{16.51 \pm 0.1} \exp[-(15300 \pm 600)/RT]\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [14]. Data measured in experiments for M = N_2 [14] were admittedly not very reliable. At high experimental scatter and, as compared to M = Ar, an unexpectedly low Arrhenius preexponential factor (in the high-pressure limit) gave rise to some doubt [14]. It was mentioned that trace impurities of O_2 (ca. 0.01%) in Ar enhanced the rate of N_2F_4 dissociation [17].

Several studies cover the fall-off region of unimolecular dissociation. The pressure at which the observed rate constant reaches one-half of the limiting high-pressure value is around 4 atm (at ca. 400 K) [14]. The fall-off behavior does not allow a direct comparison to low-pressure, termolecular NF_2 recombination rate constants, see a comment [20] on earlier dissociation rate constants [18]. Bimolecular rate constants for N_2F_4 dissociation in Ar that were calculated by the RRKM formalism exhibited a similar temperature dependence but were uniformly higher by a factor of about 13 than experimental values [14].

Rate constants for NF_2 recombination were measured in a low-pressure flow system. At 293 K and pressures between 0.75 and 3.75 Torr termolecular rate constants were as follows (all in 10^{15} $cm^6 \cdot mol^{-2} \cdot s^{-1}$): in He 2.8 ± 0.5, in Ar 4.6 ± 0.5, in O_2 3.6 ± 0.7, in NO ~2.2 (estimate), in SF_6 10.6 ± 1.1 [20]. A rate constant of $(17.4 \pm 3.6) \times 10^{15}$ $cm^6 \cdot mol^{-2} \cdot s^{-1}$ at 300 K for $M = N_2F_4$ was calculated from an experimental dissociation rate constant and the equilibrium constant [16].

Condensed Phases

When N_2F_4 was dissolved in nonpolar solvents such as perfluoro-2,3-dimethylhexane, 2,2-dichloro-3-chloroperfluorobutane, and various Kel-F oils, the NF_2 radical was easily detected at 25°C by its characteristic ESR spectrum [21]. Pure liquid N_2F_4 is weakly dissociated at 25°C (0.0045%). For comparison, a value of 0.022% was measured in the vapor phase at 25°C and 13 atm [22]. The temperature-dependent intensity of the NF_2 ESR triplet that was measured between −30 and +25°C in liquid N_2F_4 yielded a reaction enthalpy for dissociation of 19.8 ± 1.3 kcal/mol [22].

NF_2 radicals deposited in a low-temperature N_2 matrix recombined at about 40 K as was evidenced by the loss of the 573 cm^{-1} IR band for NF_2 after temperature cycling between 20 and 40 K [23].

N_2F_4 dissociated on a passivated (by N_2F_4) quartz wall with a rate constant of $(1.25 \pm 0.25) \times 10^{-4}$ s^{-1} at 300 K. Recombination of NF_2 radicals on the wall occurred with a rate constant of $(2.3 \pm 0.5) \times 10^6$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ as calculated from the equilibrium constant [16].

When 650 Torr N_2F_4 was introduced at room temperature above molecular sieves (Linde 13X, 10X, 5A, 4A, 3A with effective pore diameters of 9, 8, 5, 4, and 3 Å, respectively), NF_2 ESR spectra were obtained from 13X, 10X, and 5A sieves, but only N_2F_4 ^{19}F NMR spectra could be observed for 13X and 10X sieves. Neither adsorbed species was found for 4A or 3A sieves (the NF_2 critical diameter is estimated to be 3.7 Å). Only adsorbed N_2F_4 could be detected on silica gel. It was concluded that N_2F_4 and NF_2 followed relatively independent adsorption isotherms because the concentration of adsorbed NF_2 on 13X, 10X, and 5A sieves remained practically constant while the bulk adsorption of N_2F_4 changed by more than a factor of 20 [24].

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4.1.12.6.2.2 The Disproportionation Reaction, $6\,NF_2 \rightarrow 4\,NF_3 + N_2$

NF_2 disproportionates in the temperature range 300 to 500°C with the stoichiometry $6\,NF_2 \rightarrow 4\,NF_3 + N_2$. The gas-phase reaction was homogeneous when experiments were performed in a passivated Monel [2] or in a nickel reactor [1]. Slower reaction rates were found in Pyrex vessels. The loss of Monel passivation resulted in increased rates. Both effects indicated heterogeneous components [2]. Indeed, heterogeneous disproportionation had been observed, either on $AlCl_3$ at lower temperatures [3] (side reaction to N_2F_2 synthesis) or on a hot wire [4].

Gas-phase kinetics of NF_2 disproportionation were measured at high initial NF_2 pressures (up to 600 [2] or 1200 Torr [1]). A second-order rate law holds: $d[NF_2]/dt = -k[NF_2]^2$ with $k = 10^{11} \cdot \exp(-98\ kJ \cdot mol^{-1}/RT)\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [1] (an expression $k = 2.3 \times 10^{11}\ \exp[-(23800 \pm 1200)\ cal \cdot mol^{-1}/RT]$ would better fit published values) or $k = 10^{12.31 \pm 0.2} \cdot \exp[-(36900 \pm 500)\ cal \cdot mol^{-1}/RT]\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [2]. Largely different Arrhenius parameters are only the result of different experimental values at the low-temperature limit [2]. Additions of about 1200 Torr N_2 or NF_3 had no major effect on k. However, purification of N_2F_4 proved to be essential [2]. Preliminary rate data [5, 6] are probably influenced by NO impurities. The mechanism of disproportionation was believed to be:

(1) $2\,NF_2 \rightarrow NF_3 + NF$ rate-determining step
(2) $2\,NF + M \rightarrow N_2F_2 + M$ or (2a) $NF + NF_2 \rightarrow N_2F_2 + F$
(3) $NF_2 + N_2F_2 \rightarrow NF_3 + N_2 + F$ and (4) $NF_2 + F + M \rightarrow NF_3 + M$

where $k = 3\,k_1$ in case the reaction proceeds via step (2a) or $k = 1.5\,k_1$ in case step (2) is passed [2]. An earlier proposal included

$$2\,NF_2 \xrightarrow{k_1} N_2F_2 + F_2 \rightarrow N_2 + 2\,F_2$$

$$NF_2 + F_2 \rightarrow NF_3 + F \quad \text{and} \quad NF_2 + F + M \rightarrow NF_3 + M$$

with $k = 3\,k_1$ employing steady-state assumptions for F and F_2 [1].

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4.1.12.6.2.3 Decomposition into F_2 and N_2

NF_2, NF, F, and N_2 were the only species detected during the first 150 μs by a time-of-flight mass spectrometer coupled to a shock tube that had been used to heat NF_2 (<1% in Ar) to temperatures between 2200 and 3000 K. NF formation showed an induction period [1]. The detection of NF_3 below 1900 K [1] led to an independent investigation of the 1400 to 1800 K temperature range [2]. Initial rates of NF_2 loss, N_2 and NF_3 formation during the first 200 to 300 μs after shock heating depended on $[NF_2]$ with N_2 and NF_3 being formed in a constant ratio of 2:1. Induction periods observed for N_2 and NF_3 depended on $[NF_2]^{-1}$. A further mass peak indicated N_2F but the presence of N_2F_2 as parent compound could not be excluded [2].

First kinetic investigations in shock-heated 1:103 and 1:206 NF_2–Ar mixtures by use of the NF_2 UV absorption were limited to 1400 to 2000 K [3]. Chemiluminescence above 2000 K prevented the extension of that range [4]. Rate constants, $k(Ar) = 1.62 \times 10^{13} \cdot T^{0.5} \cdot \exp(-47838\ \text{cal} \cdot \text{mol}^{-1}/RT)\ \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ (error limits?) were first assigned to the first step of a simple mechanistic scheme: (1) $NF_2 + M \xrightarrow{k} NF + F + M$ (see also NF_2 bond energies, p. 250), and (2) $2\,NF \rightarrow N_2F_2^* \rightarrow N_2 + 2\,F$ [1, 3]. Product distributions [1, 2] indicated a more complex reaction scheme (k in $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) [2]:

(1) $NF_2 + M \rightarrow NF + F + M$	$k(Ar) = 6 \times 10^{14} \exp(-52\ \text{kcal} \cdot \text{mol}^{-1}/RT)$; (recalculation [2] of published data [3]) $k(Ne) = 2.2 \times 10^{15} \exp(-57\ \text{kcal} \cdot \text{mol}^{-1}/RT)$
(2) $2\,NF \rightarrow N_2 + 2\,F$	
(3) $NF + NF_2 \rightarrow N_2F + F_2$	$k \approx 2 \times 10^{12}$ at ~1800 K (estimated)
(4) $N_2F + NF_2 \rightarrow NF_3 + N_2$	$k \approx 10^{12}$ at ~1800 K (estimated)
(5) $F_2 + NF_2 \rightarrow NF_3 + F$	$k \approx 10^{12}$ at ~1800 K (estimated; for exact data, see p. 351)
(6) $NF_3 + M \rightarrow NF_2 + F + M$	$k_6/k_1 \approx 5$ (for independent k_6 data, see p. 206)

Independent investigations of step (5) (see e.g., [5] and p. 351) led to a further revision. The sequence (3a) $NF + NF_2 \rightarrow N_2F_2 + F$, (3b) $N_2F_2 + NF_2 \rightarrow N_2F + NF_3$ replaces [5] steps (3) and (5) in the above scheme. Uncertain secondary reactions also render kinetic data for the initial step (1) as being rather uncertain [6].

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4.1.12.6.3 Photochemical Behavior

4.1.12.6.3.1 Ultraviolet Irradiation of N_2F_4/NF_2

NF_2 and N_2F_4 absorb in the ultraviolet at 260 nm and below 240 nm, respectively; see pp. 257 and 322. Irradiation of a gaseous N_2F_4/NF_2 equilibrium mixture (6 Torr) with appropriate wavelengths from a xenon flashlamp gave N_2, F_2, N_2F_2, and NF_3 products. The proposed reaction scheme included the following steps [1]

(1) $N_2F_4 \rightleftharpoons 2NF_2$
(2) $N_2F_4 + h\nu \rightarrow N_2F_3 + F$
(3) $NF_2 + h\nu \rightarrow NF(X,a) + F$
(4) $2NF \rightarrow N_2 + 2F$
($k_4 \approx 2.5 \times 10^{13}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$, see [2])
(5) $F + N_2F_4 \rightarrow NF_3 + NF_2$
(6) $N_2F_3 \rightarrow N_2F_2 + F$, $\Delta H \approx -14$ kcal/mol
(7) $NF + N_2F_4 \rightarrow NF_2 + N_2F_2 + F$
(8) $2F + M \rightarrow F_2 + M$

Reaction (7) was believed to be the result of an initial bimolecular displacement step, (7a) $NF + N_2F_4 \rightarrow \{FN \cdots NF_2\text{–}NF_2\} \rightarrow N_2F_3 + NF_2$, $\Delta H \approx -5$ kcal/mol, followed by step (6). Earlier reaction schemes for NF_2 decomposition at 253.7 nm irradiation included steps (1), (3), (9) $F + NF_2 \xrightarrow{(M)} NF_3$ (see pp. 351/2), and (10) $2NF \rightarrow N_2F_2$ [3] or (1), (3), (6), (10), and (7a) [4]. In these schemes, emphasis was laid on the formation of N_2F_2 which was an abundant product in the photolysis of pure N_2F_4/NF_2 or in photochemical reactions thereof. Step (2) and (3) played an important role in $HF^{\dagger}$ lasing reactions where N_2F_4 had been used as the fluorine donor, see for example, [5] and "Fluorine" Suppl. Vol. 3, pp. 128/50.

Formation and decay of two transient species of different lifetimes were observed by kinetic absorption spectroscopy in the vacuum-UV after flash photolysis of N_2F_4/NF_2. Species were originally identified as NF(X) and NF(a) [6]; see p. 366 for the discussion of this assignment. When the 230 to 700 nm range was monitored after a high-energy flash, only NF_2 could be identified as transient. A search for NF was without success and overall N_2F_4 decomposition was small (NF_3 and SiF_4 side products) [7]. Heating of N_2F_4 was the only result of an early flash photolysis study [8]. A pressure change that was observed when N_2F_4 samples were irradiated with 10.6 μm from a CO_2 laser (laser intensity above the threshold value of the reaction) was ascribed to the reaction $3N_2F_4 \rightarrow 4NF_3 + N_2$ (see, however, the following section). Simultaneous irradiation with wavelengths of 220 and 450 nm was reported to increase the turnover of that reaction (450 nm is far beyond N_2F_4/NF_2 absorption!) and to shift the IR threshold value [9].

Illumination of NF_2 in a 4 K Ar or Kr matrix by a mercury lamp leads to NF and NF_3 as was observed by the disappearance of NF_2 IR bands and concomittant growth of product bands. cis- and trans-N_2F_2 formed when the photolyzed matrix was warmed to 20 K [10].

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4.1.12.6.3.2 Infrared Irradiation of N_2F_4

Rapid dissociation of gaseous N_2F_4 into two NF_2 molecules was induced by multiphoton absorption of IR photons with wavelengths around 10.6 μm [1 to 12]. With these wavelengths the N–F modes were pumped directly, but energy exchange was extremely rapid with other modes including the N–N mode. In order to verify that dissociation is the result of the interaction with a strong IR field (the N–N bond strength requires an equivalent of ca. eight 10.6-μm photons) and not the primary result of thermal heating (see an early discussion [1]) a variety of experiments have been undertaken. These included relaxation studies (see pp. 335/6), the measurement of the average energy absorption per N_2F_4 molecule versus CO_2 laser energy fluence [2 to 4], N_2F_4 pressure [2, 3], and the pressure of added Ar gas [2, 3]. The degree of laser-induced N_2F_4 dissociation was monitored in most cases by the UV absorbance of NF_2 [1 to 6, 8 to 10]. IR probing with a low-level CO_2 laser of the same wavelength as the incident pulse gave similar results [6]. The degree of dissocation was measured as a function of incident energy fluence [2, 4, 6, 9], of N_2F_4 [2] and Ar [2, 4, 9] pressures. Dissociation was found to be a threshold process that needed fluxes higher than 100 mJ/cm^2 [2, 4, 6, 7]. In the photochemical stationary state, the fraction, F, of remaining N_2F_4 molecules depended on the intensity of the laser pulse, I, according to $-d(\ln F)/d(I \cdot t) = k_{stat}$. The stationary rate constant was determined as $k_{stat} = (1.0 \pm 0.4) \times 10^6 \cdot I$ $MW \cdot cm^2 \cdot s^{-1}$ [2, 4, 5]. In time-resolved experiments, dissociation rates followed roughly the incoming pulse [6, 8, 10]. Laser energy absorption exhibited saturation independent of N_2F_4 pressure (below 16 Torr) [8]. The effect was used to determine experimentally the average number of quanta absorbed per N_2F_4 molecule at 100% dissociation, $\langle n \rangle = 8.5 \pm 0.6$ (after correction for NF_2 absorption) [8].

Collisionless multiphoton dissociation of N_2F_4 was studied in a molecular beam that was crossed at 90° by a CO_2 laser beam (976 or 1031 cm^{-1}). Dissociation into NF_2 was evidenced by NF_2^+, NF^+, and F^+ mass peaks. Absence of $N_2F_3^+$ and $N_2F_2^+$ mass peaks was noted. NF_2 fragments had only little translational energy (average 0.4 kcal/mol). The angular distribution of NF_2 peaked at 0° and was rather narrow. It did not depend on the laser energy fluence. Due to supersonic expansion, N_2F_4 molecules were rotationally cool. Multiphoton excitation did not notably increase their rotational energy. RRKM calculations could not reproduce the observed translational energy distribution very well [11] (preliminary results [12]).

N_2F_4 in low-temperature Ar, N_2, and NO matrices showed no evidence of dissociation when irradiated by 944.2 cm^{-1} CO_2 laser pulses of 1 to 2 Joule per pulse [13]. N_2F_4 disproportionation according to $3N_2F_4 \rightarrow 4NF_3 + N_2$ was claimed to take place under irradiation of >37 W/cm^2 laser pulses of 943 cm^{-1} and 10^{-2} s pulse duration. A (rather unspecific) pressure change in the irradiated cell served for diagnostics [14]. It has also been claimed that N_2F_4 gained some fluorinating ability toward NO, CO, etc. when exposed to 10.6 μm radiation, see pp. 372/3 and [14]. The molecular beam study gave, however, no evidence for N–F bond breaking [11] that would be a rather high-energy channel.

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4.1.12.6.4 Relaxation of Vibrationally-Rotationally Excited N_2F_4

A few approximate experimental data are available on the redistribution of energy after N_2F_4 has been excited by CO_2 lasers operating in the 10.6 μm region. Data on the chemical channel leading to N_2F_4 dissociation are given in the previous section.

A time constant of 47 ± 4 ns·Torr was measured with a low-power CW laser for the recovery of the levels of a N_2F_4 probe that had been previously saturated with a short, high-power laser pulse of the same wavelength (P(20) line of the 10.6 μm CO_2 transition, i.e., 944.19 cm^{-1}). The fast bimolecular process was ascribed to rotation-rotation exchange [1]. Laser-induced infrared fluorescence measured for the ranges 1400 to 2500 cm^{-1}, 1100 to 1300 cm^{-1}, and 670 to 830 cm^{-1} had a risetime of less than 0.2 μs after 0.13 to 1 mbar N_2F_4 had been excited with a 944.2 cm^{-1} CO_2 laser pulse of 5 J and 200 ns pulse duration (at the base). That time is four times shorter than the time between collisions of N_2F_4 molecules (the collision number is ca. 0.9×10^7 $s^{-1} \cdot mbar^{-1}$). Extremely rapid intramolecular relaxation between directly pumped and other vibrational levels offers a likely explanation [2, 3]. An even shorter intramolecular V–V relaxation time <15 ns for energy exchange between pumped N–F and

N–N stretching vibrations was deduced from CO_2 laser-initiated N_2F_4 dissociation [4]. These experiments were performed at considerably higher pressures (3 to 15 Torr); nevertheless, the process was claimed to be collisionless. Later experiments for $p(N_2F_4) \leq 24$ Torr resulted in a time constant of about 40 ns [5]. The decay of the 1400 to 2500 cm^{-1} laser-induced fluorescence showed a rapid initial and a slower subsequent process. The first process became more rapid with increasing N_2F_4 pressures and was ascribed to V–T relaxation with a rate constant $k_{V\text{-}T} > 10^5\ s^{-1} \cdot mbar^{-1}$ for $M = N_2F_4$ [3, 6]. Simulations of laser-induced N_2F_4 dissociation by a simple scheme resulted in a comparable time constant of $5 \leq \tau_{V\text{-}T} \leq 20$ µs·Torr for $M = N_2F_4$, He, Ar [5] and (10 to 20) µs·Torr for M = Ar [8]. The slower process observed in laser-induced fluorescence slowed down with increasing pressure and was ascribed to thermal heating of the system [3, 6]. An earlier time constant for vibrational relaxation of 10^{-6} s·atm [7] was later ascribed to thermal heating [3, 4].

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4.1.12.6.5 Behavior in Discharges. Interaction with X-Rays

A search for the NF radical proved unsuccessful when N_2F_4 was subjected to a microwave discharge [1].

Passing a flow of N_2F_4 through a high-voltage glow discharge tube made of quartz and equipped with Cu electrodes generates NF_3, $3N_2F_4 \rightleftharpoons 4NF_3 + N_2$. The NF_3 yield depends on the specific energy defined as discharge power per volume velocity of gas flow. The amount of NF_3 increases rapidly with the specific energy until almost 100% conversion is reached around 20 to 24 W·h/L. At higher specific energies, NF_3 yields are diminished by further breakdown into N_2 and F_2. At about 380 W·h/L, the yield reaches only about 20% [2, 3].

N_2, F_2, and NF_3 were detected by mass spectrometry after exposure of pure N_2F_4 samples held at 77 K to large doses of 2 to 3 MeV bremsstrahlung. At similar conditions but 105 K, N_2F_2 emerged [4].

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4.1.12.6.6 Reactions with Electrons

Thermal electrons attach to N_2F_4 at 300 K with a rate constant of $2.3\times10^{15}\ cm^3\cdot mol^{-1}\cdot s^{-1}$ [1]. An excitation function does not seem to have been published. A rather pure NF_2^+ plasma (93% purity with some NF^+ and NO^+) was obtained after a large current of low energy electrons (anode potential 12 V) had been directed onto N_2F_4 at 5×10^{-4} to 10^{-3} Torr. The quantity of NF^+ increased with the anode potential [2]. High-energy electrons of about 30 MeV decompose N_2F_4 into NF_3 (6/5), N_2 (1/5), trans-N_2F_2 (2/15), and cis-N_2F_2 (1/15) where numbers in parentheses denote the moles of product per mole of radiolyzed N_2F_4. The rate of N_2F_4 decomposition depends linearly on N_2F_4 pressure and dose. Formation rates of products are also linear functions of the dose. The radiation yield of N_2F_4 decomposition was 20 molecules per 100 eV absorbed by N_2F_4 [3].

Starting from some early preliminary results [4], interaction of medium-energy electrons (24 to 70 eV) with N_2F_4 (or NF_2) has been studied repeatedly by mass spectrometry [5 to 15, 19]. Some early measurements [5, 7] were later shown to need reinterpretation [6, 8, 9, 16]; see also the reviews [17, 18]. The source of misinterpretation was the neglect of N_2F_4 dissociation into NF_2 radicals, which had been the main species under the applied experimental conditions. Relative abundances of positive ions, measured in a mass spectrometer at 24 eV [19], 50 eV [13], and 70 eV [5 to 12, 14, 15] depend on the status of the $N_2F_4\rightleftharpoons2NF_2$ equilibrium and thus on temperature, pressure, etc. in the ionization chamber. Therefore, published relative ion currents are hardly comparable from one study to the other. Some authors [5, 6, 12, 19] consider NF^+ as the most prominent peak at high temperatures (170°C [6], ion source 200°C, and prior heating of N_2F_4 to 300°C [12], 190°C [19]), whereas others argue that NF_2^+ is responsible for the most intense mass peak at temperatures between ~190°C [11, 15] and ~200°C [7, 15]. Relative abundances of positive ions measured at 50 eV around room temperature that are thought to originate solely from N_2F_4 may under these circumstances only be taken as a first guideline: [N^+ (6.4)], F^+ (0.46), [N_2^+ (5.0)], NF^+ (16.4), F_2^+ (0.036), N_2F^+ (7.2), NF_2^+ (100), $N_2F_2^+$ (9.2), NF_3^+ (0.047), $N_2F_3^+$ (7.1), $N_2F_4^+$ (13.8) [13]. Data in brackets are from [6] for 70 eV because these ions were not observed by [13]. Despite the uncertainty in single measurements there is, however, a general trend that ion currents of $N_2F_4^+$, $N_2F_3^+$, $N_2F_2^+$, and N_2F^+ increase when the temperature in the ion source is lowered [6, 11, 15]. The temperature-dependent ratio $NF_2^+/N_2F_4^+$ was used to determine the heat of N_2F_4 dissociation (see p. 327) in the 333 to 451 K range [8, 9].

F^- yields the most intense negative ion peak at 70 eV (temperature?): N^- (25), F^- (100), F_2^- (13), N_2F^- (2.3), NF_2^- (5.1), $N_2F_2^-$ (0.9) [10]. Similar data for F^-, F_2^-, N_2F^-, and NF_2^- were published [15].

Appearance potentials (AP in eV) measured by mass spectrometry are listed in the following table along with corresponding processes. (E_i and A denote ionization potential and electron affinity, given in eV.)

(A) Reactions: $NF_2+e^-\rightarrow$ Products

(1) $\rightarrow NF_2^+ + 2e^-$ AP(NF_2^+) = 11.76 ± 0.1 [13], 11.79 ± 0.12 [11, 12], 11.8 ± 0.2 [6, 16] (revised data from [5]), 11.82 ± 0.06 [15], 12.0 ± 0.1 [8]

(2) $\rightarrow NF^+ + F^- + e^-$ AP(NF^+) = 11.8 ± 0.2 [8], 11.86 ± 0.2 [13] (assigned to E_i(NF) = 11.82 ± 0.06 [15])

(3) $\rightarrow NF^+ + F + 2e^-$ AP(NF^+) $= 15.0 \pm 2$ [6] (revised data from [5]), 15.32 ± 0.08 [15], 15.46 [13], 15.5 ± 0.2 [8]

(4) $\rightarrow NF + F^-$ AP(F^-) $= 0.18 \pm 0.09$ [15]

(B) Reactions: $N_2F_4 + e^- \rightarrow$ Products

(5) $\rightarrow N_2F_4^+ + 2e^-$ AP($N_2F_4^+$) $= 12.00 \pm 0.10$ [13], 12.04 ± 0.10 [7]

(6) $\rightarrow NF_2^+ + NF_2^- + e^-$ AP(NF_2^+) $= 12.4 \pm 0.1$ [15] (ascribed to process (7) [13])
AP(NF_2^-) $= 12.22 \pm 0.27$ [15]

(7) $\rightarrow NF_2^+ + NF + F^- + e^-$ AP(NF_2^+) $= 12.40 \pm 0.1$ [13] (ascribed to process (6) [15])

(8) $\rightarrow NF_2^+ + NF_2 + 2e^-$ AP(NF_2^+) $= 12.5$ [16] (revised data from [5]), 12.63 ± 0.1 [11, 12], 12.7 ± 0.2 [7], 12.7 ± 0.1 [13, 15]

(9) $\rightarrow N_2F^+ + F + F_2 + 2e^-$ AP(N_2F^+) $= 14.2 \pm 0.3$ [13]

(10) $\rightarrow N_2F^+ + 3F + 2e^-$ AP(N_2F^+) ≈ 16.7 [13]

(11) $\rightarrow N_2F_2^+ + 2F + 2e^-$ AP($N_2F_2^+$) $= 16.0 \pm 0.1$ [13]

(12) $\rightarrow N_2F^+ + F^- + e^-$ AP($N_2F_3^+$) $\underset{\cdot}{=} 12.8$ [8] (tentative)

(13) $\rightarrow N_2F_3^+ + F^- + 2e^-$ AP($N_2F_3^+$) $= 14.2 \pm 0.3$ [14]

(14) $\rightarrow N_2F_2 + F_2^-$ AP(F_2^-) $= 0.20 \pm 0.07$ [15]

(15) $\rightarrow N_2F_2^+ + F_2^- + e^-$ AP(F_2^-) $= 13.26 \pm 0.10$ [15]

(16) $\rightarrow NF_2 + NF_2^-$ AP(NF_2^-) $= 0.55 \pm 0.06$ [15] (yields $A \geq 0.41 \pm 0.15$)

(17) $\rightarrow N_2F^- + F_2 + F$ AP(N_2F^-) $= 0.19 \pm 0.10$ [15]

Different interpretations [13, 15] concerning processes (2), (6), and (7) basically rely on the simultaneous observation of positive and negative ions [15]. The assignment AP(NF^+) = 11.86 eV to (2) $NF_2 + e^- \rightarrow NF^+ + F^- + e^-$ [13] is opposed by the fact that there is no indication for such a process from the effective F^- ionization [15]. There is also no evidence for (7) from F^- ionization but a close agreement of AP(NF_2^+) and AP(NF_2^-) as required by process (6) [15].

The measurement of a close-to-thermal F_2^- kinetic energy for (14) $N_2F_4 + e^- \rightarrow F_2^- + N_2F_2$ provides some evidence for an excited N_2F_2 product arising from this highly exothermic reaction. Thus, formation of isomeric F_2NN instead of cis-, trans-FNNF was discussed [15]. Thermodynamic data also indicate considerable excitation of products arising from reaction (15) [15].

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4.1.12.6.7 Reactions with Elements

4.1.12.6.7.1 Interactions with Noble Gases in Excited $^3P_{0,2}$ States

Ne($^3P_2$) atoms that had been produced in a cold hollow-cathode discharge and later monitored along a flow tube by atomic absorption spectroscopy were quenched by N_2F_4 at 300 K with a rate constant of 1.4×10^{-10} cm^3·molecule^{-1}·s^{-1} [1]. Details on quenching channels have not been worked out.

At similar experimental conditions Ar($^3P_2$) atoms were quenched with a rate constant of 3.1×10^{-10} cm^3·molecule^{-1}·s^{-1} [2] (see also [3 to 6]). Separate data for quenching of Ar($^3P_0$) atoms that are produced along with Ar($^3P_2$) [2] are not available. Chemical channels that lead to eximers ArF* in B, C [3, 7], and D [3] states as well as to NF in electronically excited a and b states [7] contribute significantly to Ar ($^3P_{0,2}$) quenching. A room-temperature rate constant of 5.7×10^{-11} cm^3·molecule^{-1}·s^{-1} for Ar($^3P_{0,2}$) + N_2F_4 → ArF* + ... is based on a comparison of the ArF* emission to the ArCl* emission produced from Ar($^3P_{0,2}$) + Cl_2 [3]. Thus, the channel toward ArF* excimers has a branching ratio of 0.18 [7] (misprinted in [3, 6]). ArF* excimer emission from Ar($^3P_{0,2}$) + N_2F_4 was described earlier [8]. From later results [9] it is not obvious whether ArF* was observed in the spark emission spectrum taken from Ar–N_2F_4 mixtures in He. The reaction Ar($^3P_{0,2}$) + N_2F_4 was mentioned as a source of NF(b $^1\Sigma^+$) radicals [10].

The quenching rate constant of Ar($^3P_2$) by NF_2 (from thermal dissociation of N_2F_4 at 500 K) was expected to be similar to that for N_2F_4 [7]. Inspection of the emission from Ar ($^3P_{0,2}$) + NF_2 in a flowing afterglow showed, however, striking differences to the analogous N_2F_4 system. Neither ArF(B–X) nor ArF(C–A) emissions were observed, whereas a strong NF(b–X) and a very weak NF(a–X) emission were present. The NF(b,v′–X,v″) spectrum was about four times as intense as that from Ar($^3P_{0,2}$) + N_2F_4. The NF(b,v′) vibrational distribution in the reaction zone for v′ = 0 to 7 was approximately 100:18:11:8:5:4:3:2 [7].

Kr($^3P_2$) atoms obtained by electronic energy transfer from Ar($^3P_{0,2}$) and monitored in a flow tube by atomic absorption spectroscopy were quenched by N_2F_4 with a total room-temperature rate constant of 3.3×10^{-10} cm^3·molecule^{-1}·s^{-1} [2] (see also [4, 5]). A branching fraction of 0.5 [2] (misprinted in [6]) for the channel(s) leading to KrF* relies on the known rate constant for Kr* + Cl_2 → KrCl* + Cl and a branching fraction of 1 for Kr* + F_2 → KrF* + F. A comparison of this branching fraction to those for ArF* and XeF* formation from N_2F_4 suggests a reevaluation. KrF* emission was obtained from the reaction N_2F_4 + Kr($^3P_{0,2}$) [8]. KrF* excimer lasers were operated by use of N_2F_4 as the fluorine donor [11, 12].

A rate constant of 1.8×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for $Kr^* + NF_2 \rightarrow KrF^* + NF$ was derived from the simulation of the degradation of a KrF^* excimer laser using NF_3 as the fluorine donor [13].

While no direct measurements on the total quenching of $Xe(^3P_{0,2})$ atoms by N_2F_4 (or NF_2) have been published, information is available on chemical channels leading to XeF^* and NF^* [2, 5, 14]. The ratio of rate constants for excimer formations from $Xe(^3P_2) + Cl_2(F_2)$ and $Xe(^3P_2) + N_2F_4$ amounts to 1:0.27 [2, 5]. An absolute value of 1.66×10^{-10} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ (300 K) also relied on kinetic data for $Xe(^3P_2) + Cl_2 \rightarrow XeCl^* + Cl$ [14]. The branching ratio of 0.18 [14] for XeF^* formation from $Xe(^3P_2) + N_2F_4$ replaced earlier data [2, 6]. Spectral resolution of the XeF^* chemiluminescence from $Xe(^3P_2) + N_2F_4$ showed the presence of intense XeF(B–X) and less intense XeF(C–A) emissions [14] (earlier spectral study [8]).

Total quenching rate constants for $Xe(^3P_2)$ deactivation by N_2F_4 and NF_2 were believed to be similar; however, the rate constant for XeF^* formation from NF_2 was considerably less. The value of 1.1×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ at 300 K implied a branching ratio <0.1 [14]. Simulation of the measured decrease in NF_3 concentration and intermediate accumulation of NF_2 in a discharge excited XeF^* laser operated on the basis of an initial $He:Xe:NF_3 = 1000:3:1$ mixture yielded a (room-temperature) rate constant of 1.8×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$ for $Xe(^3P_2) + NF_2$. The variation in energy output in the above experiments and that observed for NF_3–N_2F_4–Xe–He mixtures indicated effective quenching of XeF(B) by N_2F_4 (NF_2) [16]. The chemiluminescence from $Xe(^3P_2) + NF_2$ consisted of XeF(D–X), intense XeF(B–X), less intense Xe(C–A), and NF(b–X) emissions. Vibrational excitations observed for XeF(B–X) and XeF(C–A) transitions were much less than those from the $Xe(^3P_2) + N_2F_4$ reaction. The fact suggested XeF^* formation via a bound $Xe^+NF_2^-$ intermediate [14]. Despite a relatively low NF(b–X) emission intensity, NF(b) formation must have occurred at a considerable rate (NF(b) escaped detection due to its long radiative lifetime) [14]. However, the $Xe(^3P_2) + NF_2$ system offered no advantage for NF(b) production compared to $Ar(^3P_{0,2}) + NF_2$ [7].

Degradiation studies of an excimer laser from $N_2F_4/NF_2 + Xe^*$ due to heterogeneous wall reactions of NF_2 were described [15].

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4.1.12.6.7.2 Reactions with Hydrogen

The reactions of N_2F_4 and NF_2 with H_2 or H atoms or their isotopes are strongly exoergic and lead to a number of electronically and vibrationally excited intermediates. Interest in these reactions has thus focussed on three points: (1) Thermal and photochemical stability of N_2F_4–H_2 mixtures, (2) conditions for and detection of product $HF^†$ or $DF^†$ lasing (see also "Fluorine" Suppl. Vol. 3, 1982, pp. 120/48), and (3) detection of electronically excited products, above all NF^* (see also pp. 263/71). Because of the explosive hazards, extreme care should be taken when working with these chemical systems.

$N_2F_4+H_2$

Mixtures of tetrafluorohydrazine and hydrogen autoignite at room temperature [1]. A short delay between mixing and spontaneous explosion was observed [21]. Mixtures explode upon spark ignition [1]. An N_2F_4–H_2 flame was pale blue-white but could not be characterized further [2]. Upper and lower limits of ignition of approximately 300 and 0.5 Torr at room temperature were strongly influenced by the conditions of the quartz surface of the reaction vessel [1]. The extreme irreproducibility of explosion limits in glass or stainless steel reactors could be reduced by coating the surface with Kel-F oil [3]. Under these conditions, mixtures containing 2 to 4 Torr N_2F_4 and 2 to 4 Torr H_2 exploded at about 90°C and a mixture of 20 Torr N_2F_4–40 Torr H_2 exploded below room temperature. Hydrocarbons stabilize N_2F_4–H_2 mixtures very specifically. For example, an induction period of 10 min was observed at 110°C when 6 Torr CH_4, 0.62 Torr C_3H_8, 6×10^{-2} Torr $CH_2{=}CH{-}CH{=}CH_2$, or 2×10^{-3} Torr $(CH_3)_2C{=}C(CH_3)_2$ were added to 40 Torr H_2 – 20 Torr N_2F_4 [3]. At a total pressure of 30 Torr, 2% H_2 and 1% N_2F_4 in Ar were stable for 2 ms at shock temperatures of 780, 900, and 1010 K where 0.05, 0.15, and 0.5% cis-2-butene had been added. Correspondingly, the high-temperature limit of instability rose from 1700 to 1800 and 2070 K with increasing cis-2-butene content [4]. Attempts to obtain kinetic data for H_2(excess)–N_2F_4 (down to 0.25 mol%) mixtures in He were unsuccessful. Below 40°C no reaction occurred but upon heating, the reaction went out of control (pressure pulses were registered in the system). With added O_2 a controlled steady-state reaction took place; however, rate data were irreproducible over long periods [5]. Additions of N_2F_4 to NF_3–H_2 mixtures caused self-ignition, raised the NF_3–H_2 flame speed, and lowered the pressure limit to spherical detonation [6].

An extensive study of the $N_2F_4+H_2$ reaction included the variation of reaction stoichiometry with H_2/N_2F_4 reactant ratios, with the pressure of He diluent gas (some experiments with Xe gave similar results except that higher Xe pressures were needed), and with N_2F_2 (as supposed intermediate) [3]. The reaction of 2 Torr N_2F_4 and 4 Torr H_2 at 90°C was best described by

$$N_2F_4+2H_2\rightarrow N_2+4HF$$

Three Torr N_2F_4 and three Torr H_2 reacted at 90°C according to

$$N_2F_4+H_2\rightarrow N_2+2HF+F_2$$

with a trace amount of NF_3 side product. The HF amount remained constant upon varying the inert gas pressure from 0 to 194 Torr He. Yields of N_2 and F_2 were reduced to ~65% and 11% of the values observed in the absence of He. The NF_3 yield increased by a factor of 8 at 44 Torr He and then declined again at higher He pressures. Unreacted N_2F_4 became apparent above ~70 Torr He. Products from the reaction of 4 Torr N_2F_4 and 2 Torr H_2 indicated two parallel overall reactions

$$(1)\ 4N_2F_4+2H_2\rightarrow 3N_2+4HF+2NF_3+3F_2 \text{ and}$$

$$(2)\ 4N_2F_4+2H_2\rightarrow 4HF+4NF_3+2N_2$$

Additions of up to 193 Torr He reduced the overall N_2 yield to about one-half. Yields of NF_3 and F_2 increased with low He pressures (maxima at 1.6 Torr He) and were reduced thereafter to about

20 and 25% of their values in the absence of He. Small amounts of N_2F_2 were found at high He pressures. Results were discussed in view of a chain mechanism initiated by the reactions

$$N_2F_4(+M) \rightarrow 2NF_2(+M) \qquad \text{and} \qquad NF_2 + H_2 \rightarrow NHF_2 + H$$

(see, however, a note [12] quoting the latter step as being relatively slow) and terminated by

$$F + H(+M) \rightarrow HF(+M)$$

Chain propagation steps included H and F radical reactions and intermediate N_2F_2 formation that varied with reactant ratio and reaction temperature (lowered by He) [3]. Steps remained speculative as they were only partly supported by independent work, for example, on the $NF_2 + H$ reaction (see below).

Thermodynamic data for $\frac{1}{2}N_2F_4 + \frac{1}{2}H_2 \rightleftharpoons NHF_2$, $\Delta H^\circ_{298} = -14.40$ kcal/mol, $\Delta G^\circ_{298} = -16.45$ kcal/mol [7], indicate the equilibrium to be totally on the product side.

In a series of laser-driven photochemical reactions of N_2F_4 (see e.g., $N_2F_4 + NO$, pp. 372/3), it was claimed that an (unstabilized?) mixture of 50 Torr N_2F_4 and 100 Torr H_2 reacted upon irradiation with a single 10^{-2} s, 50 Watt CO_2 laser pulse (10.6 μm) in a chemiluminescent reaction [8]

$$N_2F_4 + 2H_2 \rightarrow N_2 + 4HF$$

A study of threshold phenomena for this reaction was mentioned but no details were given [9]. HF and DF lasing after CO_2 laser irradiation of a C_2H_2 stabilized 1:1 mixture of N_2F_4 and H_2 (D_2) at a total pressure of 27 Torr was observed to need some threshold value ≥2 MW/cm² for the input radiation [10]. Explosion limits were measured for cis-2-butene-stabilized N_2F_4–H_2 mixtures (78% N_2F_4, 20% H_2, 2% C_4H_8; 26.8% N_2F_4, 72.5% H_2, 0.7% C_4H_8; and 26.8% N_2F_4, 71.5% H_2, 1.7% C_4H_8) as a function of total pressure (up to 150 Torr) and input energy (0.1 to 0.3 J) of a CO_2 laser focussed to 0.35 cm² [11]. Measured induction times (4 to 300 μs) between the input laser pulse and onset of UV-visible chemiluminescence from the exploding mixture depended strongly on input energy (above some threshold value), on total gas pressure, and composition. The laser-initiated chain reaction was discussed in terms of initiation steps

$$N_2F_4^{\dagger} + M \rightarrow 2NF_2 + M$$

(fast due to vibrational excitation) and

$$NF_2^{\dagger} + M \rightarrow NF + F + M$$

(latter in contrast to the thermal step $NF_2 + H_2$ [3]) and propagation steps

$$NF_2 + H \rightarrow NF + HF \text{ (see below)} \qquad NF + NF_2 \rightarrow N_2F_2 + F \text{ (see p. 366)}$$

$$F + H_2 \rightarrow HF^{\dagger} + H$$

Computer simulations predicted the dependence of induction times on laser input energy; however, threshold values were overestimated [11]. A 5 Torr N_2F_4 – 10 Torr H_2 mixture showed total turnover after being exposed to a 1260 J, 30 μs, UV-visible flash. Spectra of excited intermediates indicated that temperatures of 3000 K were reached. In contrast to IR irradiation, short wavelengths in the flash were believed to initiate a chain reaction starting from F atoms [13] generated by

$$N_2F_4 + h\nu \rightarrow N_2F_3 + F \qquad \text{and} \qquad NF_2 + h\nu \rightarrow NF + F$$

Vibrationally and electronically excited intermediates and products from the thermal or photochemical reaction of N_2F_4 with H_2 (D_2, T_2) were identified as $HF^{\dagger}$ [10, 14 to 17], $DF^{\dagger}$ [10, 16, 18], $TF^{\dagger}$ [16], $NH(A\,^3\Pi \rightarrow X\,^3\Sigma^-)$ [4, 10, 13], $NF_2(A \rightarrow X\,^2B)$ [13]. In case of side reactions with stabilizers or lubricant, C_2^* [11] and CN^* [11, 13] were also observed. HF lasing transitions in the 2–1 band and DF transitions in the 4–3, 3–2, and 2–1 bands were obtained from discharge-excited N_2F_4(5 Torr) – H_2(5 Torr) – He(100 Torr) [14] and N_2F_4–D_2 (ca. 1 Torr) [18] mixtures. Thermochemical calculations for 1500 K ranked a chemical HF laser based on the $N_2F_4 + H_2$ reaction close to that based on $F_2 + H_2$ [19]. Product distributions from $N_2F_4 + H_2$ (in He) were calculated for temperatures of 1500 and 2000 K [20].

$NF_2 + H(D)$

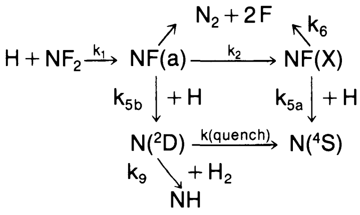
Reactants for the reaction $NF_2 + H(D)$ were prepared in most cases by thermal dissociation of N_2F_4 and by passage of a stream of $H_2(D_2)$ through a microwave discharge [22 to 26, 33]. In a few instances NF_3 was passed through a microwave discharge to obtain NF_2. Accompanying F atoms were used to generate H(D) atoms by means of $F + H_2(D_2) \rightarrow HF^{\dagger}(DF^{\dagger}) + H(D)$ [27, 29]. Also, a combination of both methods, thermal dissociation of N_2F_4 and hydrogen atom generation from $F + H_2(D_2)$, has been used [31]. Generally, the reaction was studied in fast flow systems. Branching into $HF^{\dagger}(v' \leqslant 4)$ vibrational states was studied by the techniques of arrested relaxation [26]. Chemiluminescence was further used to detect electronically excited molecules. $H(^2S)$, $N(^4S)$, $N(^2D)$, and $N(^2P)$ atom profiles were measured during the first 20 to 30 ms of the reaction by atomic resonance fluorescence [23, 24] ($N(^4S)$ also by resonance absorption [23]).

A large number of ground state and excited state molecules and atoms are formed in the chain reaction between difluoroamino radicals and hydrogen (deuterium) atoms. Identified species include HF, $HF^{\dagger}$ [25 to 27, 31, 37]; DF, $DF^{\dagger}$ [26 to 31, 33 to 35]; $NF(X\,^3\Sigma^-)$, $NF(a\,^1\Delta)$ [22 to 37], $NF(b\,^1\Sigma^+)$ [22, 25 to 29, 36, 37] (branching into NF electronic states [26]); $N_2(a\,^1\Pi_g)$, $N_2(B\,^3\Pi_g)$ [22, 24, 27, 37]; $N(^4S)$, $N(^2D)$ [23 to 25], $N(^2P)$ [24]; $NH(A\,^3\Pi)$, $NH(c\,^1\Pi)$ [24, 25]; and $ND(A\,^3\Pi)$, $ND(c\,^1\Pi)$ [25]. The following table summarizes reaction steps of the chain reaction:

	step		comment
(1a)	$NF_2 + H$	$\rightarrow NF(X,a,b) + HF(v' \leqslant 4)$	see below
(1b)	$NF_2 + D$	$\rightarrow NF(X,a) + DF(v' \leqslant 4)$	
(2)	NF(a, b)	$\rightarrow NF(X)$	see NF* quenching, pp. 288/90
(3)	$HF^{\dagger} + M$	$\rightarrow HF + M$	see "Fluorine" Suppl. Vol. 3, 1982, pp. 150/65
(4)	$NF(a) + HF(v+2)$	$\rightarrow NF(b) + HF(v)$	originally believed to be major route to NF(b) [27, 29 to 31]; practically no NF(b) found in $NF_2 + D$ reaction (larger V–E energy gap, see p. 265); the early assumption that NF(b) originated from NF(X) by energy transfer [22] was later abandoned
(5a)	$NF(X) + H(^2S)$	$\rightarrow N(^4S) + HF(X)$	$\Delta U \approx -32$ kcal/mol and $k(298\ K) = (1.5 \pm 0.3) \times 10^{11}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ for (5a) [23]; k(5a)/k(5b) = 1:3 with k(5b) in the $(2.7\ to\ 5.4) \times 10^{11}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ range; experimental ratio $N(^2P)/N(^2D) = 0.1$ [25]
(5b)	$NF(a) + H(^2S)$	$\rightarrow N(^2D) + HF(X)$	
(5c)	$NF(X,a,b) + H(^2S)$	$\rightarrow N(^2P) + HF(X)$	
(6)	NF + NF	$\rightarrow N_2 + 2F$	estimate: $k(298\ K) = (4.2 \pm 2.1) \times 10^{13}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ independent of NF electronic state [23, 24]; reaction proceeds probably via {NNF} intermediate
(7)	$N(^4S) + NF_2$	$\rightarrow 2NF$	see p. 349
(8)	$N(^2D) + NF(a)$	$\rightarrow N_2(B,a) + F$	step believed to produce $N_2(B,a)$ rather than $2N(^4S) + M \rightarrow N_2(B) + M$ and $2N(^2D) \rightarrow N_2(B,a)$; experimental vibrational temperature of $N_2(B)$ product ca. 8200 K; $k(8) \approx 1.8 \times 10^{13}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [25]

	step		comment
(9)	$N(^2D) + H_2$	$\rightarrow NH + H$	experimental rate constant for $N(^2D)$ depletion $k \approx 120\ s^{-1}$ considered as sum of rate constants for (9) and $N(^2D)$ quenching with $k(9) \gg k(\text{quench})$ [24]
(10)	$NH(X) + N_2(A)$	$\rightarrow NH(A, c) + N_2$	in comparison to chain reaction $NF_2 + D$ the step is believed to produce NH(A,c) rather than $N(^2D) + H_2 \rightarrow NH(X) + H$ ($\Delta E = -12200\ cm^{-1}$) and $N(^4S) + H_2$ ($\Delta E = +7030\ cm^{-1}$); experimental rotational temperatures of NH(A) and NH(c) reach 5500 and 900 K, respectively [25]

Clyne and co-workers [23] considered the $NF_2 + H$ reaction as an efficient, self-propagating chain reaction where the initiating step (1) is followed by rapid secondary steps that are capable of recycling H atoms with a chain length $\geqslant 20$. Major steps in the chain were believed to be steps (1) and (6) and $F + H_2 \rightarrow HF + H$. Steps (5) and (7) and wall recombination of H atoms were thought to play a minor role. Characteristic reaction profiles for $N(^2D)$ and $N(^4S)$ atoms showed $N(^2D)$ to be an initial and $N(^4S)$ to be a subsequent product. These profiles were simulated on the basis of the following simplified reaction scheme (adopted from [24]):



Reactions of the above scheme and table as well as additional reactions, such as $NF_2 + NF$ (see p. 366), NH + NH, NH quenching, $NF + H_2$, were considered in a calculation on the possibility of a chemical laser based on $H_2(H) + NF_2$ [38]. A further listing of reactions and rate data relevant to the calculation of NF(a,b) concentrations has been published [36].

The initiating reaction (1a) $NF_2 + H$ or (1b) $NF_2 + D$ was investigated in detail, motivated by the hope of achieving NF(a,b) lasing, see pp. 263/71. Primary products from the reaction $NF_2 + H$ include NF in X, a, b electronic states and $HF(v \leqslant 4)$ [26], see details given below. Of the NF species, NF(a) is produced in such a large excess that published yields of practically 100% [27, 29] or >90% [24] are reasonable approximations. Relative emission intensities from NF(a) and NF(b) that had been produced via $NF_2 + D$ amounted to 1.5 and 0.02 when compared to respective emissions from $NF_2 + H$ [27]. Additional reasoning that NF(a) might be efficiently pumped by $HF(v + 2)$ but not by DF (because of large resonance defects) led to the early speculation that NF(b) was not a primary product [27], see also [32]. Overall rate constants measured at room temperature for reaction (1a) agree: $(9 \pm 1.2) \times 10^{12}$ [23] (from the measurement of H atom removal), $(7.8 \pm 3.9) \times 10^{12}$ [26] (from the measurement of $HF(v \geqslant 1)$ formation, $k = (2.3 \pm 0.7) \times 10^{12}$, and extrapolated for all states v = 0 to 4), and 2×10^{13} [31] (all data in $cm^3 \cdot mol^{-1} \cdot s^{-1}$). The temperature dependence in the 298 to 550 K range was weak, $k = (1.1 \pm 0.3) \times 10^{13} \exp[-(30 \pm 50)/T]\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [23]. A room-temperature rate constant of $1.2 \times 10^{13}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ for reaction (1b) was published without further details [33].

Based upon energetic grounds, the following state-selective paths are possible [26]: $H + NF_2 \rightarrow HF(v) + NF(X\,^3\Sigma^-)$, where $\Delta H_0^\circ = -66$ kcal/mol allows for $v \leq 6$; $H + NF_2 \rightarrow HF(v) + NF(a\,^1\Delta)$, where $\Delta H_0^\circ = -34$ kcal/mol allows for $v \leq 3$; and $H + NF_2 \rightarrow HF(v) + NF(b\,^1\Sigma^+)$, where $\Delta H_0^\circ = -13$ kcal/mol allows for $v \leq 1$.

Initial vibrational distributions for HF(v) and DF(v) were measured for v = 1 to 4 and were shown to be independent of the NF_2 flow rate. Occupation of the v = 5 state was observed for neither HF nor DF. Experimental distributions, P_v, were used to extrapolate the occupation of the v = 0 state either from a linear log P_v vs. E_v correlation (E_v vibrational energy) or from a surprisal analysis. Resulting distributions are given below together with $\langle E \rangle$ (the mean energy being available for the NF(a) path, $\langle E \rangle = \Delta H_0^\circ + E_a$ (assumed 1 kcal/mol) + $\frac{5}{2}$ RT) and energy fractions stored in vibration, $\langle f_v \rangle$, and rotation $\langle f_r \rangle$ [26]:

	$\langle E \rangle$	$\langle f_v \rangle$	$\langle f_r \rangle$	P_v				
				v_0	v_1	v_2	v_3	v_4
$H + NF_2$*)	36	0.12	~0.03	0.71	0.22	0.06	0.01	0.003
		0.14	~0.03	0.65	0.27	0.07	0.01	—
$D + NF_2$*)	37	0.15	~0.03	0.56	0.25	0.12	0.06	0.01
		0.17	~0.03	0.51	0.28	0.14	0.06	0.01

*) Data in first line from log P_v vs. E_v, in second line from surprisal.

Initial populations of NF(a, b) vibrational states from reaction (1a) were determined by use of the assumption that Franck-Condon factors of observed transitions were practically constant [26]:

	$\langle E \rangle$	$\langle f_v \rangle$	P_v			
			v_0	v_1	v_2	v_3
$NF(a\,^1\Delta)$	36	≤ 0.05	0.73	0.19	0.08	obscured
$NF(b\,^1\Sigma^+)$	15	—	0.95	0.04	0.01	0.003

The relatively small energy fractions stored in NF(a) and HF(v) vibration and minimal rotational excitation in that channel ($J \leq 10$) indicated translationally hot product molecules.

In contrast to earlier assumptions, it was found that NF(b) was directly formed from $H + NF_2$ (the ratio of NF(b)/NF(a) was independent of the NF_2 flow) [26]. The NF(X) channel was also shown to be the source of the observed HF(v = 4) rather than energy pooling of HF(v). Thus, the initial distribution among NF electronic states was calculated from NF(a) and NF(b) emissions and the HF(v) distribution, $NF(X\,^3\Sigma^-) : NF(a\,^1\Delta) : NF(b\,^1\Sigma^+) = 0.07 : 0.91 : 0.02$ where the NF(X) fraction was admittedly rather uncertain [26].

RRKM calculations for the NF(a) channel were performed on the basis of the intermediate complex mechanism: $H + NF_2 \rightleftharpoons \{HNF_2\} \rightarrow HF + NF(a)$ [26]. The mechanism was previously cited for NF(a) formation. Spin conservation rules predicted an addition-elimination, $H(^2S) + NF_2(^2B_1) \rightarrow \{HNF_2(^1A)\} \rightarrow HF(X\,^1\Sigma^+) + NF(a\,^1\Delta)$, rather than abstraction reaction $(X + NF_2(^2B_1) \rightarrow XF^* + NF(X))$ [27, 28]. The RRKM estimate for HF elimination from $\{NHF_2\}$ was $k \leq 4.7 \times 10^{11}\ s^{-1}$ (for $E_0 \leq 75$ kcal/mol), 2 orders of magnitude higher than the rate constant for redissociation into H and NF_2. NF(X) was considered to originate also from $\{HNF_2\}$ but via singlet-triplet surface crossing. A possible quenching channel, $\{HNF_2\} + M \rightarrow HNF_2 + M$, played no role at the applied total pressures. Formation of $\{HNF_2\}$ needs an H atom approach perpendicular to the NF_2 plane. This restriction is most probably the reason for the comparatively low rate constant for the $H + NF_2$ radical reaction [26].

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4.1.12.6.7.3 Reactions with Oxygen and Nitrogen

Reactions with Oxygen

$N_2F_4 + O_2$. The controversy concerning a possible reaction

$$2\,N_2F_4 + O_2 \rightarrow 2\,FNO + 2\,NF_3$$

has been partly described [1, pp. 63/4]. Formation of FNO was refuted [1, p. 64], [2] based upon the direct IR observation of the $N_2F_4 + O_2$ system in a passivated Al cell for 1 h at 30°C [2] as well as the lack of any O_2 influence on the kinetics of the gas-phase reactions $N_2F_4 + OF_2$ [2, 3] (at 130°C) and $N_2F_4 + F_2$ [4] (at <90°C). Earlier results [5] were traced back to the presence of moisture and reactions with the glass walls [2] although two other reports [6, 7] supported FNO formation (in [7] at 400°C in a Cu reactor). Repeated experiments at room temperature in a Teflon coated reactor were also in favor of slow FNO formation without an effect from traces of H_2O [8]. With other reactors, however, a significant influence of wall materials and moisture was reported on the reaction rates [8]. It was argued [9] that the sequence

$$N_2F_4 \rightleftharpoons 2\,NF_2 \qquad \text{and} \qquad NF_2 + O_2 \rightarrow [NF_2O_2] \rightarrow FNO + 1/2\,F_2 + 1/2\,O_2$$

should be slow at room temperature because of a reaction enthalpy of +42 kcal/mol (a favorable path is given below). However, in the presence of water FNO is removed and thus the reaction is shifted toward the product side. Semiquantitative kinetic measurements made in an all Teflon cell at 25°C with O_2 saturated with H_2O showed after an induction period, a decrease in N_2F_4 concentration, intermediate FNO formation, and finally NO_2 (all species detected by IR). In dry O_2 or oxygen-free H_2O, however, N_2F_4 is claimed to be stable [9]. A report (mentioned in [1, p. 64]) quotes nitrogen oxides as products from $N_2F_4 + O_2$ at −78°C but not at temperatures between −140 and −196°C.

The gas-phase or liquid-phase (in CCl_4 at −22°C) reaction of N_2F_4 with ozonized O_2 in a glass vessel produced NO, NO_2, and SiF_4 [10]. When mixtures of N_2F_4 and O_2 were exposed to large doses of 2 to 3 MeV X-rays, mass spectrometrically identified products depended on temperature: N_2, NF_3, OF_2 at 77 K; O_3, F_2, NO at 85 K; N_2O, $ONNF_2$, FNO_2 at 123 K; and N_2O_4 at 293 K [11].

Enthalpies and free energies (in kcal/mol) for the reactions $1/2\,N_2F_4 + 1/2\,O_2 \rightleftharpoons F_2 + NO$, $\Delta H^\circ_{298} = 27.6$, $\Delta G^\circ_{298} = 11.36$, and $N_2F_4 + O_2 \rightleftharpoons F_2 + 2\,FNO$, $\Delta H^\circ_{298} = -29.6$, $\Delta G^\circ_{298} = -42.9$, predict these equilibria to be totally on the reactant and product side, respectively [12].

$N_2F_4 + O_3$. At liquid-N_2 temperatures a red color appeared at the interface of O_3 and N_2F_4 layers [10]. Upon warming, an explosive reaction occurred [7]. Products mentioned in screening investigations were NF_3, FNO, O_2 [1, p. 64], and NO_2 [7].

N_2F_4 + O. Undissociated N_2F_4 did not react with oxygen atoms at room temperature [13, 23]. Upper limits of 10^{10} [23] and (2.4 to 8.4) $\times 10^{11}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ [14] were estimated for the room-temperature rate constant for the reaction $N_2F_4 + O \rightarrow$ products. Mixing of O and N_2F_4 gas flows and quenching at $-196°C$ was reported to yield NF_3 and NO_2 [7] or N_2, N_2O, NO, and NO_2 [10] (plus side products from the attack on glass) when condensates were slowly heated.

NF_2 + O_2. Freeman [15] mentions in his review on the chemical behavior of the NF_2 radical that there is no reaction with O_2. However, FNO formation is reported at 400°C (at that temperature, initial N_2F_4 is totally dissociated) [7].

NF_2 + O_3. When NF_2 was quenched on a thin layer of O_3, six F–N–O-containing products FNO, FNO_2, $FONO_2$, F_3NO, $ONNF_2$, and O_2NNF_2 were detected by mass spectrometry (caution, the reaction can be explosive) [16].

NF_2 + O. There is considerable disagreement on products, reaction stoichiometry, and rate constants for the reaction of the difluoroamino radical with oxygen atoms. A bright, green luminescence was ascribed to the (0,0) and (0,1) bands of the $NF(^1\Sigma^+ \rightarrow X^3\Sigma^-)$ system. Additional weaker $NF(^1\Delta \rightarrow X^3\Sigma^-)$ emission was observed when $O(^3P)$ atoms reacted with excess NF_2 (both in Ar) [13]. A yellow-green luminescence from $O + NO \rightarrow NO_2^*$ was observed when oxygen atoms were in excess. The proposed reaction mechanism included three steps:

$$NF_2 + O \rightarrow NF + OF$$

$$NF + O \rightarrow NO + F$$

$$O + OF \rightarrow O_2 + F$$

The NO product was detected by mass spectrometry [13]. During the first kinetic investigations the decrease in O concentration was monitored by atomic resonance fluorescence [17]. A concentration-dependent change of the reaction stoichiometry was reported. At initial concentrations $[NF_2]/[O] \leqslant 16$, NF_2 and O were consumed in a 1:3 ratio (apparent rate constant $\sim 2.1 \times 10^{12}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 298 K), whereas for $[NF_2]/[O] \geqslant 30$ a 1:1 stoichiometry was found. For the latter conditions, $NF_2 + O \rightarrow NF + OF$ is believed to predominate with $k = 1.1 \times 10^{12}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (±50%) at 298 K [17]. In a re-examination of the $NF_2 + O$ system in He [14, 18], NF_2 was detected by laser magnetic resonance and O atoms by ESR (see [19] for experimental techniques and preliminary data). With somewhat lower initial concentrations ($[O]_0 = (0.2 \text{ to } 1) \times 10^{12}$, $[NF_2]_0 = (0.88 \text{ to } 6.7) \pm 10^{12}$ molecule/cm^3), NF_2 and O were consumed in a 1:1 ratio. One F atom formed per reaction step. An ESR search for NO as product was in vain [14, 18]. The rate constant, $k(298\ K) = (1.7 \pm 0.2) \times 10^{13}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$, was thus ascribed to

$$(1)\quad NF_2 + O \rightarrow FNO + F, \quad \Delta H = -66.6 \text{ kcal/mol}$$

The absence of NO imposed an upper limit of $(k_2 + k_3)/k_1 < 0.1$ on the channels

$$(2)\quad NF_2 + O \rightarrow NO + F_2, \quad \Delta H \approx -48.5 \text{ kcal/mol, and}$$

$$(3)\quad NF_2 + O \rightarrow NO + 2F, \quad \Delta H \approx -10.4 \text{ kcal/mol}$$

Also the channel $NF_2 + O \rightarrow NF + FO$ was suggested to be too endothermic ($\Delta H \approx 21.2$ kcal/mol) [14, 18]. RRKM calculations based on a bound complex mechanism (ONF_2) were performed in support of the revised mechanism [18]. However, no explanation was given for the observed NF* luminescence.

Reactions with Nitrogen

N_2F_4 + N_2, NF_2 + N_2. No significant interactions between molecular nitrogen and ground state or vibrationally excited N_2F_4 and NF_2 have been reported.

N_2F_4 + N. No reaction has been observed between undissociated N_2F_4 and nitrogen atoms [13, 23], $k \leq 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at room temperature [23].

$NF_2 + N$. The reaction $NF_2 + N$ is a convenient source of F atoms that can be generated practically free of F_2, see "Fluorine" Suppl. Vol. 2, 1980, p. 33. Both reactants were consumed in a 1:1 ratio [20]. Direct formation of two F atoms

$$NF_2 + N \rightarrow N_2 + 2F,\ \Delta H^\circ_{298} = -86\ \text{kcal/mol}$$

was favored over the sequence

$$NF_2 + N \rightarrow 2NF,\ \Delta H^\circ_{298} = 0\ \text{kcal/mol}$$
$$\text{and } NF + N \rightarrow N_2 + F,\ \Delta H^\circ_{298} = -156\ \text{kcal/mol}$$

which requires a 3:1 consumption of N and NF_2 [20]. Spin conservation rules forbid [18, 20]

$$NF_2 + N \rightarrow N_2 + F_2,\ \Delta H^\circ_{298} = -122\ \text{kcal/mol}$$

Two re-eximinations confirmed the 1:1 ratio of reactant consumption [18, 21].

Rate constants for $NF_2 + N \rightarrow$ products were determined at 298 K in flow systems. The decrease in N atom concentration was measured either by atomic resonance absorption and fluorescence [17, 22] or by ESR [18]: $(2.8 \pm 0.2) \times 10^{12}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [22] (previous rate constant $(1.8 \pm 0.7) \times 10^{12}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [17]; preliminary value [21]) and $(3.4 \pm 0.5) \times 10^{12}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ [18].

Investigations of the product side of the reaction led to the detection of different reaction channels. The observed fluorescence consisted of the N_2 First Positive bands $B^3\Pi_g \rightarrow A^3\Sigma_u^+$, the (0,0) and (0,1) bands of $NF(^1\Sigma^+ \rightarrow {}^3\Sigma^-)$ and with minor intensity of $NF(^1\Delta \rightarrow {}^3\Sigma^-)$ [13]. Deviating from the first proposal [20] (see above), a mechanism was discussed [13] that included a primary step

$$NF_2 + N \rightarrow 2NF$$

followed by rapid bimolecular disproportionation,

$$NF + NF \rightarrow N_2 + 2F$$

In a later publication [17] the second step was considered unlikely to proceed directly. Instead, the sequence $NF + NF \rightarrow NNF + F$ and $NNF + M \rightarrow N_2 + F + M$ was proposed [17]. The finding that instead of two [20] only one F atom formed initially per NF_2 reactant molecule provoked a new, still tentative mechanism [18]. The channel

$$\text{(a)}\ NF_2 + N \rightarrow N_2F + F$$

should be accompanied by

$$\text{(b)}\ NF_2 + N \rightarrow N_2F^* + F$$

with a branching ratio (a)/(b) near 1 and should be followed by fast reactions

$$\text{(c)}\ N_2F + F \rightarrow N_2 + 2F \quad \text{and} \quad \text{(d)}\ N_2F^* \rightarrow N_2 + F$$

An energy diagram and RRKM calculations based on the assumption of initial NNF_2 complex formation have been put forward in favor of the revised mechanism [18].

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4.1.12.6.7.4 Reactions with Halogens

Reactions with Fluorine

$N_2F_4+F_2 \rightarrow 2NF_3$. The reaction of tetrafluorohydrazine with molecular fluorine gave NF_3 as the only product [1, 2]. Kinetic experiments were performed between room temperature and 85°C in a vessel made of Mg [1] or Ni [2]. Time-dependent concentrations of F_2 or NF_3 were followed by F_2 UV absorption [1] or gas-liquid chromatography of batches with subsequent IR analysis of NF_3 [2]. Experimentally, a homogeneous gas-phase reaction was found that obeyed the rate law $-d[F_2]/dt=-k'[F_2][N_2F_4]^{1/2}$ with $k'=1.0\times10^{11.0\pm0.2}\exp[-(20400\pm400)\ \text{cal}\cdot\text{mol}^{-1}/RT]$ [1] or $k'=1.2\times10^{9}\exp[-17900\ \text{cal}\cdot\text{mol}^{-1}/RT]\ \text{L}^{1/2}\cdot\text{mol}^{-1/2}\cdot\text{s}^{-1}$ [2]. The different rate constants are thought to originate from an undetected, heterogeneous component of the reaction [3]. Diluent gases N_2 or O_2 (up to 660 Torr) and additions of NO and O_2 (<3 Torr) reportedly had no measurable effect on the reaction [1]. There was also no photochemical influence. The supposed mechanism of the reaction is [1]:

(1) $N_2F_4 + M \rightleftharpoons 2NF_2 + M$ (fast equilibrium, see pp. 326/31)
(2) $NF_2 + F_2 \rightarrow NF_3 + F$ (rate-determining step)
(3) $NF_2 + F + M \rightarrow NF_3 + M$
(4) $F + N_2F_4 \rightarrow NF_3 + NF_2$
(5) $2F + M \rightarrow F_2 + M$ (see "Fluorine" Suppl. Vol. 2, 1980, pp. 95/98)

Steps (3) and (5) are neglected in [2]. The sequence (1), (2), (3) is kinetically indistinguishable from the sequence (1), (2), (4) [1].

$NF_2 + F_2 \rightleftharpoons NF_3 + F$. The rate law for $N_2F_4 + F_2 \xrightarrow{k'} 2NF_3$ supports the assumption that $NF_2 + F_2 \xrightarrow{k_2} NF_3 + F$ ($\Delta U^\circ_{298} = -22.7$ kcal/mol [11], $\Delta H^\circ \approx -23$ kcal/mol [6]) is the rate-determining step. Thus, one has $k' = k_2K^{1/2}$, where K is the equilibrium constant for $N_2F_4 + M \rightleftharpoons 2NF_2 + M$. Based on experimental kinetic data [1] for $N_2F_4 + F_2$ and an equilibrium constant [4], $k_2 = 6.6 \times 10^9 \exp[-(10200 \pm 500)\ \text{cal}\cdot\text{mol}^{-1}/RT]\ \text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ was derived [3] (the original data for k_2 in [1] were evaluated incorrectly, see [5]). An activation energy of ~7.6 kcal/mol for k_2 emerges [3] using kinetic data from [2]. A more direct measurement of k_2 has been performed [5]. In N_2F_4–F_2–Ar (or Ne) mixtures and at temperatures between 1100 and 1600 K obtained in reflected shock waves, N_2F_4 dissociates rapidly and completely and reacts subsequently with F_2 at rate constants of $k_2 = 4.8 \times 10^{12} \exp(-14400\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [5] (k_2 values are from initial rates of NF_3 formation or disappearance of F_2 measured by sampling and time-of-flight mass spectrometry). Corrected data (derived from [1]) and those (from [5]) extrapolated toward temperatures around 80°C agree reasonably well. However, according to [3], data of [5] are to be preferred because heterogeneous reactions are thought to be negligible.

By use of equilibrium constants taken from the JANAF tables and k_2 values [5], the rate constants for the reverse reaction, $NF_3 + F \xrightarrow{k_{-2}} NF_2 + F_2$, were calculated to be $k_{-2} = 8.8 \times 10^{13} \exp(-35600\ \text{cal}\cdot\text{mol}^{-1}/RT)\ \text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [7]. An Arrhenius plot for k_{-2} in the range ~1600 to 2500 K was reported [5].

$N_2F_4 + F \rightarrow NF_3 + NF_2$. The direct reaction between tetrafluorohydrazine and fluorine atoms is thought to play some role in the thermal reaction $N_2F_4 + F_2$ [1]. The Arrhenius activation energy for this step was estimated to be between 1.5 and 4.5 kcal/mol depending on whether $F + N_2F_4$ or $F + NF_2$ dominates [1]. In the photochemical decomposition of N_2F_4/NF_2 the present reaction was supposed to be the only path to NF_3 [8].

$NF_2 + F + M \rightarrow NF_3 + M$. The reaction is the reverse of the thermal decomposition of NF_3, see p. 206. Fluorine atoms generated by photochemical decomposition of NF_2 in the gas-phase [9] or in low-temperature matrices [10] react with excess NF_2 to form NF_3. Pyrolysis of NF_2 into NF_3 and N_2 is also thought to involve this reaction step [6]. The kinetics of the gas-phase reaction $NF_2 + F + M \rightarrow NF_3 + M$ ($\Delta U^\circ_{298} = -60.4$ kcal/mol [11], $\Delta H = -58$ kcal/mol [15]) has been the object of experimental [11 to 14] and theoretical studies [16, 17]. Data are compiled below.

Termolecular rate constants (*) limiting low-pressure rate constants):

M	T in K	k in 10^{17} $\text{cm}^6\cdot\text{mol}^{-2}\cdot\text{s}^{-1}$	conditions, remarks	Ref.
He	298	3.2 ± 1.2*)	flow system with mass spectrometric detection; NF_2 from thermal dissociation of N_2F_4, F from reaction $NF_2 + N$	[11]
He	297	0.98*)	derived from laser magnetic resonance study of $NF_2 + O$	[12]

M	T in K	k in 10^{17} $cm^6 \cdot mol^{-2} \cdot s^{-1}$	conditions, remarks	Ref.
He	300	0.5	k cited in [3, 16]; $k[M] \approx 10^{10}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 3.5 Torr in original report [14]	[14]
Ne	298	0.83 (at 1 atm)	rate constants in fall-off region; NF_2 from irradiation of NF_3–Xe–Ne mixtures with 300 to 350 keV electrons; detection of NF_2 UV absorption	[13]
		0.62 (at 2 atm)		
		0.33 (at 4 atm)		
Ne	300	2.0*)	RRKM calculation on unimolecular NF_3 decomposition; efficiency adjusted to experimental value of [11]	[17]
	400	1.2*)		
N_2	300	1.0 ± 0.2	unimolecular decomposition of NF_3 using Troe formalism [18]	[16]

Bimolecular rate constants (**) limiting high-pressure rate constants):

M	T in K	k in 10^{12} $cm^3 \cdot mol^{-1} \cdot s^{-1}$	conditions, remarks	Ref.
Ne	298	3.5 (at 1 atm)	see above	[13]
		5.1 (at 2 atm)		
		5.4 (at 4 atm)		
Ne	300	26**)	RRKM calculation, see above	[17]
	400	22**)		

$NF_2 + F \rightarrow NF + F_2$. Such a reaction is too endoergic to play a role in $N_2F_4(NF_2) + F_2(F)$ systems, $\Delta H^\circ_{298} = 35$ kcal/mol [15].

Reactions with Chlorine

The photochemical reaction of chlorine with N_2F_4 is an early, renowned example of an NF_2 radical reaction (see e.g., the reviews [19 to 21] and the compilation of Lawless and Smith [22, pp. 56], [78, 80] containing some unpublished reports). Whereas reports (mentioned in [22, p. 80]) state that there is no direct chlorination of N_2F_4 at temperatures up to 285°C, under UV irradiation at lower temperatures an equilibrium reaction

$$N_2F_4 + Cl_2 \overset{h\nu}{\rightleftharpoons} 2ClNF_2$$

is established within a few minutes [23, 24]. IR analysis of the photochemically formed $ClNF_2$ from initial mixtures of about 55 Torr N_2F_4 and 116 to 520 Torr Cl_2 resulted in an equilibrium constant for which $\log K = 5.77 - 2640/T$ (41 to 83°C) [24]; see, however, [19] for a critical comment. Within some experimental scatter the equilibrium could also be verified from the reverse reaction, that is, UV photolysis of $ClNF_2$ [24]. Equilibrium constants for the reverse process $ClNF_2 \rightleftharpoons \frac{1}{2}N_2F_4 + \frac{1}{2}Cl_2$, $\log K' = -1.04 + 1092/T$, $\Delta G^\circ_{298} = -3.58$ kcal/mol, $\Delta H^\circ_{298} = -5.0$ kcal/mol were derived [25]. See also the data for the (catalyzed) decomposition of $ClNF_2$ [26]. In case K and K′ are true thermodynamic constants (see, however, [19]) the relation $K' = K^{-1/2}$ should hold. But there is considerable disagreement that becomes even worse when K′, ΔG°_{298}, ΔH°_{298} are ascribed [26] to $2ClNF_2 \rightleftharpoons N_2F_4 + Cl_2$.

Under photochemical conditions the following reaction steps appear to be involved

(1) $N_2F_4 \rightleftharpoons 2NF_2$
(2) $Cl_2 \rightleftharpoons 2Cl$
(3) $Cl + NF_2 \rightleftharpoons ClNF_2$
(4) $Cl + ClNF_2 \rightarrow Cl_2 + NF_2$

where a possible step (5) $NF_2 + ClNF_2 \rightarrow N_2F_4 + Cl$

is thought to be unlikely because of the thermal stability of $ClNF_2$ in the presence of N_2F_4 [24].

The room-temperature rate constant was measured separately for $NF_2 + Cl + Ar \rightarrow ClNF_2 + Ar$ [27]. After having mixed NF_2 (from thermal dissociation of N_2F_4 at 200°C) and Cl ($^2P_{3/2}$) atoms (by microwave discharge in Cl_2) in a low-pressure flow system, the decrease in NF_2 UV absorption was observed (too low an extinction coefficient!): $k = (9.8 \pm 1.5) \times 10^{16}\ cm^6 \cdot mol^{-2} \cdot s^{-1}$ at 293 K. With excess Cl atoms NF_2 is rapidly regenerated via step (4) [27].

Equilibrium constants [24, 25] predict that $ClNF_2$ synthesis from $N_2F_4 + Cl_2$ is favored by higher temperatures. However, $ClNF_2$ and N_2F_4 decompose above 100°C and 200°C, respectively [25, 26]. For N_2F_4 decomposition, see pp. 331/2.

At still higher temperatures a different situation arises. MacLean and co-workers [28 to 30] heated N_2F_4 and Cl_2 in Ar by shock waves to 1150 to 1550 K. They followed the reaction by monitoring simultaneously the UV absorptions of NF_2 and Cl_2 and the chlorine atom recombination emission. NF_2 was generated immediately at the shock front. After an induction period, NF_2 and Cl_2 disappeared rapidly with equal rates, while the Cl atom concentration passed through a maximum [28]. After initiation by steps (1) and (2), discussed above for the photochemical reaction, a different chain mechanism is discussed for the high temperatures. Chain propagation steps include

(6) $F + Cl_2 \rightarrow ClF + Cl$ (8) $NF + NF_2 \rightarrow N_2F_2 + F$
(7) $Cl + NF_2 \rightarrow ClF + NF$ (9) $NF + NF \rightarrow N_2 + 2F$

with $k_7 = 7.8 \times 10^{12}\ cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 1175 K [29, 30].

Reactions with Bromine and Iodine

In contrast to the N_2F_4/NF_2 reactions, with lighter halogens, no stable Br- or I-containing product has been observed [31]. Rather, UV photolysis of a 0.004 mol Br_2 and 0.002 mol N_2F_4 mixture provides a convenient route to N_2F_2 (see p. 387). Side products are N_2, NF_3 (decreases with initial $Br_2 : N_2F_4$ ratio), and some products from the attack on the glass walls [32, 33]. A rate constant $k = (3.6 \pm 0.7) \times 10^{16}\ cm^6 \cdot mol^{-2} \cdot s^{-1}$ was reported for $NF_2 + Br + Ar \rightarrow BrNF_2 + Ar$ measured in a flow system at 293 K [27]. The $BrNF_2$ product concentration remained low because of the reaction $Br + BrNF_2 \rightarrow NF_2 + Br_2$ [27].

The fate of I($^2P_{1/2}$) atoms produced by photolysis of C_2H_5I–N_2F_4 mixtures remains speculative [34].

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4.1.12.6.7.5 Reactions with Sulfur, Carbon, and Silicon

The product mixture obtained from reacting equimolar amounts of N_2F_4 and sulfur between 110 and 140°C for up to 3 h contained SF_4 (48%), unreacted N_2F_4 (30%), and minor amounts of SOF_2 (from side reaction) and SF_5NF_2 (6% each) [1].

N_2F_4 was inert to graphite from various sources. There was also no noticeable absorption of N_2F_4 [2].

Plasmas containing NF_2 were used to etch Si [3, 4].

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4.1.12.6.7.6 Reactions with Metals

According to an unpublished report (mentioned in [1, p. 61]), N_2F_4 reacted with Li at temperatures between −80 and 250°C with formation of LiF and Li_3N. When N_2F_4 was admitted to K (or Li) dissolved in NH_3 an explosion occurred [1, p. 61].

No attack of N_2F_4 on passivated Mg was mentioned [2].

NHF_2 was formed in concentrated H_2SO_4 by action of Hg. Side products were Hg_2SO_4 and some SO_2 [1, p. 58]. The quenching of excited $Hg(^3P_0)$ and $Hg(^3P_2)$ atoms by N_2F_4 included reactive channels. From the HgF(B–X) chemiluminescence observed in a flowing afterglow study, a rate constant of 3.2×10^{13} $cm^3 \cdot mol^{-1} \cdot s^{-1}$ (300 K) was derived for $Hg(^3P_2) + N_2F_4 \rightarrow HgF(B) + \ldots$ [3].

Passivated Al vessels were used for gas-phase N_2F_4 studies [4]. NF_2 loss rates (no numerical data given) were measured for the hot gas (500 K) in contact with virgin and passivated (by NF_2) Al 6061. Passivation was explained by buildup of a fluoride layer [5].

Zr foil can be ignited in an N_2F_4 atmosphere. The strongly exothermic reaction generated light of a high color temperature (4700 K) useful for flash lamps [6].

Ni or Monel are recommended materials for reaction vessels when work with N_2F_4 is performed at high temperatures [1, p. 48]. Prior passivation of Monel [7] excluded some catalytic surface effects observed in N_2F_4 thermolysis [8].

Stainless steel vessels are suited for work with N_2F_4 at normal conditions [1, p. 48]. NF_2 loss rates were plotted [5] for fresh and passivated type 304 stainless steel contacted at 500 K with an NF_2 atmosphere. Fe^{2+} reduced N_2F_4 in concentrated H_2SO_4 to NHF_2 during 17 h at 30°C in 80% yield

$$N_2F_4 + 2Fe^{2+} + 2H^+ \rightarrow 2NHF_2 + 2Fe^{3+}$$

In aqueous H_2SO_4 further reduction to NH_4^+ occurred [1, p. 58].

Metal strips made of Cu were more heavily attacked by NF_2 at 500 K than those made of Ni or Al [5]. However, a copper vessel was used at 393 K during 6 d and at 100 atm without any reported problems [9].

Some surface reaction with Pt can be inferred from data taken at 500 K [5].

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4.1.12.6.8 Reactions with Compounds

4.1.12.6.8.1 Reactions with Inorganic Compounds Containing Hydrogen

Reactions of N_2F_4 or NF_2 with simple inorganic compounds that contain bound hydrogen are compiled in Table 23. Reactions with CH_4 are added for comparison. Reactions with other hydrocarbons are surveyed on pp. 381/2.

Table 23
Reactions of N_2F_4/NF_2 with Inorganic, Hydrogen-Containing Compounds.
Underlined reactions are described in more detail in the text.

reactant	products	conditions, results, remarks	Ref.
<u>H_2O</u>	F^-, N_2, N_2O, NO, NO_2^-, NO_3^-, etc.	solubility of N_2F_4 in H_2O [6]; slow hydrolysis between 25 and 133°C with complex mechanism [1, 2]	[1 to 6]
<u>H_2O_2</u>	F, FNO, H_2O, O_2, etc.	liquid-phase reaction [1, 3, 4]; gas-phase reaction [7]	[1, 3, 4, 7]
NH	N_2, HF, F	$NF_2 + NH \rightarrow N_2 + HF + F$, $k \approx 6 \times 10^{12}$ $cm^3 \cdot mol^{-1} \cdot s^{-1}$ at 300 K, quoted in [8]	[8]
N_2H_4	N_2, HF, F	calculated flame temperature (4000 K) and specific impulse 265 s [9]; calculated product distribution at 1500 K and ranking analysis for possible HF laser [10]; F atom yields calculated for 1500 and 2000 K [11]	[9 to 11]
NH_3	NH_4F, N_2	heat of reaction for $N_2F_4(g) + {}^{16}/_{3} NH_3(g) \rightarrow 4 NH_4F(c) + {}^{5}/_{3} N_2(g)$, $\Delta H^\circ_{298} = -1603.0 \pm 0.9$ kJ/mol, from calorimetry [12], see also [5] (purity of N_2F_4 only ~94%); calculated F atom yields at 1500 and 2000 K [11]	[5, 11, 12]
NH_4HF_2	NHF_2	calculated for ${}^{2}/_{5} N_2F_4 + {}^{1}/_{5} NH_4HF_2 \rightleftharpoons NHF_2$: $\Delta H^\circ_{298} = 13.37$ kcal/mol, $\Delta G^\circ_{298} = 12.10$ kcal/mol	[27]
NH_2NO_2	NF_3, NO_x	flash decomposition into NF_3 with liquid N_2F_4; in CCl_4 solution NO_x products	[3, p. 65]
HN_3	NF_3	flash photolysis of various N_2F_4–HN_3 mixtures (5 Torr N_2F_4 and $[N_2F_4]/[HN_3] = 10$ to 0.5); NF_2 and NH intermediates detected; tentative mechanism	[13]
HNO_3	FNO, NF_3	no details available	[4]

Table 23 (continued)

reactant	products	conditions, results, remarks	Ref.
$HF + Cl_2$	NF_3, HCl	calculated data for $\frac{1}{2}N_2F_4 + HF + \frac{1}{2}Cl_2 \rightleftharpoons NF_3 + HCl$: $\Delta H^\circ_{298} = 12.54$ kcal/mol, $\Delta G^\circ_{298} = 11.89$ kcal/mol	[27]
HCl	$HF^{\dagger}$	HF lasing initiated by pulsed discharge [14] or flash photolysis [15]	[14, 15]
$HClO_4$	FNO, NF_3	reaction with aqueous $HClO_4$ (products?) needs thermal activation	[4]
HBr	$HF^{\dagger}$	HF lasing at P branches of 4–3, 3–2, 2–1 transitions initiated by pulsed discharge in 5 Torr N_2F_4–10 Torr HBr–100 Torr He	[14]
R–SH	NHF_2	NHF_2 synthesis from N_2F_4 and thiophenol or aliphatic mercaptanes, for details, see "Fluorine" Suppl. Vol. 5	[16, 17]
$BH_3 \cdot X$	(NHF_2)	NHF_2 product from X = pyridine [3, p. 57], for $X = N(CH_3)_3$ no reaction [3, p. 58]	[3]
KBH_4	KBF_4, HF	reaction at −130°C	[3, p. 61]
B_2H_6	$B_3N_3H_nF_{6-n}$	reaction between 140 and 160°C, products with n = (3), 4, 5 and additional BF_3, B_3H_9, BF_3NH_3, H_2, N_2	[18]
$\underline{CH_4}$	HF, CF_4, etc.	thermal stability [19, 20]; HF lasing [14, 15]; photochemical reaction (UV) [21]; photochemical reaction (IR) [22, 23]	[14, 15, 19 to 23, 28]
SiH_4	SiF_4, HF, N_2	explosion at 25°C, products SiF_4, N_2, H_2 [3, p. 61]; delay between mixing and explosion depends less on N_2F_4 than on SiH_4 pressure, inhibition by cis-2-butene [19]; time behavior and detailed product analysis (42% N_2, 25% SiF_4, 28% HF, 2.4 % H_2, and minor amounts of other products) of detonating 2:1 N_2F_4–SiH_4 mixtures stabilized by cis-2-butene [24]	[3, 19, 24]
$(C_6H_5)_2PH$	$(C_6H_5)_2PF_3$	54% yield of product after 1 d reaction of equimolar mixture in $C_3F_5Cl_3$	[25]

Table 23 (continued)

reactant	products	conditions, results, remarks	Ref.
AsH_3	NHF_2, As	gas mixture thermally stable at 25°C [19]; reaction at 50°C [16], for details, see "Fluorine" Suppl. Vol. 5	[16, 19]
LiH	LiF, N_2, H_2	after induction period explosive reaction $N_2F_4+4LiH \rightarrow 4LiF+N_2+2H_2$ at 0 to 50°C; same stoichiometry in ether, dioxane, or hexane [1]; intermediate step in reaction between $ClNF_2+LiH$ [26]	[1, 26]
GeH_4	—	N_2F_4–GeH_4 mixtures burn spontaneously or explode after short delay	[19]

The solubility of N_2F_4 in pure **H_2O** is low. At temperatures between 288.15 and 318.18 K the mole fraction of dissolved N_2F_4 (corrected for hydrolysis) is given by: $\log x = 6936.9/T + 45.345 \cdot \log T - 140.28$. Enthalpies of solution increase from −6.7 kcal/mol at 278.15 to −3.1 kcal/mol at 319.15 K, corresponding entropies increase from −45 to $-33\ cal \cdot mol^{-1} \cdot K^{-1}$ [6]. Slow hydrolysis of N_2F_4 in water was known for some time, see, for example [5]. There is, however, disagreement on details. A general statement implies formation of NF_3 and FNO [4] (the latter is not stable in H_2O). About 10% conversion of N_2F_4 was noted after 10 h at 80°C according to

$$3N_2F_4+7H_2O \rightarrow 12HF+2HNO_3+\tfrac{3}{2}N_2+NO \text{ (+traces of } N_2O)$$

The mechanism was believed to be [1]:

$$\begin{aligned} N_2F_4+2H_2O &\rightarrow 4HF+O_2+N_2 \quad \text{rate limiting} \\ NF_2+O_2 &\rightarrow F_2NO_2 \\ F_2NO_2+H_2O &\rightarrow 2HF+NO_2+\tfrac{1}{2}O_2 \\ 2NO_2+H_2O &\rightarrow HNO_3+HNO_2 \\ 3HNO_2 &\rightarrow HNO_3+2NO+H_2O \end{aligned}$$

Hydrolysis of N_2F_4 in acidic, basic, and neutral H_2O between 60 and 133°C was investigated in sealed borosilicate ampules with IR spectroscopy as the main detection method [2] (see also reports mentioned in [3, p. 60]). At 133°C the reaction was rapid. Formation of N_2O and NO_2^- as main products in the reaction with caustic soda is described by

$$N_2F_4+4OH^- \rightarrow 2NO+4F^-+2H_2O \quad \text{and} \quad 4NO+2OH^- \rightarrow N_2O+2NO_2^-+H_2O$$

Traces of N_2 were also observed. NO, N_2, and NO_3^- were found in neutral H_2O and aqueous HCl at 133°C. Between 60 and 100°C, H_2O and 0.5N HCl almost quantitatively convert N_2F_4 into NO with some minor amounts of NF_3. Kinetic investigations at 60°C employed 5 mL neutral H_2O and $\sim(3 \text{ to } 13)\times10^{-3}$ mol N_2F_4 (thus, according to [7], systems were not homogeneous). Data were characterized by (a) high irreproducibility, (b) long induction periods of up to 2 weeks, and (c) promotion of the reaction by NO and more effectively by O_2 (see also the reaction $N_2F_4+O_2$, p. 347). A few hydrolysis experiments in 0.5N HCl, 0.5N HF (slightly faster conversion), 2N NaOH (slow steady conversion from the very beginning), and 1N H_2SO_4 (at lower temperatures) were also described. A tentative mechanism [2] includes the reactions

$$N_2F_4 + 2H_2O \xrightarrow{\text{slow}} 2NO + 4HF$$

$$NO \xrightarrow[H_2O,\,N_2F_4]{\text{slow}} NO_2$$

$$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2 \rightleftharpoons \tfrac{2}{3}HNO_3 + \tfrac{4}{3}NO + \tfrac{2}{3}H_2O$$

$$2NO_2 + N_2F_4 \xrightarrow{\text{fast}} 4FNO$$

$$2FNO + H_2O \longrightarrow NO_2 + NO + 2HF$$

$$4FNO + SiO_2 \xrightarrow{\text{fast}} 2NO_2 + 2NO + SiF_4 \text{ (reaction with glass wall)}$$

Unpublished reports quoted in [3, p. 66] state that N_2F_4 (1) ignites with formation of NF_3 when contacted with $\mathbf{H_2O_2}$ in a glass vessel (formation of FNO and NF_3 [4]), (2) produces FNO and FNO_2 with 98% H_2O_2 in a Kel-F vessel, and (3) does not react during 45 min (at 25°C?) with 30% H_2O_2. A vigorous reaction (at room temperature?) with 3% H_2O_2 was also reported: $N_2F_4 + 2H_2O_2 \rightarrow 4HF + 2HNO_3$ (80 to 96% conversion, NF_3 side product) [1]. The gas-phase reaction between NF_2 and H_2O_2 at room temperature was studied by laser magnetic resonance to follow the NF_2 and HO_2 radical concentrations. The decrease in NF_2 shows a marked induction period and is inhibited by added H_2. Also, intermediate HO_2 formation is suppressed by H_2. Qualitative data are discussed in terms of a branched chain mechanism [7]:

initiation

$$NF_2 + H_2O_2 \rightarrow F + \cdots \text{ (F atoms are scavanged by } H_2\text{)}$$

extension and branching

$$F + H_2O_2 \rightarrow HO_2 + HF$$

$$NF_2 + HO_2 \rightarrow FNO + F + OH \quad (k \approx 1.2 \times 10^{12}\ \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \text{ at } \sim 25°\text{C})$$

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$

termination

$$HO_2 + \text{wall} \rightarrow \cdots \qquad F + HO_2 \rightarrow HF + O_2$$

$$HO + HO_2 \rightarrow H_2O + O_2 \qquad HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Mixtures of N_2F_4 and $\mathbf{CH_4}$ are thermally stable at 25°C [19]; but additions of 1% N_2F_4 effectively shorten the induction period for spontaneous ignition of CH_4–O_2 mixtures in Ar [20]. Pulsed discharge excitation of 5 Torr N_2F_4 and 10 Torr CH_4 leads to HF lasing on the P branch of the 2–1 band. The same result was obtained with natural gas (main component CH_4). Addition of 100 Torr He results in lasing on the P branches of the 3–2, 2–1, and 1–0 bands [14]. HF lasing may also be initiated by flash photolysis of N_2F_4–CH_4 [15]. The photochemical reaction between N_2F_4 and CH_4 with irradiation at 2537 Å (NF_2 absorption) reaches high conversions during relatively short times. The reaction is initiated by $NF_2 + h\nu \rightarrow NF + F$. The excited $CH_3NF_2^*$ intermediate (from $F + CH_4 \rightarrow CH_3 + HF$ and $CH_3 + NF_2 \rightarrow CH_3NF_2^*$) may be deactivated (preferentially at high CH_4 pressures) or may eliminate HF, $CH_3NF_2^* \rightarrow HCN + 2HF$ (preferentially at low CH_4 pressures). Final products are thus CH_3NF_2, HF, HCN, and N_2F_2 with the total amount of CH_3NF_2 and HCN being independent of initial CH_4 pressure [21]. N_2F_4 reportedly gained fluorinating capabilities toward CH_4 when the N–F stretching vibrations were excited by near-resonant 10.6 μm CO_2 laser irradiation [22]. Exposure of 1:1 or 2:1 N_2F_4–CH_4 mixtures (150 or 114 Torr CH_4, respectively) to a 40 or 50 W laser pulse led in a chemiluminescent reaction to about 22% CF_4 as well as to HF and N_2 [22]. Irradiation with 30 W yielded HF but no fluorinated hydrocarbon. Instead 35% C_2H_2, 7% C_2H_4, 3% CH_4, 5% H_2, and 25% N_2 were listed as products from a 100 Torr N_2F_4–300 Torr CH_4 mixture [23].

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4.1.12.6.8.2 Reactions with Halides and Perhalogenated Compounds

Table 24 provides a survey of the reactions of N_2F_4 and NF_2 with halides M_iX_j, where M is a metal or nonmetal and X stands for F, Cl, Br, or I or a combination thereof. Added are the reactions with some perhalogenated compounds, above all, sulfur compounds that contain the substituents CF_3, $CF_3N{=}$, etc.

Table 24

Reactions of N_2F_4/NF_2 with Halides and Perhalogenated Compounds. Underlined reactions are described in the text.

reactant	products	conditions, remarks	Ref.
ClF_3	NF_3, ClF	gas-phase kinetics [1]; contradictory results [2, p. 63]: no reaction at 195°C in Teflon reactor, conversion into NF_3 at 100°C; no conclusive results at 25°C [3]	[1 to 3]
CF_3SCl	$ClNF_2$, $(CF_3)_2S_2$	photochemical reaction [2, p. 56]	[2]
CF_3SSCF_3	CF_3SNF_2	photochemical reaction (also in electrical discharge), coupling of NF_2 and CF_3S radicals	[4]
SF_4	SF_5NF_2, N_2F_2	equimolar reactants irradiated for 80 h with low-pressure Hg lamp, 30% yield of SF_5NF_2 [5, 6]; no thermal reaction at 80°C but N_2, SF_6, and some NF_3 from $N_2F_4 + SF_4 + NaN_3$ at 80°C [54]	[5, 6, 54]
$SF_4 + N_2F_2$	SF_5NF_2, NF_3, N_2	$SF_4:N_2F_4:N_2F_2 = 1:1.1:1$ heated to 100°C for 17 h, relative product yields: SF_5NF_2 (1), N_2 (0.9), NF_3 (0.8); N_2F_4 used as radical trap	[7]
$SF_4 + CF_3OF$	SF_5NF_2, $CF_3OSF_4NF_2$	$SF_4:N_2F_4:CF_3OF = 4:3:5$ at 25°C for 7 d; $CF_3OSF_4NF_2$ yield 14%; other products COF_2, SOF_2, CF_3OOCF_3	[8]
CF_3SF_3	$CF_3SF_4NF_2$, SF_6, etc.	about equimolar mixture irradiated with low-pressure Hg lamp for 7 h; yields SF_6 (40%), SF_4 (17%), $CF_3SF_4NF_2$ (8%), reactants (10% each), SO_2 (8% impurity)	[5]
$R_fN{=}SF_2$	SF_5NF_2, N_2, R_fF	$R_f = CF_3$, C_2F_5, C_3F_7; only photochemical reaction, stoichiometry $R_fN{=}SF_2 + 1.5\,N_2F_4 \rightarrow R_fF + SF_5NF_2 + 1.5\,N_2$, yields of SF_5NF_2: 93% (CF_3), 65% (C_2F_5), 66% (C_3F_7)	[9]

Table 24 (continued)

reactant	products	conditions, remarks	Ref.
SF_6	—	no thermal reaction at ~350 K [10]; for irradiation with 2 to 3 MeV X-rays, only N_2F_4 decomposition [11]	[10, 11]
SF_5Cl	SF_5NF_2, Cl_2	$SF_5Cl:N_2F_4 = 1.6:1$ mixture irradiated with low-pressure Hg lamp for 120 h, yields: SF_5NF_2 34%, Cl_2 30%	[5]
R_fSF_5	R_fNF_2, SF_4, SF_6, R_fF, NF_3	$R_f = C_2F_5$, cyclo-C_6F_{11}; reactions at <10 Torr and >700°C or 1 atm and >500°C; up to 77% yield of $C_2F_5NF_2$; 16% $C_6F_{11}NF_2$	[12]
$R_f'SF_4R_f$	$R_f'NF_2$, R_fNF_2, etc.	$R_f' = R_f = C_2F_5$; $R_f' = CF_3$, $R_f = C_2F_5$; reactions around 700°C and below 10 Torr; high yields of $R_f'NF_2$, R_fNF_2	[12]
$\overline{(CF_2)_2SF_4(CF_2)_2O}$	$O(CF_2CF_2)_2$	only cyclic ether as product between 520 and 745°C and 5 to 760 Torr	[12]
S_2F_{10}	SF_5NF_2	ca. 60% yield at 140°C and Monel reactor [13]; lower yield at 150°C and stainless steel reactor [14]; considerable turnover at ca. 25°C with 300 CO_2 laser pulses of 10^{-7} s (0.3 J, 933 cm^{-1}) or a single 0.3 J ArF laser pulse [15]; coupling of NF_2 and SF_5 radicals	[13 to 15]
S_2Cl_2 or SCl_2	—	no $ClNF_2$ [2, p. 83]	[2]
N_3F	NF_3	[2, p. 105]	[2]
$\underline{N_2F}$	NF_3, N_2	step in thermal NF_2 decomposition	[16 to 19]
$\underline{NF}$	N_2F_2, F	step in thermal NF_2 decomposition [16 to 18]; chain propagation step in $Cl_2 + N_2F_4$ reaction [19]; rate constants for ground state and excited NF [20, 21, 55]; $NF + N_2F_4 \rightarrow NF_2 + N_2F_2 + F$ postulated in photochemical NF_2 decomposition [22]	[16 to 23, 55]

Table 24 (continued)

reactant	products	conditions, remarks	Ref.
$\underline{N_2F_2}$	N_2F, NF_3	$NF_2+N_2F_2$ step in thermal NF_2 decomposition [17, 18]; $N_2F_4+N_2F_2+SF_4$ [7], see above; $N_2F_4+N_2F_2+SO_2$, see p. 371; no N_4 species from $N_2F_4+N_2F_2$ at 6200 atm [2, p. 43]; reaction $N_2F_4+N_2F_2$ at 110°C [53]	[2, 7, 17, 18, 53]
$\underline{NF_2}$	N_2F_4, NF_3, NF	$2NF_2 \rightarrow N_2F_4$: see pp. 326/31; $2NF_2 \rightarrow NF_3+NF$: see p. 331; $NF_2+N_2F_4 \rightarrow NF_3+N_2F_3$ considered unlikely because of endothermicity [24]	[24]
NF_3	—	no reaction between 950 and 1120 K	[25]
NCl_3	—	no $ClNF_2$ formation observed [2, p. 83]	[2]
PF_3	—	no reaction at 100°C [26]; thermochemical calculations on F atom generation at 1500 and 2000 K [27]; formation of N_2, PF_5 in the presence of NaN_3 [54]	[26, 27, 54]
PF_2I	F_2NPF_2, I_2	synthesis of F_2NPF_2 in 26% yield from equimolar reactants at 23°C for 45 h, photochemical reaction leads to vigorous explosion	[56]
$(CF_3)_2PI$	—	no reaction at conditions mentioned above	[56]
PF_5	—	no reaction at 25°C; no association down to −120°C	[28]
PCl_3	$NFPCl_2PCl_4$	reaction in autoclave at 100°C and $POCl_3$ solvent [26]; no $ClNF_2$ formation observed [2, p. 83]	[2, 26]
PCl_5	—	no $ClNF_2$ formation observed [2, p. 83]	[2]
$\underline{AsF_5}$	$N_2F_3^+AsF_6^-$	formation of $N_2F_3^+$ salt [29, 30], identification of product [30 to 32]; low-temperature $N_2F_4 \cdot 2AsF_5$ complex [29], see also [2, pp. 94/5]	[2, 29 to 32]

Table 24 (continued)

reactant	products	conditions, remarks	Ref.
AsF_5 in C	trans-N_2F_2	reaction of 1st stage AsF_5 intercalates [33, 34], mechanism [35]	[33 to 35]
SbF_5	$N_2F_3^+SbF_6^-$, $N_2F_3^+Sb_2F_{11}^-$	synthesis of $N_2F_3^+SbF_6^-$ [30, 36], $N_2F_3^+Sb_2F_{11}^-$ [32]	[30, 32,36]
SbF_5 in C	trans-N_2F_2	reaction of 1st stage SbF_5 intercalates	[33]
AsF_3SbF_5	$N_2F_3^+Sb_2F_{11}^-$, $N_2F_3^+Sb_3F_{16}^-$	preliminary results [37], $N_2F_3^+$ identified [38], see also [2, p. 92]	[2, 37, 38]
$N_2F_3Sb_3F_{16}$	$N_2F_3^+Sb_2F_{11}^-$	with excess N_2F_4	[38]
$SbCl_5$	$ClNF_2$	formation of $ClNF_2$ at 150°C [2, pp. 57, 80]	[2]
CF_4–NO	CO_2, F_2CO	CO_2 and F_2CO [39] products mentioned in CO_2 laser-initiated reaction of N_2F_4–NO–CF_4 mixtures; no thermal reaction [39]	[39 to 41]
CF_3I	CF_3NF_2, I_2, etc.	photochemical (1 h UV irradiation at 26°C) and thermal (120°C) reaction, CF_3NO and CF_3NONF side products due to reactions with glass	[42]
CF_3I–NO	CF_3NONF	45% CF_3NONF yield from thermal reaction (120°C, 1 h); photochemical reaction at 26°C: 12% CF_3NO, 17% CF_3NONF	[42]
$CFBr_3$	$CFBr_2NF_2$	photochemical and thermal reaction, 45% yield of $CFBr_2NF_2$ in 1st step of photochemical reaction at 100°C (irradiation for 52 h), in 2nd step reaction to syn- and anti-BrFC=NF	[43]
CCl_4	CF_3Cl, CF_2Cl_2, etc.	various products at 2 to 3 MeV X-ray irradiation between 87 and 293 K	[11]
NF_4GeF_5	—	only minor traces of GeF_6^- after treatment with large excess of N_2F_4 at −78°C	[44]
$SnCl_2$	N_2F_2	less effective than $AlCl_3$ [2, p. 40]	[2]

Table 24 (continued)

reactant	products	conditions, remarks	Ref.
SnF_4	—	no $N_2F_3^+$ salt from suspension of SnF_4 in liquid HF and threefold excess of N_2F_4 (SnF_4 remains polymerized)	[30]
BF_3	(BF_4^-)	claimed synthesis of $N_2F_5^+BF_4^-$ in presence of F_2 [45] refuted [46]; no product at −78°C [30]; only weak interaction in BF_3–N_2F_4 system below −120°C [28, 47]; some BF_4^- IR bands found after irradiation with CO_2 laser [48]	[28, 30, 45 to 48]
B_2F_4	BF_3, N_2	[2, p. 61]	[2]
BCl_3	(BF_3, BF_4^-)	only weak association below −78°C [28, 47]; after irradiation with 10.6 μm CO_2 laser: BF_3 and chlorine fluorides [40]; BF_3 and BF_4^- [48]	[28, 40, 47, 48]
$AlCl_3$	trans-N_2F_2, Cl_2	synthesis of N_2F_2 at −80°C, 15 to 20 Torr pressure (cf. p. 386)	[49]
CaX_2	N_2F_2	X = Cl [2, p. 41], X = I [2, p. 40]	[2]
NaI	N_2F_2	less effective N_2F_2 synthesis [2, p. 40]	[2]
KI	I_2, KF, N_2, etc.	reaction in aqueous solution [50]; in CH_3CN solution [2, p. 61]	[2, 50]
VF_5	—	no thermal reaction at 25°C; N_2F_4 does not sensitize VF_5 decomposition at 946 cm^{-1} CO_2 laser irradiation	[51]
MCl_2	N_2F_2	M = Mn, Fe, Co, Ni; less effective N_2F_2 synthesis [2, p. 40]	[2]
PtF_n	NF_3, PtF_{n-1}	n = 5, 6; with excess PtF_6: $N_2F_4 + 2PtF_6 \rightarrow 2NF_3 + 2PtF_5$; with equimolar reactants also $N_2F_4 + 2PtF_5 \rightarrow 2PtF_4 + 2NF_3$ (reactions at 25°C for 1 d plus 1 d at 70°C)	[52]

Unpublished reports (cited in [2, p. 63]) disagree on whether NF_2 is fluorinated by **ClF_3**, the reactor material obviously playing some role. On the other hand, a homogeneous gas phase reaction, $(N_2F_4 \rightleftharpoons 2NF_2) + ClF_3 \rightleftharpoons 2NF_3 + ClF$ was reported to occur in a passivated Al vessel at temperatures between 180 and 210°C [1]. The kinetics of the reaction, which were followed by the increase of pressure, obeyed the rate law $d[NF_3]/dt = -\frac{1}{2}d[ClF_3]/dt = k[NF_2][ClF_3]$ with $k = 1.49\times10^{12}\exp[-(23500\pm200)\ cal\cdot mol^{-1}/RT]\ cm^3\cdot mol^{-1}\cdot s^{-1}$. Addition of products did not change the course of the reaction. Moreover, experimental rate constants were not affected by a large excess of added N_2 or O_2 [1]. Four steps are discussed for the reaction mechanism:

(1) $N_2F_4 \rightleftharpoons 2NF_2$

(2) $NF_2 + ClF_3 \rightleftharpoons NF_3 + ClF_2$

(3) $NF_2 + ClF_2 \rightleftharpoons NF_3 + ClF$

(4) $ClF_2 + ClF_2 \rightleftharpoons ClF_3 + ClF$

where kinetic results do not allow one to distinguish whether intermediate ClF_2 radicals react via (3) [with the consequence $k = 2k_2$] or more probably via (4) [$k = k_2$] [1].

The reactions between NF_2 and $\mathbf{N_2F}$, **NF**, $\mathbf{N_2F_2}$, or $\mathbf{NF_2}$ occur or are believed to occur during thermal and photochemical decomposition of NF_2, see also pp. 326/33. The postulated step $NF_2 + N_2F \rightarrow NF_3 + N_2$ with an approximate rate constant of $10^{12}\ cm^3\cdot mol^{-1}\cdot s^{-1}$ in the 1400 to 2000 K range [16] follows in the mechanism of NF_2 decomposition the step $NF + NF_2 \rightarrow N_2F + F_2$, $k \approx 2\times10^{12}\ cm^3\cdot mol^{-1}\cdot s^{-1}$ in the 1400 to 2000 K range [16]. The latter step, however, was later replaced by $NF + NF_2 \rightarrow N_2F_2 + F$ followed by $N_2F_2 + NF_2 \rightarrow N_2F + NF_3$ [17, 18]. A variant formulation for $N_2F_2 + NF_2 \rightarrow NF_3 + N_2 + F$, $\Delta H \approx -41$ kcal/mol, relies on the observation that a mixture of N_2F_4 and N_2F_2 (40 Torr each) reacts smoothly at 110°C (half life ca. 1 h) to give NF_3 and N_2 in a 2:1 ratio [53]. The removal of two transient species that had been generated by flash photolysis of NF_2 was first ascribed to the chemical reactions $NF(X) + NF_2$ and $NF(a) + NF_2$ (for the notation, see pp. 263/4) with rate constants at 450 K of $1.2\times10^{11}\ cm^3\cdot mol^{-1}\cdot s^{-1}$ and $3.0\times10^{12}\ cm^3\cdot mol^{-1}\cdot s^{-1}$, respectively [20]. Based on some general arguments on the role of electron spin conservation in NF kinetic systems, processes were later reassigned to reactions of NF(a) (slower process with assumed $E_a \approx 4$ kcal/mol) and of NF(b) (faster process) [21]. Referring to published data [20, 21], a further reassignment to $NF(a) + NF_2 \rightarrow N_2F_2 + F$ (slower process) and $NF(X) + NF_2 \rightarrow N_2F_2 + F$ (faster process) has been done in model calculations of the $H_2 + NF_2$ reaction (see NF laser) [23]. Similarly, the rate constant $3\times10^{12}\ cm^3\cdot mol^{-1}\cdot s^{-1}$ was adequate for the description of the partial process $NF_2 + NF \rightarrow N_2F_2 + F$ that occurred during the degradation of the NF_3 working gas of a XeF excimer laser [55].

The reactions of N_2F_4 with $\mathbf{AsF_5}$ and $\mathbf{SbF_5}$ constitute rare examples where product $N_2F_3^+$ ions (see p. 383) indicate that the weak N–N bond has remained intact.

Fluorinated and unfluorinated first-stage $\mathbf{AsF_5}$ **intercalates** react with N_2F_4 to yield 90% trans-N_2F_2, 5% NF_3, and 5% N_2: $C_{10}AsF_{5+x}$(blue) + $N_2F_4 \rightarrow C_{10}AsF_{7+x}$(black) + trans-$N_2F_2$, x = 0 to 0.5. Equivalent amounts of reactants are needed to complete the reaction [33, 34]. The high stereospecifity for the trans-N_2F_2 product is best explained by intermediate $N_2F_3^+AsF_6^-$ formation followed by fluoride abstraction by the graphite [34]. The reaction $N_2F_4 \rightarrow N_2F_2 + 2F$, $\Delta H \approx 235$ kJ/mol, is even better compensated by an ionic path C^+(trigonal) + $F^- \rightarrow F$–$C(sp^3)$, $\Delta H \approx -1042$ kJ/mol, than by $2C(sp^2) + N_2F_4 \rightarrow 2F$–$C(sp^3) + N_2F_2$, $\Delta H \approx -685$ kJ/mol [35]. Second- and third-stage intercalates, $C_{17}AsF_{5+x}$ and $C_{25\ to\ 28}AsF_{5+x}$, rapidly adsorb N_2F_4 up to a ratio N_2F_4/intercalate = 0.5. However, N_2F_4 uptake is completely reversible and no N_2F_2 formation occurs [33]. Second- and third-stage intercalates might not furnish the electrons needed for $2AsF_5 + F_2 + 2e^- \rightarrow 2AsF_6^-$ [35].

First-stage $C_{6.3}SbF_5$ does not react with N_2F_4 at 25°C but absorbs N_2F_4 partly at 75°C under formation of $N_2F_3Sb_2F_{11}$ and higher stage C_nSbF_5. The mixture liberates trans-N_2F_2 at room temperature. An intercalate of the average composition C_8SbF_5 (mixture of $C_{6.3}SbF_5$ and $C_{18}SbF_5$) completely converts N_2F_4 into trans-N_2F_2 (70%) and $NF_3 + N_2$ (30%) at 75°C. $C_{18}SbF_5$ does not reduce N_2F_4 [33].

The reaction of N_2F_4 with **$AlCl_3$** used to prepare trans-N_2F_2 in about 45% yield at −80°C at a total pressure of 15 to 20 Torr (cf. p. 386) is accompanied by some unwanted side reactions

$$(1)\ 3\,N_2F_4 + 4\,AlCl_3 \rightarrow 3\,N_2 + 6\,Cl_2 + 4\,AlF_3 \qquad (2)\ 3\,N_2F_4 \xrightarrow{AlCl_3} 4\,NF_3 + N_2$$

$$(3)\ 3\,N_2F_2 + 2\,AlCl_3 \rightarrow 3\,N_2 + 3\,Cl_2 + 2\,AlF_3$$

Disproportionation of N_2F_4 (reaction (2)) is quantitative at room temperature even in the presence of traces of $AlCl_3$ and depends strongly on N_2F_4 pressure. Reaction (3) is extremely slow at −80°C whereas the others are still fast. These constraints explain optimal conditions for N_2F_2 formation [49]. Activated $AlCl_3$ absorbs some N_2F_4 below −132°C. On heating N_2F_4, N_2F_2, N_2, and Cl_2 desorb. Some solid side products of unknown composition that form during the $N_2F_4 + AlCl_3$ reaction give N_2 and Cl_2 upon decomposition [49].

N_2F_4 reacts slowly (several days) with a 5% aqueous solution of **KI** at temperatures between 20 and 80°C, N_2F_4 pressures of 0.6 to 1 bar, and initial pHs of ~1.4 or 7. The increase of the pH from 1.4 to final values of 2.8 to 3 and analyzed product ratios N_2/NH_4^+ and I_2/F^- are described by two parallel paths

$$(1)\ (N_2F_4 \rightleftharpoons 2\,NF_2) + 10\,I^- + 8\,H^+ \rightarrow 5\,I_2 + 4\,F^- + 2\,NH_4^+$$

$$\text{and} \qquad (2)\ (N_2F_4 \rightleftharpoons 2\,NF_2) + 4\,I^- \rightarrow 2\,I_2 + 4\,F^- + N_2$$

Independent of temperature, path (1) contributes about 35% at an initial pH of 1.4 and 10% at pH 7 [50].

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4.1.12.6.8.3 Reactions with Oxides

The reactions of N_2F_4/NF_2 with oxides X_lO_m are surveyed in Table 25. Thermal reactions $NF_2 + NO$ and $N_2F_4(NF_2) + N_2O_4(NO_2)$ and reactions of vibrationally excited N_2F_4 with NO, SO_2, or CO are described in some detail in the following text.

Table 25

Reactions of N_2F_4/NF_2 with Oxides.

reactant	products	conditions, results, remarks	Ref.
N_2O	—	little or no thermal or photochemical reaction	[1, p. 65]
	$(NF_2)_2O$	claim of $(NF_2)_2O$ synthesis at a Pt catalyst	[2]
	NO, NF_3, N_2F_2, etc.	various products from irradiation with 2 to 3 MeV X-rays at temperatures between 77 and 237 K	[3]
	NF_3, NO_2	at 10.6 μm irradiation (40 W CO_2 laser) of 300 Torr N_2F_4–150 Torr N_2O, 49% NO_2 and 38% NF_3	[4, 5]
	FNO	at irradiation with CO_2 laser	[47]
NO	F_2NNO	thermal equilibrium reaction of NF_2 [6 to 9]; mass spectroscopic evidence for reaction [10, 11]; unidentified red (side) product at low temperatures [1, p. 106], [12, 27]; early statements that either ignition below 25°C in glass reactor or no thermal or photochemical reaction in coated reactor [1, p. 64]; probable step toward F_2NNO product in ^{60}Co γ-irradiated NF_3–NO mixtures [13]; see also text	[1, pp. 64, 106], [6 to 13, 27]
	FNO, etc.	reaction of vibrationally excited N_2F_4; for details, see text	[4, 15 to 23, 47]
	N_2, NF_3, FNO, etc.	various products from irradiation with 2 to 3 MeV X-rays between 77 and 293 K	[3]
NO–NaN_3	N_2O, NaF	reaction at 80°C, different products as compared to reaction of N_2F_4 with NaN_3	[14]

Table 25 (continued)

reactant	products	conditions, results, remarks	Ref.
NO_2/N_2O_4	FNO	vigorous reaction at 25°C [25, 26]; stoichiometry and side products [1, p. 65], [11, 12, 25 to 27]; F_2NNO_2 intermediate [2, 28], see also text	[1, p. 65], [2, 11, 12, 24 to 28]
	—	N_2F_4 used to remove H_2O from N_2O_4 (caution, see [25])	[29]
	NF_3, FNO, etc.	various products from irradiation with 2 to 3 MeV X-rays between 77 and 151 K	[3]
	FNO	at irradiation with CO_2 laser	[47]
N_2O_4–NO	NF_3, FNO, FNO_2	product distribution very sensitive to ratio of reactants	[1, p. 65]
N_2O_4–FNO	NF_3	immediate reaction at 25°C (FNO alone does not react), F_2NNO_2 intermediate postulated (at 185°C!).	[1, p. 65]
N_2O_5	F_2NNO_2	claim of F_2NNO_2 synthesis below 21°C (see, however, [28])	[2]
	FNO, FNO_2, NO_2	—	[1, p. 65]
OF_2	—	see p. 53	
O_2F_2	NF_3, O_2	reaction at 170 K [30]; explosion [1, p. 216]	[1, p. 216], [30]
	$FONF_2$	claim of $FONF_2$ synthesis in a glow discharge at −100 to −200°C	[2]
ClO_2	FNO, NF_3	reaction subsumed under general type $XO + N_2F_4 \rightarrow X + FNO + NF_3$ [27], no ClO_2NF_2 [1, pp. 66, 171]	[1, pp. 66, 171], [27]
Cl_2O_6	$NOClO_4$, etc.	reaction in liquid ($NOClO_4$ main product and NF_3, N_2O, NO_2, FNO, ClO_2) and in gas phase (additional products ClNO, $ClNO_2$, NO_2, ClO_4)	[1, pp. 66, 172]
Cl_2O_7	$FClO_2$, $FClO_3$	reaction at 100°C in Teflon reactor formed $FClO_2$, $FClO_3$, etc. [12]; no reaction in CCl_4 or CF_3COOH solution, no NF_2ClO_4 found, $NOClO_4$ is often formed [1, pp. 66, 172/3, 188]	[1, pp. 66, 172/3, 188], [12]
SO_2	FSO_2NF_2	thermal reaction of equimolar reactants at 120°C and 100 atm for 6 d: 80% SO_2 consumed, 60% yield of FSO_2NF_2, by-products: N_2, SO_2F_2, SOF_2, and some NF_3, NO_x [31]; below 0°C at normal pressure neither reaction nor weak association [32]	[31, 32]

Table 25 (continued)

reactant	products	conditions, results, remarks	Ref.
SO_2	FSO_2NF_2	photochemical reaction at 2537 Å irradiation: $N_2F_4 + SO_2 \rightarrow FSO_2NF_2 + \frac{1}{2} N_2F_2$, 89% yield of FSO_2NF_2 after 2.5 h and 0.01 mol reactants each, yield of N_2F_2 60%; mechanism: initial F atom attack on SO_2	[31, 33 to 35]
	SO_2F_2	photochemical reaction at 10.6 μm irradiation (CO_2 laser); for details, see text	[16, 17, 19, 21]
	NF_3, N_2F_2, SO_2F_2, etc.	various products at irradiation with 2 to 3 MeV X-rays between 77 and 163 K	[3]
SO_2–N_2F_2	FSO_2NF_2	0.52 mmol N_2F_2 + 0.52 mmol N_2F_4 + 0.62 mmol SO_2 give at 100°C after 21 h 0.63 mmol FSO_2NF_2, 0.11 mmol NF_3, 0.4 mmol N_2 + some unconsumed N_2F_2, N_2F_4	[36]
SO_2–NaN_3	SO_2F_2	reaction at 80°C for 18 h, also traces of SF_6 product, caution explosions	[14]
SO_3	FSO_3NF_2	photochemical reaction ($\lambda = 2537$ Å) gives after 10 to 20 min from equimolar reactants (0.01 mol each) FSO_3NF_2 in 55% yield, by-products: SO_2F_2, NF_3, N_2F_2, N_2, NO, N_2O [34, 35]; first step in convenient $ClNF_2$ synthesis [37]	[34, 35, 37]
CO	CF_4, COF_2, etc.	thermal reaction at temperatures up to 200°C and pressures up to 200 atm leads to CF_4, COF_2, N_2O, NO_2, CO_2, FNO	[38]
	F	thermochemical calculations on F-atom concentrations at 1500 and 2000 K	[39]
	NF_2CFO	10 to 15% yield after 2 to 5 h UV irradiation of 0.016 mol N_2F_4 and 0.032 mol CO, side products: N_2F_2, N_2O, COF_2, CO_2, etc.	[35, 38]
	FCO	transient FCO radical detected after irradiating 4 Torr N_2F_4–20 Torr CO in large excess of N_2 (or Ar, or He) with 800 J Lyman flash lamp	[40]
	COF_2	threshold values for UV-visible and IR two frequency irradiation	[41]
	COF_2, CF_4	photochemical reaction at 10.6 μm irradiation (CO_2 laser), for details, see text	[5, 16, 17, [19 to 21]
CO–NaN_3	CF_4, CO_2	reaction at 80°C for 18 h (caution explosions), other products N_2 and some N_2O_4	[14]
CO_2	N_2F_2, COF_2, etc.	various products from irradiation with 2 to 3 MeV X-rays between 87 and 151 K	[3]

Table 25 (continued)

reactant	products	conditions, results, remarks	Ref.
SiO_2	SiF_4	no etching of pure SiO_2 by NF_2 (or plasma); but considerable etching of SiO_2 contaminated by impurities (e.g., carbon) [42]; etching of SiO_2 on Si wafer [43]; used as mask in Si etching [44]	[42 to 44]
KO_2	FNO_2, NF_3, FNO	reaction slightly above 25°C with excess N_2F_4 and KO_2 diluted with Teflon powder [45]; no reaction at −130°C, slow reaction at −80°C to form unidentified product that liberates NF_3 and FNO upon decomposition [1, p. 66]	[1, p. 66], [45]
Al_2O_3	AlF_3	loss of resolution of γ-Al_2O_3 chromatographic column for N_2F_4-containing gas mixtures, ascribed to AlF_3 formation	[46]
MnO_2	NF_3, FNO	reaction subsumed under general type $XO + N_2F_4 \rightarrow X + FNO + NF_3$	[27]

Low-temperature mixing (−78°C) or co-condensation (−196°C) of N_2F_4 and **NO** does not lead to any reaction. When N_2F_4 is first dissociated at 300°C, then mixed with a tenfold excess of NO, and finally quenched to −196°C, the dark blue-violet or almost black color of F_2NNO appears [6] (see also the illustrations given in [9]). Spectrophotometric studies at 25°C in the gas phase show the presence of the $N_2F_4 + 2NO \rightleftharpoons 2F_2NNO$ equilibrium with $K_c = [F_2NNO]^2/([NO]^2[N_2F_4])$. The 550 nm absorption of F_2NNO obeys Lambert-Beer's law, $A \propto \varepsilon K_c^{1/2}[NO][N_2F_4]^{1/2}$ with an average value of $\varepsilon K_c^{1/2} = 0.167\ L^{3/2} \cdot mol^{-3/2} \cdot cm^{-1}$ (at 25°C). The reaction enthalpy is derived from the temperature dependence (range?) of A, $\Delta H = -0.4 \pm 0.2$ kcal/mol (preferred value measured at constant volume) or $\Delta H = -1.1 \pm 0.3$ kcal/mol (measured at constant pressure) [8]. A best guess for $\Delta S = 40.5\ cal \cdot mol^{-1} \cdot K^{-1}$ and $K_c^{298} \approx 2.7 \times 10^{-6}$ L/mol relies on an estimated value $\varepsilon_{550} = 110\ L \cdot mol^{-1} \cdot cm^{-1}$ [8].

Room-temperature mixing of N_2F_4 and **N_2O_4** may lead to a vigorous reaction that is accompanied by ignition. Quantitative conversion into FNO according to $N_2F_4 + N_2O_4 \rightarrow 4FNO$ (however, with impure N_2F_4) [25] is supported by a more detailed product analysis: 97% FNO, 3% FNO_2, and 0.3% NF_3 [11]. These data are at variance with an earlier report claiming equimolar formation of FNO and NF_3 [27]. The early speculation that nitryldifluoroamine is an intermediate [25, 26], which subsequently decomposes into FNO, gained support from the following observation. Highly unstable, white solid F_2NNO_2 is formed in 50 to 75% yield by passing N_2F_4 through a furnace at 310°C, mixing the resulting NF_2 with equimolar NO_2, and quenching the mixture immediately to −196°C [28]. An upper temperature limit of 21°C for F_2NNO_2 formation from N_2O_4 (and N_2O_5) and N_2F_4 [2] may thus be too high. The reaction enthalpy for the overall process $NF_2 + NO_2 \rightarrow 2FNO$ is −49.2 kcal/mol [25].

A series of publications [4, 5, 15 to 22, 41] claim that the thermodynamically favorable reactions

$$N_2F_4 + 4NO \rightarrow 4FNO + N_2,\ \Delta H = -149\ \text{kcal/mol}$$

$$N_2F_4 + 2CO \rightarrow 2COF_2 + N_2,\ \Delta H = -250\ \text{kcal/mol}$$

$$N_2F_4 + 2SO_2 \rightarrow 2SO_2F_2 + N_2,\ \Delta H = -337\ \text{kcal/mol}\ [21]$$

proceed readily when the N–F stretching vibrations of N_2F_4 are excited by 10.6 μm IR radiation from a CO_2 laser. FNO formation from N_2F_4–NO (N_2O or NO_2) mixtures that were irradiated with a CO_2 laser was also recently claimed [47]. On the other hand, FNO, COF_2, and SO_2F_2 are only minor products at thermal conditions or upon UV irradiation. The vibrational specificity of CO_2 laser-induced reactions of N_2F_4 with NO, CO, SO_2 (and N_2O, CH_4) was not confirmed for the N_2F_4 + NO reaction in experiments with pulsed lasers and time-resolved product detection [23]. Original arguments that $N_2F_4^†$ excited in the NF stretching vibrations gains fluorinating properties toward NO, CO, and SO_2 are based on the following observations. (1) Additions of inert gases that are believed to deactivate $N_2F_4^†$ change the product distribution. For example, 100 Torr N_2F_4 and 100 Torr NO irradiated with 40 W/cm^2 gave 28% FNO, 3% NF_3, 24% N_2, and 45% F_2. Addition of 460 Torr N_2 and irradiation with 70 W/cm^2 leads to N_2O, N_2, and NO_2 [5]. (2) There are threshold values of the laser intensity that depend on total pressure, composition of the gas mixture, pulse duration, laser beam diameter [16, 17, 21], and heat transfer in the reaction zone [16]. For example, no reaction occurs when 200 Torr N_2F_4 and 100 Torr SO_2 are irradiated with 6000 laser pulses of 5×10^{-2} s, 0.8 cm beam diameter, and 29 W/cm^2. At otherwise identical conditions a single 31 W/cm^2 pulse is sufficient to initiate 100% conversion [16]. (3) Calculated maximal temperature rises and independent thermal experiments above 200°C [19] make a thermal explosion initiated by laser heating unlikely, see also [16]. Threshold values for CO and N_2F_4 mixtures are lower for simultaneous excitation with IR-UV/visible frequencies than for 10.6 μm radiation alone [41].

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4.1.12.6.8.4 Reactions with Miscellaneous Inorganic Compounds

Reactions of N_2F_4/NF_2 with inorganic compounds that cannot be subsumed under Sections 4.1.12.6.8.1 to 4.1.12.6.8.3 are listed in Table 26. The table is supplemented with reactions with a few organometallic compounds and some reactions with $\geqslant$COF, –CN, >C=S, $\geqslant$C–SFO groups that may be classified as organic reactions.

Table 26
Reactions of N_2F_4/NF_2 with Miscellaneous Compounds.

reactant	products	results, conditions, remarks	Ref.
FNO	—	no reaction at 200°C [1, p. 63]; thermodynamic values for $\frac{1}{2}N_2F_4 + FNO \rightarrow NF_3 + NO$; $\Delta H^\circ_{298} = 7.8$ kcal/mol, $\Delta G^\circ_{298} = 3.1$ kcal/mol [2]	[1, p. 63], [2]
	NO, NF_3, etc.	various products from irradiation with 2 to 3 MeV X-rays between 77 and 238 K	[3]
$FNO + Cl_2$	NF_3, ClNO	thermodynamic values for $\frac{1}{2}N_2F_4 + FNO + \frac{1}{2}Cl_2 \rightarrow NF_3 + ClNO$: $\Delta H^\circ_{298} = -1.27$ kcal/mol, $\Delta G^\circ_{298} = -2.09$ kcal/mol	[2]
FNO_2	—	no reaction at 25°C	[1, p. 63]
$FONO_2$	NF_3, FNO_2, FNO	102 Torr $FONO_2$ + 70 Torr N_2F_4 react in glass or Ni vessel [4]; no reaction in coated reactor [1, p. 63]; slight reaction at −160°C, detonation at −78°C [1, p. 165]	[1, pp. 63, 165], [4]
F_3NO	NF_3, FNO	photochemical reaction (Hg lamp) in passivated Ni cell: $N_2F_4 + F_3NO \xrightarrow{h\nu} 2NF_3 + FNO$, almost complete conversion during 1 h; side reactions (of FNO) in quartz cell	[5]
ClNO	(NF_2Cl, NO)	thermodynamic values for $\frac{1}{2}N_2F_4 + ClNO \rightarrow NF_2Cl + NO$: $\Delta H^\circ_{298} = 13.23$ kcal/mol, $\Delta G^\circ_{298} = 5.0$ kcal/mol, $\Delta G^\circ = 0$ at ca. 200°C; equilibrium also experimentally at reactant side (at low temperatures)	[6]

Table 26 (continued)

reactant	products	results, conditions, remarks	Ref.
$FClO_2$	FNO_2, NF_3, O_2	no reaction at 25°C for 8 d, products from equimolar mixture held at 90°C for 12 h: O_2, NF_3, FNO_2 (major product), FNO (small amount), ClO_2 [7]; NF_3, FNO_2, FNO products at 30°C [1, p. 63]	[1, p. 63], [7]
$FClO_3$	NF_3, FNO	oxidation of N_2F_4 at 115°C [1, p. 62]; no or little reaction at 200°C [1, p. 63]; NF_3 and FNO products upon heating [8]	[1, pp. 62/3], [8]
$FOClO_3$	NF_3, NO_x, NO^+	reaction in glass vessel (at 25°C?) [1, p. 63]; no miscibility or reaction between −160 and −78°C [1, p. 165]	[1, pp. 63, 165]
ClF_3O	NF_3, FNO, ClF	thermal reaction above 100°C; stoichiometry $ClF_3O + 2N_2F_4 \rightarrow 3NF_3 + FNO + ClF$, traces of FNO_2, F_3NO, and $FClO_2$ as side products; photochemical (UV) reaction at 25°C	[9]
ClO_4^-	NF_3, N_2, NO, NO_2	reaction in CH_3CN; no reaction with solid perchlorates	[1, p. 67]
SOF_2	SOF_4	photochemical reaction ($\lambda = 2537$ Å) with twofold excess of N_2F_4 gives after 30 min 20% SOF_4 (SO_2F_2, SF_4, SF_5 side products)	[10]
$SOCl_2$	$ClNF_2$	photochemical reaction (UV) of 6×10^{-3} mol $SOCl_2$ and 1×10^{-3} mol N_2F_4 gives after 1 h 65 to 70% $ClNF_2$ (side products: S, $SOCl_2$, SO_2, SOClF, SO_2ClF, (SiF_4 from quartz), Cl_2, SOF_2, NF_3); no thermal reaction at 100 or 175°C	[11]
$SOBr_2$	N_2F_2	products are identical to those from $N_2F_4 + Br_2 + h\nu$, see p. 353	[11]
SOF_4	—	no photochemical reaction (equimolar reactants UV irradiated for 1 h)	[10]
SF_5OF	SF_5ONF_2	at 25°C complete consumption of reactants (80 Torr each in Pyrex bulb), 40% SF_5ONF_2 and side products NF_3, NO, SiF_4 (from glass), SF_6, SO_2F_2, SOF_4, NO_2; at lower initial pressure only side products, in Ni bulb only 20% conversion into side products; at UV irradiation of 140 Torr N_2F_4 and 140 Torr SF_5OF in Pyrex bulb during 21 h 60% SF_5ONF_2, unconsumed reactants, minor amounts of NO, NO_2, SiF_4, SF_6, SO_2F_2; hardly reproducible yields from thermal reaction confirmed [13]	[12, 13]

Table 26 (continued)

reactant	products	results, conditions, remarks	Ref.
FSO_2	FSO_2NF_2	reaction is believed to be the final step in the photochemical reaction $N_2F_4+SO_2$	[14]
SO_2Cl_2	$ClSO_2NF_2$	UV irradiation of 4×10^{-3} mol SO_2Cl_2 and 2×10^{-3} mol N_2F_4 in quartz bulb gives after 4 h 62% $ClSO_2NF_2$ and side products SO_2, SO_2F_2, Cl_2, SiF_4, N_2	[15]
F_2SO_3	FSO_3NF_2, NF_3	rate law of mostly homogeneous gas-phase reaction in quartz or Al vessel at ca. 80°C: $-d[F_2SO_3]/dt=+d[NF_3]/dt=k[N_2F_4]^{1/2}[F_2SO_3]$; no rate constants because of high scatter	[16]
$S_2O_6F_2$	FSO_3NF_2	slow reaction at 25°C with single FSO_3NF_2 product [17]; kinetics of homogeneous gas-phase reaction measured between −15°C and +15°C: $-d[S_2O_6F_2]/dt=k[S_2O_6F_2]$ with $k=3.98\times10^{15}\exp[-(24000\pm500)\ cal\cdot mol^{-1}/RT]\ s^{-1}$, decomposition of $S_2O_6F_2$ is rate determining [16]	[16, 17]
$(CN)_2$	(N_2, NF_2CF_2CN, etc.)	no thermal reaction at 25°C; photochemical (UV) reaction of 1:2, 1:1, and 2:1 $(CN)_2$–N_2F_4 mixtures gives varying amounts of N_2, NF_2CF_2CN, $(NF_2CF_2)_2$, and $C_2F_5NF_2$	[18]
	NF_3, FCN, $C_2F_5NF_2$, $(CF_3)_2NF$	various products from irradiation with 2 to 3 MeV X-rays at temperatures between 77 and 293 K	[3]
	F	thermochemical calculations on F-atom generation at 1500 and 2000 K	[19]
CF_3OF	CF_3ONF_2	thermal reaction at 23°C with twofold excess of CF_3OF gives after 1 d CF_3ONF_2 and a number of side products (CF_4, NF_3, COF_2, etc.) [20]; photochemical reaction (UV) gives 33 to 40 mol% CF_3ONF_2 [12, 20]	[12, 20]
CF_3OF+SF_4	$CF_3OSF_4NF_2$, SF_5NF_2, etc.	N_2F_4, SF_4, and CF_3OF in ca. 3:4:5 molar ratio give after 7 d at 25°C unconsumed CF_3OF, N_2F_4 reactants and COF_2, SOF_2, CF_3OOCF_3, SF_5NF_2, and $CF_3OSF_4NF_2$ (14% yield)	[21]
$(CF_3)_3COF$	$[(CF_3)_3CO]_2$, NF_3	photochemical reaction at −90°C in n-C_5F_{12}, NF_2 acts as F-atom acceptor: $2(CF_3)_3COF+N_2F_4\rightarrow(CF_3)_3COOC(CF_3)_3+2NF_3$	[22]
	—	claim to have synthesized $N_2F_5^+(CF_3)_3CO^-$ salt [23] refuted [24]	[23, 24]

Table 26 (continued)

reactant	products	results, conditions, remarks	Ref.
ClCN	CF_4, CF_3Cl, CF_2Cl_2	UV irradiation of equimolar $ClCN-N_2F_4$ in a Ni vessel gives 20% CF_4, 50% CF_3Cl, 20% CF_2Cl_2; in quartz vessel only small turnover to CF_3Cl	[25]
$(ClCO)_2$	NF_2CClO	UV irradiation of 2:3 $(ClCO)_2-N_2F_4$ mixture gives after 2 d [26], 6 h [27] 20% [26], 40% NF_2CClO [27]; side products: N_2F_2, $ClNF_2$, COFCl, COF_2, etc.	[26, 27]
CS_2	?	N_2F_4 and CS_2 burn with a blue-white flame	[28]
	F	thermochemical calculations on F-atom generation at 1500 K	[19]
CF_3SFO	CF_3NF_2, SOF_2	equimolar mixture heated in Ni vessel to 300°C for 48 h	[29]
$CSCl_2$ $(+SOCl_2)$	NF_2Cl_2CSCl	photochemical reaction (UV) with two- to threefold excess of $CSCl_2$: ca. 22% yield of NF_2Cl_2CSCl, yield increases slightly in the presence of $SOCl_2$, large number of side products	[30]
$CSCl_2+Cl_2$	NF_2CCl_3	photochemical reaction gives NF_2CCl_3 in ca. 16% yield and no NF_2Cl_2CSCl	[30]
$B(CH_3)_3$	CF_4, HF	irradiation of mixture with CO_2 laser ($\sim$933 cm^{-1}, 50 W); side products HCN, HCF_3; chemiluminescence contains CN and C_2 emissions	[31]
$B(C_5H_{11})_3$	$NF_2B(C_5H_{11})_2$	—	[32]
$B(N(CH_3)_2)_3$	?	products not identified	[1, p. 58]
POF_3	$NOPF_6$	50% yield of $NOPF_6$ at UV photolysis of equimolar mixture for 35 min, primary product is probably F_4PONF_2 that rearranges and subsequently decomposes into $FNO+PF_5$	[10]
$P(C_6H_5)_3$	$F_2P(C_6H_5)_3$, N_2	room-temperature reaction in C_6H_5Cl gives 45% yield of $F_2P(C_6H_5)_3$ employing slight excess of N_2F_4	[33]
$P(OC_6H_5)_3$	$N_2F_4 \cdot P(OC_6H_5)_3$	reaction at ca. 100°C in benzene (autoclave) gives a black paramagnetic product (85% yield) that is probably a charge-transfer complex	[34]
O_2AsF_6	—	no reaction	[1, p. 219]

Table 26 (continued)

reactant	products	results, conditions, remarks	Ref.
$LiClO_3$	—	products depend on material of reactor, see entry for $NaClO_2$	[1, p. 67]
n-C_4H_9Li	H_2, N_2, LiF, etc.	high reaction rate in hexane solution at −78°C, products: H_2, N_2, LiF, C_4H_{10}, C_4H_8, $C_{10}H_{22}$, $N(C_4H_9)_3$	[35]
NaN_3	NF_3, N_2, NaF	reaction between 45 and 85°C [36]; no reaction between 25 and 100°C [1, p. 61]; from variation of products with reactant concentrations and from pressure dependence of NF_3 yield two simultaneous paths postulated: $NaN_3 + N_2F_4 \rightarrow NaF + NF_3 + 2N_2$ and $4NaN_3 + N_2F_4 \rightarrow 4NaF + 7N_2$ [36]	[1, p. 61], [36]
$NaNO_2$	FNO, NO, NaF	reaction at 25°C: $2NaNO_2 + N_2F_4 \rightarrow 2NaF + 2FNO + 2NO$ and minor path $NaNO_2 + FNO \rightarrow NaF + NO + NO_2$, also trace of NF_3 product	[7]
$NaNO_3$	FNO, NF_3	reaction subsumed under general type $XO + N_2F_4 \rightarrow X + FNO + NF_3$	[8]
$NaClO_2$ (+ H_2O)	—	no reaction at 25°C in Teflon vessel; $NaClO_3$, $ClNO_2$, etc. as products when traces of H_2O are present	[1, p. 67]
KNO_3	FNO, KF	reaction $KNO_3 + N_2F_4 \rightarrow KF + 3FNO$ investigated between 80 and 220°C; at 90°C with equimolar reactants between 41 and 76% yield of FNO; side products NO, N_2O_4, NF_3	[7]
$KClO_3$	FNO_2, $FClO_2$	with twofold excess of $KClO_3$ after 4 d at 25°C: FNO_2 and $FClO_2$ in 2:1 molar ratio but varying yields; minor products O_2, Cl_2, ClO_2, FNO, NF_3	[7]
$KClO_4$	—	no reaction at 200°C and 1 atm	[7]
$Al(C_2H_5)_3$	$NF_2Al(C_2H_5)_2$	reaction performed at 25°C by diffusion of N_2F_4 on $Al(C_2H_5)_3$ under He	[32]
$AgNO_3$	FNO, NF_3	reaction below 90°C, yields of FNO between 35 and 74%, minor products: NO, NF_3, N_2O_4 [7]; reaction according to general type $XO + N_2F_4 \rightarrow X + FNO + NF_3$ [8]	[7, 8]
$AgClO_4$	FNO, NF_3	reaction according to general type $XO + N_2F_4 \rightarrow X + FNO + NF_3$ needs substantial heating	[8]

Table 26 (continued)

reactant	products	results, conditions, remarks	Ref.
M, $M(CO)_n$ $M(NH_2)_m$	—	M = metal; general remark that no $M^+NF_2^-$ salts have been obtained from N_2F_4 and metals, metal carbonyls, and metal amides	[1, p. 99]

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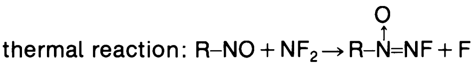
4.1.12.6.9 Survey on Reactions with Organic Compounds

The reactions of N_2F_4 or NF_2 with a great variety of organic compounds are extensively reviewed in the first four general references given on pp. 299/300. The most recent review of Fokin and Studnev (59 references) considers some selected reactions published up to the mid-1970s. The more general compilation of Fokin, Studnev, and Kuznetsova lists reaction products obtained from N_2F_4, NF_3, NHF_2, F_2, etc. and organic reactants. Out of the 819 references up to 1973, approximately 120 are concerned with N_2F_4. NF_2 gas-phase reactions and their kinetics are reviewed by Trotman-Dickenson et al. (16 references up to 1970) and by White (113 references up to 1973). Numerous examples of organic reactions are also described in the reviews of Lawless and Smith, Freeman, and Colburn (from 1966) cited on p. 300. A survey of the literature from 1972 to 1985 shows that the activity in the field has ceased. Less than one dozen publications seem to have appeared after 1980.

Under thermal conditions, the chemical reactivity of N_2F_4 toward organic compounds is governed by the NF_2 radical. For photochemical conditions, either N_2F_4/NF_2 or the organic compound can be activated. Reactive species are thus either F atoms and NF or organic radicals. The NF_2 radical is a moderately reactive, electrophilic radical. A large number of its reactions fall into three classes: (1) Labile H atoms, for instance, in aldehydes, thiols, ethers, and ketones (α-positions), are abstracted. Products are NHF_2 and difluoroamides, disulfides, α-difluoroamino ethers, and alkyldifluoroamines, respectively. At higher temperatures, hydrogen abstraction occurs also for alkanes (more easily at tertiary than at secondary and primary carbons) and for alkenes. (2) NF_2 radicals add to olefins, acetylenes, and nitroso compounds. The reaction with olefins is a typical radical reaction. It is nonstereospecific. With electron-rich olefins, for instance, vinyl ethers, styrenes, and dienes, the reaction proceeds easily. The reactivity is less for halogenated olefins, and no reaction occurs with electron-poor olefins, for instance, with maleic anhydride. (3) NF_2 couples with a wide variety of organic radicals that have been generated either thermally or photochemically. Aliphatic radicals derived from azo compounds, aliphatic iodides, and hexaphenylethane, as well as acyl radicals obtained from aldehydes or ketones, provide some examples. NF_2 behaves as a moderately reactive scavenger for these radicals, it does not couple with some very stable radicals such as RS•.

The following generalized listing of some typical reactions of N_2F_4/NF_2 with organic compounds is not intended for specific cases. Neither every compound of the class reacts in the stated manner, nor are reaction paths and products complete.

organic reactant	conditions, products
alkanes	at 80 to 300°C: $RH + NF_2 \rightarrow R\bullet + NHF_2$, $R\bullet + NF_2 \rightarrow RNF_2$, RNF_2 decomposes at higher temperatures into NF_2 and olefins; at photochemical conditions formation of $HF^{\dagger}$, elimination of HCN from excited RNF_2 intermediate
halogenated alkanes	photochemical substitution of I and Br; Hg-catalyzed substitution of Cl at tertiary carbons
hypofluorites, hypochlorites	photochemical or thermal reaction: $R_fOX + NF_2 \rightarrow R_fONF_2 + \frac{1}{2} X_2$, $X = F, Cl$
acyl fluorides, acyl chlorides	photochemical reactions: $R_fCFO + N_2F_4 \xrightarrow{h\nu} R_fNF_2 + \cdots$ and $(ClCO)_2 + N_2F_4 \xrightarrow{h\nu} 2\,F_2NCClO$
aldehydes	at thermal conditions abstraction of H atom, formation of NHF_2, $RCONF_2$, RNF_2
ketones	at thermal conditions abstraction of H atom, formation of RNF_2; photochemically: $RCOR + N_2F_4 \xrightarrow{h\nu} RNF_2 + RCONF_2 + \cdots$
ethers	photochemically: formation of α-difluoroamino ethers
peroxides	$R_fOOR_f + N_2F_4 \rightarrow 2\,R_fONF_2$
thiols, thiophenols	thermal H-atom abstraction, formation of NHF_2 and RSSR
nitriles	photochemically: $R\text{–}C{\equiv}N + N_2F_4 \xrightarrow{h\nu} RCF_2NF_2 + RNF_2 + \cdots$
azo compounds	thermal reaction: $R_f\text{–}N{=}N\text{–}R_f + 2\,NF_2 \rightarrow 2\,R_fNF_2 + N_2$; photochemical reaction: $R_f\text{–}N{=}N\text{–}R_f + N_2F_4 \xrightarrow{h\nu} R_fN(NF_2)NFR_f$
nitroso compounds	 thermal reaction: $R\text{–}NO + NF_2 \rightarrow R\text{–}\overset{\overset{O}{\uparrow}}{N}{=}NF + F$
allyl compounds	H-atom abstraction and Br or I substitution at allylic positions; addition of NF_2 to double bond
olefins	thermal reaction: $R^1R^2C{=}CR^3R^4 + N_2F_4 \rightarrow R^1R^2C(NF_2)C(NF_2)R^3R^4$ (all isomers); in the presence of HF acceptors, subsequent formation of N-fluoroiminonitriles; at higher temperatures also H-atom abstraction
dienes	conjugated double bonds: only 1,2 or 1,4 addition; isolated double bonds: partial addition to one double bond, full addition needs more severe conditions; accumulated double bonds: $C{=}C{=}C + N_2F_4 \rightarrow [C{=}C(NF_2)\text{–}C(NF_2)] \rightarrow CF\text{–}C({=}NF)\text{–}C(NF_2)$
anthracene	formation of 9,10-difluoroaminoanthracene
acetylenes	thermal addition of only $2\,NF_2$ groups: $R^1C{\equiv}CR^2 + N_2F_4 \rightarrow R^1C(NF_2){=}C(NF_2)R^2 \xrightarrow{\Delta} R^1C({=}NF)\text{–}CFR^2(NF_2) + R^1F(NF_2)C\text{–}C({=}NF)R^2$

4.1.13 The $N_2F_3^+$ Ion

CAS Registry Number: *[39448-70-9]*

Formation. Preparation

The ion was observed in the N_2F_4 mass spectrum. Its relative abundance depends on the temperature, that is, on the $N_2F_4:NF_2$ ratio in the gas. Relative to 100 for NF_2^+, the abundances of $N_2F_3^+$ were 17.3 at −190°C, 13.6 at −160°C [1], 7.1 [2], 7.2 [3], 6.6 [4] at room temperature, 7.1 also at about room temperature (ionization chamber at 197°C and cooling jacket with liquid nitrogen) [19], 1.3 at 170°C [4], and 2.3 at 197°C [19]. The appearance potentials $AP(N_2F_3^+) = 12.0$ and 15.6 eV were ascribed to the processes $N_2F_4 \rightarrow N_2F_3^+ + F^-$ and $N_2F_4 \rightarrow N_2F_3^+ + F + e^-$, respectively [5].

The recommended value for the heat of formation, $\Delta H^\circ_{f,298} = 339$ kcal/mol [6], is based on the above appearance potentials.

Salts of $N_2F_3^+$ with $Sb_2F_{11}^-$, $Sb_3F_{16}^-$, SbF_6^-, AsF_6^-, and SnF_5^- are known. They have been prepared as follows. The reaction of SbF_5 with an excess of N_2F_4 in AsF_3 solution produced, depending on the pressure of N_2F_4, either a 1:2 adduct $N_2F_4 \cdot 2SbF_5$ (1 to 2 atm, −10°C) or a 1:3 adduct $N_2F_4 \cdot 3SbF_5$ (<100 Torr, −10°C). The latter can be converted into the former by reaction with SO_2 at −45°C. The complex $N_2F_4 \cdot 2SbF_5$ was shown to be the salt $N_2F_3^+Sb_2F_{11}^-$ by ^{19}F NMR and IR spectroscopy (see below) [7 to 9] (see also [10]). For the complex $N_2F_4 \cdot 3SbF_5$ the formulation $N_2F_3^+Sb_3F_{16}^-$ (presumably by analogy to $N_2F_4 \cdot 2SbF_5$) was given by [11].

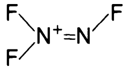
If the reaction of SbF_5 with an excess of N_2F_4 (~1 atm) is carried out in anhydrous HF solution at room temperature, the salt $N_2F_3^+SbF_6^-$ is obtained [11, 12].

The salt $N_2F_3^+AsF_6^-$ results from the reaction of AsF_5 with N_2F_4 without any solvent at −78°C according to [13] and at room temperature according to [11]. The reaction of AsF_5 with N_2F_4 without solvent or in anhydrous HF solution resulted in the adducts $N_2F_4 \cdot 2.3AsF_5$ at −78°C and $N_2F_4 \cdot 1.33AsF_5$ at room temperature. The room temperature existence of $N_2F_3^+$ was proved by ^{19}F NMR and IR spectroscopy [14].

The $N_2F_3^+SnF_5^-$ salt could not be directly prepared from N_2F_4 and SnF_4, but by a metathetical reaction between $N_2F_3^+SbF_6^-$ and Cs_2SnF_6 at −78°C in the presence of anhydrous HF [11, 15] according to $2N_2F_3SbF_6 + Cs_2SnF_6 \rightarrow 2CsSbF_6\downarrow + N_2F_3SnF_5 + N_2F_4$.

Structure. Spectra

On the basis of IR and Raman spectroscopy [11] and ^{19}F NMR [8, 9, 11, 14] and ^{14}N NMR [16], $N_2F_3^+$ possesses a planar structure (point group C_s) with three nonequivalent fluorines, two nonequivalent nitrogens, and with a strongly hindered rotation about the N–N axis, consistent with the structural formula



The ^{19}F NMR spectra of $N_2F_3^+AsF_6^-$ and $N_2F_3^+SbF_6^-$ were recorded at 84.6 MHz in SO_2, BrF_5, SbF_5, and HF solutions between −70 and +150°C. The $N_2F_3^+$ cation exhibits an ABX spectrum with an area ratio of 1:1:1 and chemical shifts $\delta_A = -127$, $\delta_B = -154$, and $\delta_X = -187$ ppm downfield from CCl_3F (external standard) nearly independent of solvent and temperature. No averaging of the resonances was noticeable up to 150°C indicating a strongly hindered rotation about the N–N axis [11]. These findings agree with the results for $N_2F_3^+AsF_6^-$ in anhydrous HF solution at room temperature ($-\delta = 122$, 146, and 180 ppm) [14] and for $N_2F_3^+Sb_2F_{11}^-$ in SO_2 at −70 and +25°C and for the melt at 120°C ($-\delta = 128.8$, 154.0, and 189.8 ppm) [8]. The low-temperature spectra (−70 to −90°C) in either BrF_5 or acidified HF solutions exhibit fine structure due to spin-spin couplings. Both the A and B signals consist of a doublet of doublets, the X signal of a 1:2:1 triplet, giving spin coupling constants J(AB) = 317 Hz and J(AX) = J(BX) = 78 Hz [11]. (J(AB) = 397 Hz, J(AX) = 81 Hz, J(BX) = 45 Hz were reported for the poorly resolved spectrum [8].) The B signal was assigned to the unique fluorine (NF), the A and X signals to the fluorines of the NF_2 group with A trans and X cis with respect to B [11].

The ^{14}N NMR spectrum of $N_2F_3^+AsF_6^-$ in anhydrous HF solution at room temperature exhibits two signals at $\delta(F_2N) = 75.9$ ppm upfield and $\delta(FN) = -26.0$ ppm downfield from liquid CD_3NO_2 [16]. Only one signal at −22 ppm downfield from NO_3^- (external 4.5 M NH_4NO_3 in 3 M HCl) was reported for $N_2F_3^+AsF_6^-$ in anhydrous HF solution at 25°C [17].

The IR and Raman spectra of solid $N_2F_3^+SbF_6^-$, $N_2F_3^+AsF_6^-$, $N_2F_3^+SnF_5^-$ and the polarization behavior of the Raman bands of $N_2F_3^+SbF_6^-$ and $N_2F_3^+AsF_6^-$ in HF solution agree with the results expected for the planar $N_2F_3^+$ ion. A total of nine IR and Raman active fundamentals, six belonging to species a′ giving rise to polarized Raman bands, and three belonging to species a″ giving rise to depolarized Raman bands, were identified (see Table 27) in addition to a number of overtones and combination bands up to 2900 cm^{-1} [11]. An earlier analysis of the IR and Raman spectra of solid $N_2F_3^+Sb_2F_{11}^-$ and $N_2F_3^+AsF_6^-$ in terms of a nonplanar structure of C_1 symmetry (which based on the argument that the 1520 cm^{-1} band expected for an N=N bond could not be observed in the Raman spectra) [18] was thus disproved. IR spectra without assignments were reported for solid $N_2F_3^+Sb_2F_{11}^-$ [7, 8] and solid $N_2F_3^+AsF_6^-$ [13, 14].

Table 27

$N_2F_3^+$ Ion. Fundamental Frequencies and Assignments in Point Group C_s [11].

mode	approximate description	wavenumber in cm^{-1}
$\nu_1(a')$	N=N stretch	1522
$\nu_2(a')$	NF_2 stretch, antisymmetric	1307
$\nu_3(a')$	NF stretch	1127
$\nu_4(a')$	NF_2 stretch, symmetric	925
$\nu_5(a')$	NF_2 in-plane deformation	516
$\nu_6(a')$	$FN{=}NF_2$ in-plane deformation	310
$\nu_7(a'')$	$FN{=}NF_2$ out-of-plane deformation, antisymmetric	671
$\nu_8(a'')$	$FN{=}NF_2$ out-of-plane deformation, symmetric	497
$\nu_9(a'')$	N=N torsion	344

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4.1.14 Dinitrogen Difluoride, N_2F_2

Other names: Difluorodiazene, difluorodiimine

CAS Registry Numbers: N_2F_2 *[10578-16-2]*, trans-N_2F_2 *[13776-62-0]*, cis-N_2F_2 *[13812-43-6]*

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Review

Dinitrogen difluoride is a colorless gas at normal conditions. It exists as a mixture of cis and trans isomers which can be separated. Most methods for preparing N_2F_2 yield a mixture of both isomers, but there are also methods which produce only the trans or cis form. The two isomers are thermally interconvertible. The reactivity of N_2F_2 is characterized by its ability to behave as a fluorination agent or both as a deoxygenation and fluorination agent. In some reactions, cis-N_2F_2 proves to be the more reactive isomer.

The first work on N_2F_2 was done in 1942 and is described in "Fluor" Erg.-Bd. 1, 1959, pp. 246/7.

4.1.14.1 Isomerism

It has been known since 1959 that N_2F_2 exists in two isomeric forms which differ in their physical and chemical properties, i.e., their melting points, boiling points [1, 2], vapor pressures, critical temperatures, heats of vaporization [1], mass-spectral fragmentation patterns [1, 3, 4], and chemical reactivity towards, e.g., glass or mercury [1, 5]. It has been firmly established by electron diffraction [6], vibrational IR spectra [1, 4, 7], ^{14}N and ^{19}F NMR spectra [8], rotational microwave spectra [9], and mass-spectral fragmentation patterns [1, 3, 4] that the two isomers are the cis and trans forms of planar dinitrogen difluoride, F–N=N–F, as had been conjectured soon after the discovery of N_2F_2. Of the two, the cis compound is the higher boiling and more reactive (thus, formerly frequently designated as "active" N_2F_2). Arguments were once given in favor of a 1,1-difluorodiazene structure, N=NF$_2$, instead of cis-F–N=N–F [4], but most of them, in particular the most crucial argument (IR band shapes), proved to be incorrect [10, 11].

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4.1.14.2 Preparation

Methods

Several well-defined routes with respect to working conditions, product yields, and purities are known for preparing N_2F_2:

(1) Reaction of elemental fluorine with sodium azide

$$2\,NaN_3 + 2\,F_2 \rightarrow 2\,NaF + N_2F_2 + 2\,N_2$$

Fluorine gas is passed over NaN_3 or a NaN_3–CaF_2 (1:4) mixture at room temperature in a copper or nickel reactor, and the effluent gases are heated (60 to 100°C) to promptly decompose intermediately formed N_3F into N_2 and NF radicals which then combine to give N_2F_2 [1 to 5]. Sodium azide must be present in excess to avoid further fluorination of N_2F_2 to NF_3. The product is collected in a liquid-nitrogen cold trap and purified by high-vacuum distillation. Use of moist NaN_3 or preferably admixture of HF to the F_2 stream increases the yield of N_2F_2, which is reported to be 34% based on charged F_2. When the product gases are heated to 60°C, the N_2F_2 formed is essentially pure trans isomer [1, 2]. At higher temperatures the abundance of cis-N_2F_2 increases [1 to 4].

(2) Defluorination of N_2F_4 by $AlCl_3$

$$3\,N_2F_4 + 2\,AlCl_3 \rightarrow 3\,N_2F_2 + 3\,Cl_2 + 2\,AlF_3$$

Gaseous N_2F_4 at pressures of 15 to 20 Torr is allowed to come into contact with an excess of $AlCl_3$ at −80°C in a static or flow system. The conditions of low pressure, low temperature, and excess $AlCl_3$ must be kept to suppress other efficient reactions with $AlCl_3$, namely reduction of N_2F_2 and disproportionation of N_2F_4 into NF_3 and N_2. The product obtained after washing with aqueous NaOH and trap-to-trap vacuum distillation is trans-N_2F_2 at 45 to 48% yield [6].

(3) Dehydrofluorination of difluoroamine with an alkali fluoride

$$2\,NHF_2 + 2\,MF \rightarrow N_2F_2 + 2\,MHF_2,\quad M = K, Rb, Cs$$

Contact between gaseous NHF_2 and dry alkali fluoride at ambient temperature is made in a static or flow system (a flow system at low pressure is preferable to reduce explosion hazards with NHF_2). The product gases are separated by trap-to-trap distillation between −142 and −196°C in a high-vacuum line. The yield of N_2F_2, a mixture of cis and trans, may be quantitative based on consumed NHF_2. The reaction in aqueous solution at pH 8.6 gave lower yields [7].

(4) Basic hydrolysis of N,N-difluorourea

$$2\,NF_2CONH_2 + 2\,H_2O \rightarrow N_2F_2 + 2\,NH_4F + 2\,CO_2$$

A concentrated KOH solution is added dropwise to aqueous difluorourea cooled to about −10°C. The products are passed through a KOH scrubber and condensed in a liquid-nitrogen cold trap. Water is removed in a CO_2-acetone cold trap. A 3:1 mixture of trans- and cis-N_2F_2 is obtained with a maximum yield of 42%. The use of dilute base at 25°C or above only yields traces of N_2F_2 [8]. The procedure is reported to work under nonaqueous conditions as well [9].

(5) Liberation of N_2F_2 from any N,N-difluorocarbamate under nonaqueous conditions

$$2\,F_2NCOOR + 2\,KOC(CH_3)_3 \rightarrow 2\,(CH_3)_3COCOOR + N_2F_2 + 2\,KF$$
$$R = \text{isopropyl [10] or 2-ethyl hexyl [11]}$$

The reaction is performed in chilled 1,1,2,2-$C_2H_2Cl_4$ [10] or in diglyme [11]. The product collected in a liquid-nitrogen [10] or CO_2-acetone [11] cold trap is a mixture of cis- and trans-N_2F_2, with a greater abundance of trans [10, 11].

(6) Electrolysis of molten NH_4HF_2, or NH_4HF_2 in anhydrous HF

$$2\,NH_4HF_2 + 4\,F_2 \rightarrow N_2F_2 + 10\,HF$$

Electrolysis in anhydrous HF (0.1 to 1.0 M NH_4HF_2, 2.1 to 264 mA/cm^2) gave trans-N_2F_2 as the only NF species [12], whereas in molten NH_4HF_2 (125 to 145°C) both cis- and trans-N_2F_2 occurred as minor products besides NF_3 and NHF_2 [13 to 16]. The latter could be destroyed without explosion hazards by passing over $MnO_2 + KMnO_4$ and N_2F_2 isolated by high-vacuum distillation into a liquid-nitrogen cold trap [13, 14]. The yield of N_2F_2 increases considerably with increasing current density; no N_2F_2 was observed at $\leq 2.1\ mA/cm^2$ in NH_4HF_2–HF [12].

(7) UV photolysis of N_2F_4 in the presence of Br_2.

The photolysis products are separated by trap-to-trap distillation between −140 and −195°C. The fraction of N_2F_2 in the photolysis products, which contain NF_3 and SiF_4 (glass vessel), is 70% (53% trans) [17]. Occurrence of N_2F_2 in the N_2F_4/NF_2 photolytic system was reported earlier by others [18].

Various other methods of preparing N_2F_2 have been reported, but appear to be less convenient or efficient: Reaction of gaseous BrF_5 with Mg_3N_2 [19]; of elemental fluorine with NH_4Cl in the presence of NaF [20], cf. "Fluorine" Suppl. Vol. 2, 1980, p. 184; of elemental fluorine with certain solids or liquids containing NH groups, e.g., $LiNH_2$ or N_2H_4, in the presence of a metal fluoride [21]; of elemental fluorine with excess NH_3 [22], cf. "Fluorine" Suppl. Vol. 2, 1980, p. 165; of N_2F_4 with first-stage graphite intercalation compounds of AsF_5, fluorinated or unfluorinated ($C_{10}AsF_{5+x}$, $0 \leq x \leq 0.5$, this method gave almost pure (90%) trans-N_2F_2 with little NF_3 and N_2 and no cis-N_2F_2) [23], see also p. 366; recovery of pure cis-N_2F_2 from the solid adduct $N_2F_2 \cdot AsF_5$ (see p. 403) by reaction with, e.g., NaF in anhydrous HF [24] or from $N_2F_2 \cdot 2\,SbF_5$ (see p. 403) by thermal decomposition at 200°C [25]; reduction of $N_2F_4 \cdot 2\,SbF_5$ (see p. 403) by, e.g., ferrocene or iodine in AsF_3 or in liquid SO_2 to give pure trans-N_2F_2 [25, 26]; pyrolysis of NF_3 or N_2F_4 at >1000°C and quick quenching to below 100°C [27]; reaction of NF_3 or N_2F_4 with $Fe(CO)_5$ [28, 29], cf. "Eisen-Organische Verbindungen" B 3, 1979, p. 118; electric discharge in NF_3 in the presence of Hg vapor [30]; radiolysis of an N_2–F_2 mixture by 30-MeV electrons [31]; by U fission fragments or mixed $(n+\gamma)$ radiation [32, 33].

In addition, Lawless and Smith [43] reported N_2F_2 to be present in the products of the reactions $F_2 + NH_2CONF_2$, $NF_2Cl + NaN_3$ or aqueous KOH, $N_2F_4 + CaCl_2$, $N_3F + H_2O_2$ or KO_2; this work was mostly done under contracts during the period 1959 to 1964 and does not appear to have been published elsewhere.

Purification

Besides fractional distillation, gas-phase absorption or partition chromatography can be used to separate cis- and trans-N_2F_2 from other products and from each other. For instance, NF_3, trans-N_2F_2, and cis-N_2F_2 elute in that order with helium from columns packed with firebrick or silica gel [3, 17]. Separation of nitrogen fluorides from other products and from each other by gas-phase chromatography with various column fillings has been reported [34, 35].

Heat of Formation ΔH_f°

Published data are controversial: From a calorimetric measurement of the enthalpy of the reaction $N_2F_2(g) + \frac{8}{3}NH_3(g) \rightarrow 2NH_4F(c) + \frac{1}{3}N_2(g)$ for mixtures with both isomers of N_2F_2 in different proportions, the values $\Delta H^\circ_{f,298}(\text{cis-}N_2F_2) = +16.4 \pm 1.2$ and $\Delta H^\circ_{f,298}(\text{trans-}N_2F_2) = +19.4 \pm 1.2$ kcal/mol were deduced [36] and were adopted in the JANAF Tables [37]. However, $\Delta H^\circ_{f,298} = +25.6 \pm 1.3$ kcal/mol for both isomers (earlier: 25.3 ± 2.0 kcal/mol for cis-N_2F_2 alone [38]) had been derived [39, 40] from the enthalpy of the reaction $N_2F_2 + 3KI \rightarrow 2KF + KI_3 + N_2$ in aqueous solution (pH 3) [38], and from an apparent $\Delta H = 0$ for the isomeric conversion of N_2F_2 [41]. But, both the value for the enthalpy difference between the cis and trans isomer, $\Delta H = 0$ [41] and that implied by the data of [36], $\Delta H = 3.0$ kcal/mol (cis-N_2F_2 more stable), are open to question, cf. p. 394.

Handling. Storage

N_2F_2 is potentially explosive. When it is mixed with organic compounds, explosions usually result, in particular with condensed N_2F_2 [8, 13, 15, 17]. Explosion hazards of organic material in contact with gaseous N_2F_2 appear to be less serious [11].

The cis isomer reacts slowly with glass at room temperature and high pressure while the trans isomer is essentially unchanged under the same conditions [15]. Stainless steel and Monel are attacked below 100°C by N_2F_2 [42].

Both isomers are thermodynamically unstable at room temperature. Thus, N_2F_2 partly decomposes into N_2 and F_2 when stored in a metal bomb for several months [1]. However, the trans compound is reported stable upon prolonged storage in mixtures with NF_3 in a stainless steel bomb, whereas cis-N_2F_2 decomposes under the same conditions [22].

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4.1.14.3 Molecular Properties and Spectra

Electron Configurations. Ionization Energies

The molecules trans- and cis-N_2F_2 are planar with C_{2h} and C_{2v} symmetry, respectively [1]. Ab initio MO calculations predict the following sequences of doubly occupied orbitals for both molecules; the sequences start at the K shells of the elements:

trans-N_2F_2 [2, 3, 4]: $1a_g$ $1b_u$ $2a_g$ $2b_u$ $3a_g$ $3b_u$ $4a_g$ $4b_u$ $5a_g$ $5b_u$ $1a_u$ $1b_g$ $6a_g$ $6b_u$ $2a_u$ $7a_g$
cis-N_2F_2 [2]: $1a_1$ $1b_2$ $2a_1$ $2b_2$ $3a_1$ $3b_2$ $4a_1$ $4b_2$ $5a_1$ $6a_1$ $1b_1$ $1a_2$ $5b_2$ $7a_1$ $2b_1$ $6b_2$

For both trans- and cis-N_2F_2, the highest MO is a combination of nitrogen lone pairs, a symmetric combination (n^+) in the case of trans-N_2F_2 [2, 3, 4], and an antisymmetric combination (n^-) in the case of cis-N_2F_2 [2] (the "+" and "−" labels define the behavior of the orbital wave functions under a rotation about the twofold symmetry axes). The other combinations, n^- for trans-, n^+ for cis-N_2F_2, are assigned to the third valence orbitals, $6b_u$ for trans-N_2F_2 [2, 4], $7a_1$ for cis-N_2F_2 [2]. The second-highest valence orbitals, $2a_u$ for trans-, $2b_1$ for cis-N_2F_2, are π-bonding orbitals in both molecules [2].

Ionization energies were obtained for trans-N_2F_2 by excitation with He I and He II radiation and, by comparison with MO calculations, were assigned to molecular orbitals as follows:

E_i (vertical) in eV [3]	13.4	14.1	15.1	16.85	17.2	18.70	19.80	21.0	22.7
E_i (adiabatic) in eV [3]	12.8	13.65	—	—	—	18.0	—	—	22.3
orbital assignment [2, 3]	$7a_g$	$2a_u$	$6b_u$	$6a_g$	$1b_g$	$1a_u$	$5b_u$	$5a_g$	$4b_u$

The value for the first ionization energy is in approximate agreement with a mass spectrometric appearance potential of trans-$N_2F_2^+$, 13.1±0.1 eV [5].

Up to five bands may be detected in the 15- to 18-eV range of binding energies in the experimental photoelectron spectrum, whereas only three are to be expected. Thus, the orbital assignment in this range is tentative and based solely on a many-body Green's function calculation of ionization energies [2]. Other photoelectron lines in that range may be due to cis-N_2F_2 or other impurities, or may form part of a complex band structure of trans-N_2F_2 itself [2, 3]. The assignment of photoelectron bands of trans-N_2F_2 at >18 eV is doubtful in view of more advanced many-body calculations indicating the presence of several satellite lines in the

20- to 25-eV region. Thus, the band at 21.0 eV may be a satellite, and the bands with maxima at 18.70 and 19.80 may arise from three different ionization processes [2].

No ionization energies appear to have been measured for cis-N_2F_2 so far.

Excited States. Electronic Spectra

Ab initio MO plus CI calculations for trans-N_2F_2 predict five spin-allowed transitions to singlet states in the 6- to 12-eV region (48000 to 96000 cm^{-1}) [4]. Experimental results are contradictory, one group of workers reporting a single strong band at 66000 cm^{-1} (~154 nm) with no indication of any absorption at lower wavenumbers [6], whereas other authors [7] report trans- and cis-N_2F_2 to have prominent absorption maxima at 196 and 199 nm (~51000 and 50200 cm^{-1}), respectively.

Dipole Moment μ

For cis-N_2F_2, $\mu = 0.16 \pm 0.01$ D was determined from the Stark effect of the $2_{1,1} \leftarrow 2_{0,2}$ transition in the rotational microwave spectrum. As in the case of NF_3 or N_2F_4, the small value of the molecular dipole moment is attributed to the hybridized lone pair of the nitrogen atoms counteracting the NF bond moments [8]. For trans-N_2F_2, $\mu = 0$ for symmetry reasons.

Nuclear Magnetic Resonance

The ^{19}F NMR spectra of trans- and cis-N_2F_2 are very similar, showing a symmetric five-line pattern with three strong center lines and two weak outer lines. Together with ^{19}F-$\{^{14}N\}$ double resonance spectra they were analyzed to give the following values of chemical shifts δ, relative to internal CCl_3F for ^{19}F and to external NF_3 for ^{14}N, positive in the high field direction, and spin coupling constants J [9]:

molecule	$\delta(^{19}F)$ in ppm	$\delta(^{14}N)$ in ppm	$^1J(N\text{-}F)$ in Hz	$^2J(N\text{-}F)$ in Hz	$^3J(F\text{-}F)$ in Hz
trans-N_2F_2	−94.9	−75.2	±136	∓73	322
cis-N_2F_2	−133.7	−13.3	±145	∓37	99

The $\delta(^{19}F)$ values approximately agree with $\delta = -94.4$ for trans-, $\delta = -136.1$ ppm for cis-N_2F_2, reported relative to internal CCl_3F for the center of an apparent three-line pattern [10]. For earlier ^{19}F and ^{14}N NMR results, see [28] and [12], respectively.

A reanalysis of the five-line ^{19}F NMR spectrum of cis-N_2F_2 showed that an additional spin coupling constant, $J(N\text{-}N) = \mp 33$ Hz (sign opposite to $^1J(N\text{-}F)$) has to be taken into account [11].

There does not appear to be any way of reconciling the ^{14}N and ^{19}F NMR spectra of cis-N_2F_2 with the proposed structural alternative, 1,1-difluorodiazene, $N{=}NF_2$. In particular, observation of an identical chemical shift for both nitrogen atoms opposes that structure [9, 12].

Rotational Constants. Bond Distances and Angles

Rotational constants A, B, and C of the vibrational ground state have been obtained only for cis-N_2F_2 which is amenable to microwave spectra due to its dipole moment. The values (in MHz) A = 19686.64, B = 7946.76, and C = 5651.38 for $^{14}N_2F_2$, A = 19302.87, B = 7901.20, and C = 5596.44 for $F^{14}N^{15}NF$ were obtained from transitions between low-J levels, neglecting centrifugal distortion. Rotational constants for an excited vibrational state are also given [8]. For trans-

N_2F_2, only $\frac{1}{2}(B+C)=0.14876$ and $0.14821\ cm^{-1}$ were derived from analyses of the ν_5 and $(\nu_2+\nu_5)$ vibration-rotation bands [13].

Bond distances and angles have been determined for the cis isomer from the above rotational constants, and for both isomers by electron diffraction:

molecule	r(N–N) in Å	r(N–F) in Å	α(FNN)	method	Ref.
trans-N_2F_2	$1.230_5 \pm 0.010$	$1.396_2 \pm 0.008$	$105.5_0° \pm 0.7°$	electron diffraction	[1]
cis-N_2F_2	$1.213_9 \pm 0.012$	$1.410_1 \pm 0.009$	$114.4_4° \pm 1.0°$	electron diffraction	[1]
cis-N_2F_2	1.214 ± 0.005	1.384 ± 0.010	$114.5° \pm 0.5°$	microwave spectroscopy	[8]

Although the physical meaning of the bond lengths and angles α obtained by microwave spectroscopy or electron diffraction is not quite the same (r(N–N) of cis-N_2F_2 from microwave spectra refers to a substitution structure, r_s, the corresponding r(N–F) and α(FNN) values to an effective structure, r_0 and α_0, whereas structural parameters from electron diffraction are thermal-average values, cf. [14]), this cannot account for the large (0.026 Å) difference between the r(N–F) values of cis-N_2F_2 obtained by the two methods [1].

Vibrational Frequencies

Both trans- and cis-N_2F_2 have six normal modes of vibration. Their symmetry species, selection rules (IR or Ra = IR or Raman active) and approximate mode descriptions (based on a six-parameter force field [15]) are given in the following tabulation. The numbering of fundamentals is that used by King and Overend [16, 17]. The setting of coordinate axis is that used in [15] and is in accord with IUPAC recommendations for planar molecules with C_{2v} symmetry, that is, the molecule is in the yz plane (xz plane in [17]) with $z=C_2$ axis [18]. This implies the ν_5 and ν_6 fundamentals of cis-N_2F_2 to be labeled as b_2 (in [17] b_1).

molecule	mode[a]	selection rules	approximate mode description[b]
trans-N_2F_2 [15, 16, 19]	$\nu_1(a_g)$	Ra	$\nu(N{=}N)$
	$\nu_2(a_g)$	Ra	$\delta_s(FNN)+\nu_s(N{-}F)$
	$\nu_3(a_g)$	Ra	$\nu_s(N{-}F)+\nu(N{=}N)+\delta_s(FNN)$
	$\nu_4(a_u)$	IR	out-of-plane torsion
	$\nu_5(b_u)$	IR	$\nu_{as}(N{-}F)$
	$\nu_6(b_u)$	IR	$\delta_{as}(FNN)$
cis-N_2F_2 [15, 17]	$\nu_1(a_1)$	IR, Ra	$\nu(N{=}N)$
	$\nu_2(a_1)$	IR, Ra	$\nu_s(N{-}F)$
	$\nu_3(a_1)$	IR, Ra	$\delta_s(FNN)$
	$\nu_4(a_2)$	Ra	out-of-plane torsion
	$\nu_5(b_2)$	IR, Ra	$\nu_{as}(N{-}F)$
	$\nu_6(b_2)$	IR, Ra	$\delta_{as}(FNN)$

[a] Point groups C_{2h} (trans-N_2F_2) and C_{2v} (cis-N_2F_2). – [b] Only leading terms of calculated potential energy distributions [15] are given.

Observed fundamental frequencies, in cm^{-1}, for trans- and cis-N_2F_2 are presented in the following table.

molecule	trans-N_2F_2	trans-N_2F_2	trans-N_2F_2	trans-N_2F_2
spectrum	Ra	IR	IR	Ra
conditions[a]	liquid, 145 K	gas, RT	solid, 77 K	gas, 8 atm, RT
ν_1	1522	—	—	1523
ν_2	1010	—	—	1018
ν_3	600	—	—	603
ν_4	—	363.5	367, 370	—
ν_5	—	990[b]	970	—
ν_6	—	423	418	—
Ref.	[16]	[16]	[16]	[20]

molecule	trans-N_2F_2	trans-N_2F_2	cis-N_2F_2	cis-N_2F_2
spectrum	IR	IR	Ra	IR
conditions[a]	gas, RT	gas, RT	liquid, 151 K	gas, RT
ν_1	—	(1636)[c]	1526	1525
ν_2	—	(1010)[c]	884	896
ν_3	—	(592)[c]	341[d]	341[d]
ν_4	362	360	550(?)[e]	550(?)[e]
ν_5	990[b]	989	945	952
ν_6	420	421	729	737
Ref.	[20]	[19]	[17]	[17]

[a] RT = room temperature. – [b] Band origin 991.01 cm^{-1} [13]. – [c] Values derived from IR combination bands and obsolete in particular for ν_1. – [d] From relative intensities of vibrational satellites in rotational microwave spectra, $\nu_3 = 300 \pm 35\ cm^{-1}$ was estimated [8]. – [e] Questionable assignment. IR forbiddenness of a_2 fundamental must be lifted by, e.g., Coriolis resonance with ν_6, ν_3, or both [17].

Several IR overtone and combination bands have been found for both cis-N_2F_2 [17] and trans-N_2F_2 [13, 16, 19, 20]. The $\nu_2+\nu_4$, $\nu_2+\nu_5$, and $\nu_2+\nu_6$ bands of trans-N_2F_2 were analyzed in greater detail [13]. The $2\nu_6$ overtone of trans-N_2F_2 also appeared in the Raman spectrum of the liquid [16].

Vibrational Amplitudes

Experimental values, in Å, from electron diffraction are [1]:

trans-N_2F_2: $u(N{=}N) = 0.036_9 \pm 0.009$, $u(N{-}F) = 0.056_5 \pm 0.005$
cis-N_2F_2: $u(N{=}N) = 0.060_4 \pm 0.011$, $u(N{-}F) = 0.063_3 \pm 0.007$

Values calculated from force fields [21 to 23] differ from these and from each other. None of the calculations reproduces the large difference of amplitudes found experimentally for the bonded distances, in particular for u(N=N), between the two isomers. It appears questionable, however, whether this effect is real [21].

Coriolis Coupling Constants

For trans-N_2F_2, $\zeta_{46}^{(a)} = 0.962$ was obtained from an analysis of the overlapping ν_4 and ν_6 IR bands, with values of rotational constants calculated from the molecular geometry [13]. Calculated values from force fields are $\zeta_{46}^{(a)} = 0.978$, $\zeta_{46}^{(b)} = 0.207$ [16], and $\zeta_{46}^{(a)} = 0.968$, $\zeta_{46}^{(b)} = 0.251$ [21].

Force Constants

A general force field for cis- or trans-N_2F_2 contains ten independent potential constants. In internal coordinates these are two stretching constants, f_R and f_r, with R = r(N=N) and r = r(N–F), two angle deformation constants, f_α and f_φ, with $\alpha = \sphericalangle$FNN and φ = dihedral angle of out-of-plane torsion, and six interaction constants, f_{Rr}, f_{rr}, $f_{R\alpha}$, $f_{r\alpha}$, $f'_{r\alpha}$ (the latter two refer to interactions between the FNN angle and an adjacent and nonadjacent N–F bond, respectively), and $f_{\alpha\alpha}$. With only six normal frequencies and no further spectroscopic data given, only six constants can be uniquely determined. Three such six-parameter force fields have been calculated for trans-N_2F_2, two for cis-N_2F_2, and the resulting constants are listed below. Zero values are arbitrarily chosen as such. It should be noted that f_R for trans-N_2F_2 in the third set [19] is based on $\nu_1 = \nu$(N=N) = 1636 cm^{-1}, a value now known to be invalid. All constants are in mdyn/Å.

molecule	f_R	f_r	f_α	f_φ	f_{Rr}	f_{rr}	$f_{R\alpha}$	$f_{r\alpha}$	$f'_{r\alpha}$	$f_{\alpha\alpha}$	Ref.
trans-N_2F_2	8.117	4.348	1.457a)	0.331a)	0	0	0	1.105a)	0	0.144a	[15]
trans-N_2F_2	11.138	4.523	1.185	0.304	0	0	0.246	0.528	0	0	[24]
trans-N_2F_2	11.10	4.60	1.02	0.29	0.95	0	0.20b)	0.42	0	0	[19]
cis-N_2F_2	7.934	4.966	1.171a)	0.263a)	0	0	0	0.774a)	0	0.353a)	[15]
cis-N_2F_2	8.956	3.987	1.028	0.288	0	0	0.229	0.509	0	0	[24]

a) Values of the original reference [15] for f_α, f_φ, and $f_{\alpha\alpha}$ have been normalized here to r·R, those for $f_{r\alpha}$ to $(r \cdot R)^{1/2}$, to obtain units of mdyn/Å throughout. This normalization is chosen in [24], and except for $f_{r\alpha}$ also in [19] (there $f_{r\alpha}$ normalized to r). The bonded distances are taken from [1]. – b) Preselected value.

Force fields with ten potential constants have been calculated in two papers [21, 25] without specifying the methods of approximation.

Bond Dissociation Energies D. Atomization Energy ΔH°_{at}

Published values reflect the uncertainty which still exists for the enthalpies of formation, ΔH°_f, of the two N_2F_2 isomers, see p. 388 (D, ΔH°_{at}, and ΔH°_f in kcal/mol): Thus, for trans-N_2F_2, Armstrong and Marantz [26] have assumed D(N=N) = 107.9 and calculated D(N–F) = 68.2 from ΔH°_{at} = 244.3, which they derived from their value ΔH°_f = 19.4. Herron and Dibeler [5] obtained D(N=N) = 103 ± 10 for trans-, 106 ± 10 for cis-N_2F_2 from D(N=N) = $2\Delta H^\circ_f$(NF) – $\Delta H^\circ_f(N_2F_2)$ with ΔH°_f(NF) = 64 and $\Delta H^\circ_f(N_2F_2)$ from a preliminary communication of the values of Armstrong and Marantz. These bond dissociation energies appeared consistent with D(N=N) ≤ 106 = AP(NF^+) – IP(NF) for both isomers, where AP(NF^+) is the appearance potential of NF^+ in mass spectra of N_2F_2 and IP(NF) is the ionization potential of the NF radical determined mass spectrometrically [5]. With ΔH°_f = 25.6 for both isomers, Zercheninov et al. [27] have calculated D(N=N) = 97.2, D(N–F) = 70.5 (assigned value).

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4.1.14.4 Quantum Chemical Calculations

A synopsis of ab initio calculations presenting the methods for computing wave functions and the derived molecular properties is given in Table 28. References for calculations with semiempirical methods are given below. The abbreviations and symbols are explained on p. 235.

The following molecular properties have been calculated by CNDO, INDO, or related methods: ε_i [7, 10 to 13], μ [10, 11, 14, 15], ΔE [16], electron affinity [12], $\sigma(^{14}N)$ [17, 18], $\sigma(^{19}F)$ [19, 20], J(F-N) [21], geometry parameters [9 to 11, 13, 17, 22 to 25], ΔH_f°, ΔH_{at}° [11, 13], D(FN=NF) [9], E(cis) − E(trans), barrier to isomeric conversion, and transition rate [12, 15, 24 to 27]. Properties calculated by the extended Hückel or similar methods: ε_i [28], ΔH°_{at}, barrier to isomeric conversion [29], ^1J(N-F) and ^2J(N-F) [32]. Properties calculated by the HAM ("hydrogen atoms in molecules") method: ε_i [7, 30].

Table 28

Ab Initio MO Calculations for trans- and cis-N_2F_2.

N_2F_2 isomer	basis set	$-E_T$ in a.u.	calculated molecular properties	Ref.
trans, cis	extended GTO and smaller sets	307.66402 (trans), 307.66305 (cis)	r(N=N), r(N–F), $\sphericalangle$FNN, μ; sign of E_T(cis) − E_T(trans) dependent on basis set	[1]
trans, cis	extended GTO	307.576333 (trans), 307.573209 (cis)	ε_i, E_i (many-body Green's function calculations)	[2]
trans	DZ GTO	307.5104	ε_i, pop., moments of charge distribution	[3, 4]
trans	DZ GTO	307.5073, 307.6677(CI)	vertical excitation energies	[5]
trans, cis	4-31G, STO-3G	307.13832(trans), 307.13397(cis)	r(N=N), r(N–F), $\sphericalangle$FNN; sign of E_T(cis) − $E_T$trans) dependent on basis set	[6]
trans, cis	STO-3G	303.44085(trans), 303.44098(cis)	r(N=N), r(N–F), $\sphericalangle$FNN, pop.	[31], see also [33]
trans	4-31G, STO-3G	—	ε_i	[7]
cis	STO-3G	—	r(N=N), r(N–F), $\sphericalangle$FNN	[8]
trans, cis	GTO	—	D(FN=NF)	[9]

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4.1.14.5 Thermal Properties

The following experimental values have been published without details of the means by which they were determined:

property	trans-N_2F_2	cis-N_2F_2	Ref.
density in g/cm^3	—	1.809 (−183°C)	[1]
melting point in °C	−172	below −195	[2, 3]
boiling point in °C	−111.4	−105.7	[2, 3]
vapor pressure equation	$\log(p/\text{Torr}) = -742.3/T + 7.470$	$\log(p/\text{Torr}) = -803.0/T + 7.675$	[2]
	$\log(p/\text{atm}) = -745/T + 4.58$*)	$\log(p/\text{atm}) = -793/T + 4.72$*)	[4]
heat of vaporization in kcal/mol	3.40	3.67	[2]
critical temperature in K	260	272	[2]
critical pressure in atm	46.6*)	46.6*)	[4, 5]

*) A critical temperature of cis-N_2F_2 given in [4] appears to be averaged from an "experimental value", 260.2 K, and a value calculated empirically on the basis of a concept of atomic

increments, see [5]. The same concept was used to calculate critical pressures [4, 5]. The constants of the vapor pressure equation were obtained by inserting boiling- and critical-point data [4].

Among the published papers containing calculated thermodynamic functions for the ideal gas [6 to 10], current data for molecular frequencies (from [16] and [17] on p. 395) have been used in only two papers [6, 7]. The calculated values for the molar heat capacity C_p°, entropy S°, enthalpy $H_T^\circ - H_0^\circ$, and Gibbs free energy $(G^\circ - H_0^\circ)$ are given below:

trans-N_2F_2 [6]

T in K	C_p° in cal·mol^{-1}·K^{-1}	S° in cal·mol^{-1}·K^{-1}	$H^\circ - H_0^\circ$ in kcal/mol	$-(G^\circ - H_0^\circ)/T$ in cal·mol^{-1}·K^{-1}
200	10.742	59.714	1.759	50.917
298.16	12.777	64.402	2.918	54.616
400	14.430	68.389	4.305	57.626
600	16.557	74.697	7.427	62.318
800	17.720	79.630	10.864	66.050
1000	18.395	83.677	14.488	69.189
1200	18.798	87.016	18.196	71.853
1400	19.062	89.991	21.995	74.280
1600	19.238	92.500	25.814	76.366
1800	19.364	94.741	29.675	78.255
2000	19.459	96.789	33.566	80.006

cis-N_2F_2 [7]

T in	C_p° in cal·mol^{-1}·K^{-1}	S° in cal·mol^{-1}·K^{-1}	$H^\circ - H_0^\circ$ in kcal/mol	$-(G^\circ - H_0^\circ)/T$ in cal·mol^{-1}·K^{-1}
200	10.312	58.249	1.729	49.603
298.16	12.450	62.770	2.847	53.217
400	14.247	65.688	4.211	55.161
600	16.492	72.934	7.307	60.755
800	17.700	77.875	10.742	64.448
1000	18.381	81.904	14.356	67.548
1200	18.722	84.511	17.832	69.651
1400	19.055	88.180	21.851	72.572
1600	19.236	90.749	25.688	74.694
1800	19.363	93.041	29.551	76.624
2000	19.457	95.044	33.430	78.329

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4.1.14.6 Chemical Behavior

Cis-Trans Isomerization

When heated, trans-N_2F_2 is converted into the cis isomer. The first isomerization study was done in a flow system with a heated copper tube by Colburn et al. [6]. Isomerization was reported to occur above 225°C and analysis of mixtures of various starting compositions indicated the existence of an equilibrium between the two isomers: At 285°C, for instance, the equilibrium mixture contained about 13% trans-N_2F_2 [6]. In contrast to these results, it was found that the conversion of trans-N_2F_2 into cis-N_2F_2 takes place below 100°C nearly quantitatively [18] or at least with a 90% yield [35] in a stainless steel reactor. 94% conversion of trans- into cis-N_2F_2 at 74°C in a stainless steel reactor was obtained by adding a small amount of fluorine [36]. The equilibrium concentration of cis-N_2F_2 was also found by others to be 90.5%, but independent of temperature in the range 25 to 150°C [3]. The isomerization process is very slow at room temperature [6]; the equilibrium is reached only within a period of several months [3].

Thermochemical data on the isomeric equilibrium of N_2F_2 are inconclusive as demonstrated by the following compilation. ΔH and ΔS are the enthalpy and entropy of trans→cis isomerization and K is the equilibrium constant for trans-$N_2F_2 \rightleftharpoons$ cis-N_2F_2:

ΔH in kcal/mol	ΔS in $cal \cdot mol^{-1} \cdot K^{-1}$	T in K	method	Ref.
-1.005 ± 0.104	$+1.13 \pm 0.31$	283 to 423	2nd-law analysis[a]	[1, 2]
0	$+4.47$	298 to 423	K = 9.5 independent of T	[3]
-3.0	—	298	$\Delta H = \Delta H^\circ_{f,298}(cis) - \Delta H^\circ_{f,298}(trans)$	[4]
-2.52 ± 0.05	—	298	from K measured at T = 558 K [6] by 3rd-law analysis [5][b]	[5, 6]

[a] Preliminary data: $\Delta H = -2.070 \pm 0.145$ kcal/mol, $\Delta S = -1.55 \pm 0.37$ $cal \cdot mol^{-1} \cdot K^{-1}$ from 2nd-law analysis between 373 and 423 K [2]. – [b] A previously reported heat of isomerization (sic), ΔH = 27.5 kcal/mol [6], is certainly in error [4, 5, 7, 8].

The discrepancies may be due to shortcomings of the analytical methods for determining K [1] (gas chromatography [1 to 3] and IR spectroscopy [1]).

From ab initio MO-SCF calculations, ΔH is obtained as a difference of total energies, $E_T(cis\text{-}N_2F_2) - E_T(trans\text{-}N_2F_2)$. In order to get a meaningful result, calculations have to be carried out at fully-optimized molecular geometries [9]. However, so far the magnitude and size of ΔH, obtained from calculations carried out in that manner, are sensitive to the choice of the basis set and the optimization procedures (cf. p. 396), so no conclusions can be drawn.

The kinetics of trans→cis isomerization show three different time regimes: An initial induction period, during which trans-N_2F_2 remains almost unchanged, is followed by a sharp increase of reaction rate, after which equilibrium is reached [2, 3]. This indicates a self-catalyzed process, the catalyst being atomic fluorine [2], which, when intentionally added to trans-N_2F_2, e.g., by photolysis of the trans-N_2F_2–F_2–O_2 system, considerably accelerates isomeric conversion of trans-N_2F_2. Equilibrium is then reached within a few hours even at room temperature [1, 10, 11]. These findings are at variance with a unimolecular rate process which was assumed earlier [12], to analyze rate constants of trans→cis isomerization. Measurements in a shock tube at 570 to 615 K yielded $k=10^{14}\exp(-32.2/RT)\ s^{-1}$. The apparent activation energy of 32.2 kcal/mol derived therefrom [12] has been questioned [13], since both ab initio [14] and CNDO calculations [13] indicate a barrier to isomerization about a factor of two or more greater than this, provided the top of the barrier is represented by a linear N=N–F unit. This discrepancy results in a difference of about ten orders of magnitude or more between measured and calculated rate constants, and it appears impossible to reasonably explain such a large difference, not even by the quantum-mechanical tunnel effect [13, 15].

Mass Spectrum

Relative abundances RA of parent and fragment ions and their appearance potentials AP are compiled below:

	trans-N_2F_2			cis-N_2F_2		
ion	RA in % [6]	RA in % [16]	AP in eV [8]	RA in % [6]	RA in % [16]	AP in eV [8]
$N_2F_2^+$	25.3	21.56	13.1 ± 0.1	0.5	0.16	—
N_2F^+	43.4	100	13.9 ± 0.2	100	100	14.0 ± 0.2
NF^+	5.0	11.76	17.0 ± 0.2	6.0	5.53	16.9 ± 0.2
N_2^+	100	99.02	—	84.5	58.73	—
F^+	1.8	6.37	—	5.3	8.60	—
N^+	11.6	26.26	—	10.5	13.38	—

Thermal Decomposition

Since formation of N_2F_2 from the elements is endothermic, both isomers decompose into N_2 and F_2 but trans-N_2F_2 does so less rapidly [17]. Decomposition does not take place at 25 to 50°C [3], however, partial decomposition was reported to occur when N_2F_2 is stored in a stainless steel bomb for several months [17]. Decomposition is appreciable at 100°C and above, and complete in 20 min at 200°C [3]. A sample of cis-N_2F_2 allowed to stand at 100°C for 24 h was completely decomposed, whereas trans-N_2F_2 only isomerized to cis-N_2F_2 with little decomposition when heated to 95°C for 14 h [18].

Hydrolysis

Both isomers are unaffected by water at 60°C over a period of 15 h. At 74°C, the cis isomer hydrolyzes slowly (30% in 17 h), while the trans isomer reacts at a similar rate at 89°C. In each case the major products are N_2, O_2, and HF [19]. Both isomers are also reported stable against nonreducing acids and bases [20, 21].

Reactions with Elements

N_2F_2 does not take up fluorine or chlorine at room temperature [20, 21]. Also, Lawless and Smith [34] report unsuccessful attempts to observe addition reactions of the N=N bond with F_2 (at 5850 atm), with H_2, and with Cl_2, and to react N_2F_2 with sulfur at 150°C; this work was done under contract during the periods 1957 to 1960 and 1964 to 1965, and does not appear to have been published elsewhere. Na in liquid NH_3 quantitatively reduces N_2F_2 to N_2 and NaF [20, 21]. Molten Na under vacuum appears to function similarly [22]. The two N_2F_2 isomers differ in their reactivity toward Hg (no products reported) [6, 23], i.e., cis-N_2F_2 reacts much faster [6].

Reactions with Inorganic Compounds

The reaction with KI in acid solution proceeds quantitatively according to $N_2F_2 + 2I^- \rightarrow 2F^- + N_2 + I_2$ and thus is useful for quantitative analysis of N_2F_2 [20 to 22]. Reaction with NO gives FNO, N_2O, and NO_2 [17]. Toward SO_2 and SO_3, N_2F_2 behaves as both a fluorinating and deoxygenating agent. Mixtures of N_2F_2 and SO_2 at 100 to 300°C and a total pressure of 80 to 100 atm mainly give SO_2F_2, SOF_2, N_2O, and N_2 [17, 18]. UV photolysis of the N_2F_2–SO_2 system essentially yields the same products [24]. In the presence of Cl_2 [17] or Br_2 [18], SO_2FCl [17] or SO_2FBr [18] are formed. Principal reaction products with SO_3 are $S_3O_8F_2$, $S_2O_5F_2$, SO_2F_2, and N_2O. Their relative abundance depends on reactant ratios and also on the material of the reactor vessel used. Toward SF_4, SOF_2, and PF_3, N_2F_2 acts as a fluorinating agent. A mixture with SF_4 at 100°C mainly gives S_2F_{10} besides SF_6 and N_2 [18]; at 300°C and 100 atm, no S_2F_{10} occurs [17]. With SOF_2 at 100°C, N_2F_2 reacts to form SOF_4 and N_2; with PF_3 at room temperature, PF_5 and N_2 are obtained. Deoxygenation and fluorination occur with POF_3 at 85°C, the products being PF_5, N_2, and O_2 [18]. The unpublished work with elements H_2, F_2, Cl_2, and sulfur, done under contract and apparently reported only by Lawless and Smith [34], see above, was also performed with some inorganic compounds: Studies with N_2F_4 and NO under high pressure (~6000 atm) and with HI and HBr also failed to give addition reactions of the N=N bond. Furthermore, no reaction was observed for N_2F_2 with COS (100°C), $AgClO_4$, or CF_3COOH (25°C). Ammonia apparently reacted at 265°C to give NH_4F and N_2 [34].

At room temperature or below, the Lewis acids BF_3, AsF_5, and SbF_5 form solid 1:1 adducts with cis-N_2F_2 [17, 25 to 27]. Under the same conditions, trans-N_2F_2 does not react [17, 26, 27]. However, from SbF_5 at 40 to 50°C, an adduct $N_2F_2 \cdot 2SbF_5$ can be obtained with both isomers of N_2F_2 [28]. Preparation of an adduct of composition $N_2F_2 \cdot 1.3SbF_5$ from a mixture of cis- and trans-N_2F_2 at low temperatures has also been reported [33]. For more details, see p. 403.

Reactions with Organic Compounds

Treatment of $(C_6H_5)_3SiLi$ with N_2F_2 in various ethers gave $Si_2(C_6H_5)_6$ besides LiF and N_2. No identifiable organic products could be obtained with C_6H_5Li or C_6H_5MgBr under the same conditions. Thus it was not be proved whether the diazo group could be inserted into organic compounds by N_2F_2 [20]. Cyclic ketones have been α-fluorinated by N_2F_2. The reactions were performed in two steps, first a reduction of the ketone to an enamine by an amine (morpholine) and subsequent conversion of the enamine into an α-fluorinated ketone by N_2F_2 [29].

Some early papers and patents have dealt with the possibility of using N_2F_2 as a curing agent for many kinds of polymers [6, 30 to 32].

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4.1.15 Dinitrogen Monofluoride, N_2F

CAS Registry Number: *[36882-12-9]*

The existence of N_2F has been postulated as an intermediate in several reactions. Examples are the reactions of NF_2 with N or H atoms (cf. p. 349 and p. 343, respectively) or the thermal decomposition of NF_2 above 1000 K (cf. p. 332).

MO calculations using a minimum basis set of Slater-type orbitals and assumed geometric parameters were carried out. The highest amount of the calculated unpaired electron density is at the central nitrogen nucleus of the NNF radical.

Reference:

D. C. McCain, W. E. Pahlke (J. Chem. Phys. **56** [1972] 4957/65, 4961).

4.1.16 The N_2F^+ Ion

CAS Registry Number: *[33687-51-3]*

Occurrence

The adduct which cis-N_2F_2 forms with AsF_5 at room temperature or below is a salt of composition $N_2F^+AsF_6^-$, as indicated by NMR and vibrational IR spectra. The ^{19}F NMR spectrum suggests that only one type of fluorine is bonded to nitrogen. The N-F coupling constant is more than twice as large as in cis- or trans-N_2F_2, which is consistent with a change of orbital hybridization from sp^2 to sp on going from N_2F_2 to N_2F^+. Furthermore, the occurrence of only one infrared N–F stretching band, shifted to higher wavenumber with respect to cis-N_2F_2, excludes the possibility that the adduct may be composed of neutral N_2F_2 coordinated to the Lewis acid through fluorine or nitrogen [1]. The single, strong N–F stretching band is also found at approximately the same position in the adducts $N_2F_2 \cdot xSbF_5$ formed from cis-N_2F_2 with $x=1$ [2, 3], $x=1.3$ [4], and $x=2$ [5], and in $N_2F_2 \cdot BF_3$ [2]. The compound $N_2F_2 \cdot 2SbF_5 \triangleq N_2F^+Sb_2F_{11}^-$ also forms from trans-N_2F_2 [5]. In an IR spectrum of $N_2F_2 \cdot SbF_5$ dissolved in CCl_4 a band at 835 cm^{-1} was assigned to a second N–F stretching mode; nevertheless, $N_2F^+SbF_6^-$ was proposed [3].

Heat of Formation

From the appearance potentials of N_2F^+ in mass spectra of cis-N_2F_2 (14.0 eV) and trans-N_2F_2 (13.9 eV) [6], $\Delta H_f^\circ = 321$ kcal/mol for gaseous N_2F^+ was derived [7].

Structure. Bond Distance

Of the two plausible valence structures

$$:N{\equiv}\overset{+}{N}{-}F \text{ and } :\overset{+}{N}{=}\ddot{N}{-}F$$

(a third with a positive fluorine being reasonably excluded), the first is more likely, since the N–N stretching frequency is typical for a triple bond. It may then be assumed that the ion is linear (point group $C_{\infty v}$), since the central nitrogen atom has no free electron pair as it would have in the second structure. With that structure, the molecule should most likely be bent due to repulsive forces exerted by the free electron pair on the terminal atoms [8]. Assuming the differences between calculated and experimental distances to be the same as for isoelectronic

FCN, geometry-optimized MO–SCF calculations for linear N_2F^+ gave bond distances r(N–N) = 1.10 and r(N–F) = 1.28 Å [9]. Contrary to a previous assumption [4], the NF bond is probably much shorter than in NF_3 (1.37 Å) [9].

Nuclear Magnetic Resonance

Chemical shifts δ and coupling constants $J(^{14}N\text{-}^{19}F)$ obtained from room temperature ^{19}F and ^{14}N NMR spectra of $N_2F^+AsF_6^-$ dissolved in anhydrous HF are given below:

nucleus	δ in ppm	standard	$J(^{14}N\text{-}^{19}F)$ in Hz	Ref.
^{14}N	−191.2[a] (central N) −166.1[a] (terminal N)	CD_3NO_2 (neat liq.)	339	[10]
^{19}F	−179.4[b]	CF_3COOH	328	[1]

[a] Negative δ upfield. – [b] Negative δ downfield.

Molecular Vibrations. Force Constants

For the three fundamentals $\nu_1(\sigma)$, $\nu_2(\pi)$, and $\nu_3(\sigma)$ of N_2F^+, the following wavenumbers in cm^{-1} were obtained from IR and Raman (Ra) spectra of solid $N_2F^+AsF_6^-$:

ν_1	ν_2	ν_3	Ref.
1058 IR,	391 IR,		[4]
1057 Ra	391 Ra	2371 Ra	
1056 Ra		2370 Ra	[8]

A weak Raman band at 803 cm^{-1}, previously assigned as the bending frequency ν_2 [8], could not be found later either in a Raman or IR spectrum. Thus, assignment of a band at 391 cm^{-1} for ν_2 was preferred by analogy with isoelectronic FCN. This band also appeared in the Raman spectrum of $N_2F_2 \cdot 1.3SbF_5$, which was taken as additional evidence for this assignment, since the SbF_6^- anion does not absorb in this spectral region, whereas AsF_6^- does [4].

From observed frequencies, the stretching force constants f(N–N) = 21.23 ± 0.75 and f(N–F) = 8.17 ± 0.29 mdyn/Å were calculated with a stretch-stretch interaction constant of 0.5 ± 0.5 mdyn/Å [4]. An interaction constant of zero yielded corresponding values of 20.45 and 8.42 mdyn/Å [8]. Values of this constant close to zero and positive were obtained by ab initio calculations with two different basis sets [9]. A bending force constant of 0.202 mdyn/Å was calculated from $\nu_2 = 390\ cm^{-1}$, using the same bond distances as in N_2, r(N–N) = 1.10 and in NF_3, r(N–F) = 1.37 Å [4].

Bond Dissociation Energy

From heats of formation taken from [7] (ΔH_f° for N_2F^+ as given on p. 403), $D_0(N_2^+\text{-}F)$ = 57 kcal/mol has been derived by summing $-\Delta H_f^\circ(N_2F^+) + \Delta H_f^\circ(N_2^+) + \Delta H_f^\circ(F)$ [11].

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4.1.17 Trinitrogen Fluoride, N_3F

Other names: Fluorine azide, azidium fluoride

CAS Registry Number: *[14986-60-8]*

General References:

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Review

The commonly used name, fluorine azide, is used in this text.

Fluorine azide is a greenish-yellow gas at normal conditions with an odor resembling that of ClO_2. Like the other halogen azides, N_3F is a very explosive substance. Only a few data concerning the chemical and physical properties are known.

Fluorine azide has been known since 1942; the results of previous investigations are given in "Fluor" Erg.-Bd. 1, 1959, pp. 247/8.

Preparation. Formation

Fluorine azide is best prepared from dry hydrazoic acid and fluorine, diluted with nitrogen, in the gas phase at 25°C [1] according to

$$4\,HN_3 + 2\,F_2 \rightarrow 3\,N_3F + N_2 + NH_4F$$

A detailed report on the synthesis of N_3F, based on the dissertation of Haller [2], is given in "Fluor" Erg.-Bd. 1, 1959, p. 247. The amounts of HN_3, F_2, and inert gases (N_2, He) required to give a maximum yield of N_3F and a nonexplosive reaction were determined in later studies [3, 10]. N_3F also forms as an intermediate at room temperature in the synthesis of N_2F_2 from F_2 and solid NaN_3 (cf. p. 386), moistened with traces of H_2O [5] or diluted with CaF_2 (or other metal fluorides) [6] to avoid localized increases in temperature [1, 7]. At 35 to 45°C, this reaction mixture gave N_2F_2, NF_3, N_2, and also N_3F [6].

$^{15}N^{14}N_2F$ trapped in an Ar matrix was prepared from a sample of 97% enriched $Na^{15}N^{14}N_2$ [4].

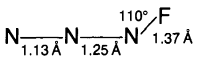
Handling. Toxicity

N_3F is a dangerous explosive and should be handled in small amounts, with caution, and protective shielding. It is advisable to dilute gaseous N_3F with an inert gas. Explosions can occur upon sudden change of pressure. Especially dangerous is N_3F in the condensed phases. Evaporation of the condensate generally causes a violent explosion [1, 2, 7].

The toxicity of N_3F, like that of the other halogen azides, has not yet been investigated. However, it can be assumed that N_3F is at least as toxic as the halogens or HN_3 [1].

Physical Properties

Experimental data for similar molecules, ab initio SCF-MO calculations, and general bonding considerations predict a planar structure for N_3F with the following geometric parameters [8]:



Semiempirical SCF-MO calculations (MNDO) gave as values for the angles, $\sphericalangle FNN = 113.5°$ and $\sphericalangle NNN = 165.3°$ [9].

The IR spectrum in an Ar matrix, taken at 4 K in the range 400 to 4000 cm^{-1} [4], is consistent with the molecular symmetry C_s (planar bent molecule) [1, 7]. The IR vibrational frequencies of N_3F (ν in cm^{-1}), are [4]:

molecule	$\nu(N-F)$	$\nu_{as}(N_3)$	$\nu_s(N_3)$	$\gamma(N_3)^{*)}$	$\delta(N_3)$
N_3F	869	2034	1086	503	654
$^{15}N^{14}N_2F$	853, 869	2010, 2024	1067	—	—

*) Out-of-plane deformation vibration.

An additional absorption band at 2164 cm^{-1} was interpreted as an overtone $2\nu_s$ [4]. The position of frequencies and the weaker N-halogen bond were compared to those of the other halogen azides [7].

N_3F exhibited an absorption maximum in the visible spectrum at 410 nm [3].

Chemical Behavior

Controlled thermal decomposition of N_3F in the diluted gas phase results in N_2F_2 according to the reaction

$$2N_3F \rightarrow N_2F_2 + 2N_2$$

The decomposition probably proceeds by means of the biradical NF [2, 5, 6].

UV photolysis of N_3F trapped in an Ar matrix at 4 K generated the free radical NF as indicated by absorptions at 1115 cm^{-1} (^{14}NF) and 1094 cm^{-1} (^{15}NF). Warming the photolyzed N_3F-Ar system to 40 K and recooling it led to absorptions assigned to cis- and trans-N_2F_2 [4].

N_3F reacted with O_2 at 40 to 80°C to give N_2F_2 plus NF_3 [12].

N_3F diluted with helium (1:3 volume ratio) reacted with an excess of chlorine at 50 to 85°C, preferably at 75°C, at about 103 Torr, and a residence time of 60 to 90 s to give $ClNF_2$ besides N_2F_2 and N_2 (and traces of CO_2, CF_4, and SiF_4) [10] according to the overall reaction

$$4N_3F + Cl_2 \rightarrow 2ClNF_2 + 5N_2$$

There was no reaction with Br_2 at 53°C [12].

N_3F reacted with H_2O_2 (98%) to give NF_3 plus N_2F_2 plus others; and with KO_2 to yield N_2F_2 [12]. No reaction occurred with OF_2, but upon UV irradiation, NF_3 was formed [12, 13], see also p. 178. The reactions with NO at −40 to −25°C and with N_2F_4 yielded NF_3 plus by-products [12].

Passing N_3F through liquid FNO or ClF_3 in a tubular Ni reactor maintained at −70 to −60°C gave NF_3 as a gas leaving the reactor [11, 12]. The reaction with ClF gave $ClNF_2$ plus by-products [12].

N_3F reacted with CO to give NF_3, N_2F_2, COF_2, plus CF_3OF [12].

The reaction of N_3F with C_2H_4 gave small amounts of unidentified liquid products. The reaction of N_3F with a number of organic compounds with functional groups such as chloro, amino, amido, oxo, and azo did not show a definite reaction pattern [12].

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Table of Conversion Factors

Following the notation in Landolt-Börnstein [7], values which have been fixed by convention are indicated by a bold-face last digit. The conversion factor between calorie and Joule that is given here is based on the thermochemical calorie, $\text{cal}_{\text{th ch}}$, and is defined as 4.184**0** J/cal. However, for the conversion of the "Internationale Tafelkalorie", cal_{IT}, into Joule, the factor 4.1868 J/cal is to be used [1, p. 147]. For the conversion factor for the British thermal unit, the Steam Table Btu, BTU_{ST}, is used [1, p. 95].

Force	N	dyn	kp
1 N (Newton)	1	10^{5}	0.1019716
1 dyn	10^{-5}	1	1.019716×10^{-6}
1 kp	$9.8066\mathbf{5}$	$9.8066\mathbf{5} \times 10^{5}$	1

Pressure	Pa	bar	kp/m²	at	atm	Torr	lb/in²
1 Pa (Pascal) = 1 N/m²	1	10^{-5}	1.019716×10^{-1}	1.019716×10^{-5}	0.986923×10^{-5}	0.750062×10^{-2}	145.0378×10^{-6}
1 bar = 10^{6} dyn/cm²	10^{5}	1	10.19716×10^{3}	1.019716	0.986923	750.062	14.50378
1 kp/m² = 1 mm H_2O	$9.8066\mathbf{5}$	$0.98066\mathbf{5} \times 10^{-4}$	1	10^{-4}	0.967841×10^{-4}	0.735559×10^{-1}	1.422335×10^{-3}
1 at = 1 kp/cm²	$0.98066\mathbf{5} \times 10^{5}$	$0.98066\mathbf{5}$	10^{4}	1	0.967841	735.559	14.22335
1 atm = 76**0** Torr	$1.0132\mathbf{5} \times 10^{5}$	$1.0132\mathbf{5}$	1.033227×10^{4}	1.033227	1	760	14.69595
1 Torr = 1 mm Hg	133.3224	1.333224×10^{-3}	13.59510	1.359510×10^{-3}	1.315789×10^{-3}	1	19.33678×10^{-3}
1 lb/in² = 1 psi	6.89476×10^{3}	68.9476×10^{-3}	703.069	70.3069×10^{-3}	68.0460×10^{-3}	51.7149	1

Work, Energy, Heat	J	kWh	kcal	Btu	MeV
1 J (Joule) = 1 Ws = 1 Nm = 10^7 erg	1	2.778×10^{-7}	2.39006×10^{-4}	9.4781×10^{-4}	6.242×10^{12}
1 kWh	$3.\mathbf{6}\times10^{6}$	1	860.4	3412.14	2.247×10^{19}
1 kcal	4184.**0**	1.1622×10^{-3}	1	3.96566	2.6117×10^{16}
1 Btu (British thermal unit)	1055.06	2.93071×10^{-4}	0.25164	1	6.5858×10^{15}
1 MeV	1.602×10^{-13}	4.450×10^{-20}	3.8289×10^{-17}	1.51840×10^{-16}	1

1 eV ≙ 23.0578 kcal/mol = 96.473 kJ/mol

Power	kW	PS	kp·m/s	kcal/s
1 kW = 10^{10} erg/s	1	1.35962	101.972	0.239006
1 PS	0.73550	1	**75**	0.17579
1 kp·m/s	$9.8066\mathbf{5}\times10^{-3}$	0.01333	1	2.34384×10^{-3}
1 kcal/s	4.184**0**	5.6886	426.650	1

References:

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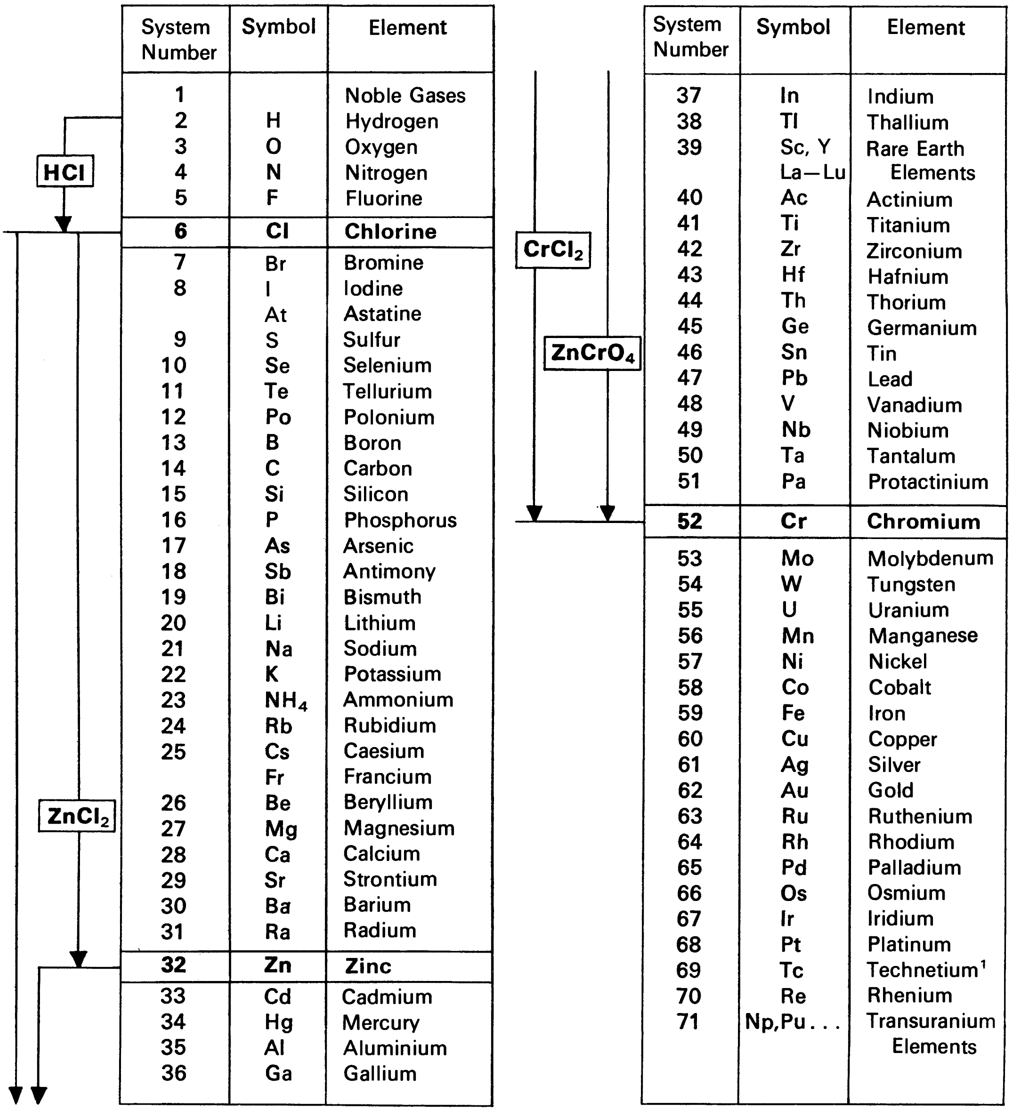
Key to the Gmelin System of Elements and Compounds



System Number	Symbol	Element
1		Noble Gases
2	H	Hydrogen
3	O	Oxygen
4	N	Nitrogen
5	F	Fluorine
6	**Cl**	**Chlorine**
7	Br	Bromine
8	I	Iodine
	At	Astatine
9	S	Sulfur
10	Se	Selenium
11	Te	Tellurium
12	Po	Polonium
13	B	Boron
14	C	Carbon
15	Si	Silicon
16	P	Phosphorus
17	As	Arsenic
18	Sb	Antimony
19	Bi	Bismuth
20	Li	Lithium
21	Na	Sodium
22	K	Potassium
23	NH$_4$	Ammonium
24	Rb	Rubidium
25	Cs	Caesium
	Fr	Francium
26	Be	Beryllium
27	Mg	Magnesium
28	Ca	Calcium
29	Sr	Strontium
30	Ba	Barium
31	Ra	Radium
32	**Zn**	**Zinc**
33	Cd	Cadmium
34	Hg	Mercury
35	Al	Aluminium
36	Ga	Gallium

System Number	Symbol	Element
37	In	Indium
38	Tl	Thallium
39	Sc, Y La—Lu	Rare Earth Elements
40	Ac	Actinium
41	Ti	Titanium
42	Zr	Zirconium
43	Hf	Hafnium
44	Th	Thorium
45	Ge	Germanium
46	Sn	Tin
47	Pb	Lead
48	V	Vanadium
49	Nb	Niobium
50	Ta	Tantalum
51	Pa	Protactinium
52	**Cr**	**Chromium**
53	Mo	Molybdenum
54	W	Tungsten
55	U	Uranium
56	Mn	Manganese
57	Ni	Nickel
58	Co	Cobalt
59	Fe	Iron
60	Cu	Copper
61	Ag	Silver
62	Au	Gold
63	Ru	Ruthenium
64	Rh	Rhodium
65	Pd	Palladium
66	Os	Osmium
67	Ir	Iridium
68	Pt	Platinum
69	Tc	Technetium[1]
70	Re	Rhenium
71	Np,Pu. . .	Transuranium Elements

Material presented under each Gmelin System Number includes all information concerning the element(s) listed for that number plus the compounds with elements of lower System Number.

For example, zinc (System Number 32) as well as all zinc compounds with elements numbered from 1 to 31 are classified under number 32.

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[1] A Gmelin volume titled "Masurium" was published with this System Number in 1941.

A Periodic Table of the Elements with the Gmelin System Numbers is given on the Inside Front Cover