REACTION CHEMISTRY OF HN_3 WITH HF, HALOGENS AND PSEUDOHALOGENS

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Background on FN_3

- FN_3 was first prepared and studied by J. F. Haller at Cornell University in 1942
- Very little work was done with FN_3 because of its extreme shock sensitivity and thermal instability
- Characterized by D. J. Benard at Rockwell's Science Center in 1986, and by H. Willner at Universität Hannover in 1987 on very small scale
- Yields were low, and purification and handling presented major problems
- Development of a safe high yield process for pure FN_3 was mandatory for studying its reaction chemistry

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Theoretical Heat of Reaction for FN_3

- Thermochemical Calculation for Reaction of HN_3 with F_2 to give FN_3 (Jerry Boatz, AFRL)

  [B3LYP(5)/6-311++G(2d,p)]

$$HN_3 + F_2 \longrightarrow FN_3 + HF$$

?H (0K) = -57.2 kcal/mol (±5 kcal/mol)

Previous Approaches to FN_3

- Haller, Benard, Willner, 1942, 1985, 1986

$$HN_3 + F_2 \xrightarrow[\text{Metal Catalyst, RT}]{\text{Gas Phase, } N_2 \text{ Diluent}} FN_3 + HF$$

- Pankratov, 1966

$$NaN_3 + F_2 \longrightarrow [FN_3] + NaF$$

- AFRL, 2002

$$NF_4SbF_6 + 2\ HN_3 \xrightarrow{HF} [FN_3] + NF_3 + H_2N_3SbF_6$$

$$(N_5)_2SnF_6 \xrightarrow[\Delta]{} FN_3 + N_5SnF_5 + N_2$$

New Results

- Repeating previous preparations was found to give impure products and yields of 50% or less
- Carrying out the fluorination reactions in solution at low temperatures resulted in quantitative yield and high purity of FN_3
- HF is not a good solvent because it protonates HN_3 to give $H_2N_3^+HF_2^-$

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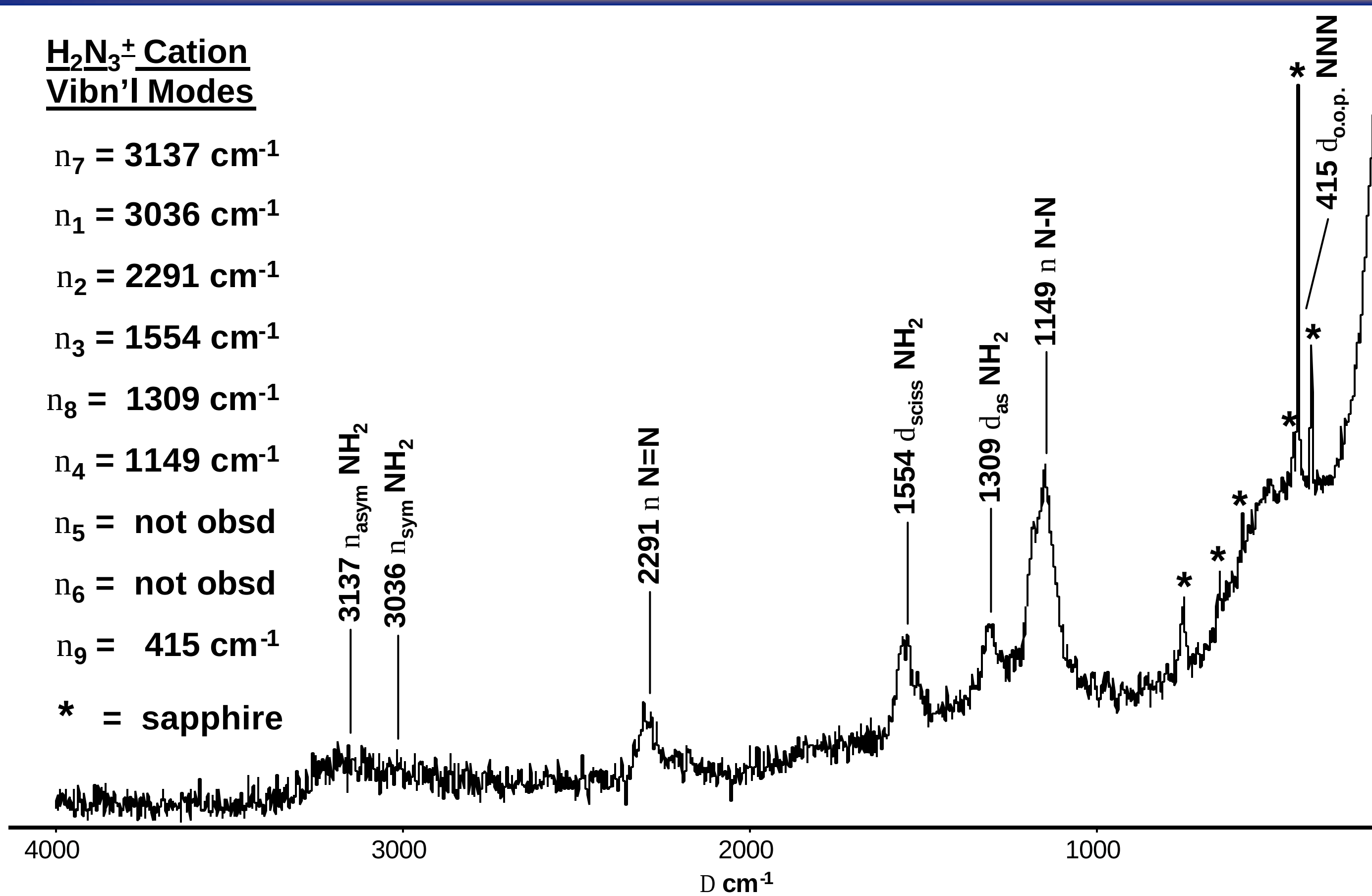
Raman Spectrum of $H_2N_3^+HF_2^-$ in HF

$H_2N_3^+$ Cation
Vibn'l Modes

- n_7 = 3137 cm^{-1}
- n_1 = 3036 cm^{-1}
- n_2 = 2291 cm^{-1}
- n_3 = 1554 cm^{-1}
- n_8 = 1309 cm^{-1}
- n_4 = 1149 cm^{-1}
- n_5 = not obsd
- n_6 = not obsd
- n_9 = 415 cm^{-1}
- * = sapphire



New Results (cont)

- Repeating previous preparations was found to give impure products and yields of 50% or less
- Carrying out the fluorination reactions in solution at low temperatures resulted in quantitative yield and high purity of FN_3
- HF is not a good solvent because it protonates HN_3 to give $H_2N_3^+HF_2^-$
- Suitable solvents are fluorocarbons that are compatible with F_2
- Product purity was established by Raman spectroscopy

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Raman Spectrum of FN_3 in $CFCl_3$ at -30°C

- FN3 was generated by fluorinating HN_3 in $CFCl_3$ and was stable at ¡ -30°C

<u>FN_3 Vibn'l Modes</u>

n_1 = 2034 cm^{-1}

[n_2 = 1085 cm^{-1}]

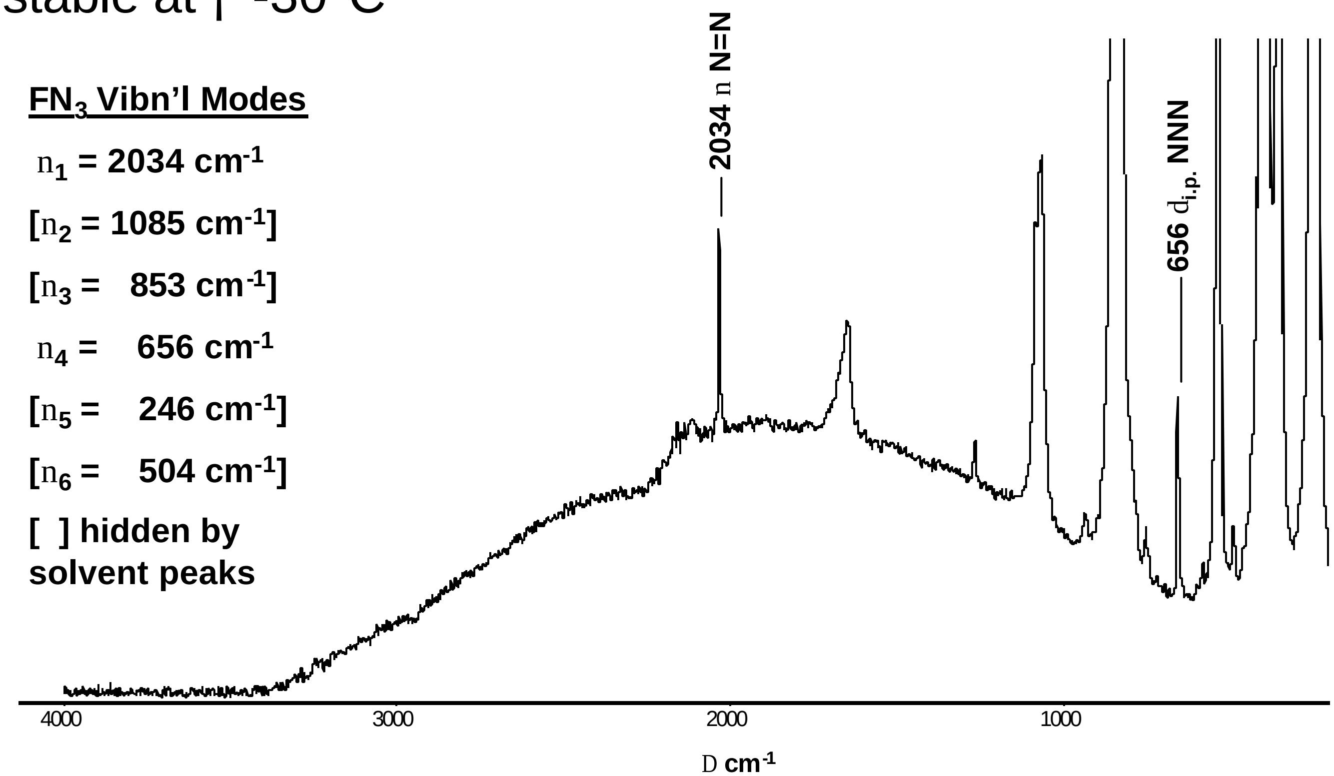
[n_3 = 853 cm^{-1}]

n_4 = 656 cm^{-1}

[n_5 = 246 cm^{-1}]

[n_6 = 504 cm^{-1}]

[ ] hidden by solvent peaks



Raman Spectrum of FN_3 in CF_3CHFCF_3 at -64°C

<u>FN_3 Vibn'l Modes</u>

n_1 **= 2037 cm^{-1}**

n_2 **= 1085 cm^{-1}**

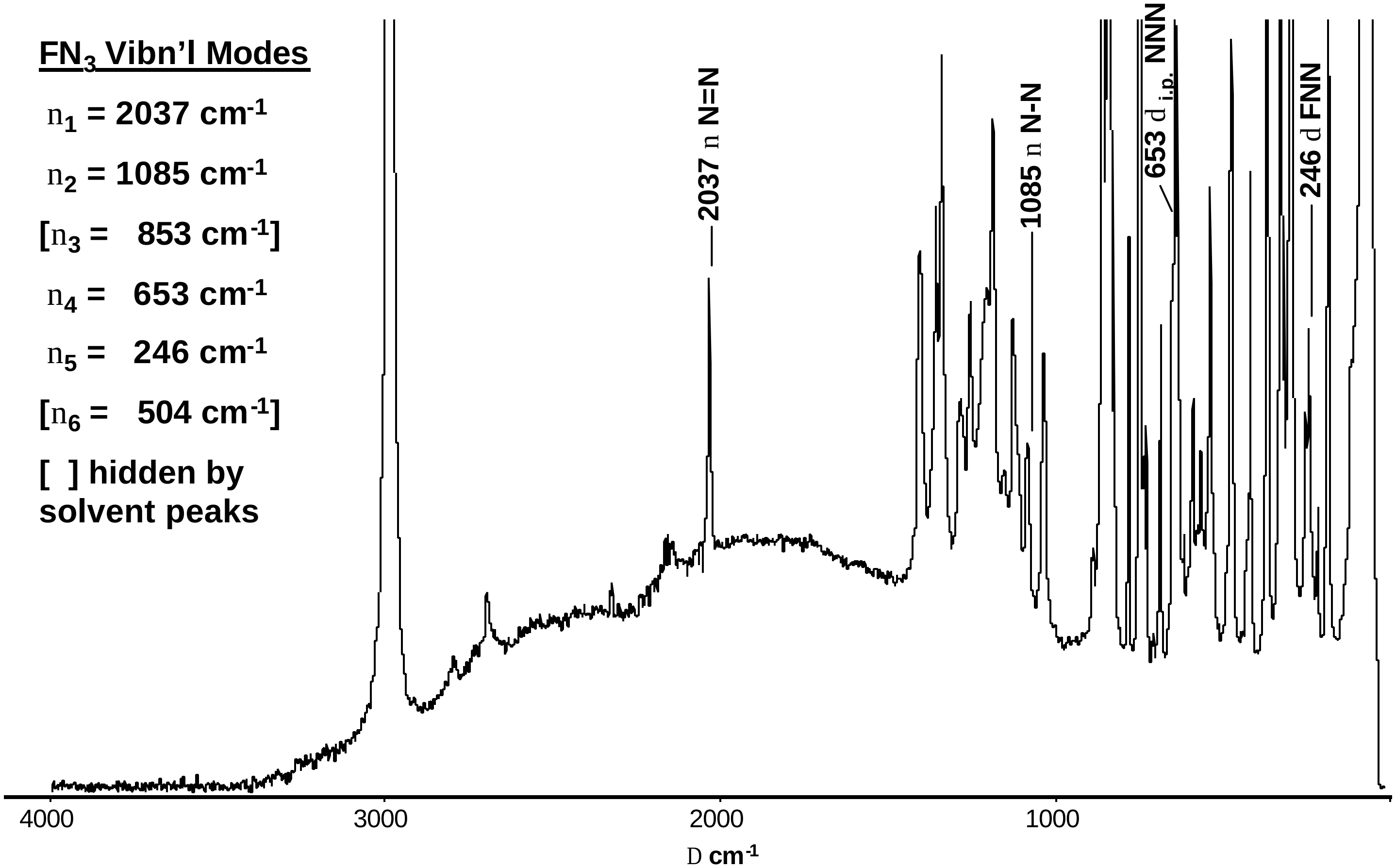
[n_3 = 853 cm^{-1}]

n_4 **= 653 cm^{-1}**

n_5 **= 246 cm^{-1}**

[n_6 = 504 cm^{-1}]

[ ] hidden by solvent peaks



Solutions of FN_3 in CF_3CHFCF_3

Consequences of Reacting F_2 with HN_3 that is Not in Solution

Safe Production of FN_3

- Shock sensitive HN_3 was replaced by insensitive $(CH_3)_3SiN_3$

$$(CH_3)_3SiN_3 + F_2 \xrightarrow[\text{Solvent}]{\text{Pure or diluted } F_2} FN_3 + (CH_3)_3SiF$$

- FN_3 was also produced in quantitative yield and high purity

Extension of Synthesis from FN_3 to ClN_3

- Natural Progression in Search for Polynitrogen Precursor
- ClN_3 extremely Shock Sensitive and Thermally Unstable
- Reaction Chemistry of ClN_3 Relatively Unstudied
- Improved Synthesis Needed

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Prior Syntheses of ClN_3

- Raschig, 1908

  $$HN_3 + HOCl \longrightarrow ClN_3 + H_2O$$

- Browne, 1943

  $$AgN_3/Et_2O + Cl_2 \longrightarrow ClN_3 + AgCl$$

- Coombe, 1981

  $$NaN_3/H_2O + Cl_2 \longrightarrow ClN_3 + HN_3$$

- Klapötke, 1994

  $$3\ (CH_3)_3SiN_3 + 3\ ClNO_2 \longrightarrow 2\ ClN_3 + 2\ N_2O + \text{“}N_2O_3\text{”} + (CH_3)_3SiCl + (CH_3)_3SiOSi(CH_3)_3$$

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Synthesis of ClN_3

- Modification of Synthetic Method Substituting Cl_2 for F_2

- Theoretical Calculation [B3LYP(5)/6-311++G(2d,p)]

$$HN_3 + Cl_2 \xrightarrow{} ClN_3 + HCl$$

Gas Phase, -273°C

?H (0K) = +2.2 kcal/mol (±5 kcal/mol)

- Reaction Essentially Thermochemically Neutral

- Equilibrium Reactions in $CFCl_3$ and CF_3CHFCF_3 at -40°C

$$HN_3 + Cl_2 \rightleftarrows ClN_3 + HCl$$

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Synthesis of ClN_3 (cont)

- Modification of Synthetic Method Substituting ClF for F_2

- Theoretical Calculation [B3LYP(5)/6-311++G(2d,p)]

  $$HN_3 + ClF \longrightarrow ClN_3 + HF$$

  Gas Phase, -273°C

  ?H (0K) = -26.6 kcal/mol (±5 kcal/mol)

- Quantitative Reaction in CHF_3 at -70°C

  $$HN_3 + ClF \longrightarrow ClN_3 + HF$$

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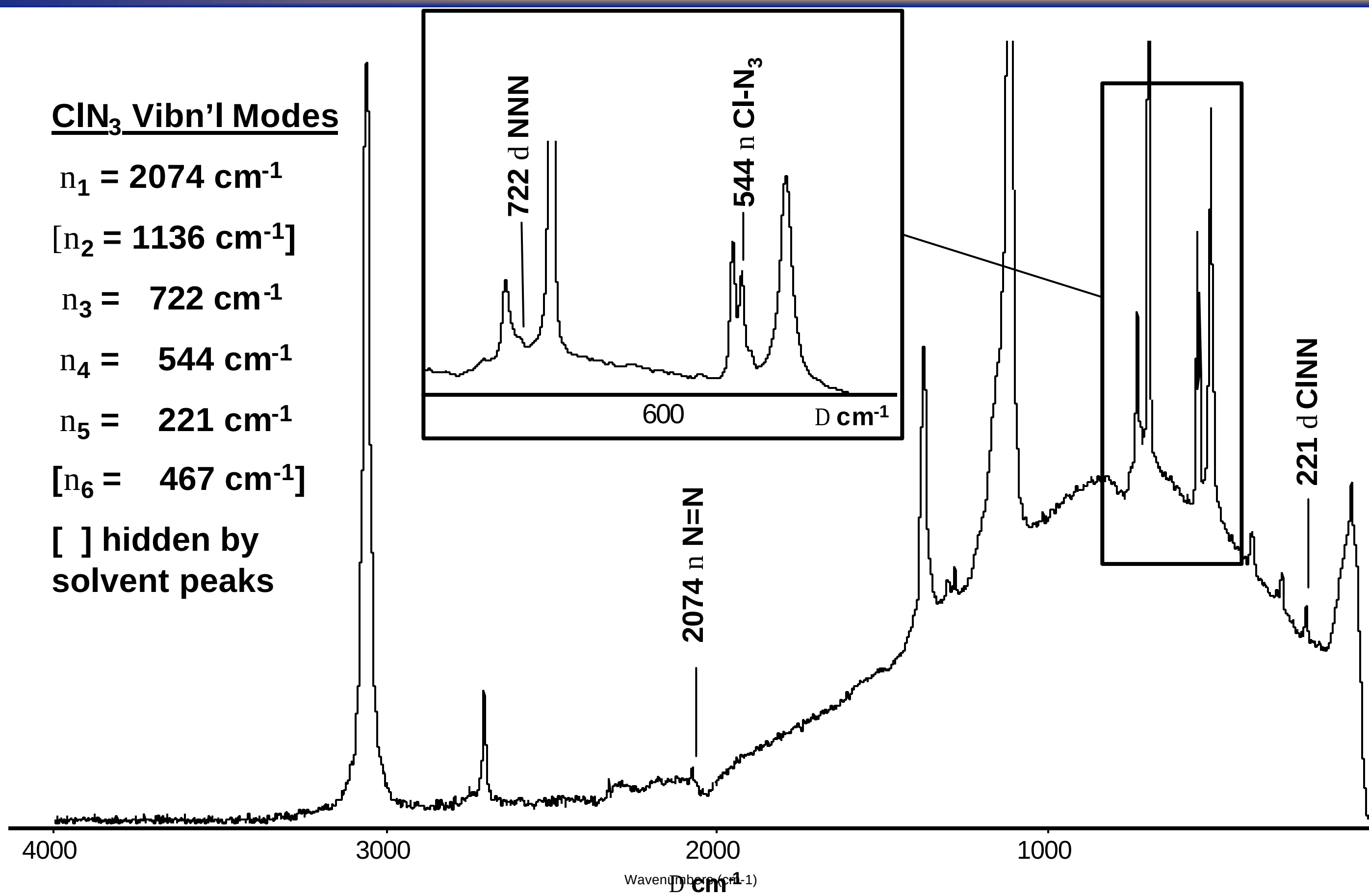
Raman Spectrum of ClN_3 in CHF_3 at -70°C

<u>ClN_3 Vibn'l Modes</u>

- ν_1 = **2074 cm^{-1}**
- [ν_2 = **1136 cm^{-1}**]
- ν_3 = **722 cm^{-1}**
- ν_4 = **544 cm^{-1}**
- ν_5 = **221 cm^{-1}**
- **[ν_6 = 467 cm^{-1}]**

[ ] hidden by solvent peaks



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Bromine Azide and Iodine Azide Syntheses

- Theoretical Calculations [B3LYP(5)/6-311++G(2d,p)]

$HN_3 + Br_2 \longrightarrow BrN_3 + HBr$

?H (0K) = +12.9 kcal/mol (±5 kcal/mol)

Unfavorable Endothermic Reaction

$HN_3 + BrF \longrightarrow BrN_3 + HF$

?H (0K) = -19.8 kcal/mol (±5 kcal/mol)

$3\ BrF \longrightarrow BrF_3 + Br_2$

$HN_3 + I_2 \longrightarrow IN_3 + HI$

?H (0K) = +21.1 kcal/mol (±5 kcal/mol)

Unfavorable Endothermic Reaction

$HN_3 + IF \longrightarrow IN_3 + HF$

?H (0K) = -11.1 kcal/mol (±5 kcal/mol)

$5\ IF \longrightarrow IF_5 + 2\ I_2$

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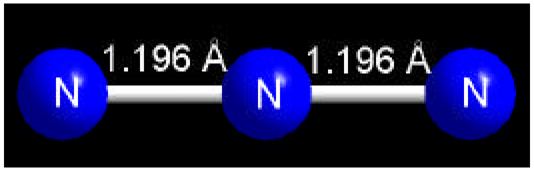
Search for a Bulk Synthesis of N_3^+



- Theoretical calculations predict the N_3^+ cation to be 80.1 K*cal/mol* more stable than its most likely decomposition products, N^+ and N_2
- The N_3^+ cation has been observed in nitrogen plasma, but has neither been isolated in bulk nor been well characterized
- The N_3^+ cation would make a good candidate for an all-nitrogen ionic salt because of its high kinetic barrier and the fact that the corresponding parent radical, N_3, is vibrationally stable
- Extensive experimental efforts are presently being made to prepare and characterize this ion

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Attempt to Prepare N_3SbF_6

- FN_3 was reacted with SbF_5 in $CFCl_3$ solution
- White, room temperature stable solid was obtained which was identified as $SbCl_4^+SbCl_xF_{(6-x)}^-$
- SbF_5 undergoes rapid F/Cl exchange with $CFCl_3$
- Solutions of FN_3 in CF_3CHFCF_3 and SbF_5 in HF were reacted at -64°C
- White, room temperature stable solid was obtained which was identitified as $NH_2F_2^+SbF_6^-$ by its Raman spectrum and confirmed by x-ray diffraction

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Explanation for $NH_2F_2^+$ Formation

- Most likely mechanism is an *a*-nitrogen-bridged donor/acceptor adduct between FN_3 and SbF_5, followed by N_2 elimination and addition of two HF molecules

$$\text{N-N-N(F)} \rightarrow SbF_5 \xrightarrow{-N_2} \text{F-N} \rightarrow SbF_5 \xrightarrow{+2\,HF} NH_2F_2^+SbF_6^-$$

Reaction of FN_3 with SbF_5 in the Presence of $(CH_3)_3SiF$

- FN_3 was generated from $(CH_3)_3SiN_3$ and F_2 in CF_3CHFCF_3 solution and mixed with SbF_5

- White solid product was obtained in CF_3CHFCF_3 solution

- Raman spectrum showed bands characteristic for a $(CH_3)_3Si$-containing compound with SbF_6^-

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Summary

- A scalable method for the safe production and handling of FN_3 has been developed by direct fluorination of either HN_3 or $(CH_3)_3SiN_3$ in polyfluorohydrocarbon or perhalocarbon solutions
- HF protonates HN_3 to give $H_2N_3^+HF_2^-$ in HF solution
- A new method for the synthesis of ClN_3 is reported
- SbF_5 undergoes rapid F/Cl exchange with $CFCl_3$ to give $SbCl_4^+$ antimonates
- FN_3 undergoes N_3/Cl exchange with $CFCl_3$ at >-20°C
- In the presence of HF, FN_3 forms with SbF_5 the $NH_2F_2^+SbF_6^-$ salt
- $(CH_3)_3SiF$ forms a solid compound with SbF_5

Project Sponsors

Blooms in the Mojave Desert

Sunset in the Mojave Desert near the Air Force Research Laboratory