IMPROVED SYNTHESIS AND REACTION CHEMISTRY OF FN_3

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Background

- FN_3 was first prepared 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 in 1986 and by H. Willner 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

Previous Approaches

- Haller, Benard, Willner

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

- Pankratov

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

- AFRL

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

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

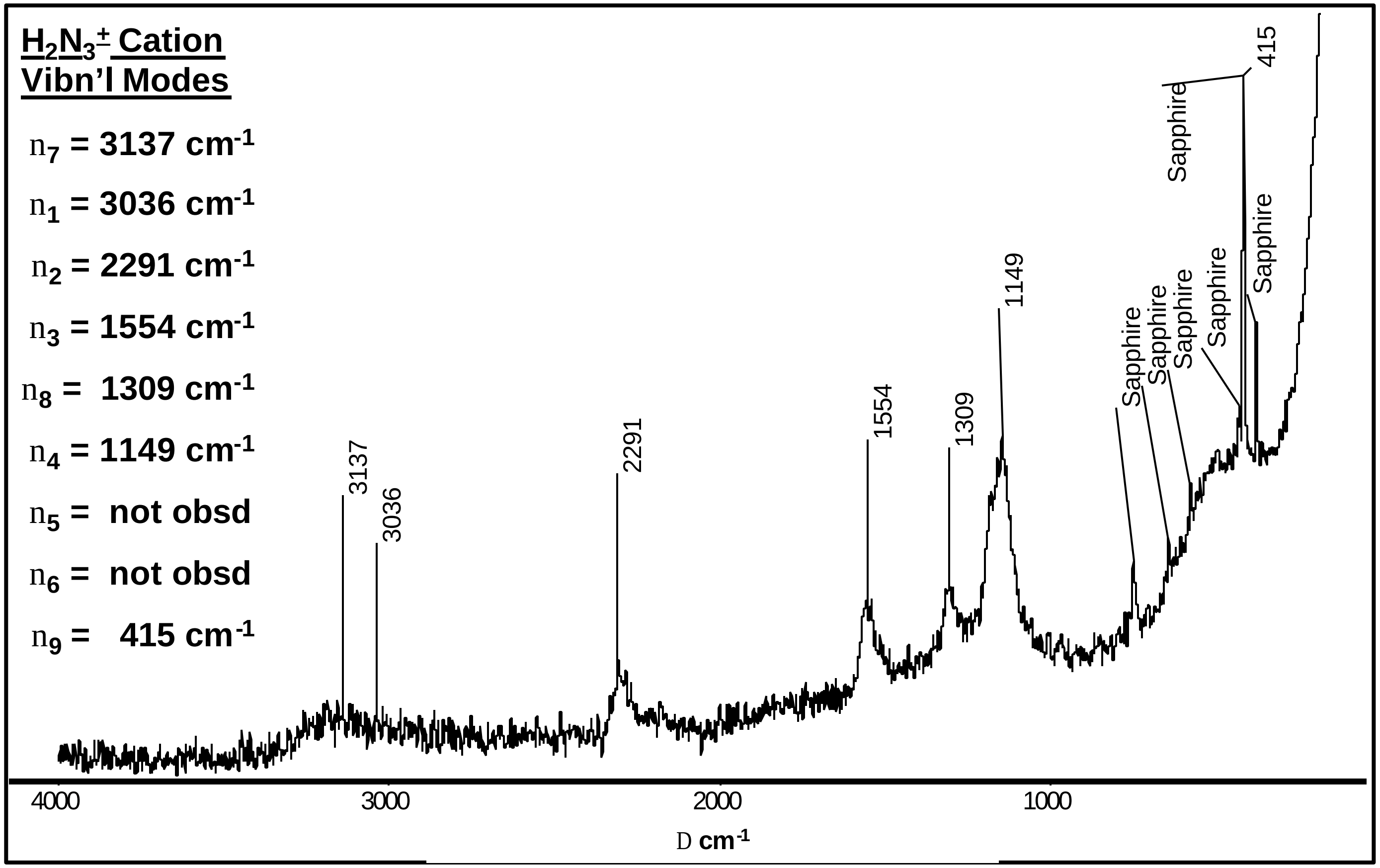
New Results

- 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 $H_2N_3^+HF_2^-$

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

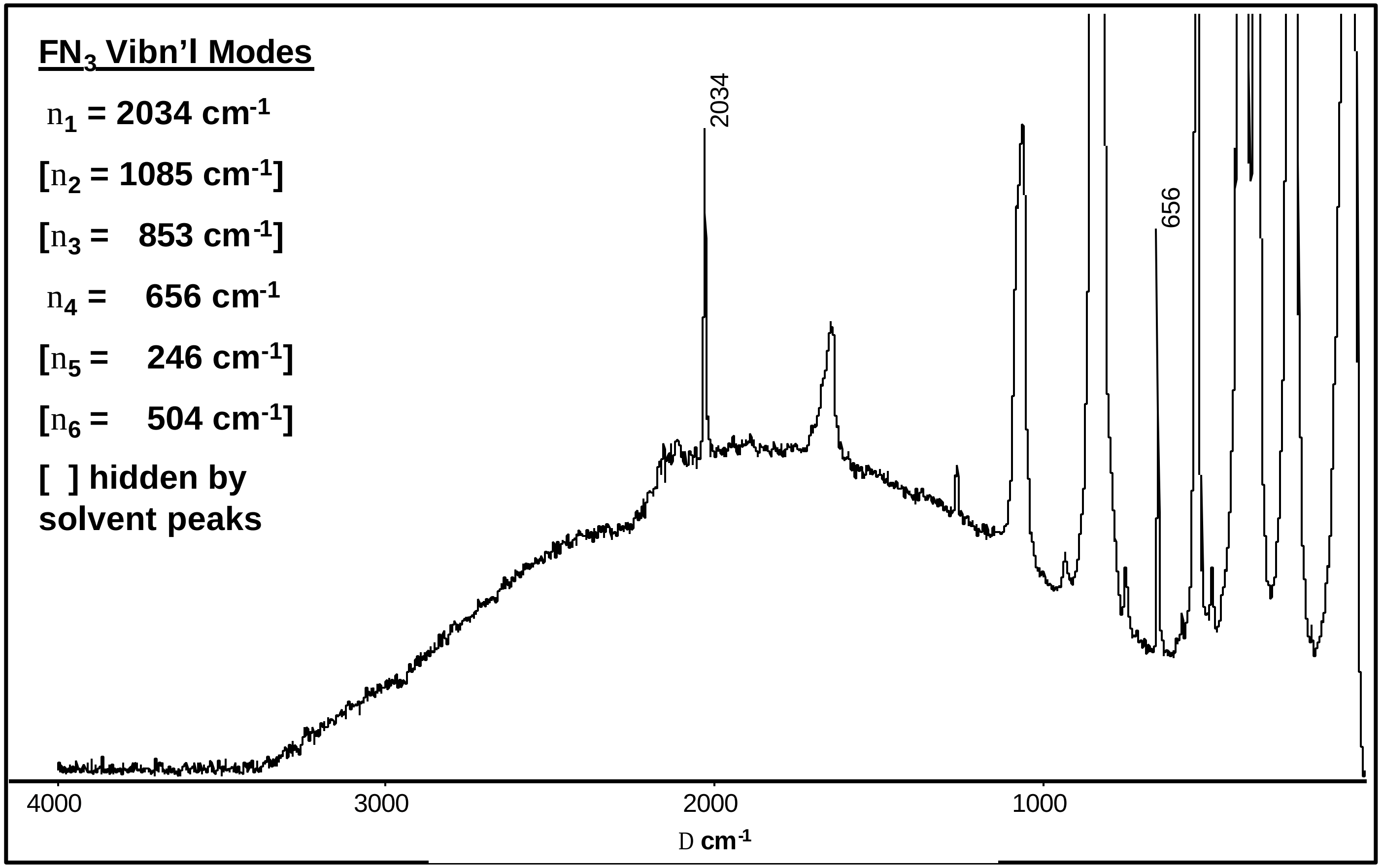
n_6 = not obsd

n_9 = 415 cm^{-1}

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 $H_2N_3^+HF_2^-$
- Suitable solvents are fluorocarbons that are compatible with F_2
- Product purity was established by Raman spectroscopy

Raman Spectrum of FN_3 in CF_3Cl



FN$_3$ Vibn'l Modes

n_1 = 2034 cm^{-1}

[n_2 = 1085 cm^{-1}]

[n_3 = 853 cm^{-1}]

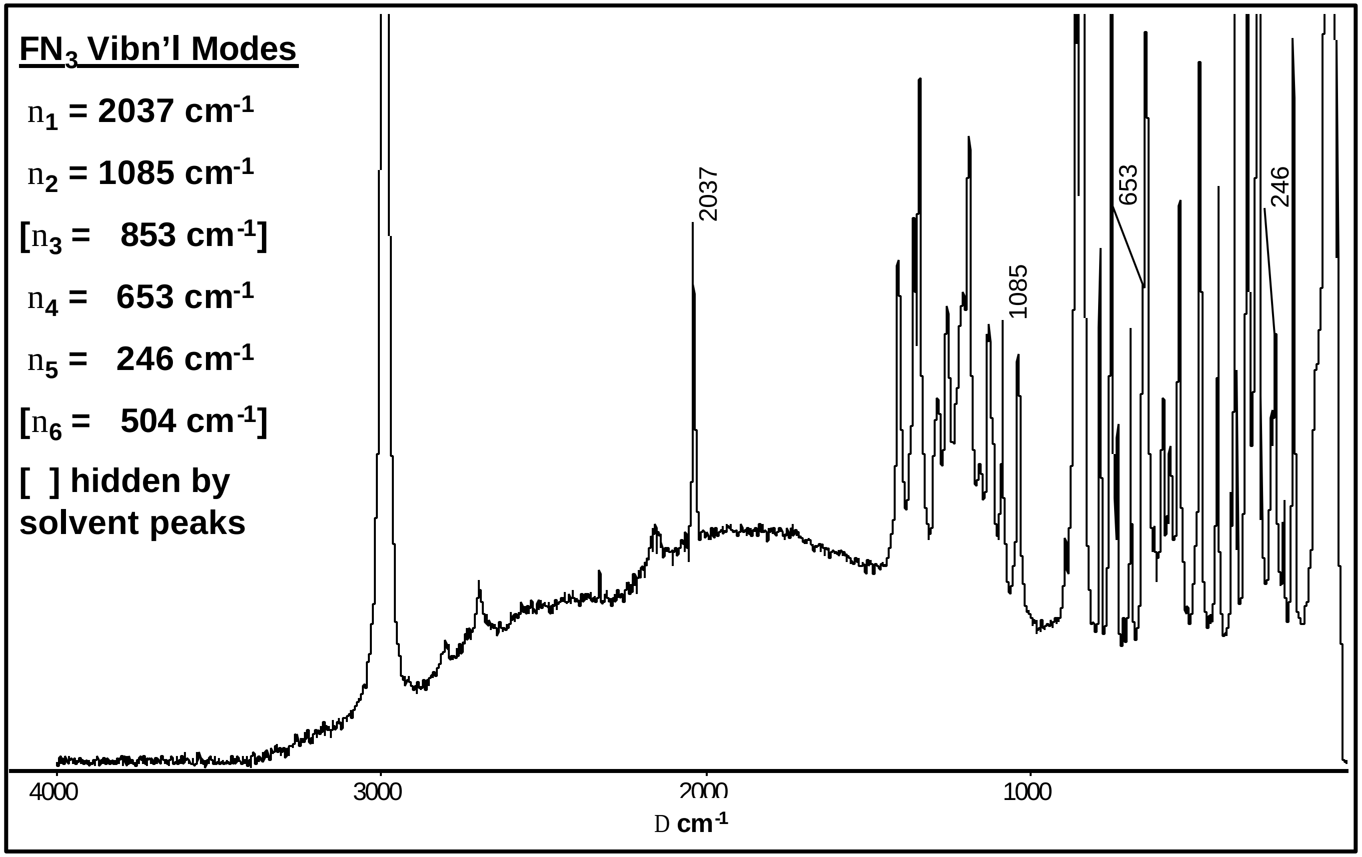
n_4 = 656 cm^{-1}

[n_5 = 246 cm^{-1}]

[n_6 = 504 cm^{-1}]

[ ] hidden by solvent peaks

Raman Spectrum of FN_3 in CF_3CHFCF_3



FN_3 Vibn'l Modes

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

Consequences of Reacting HN_3 with F_2 Not in Solution

Safe Production of FN_3

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

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

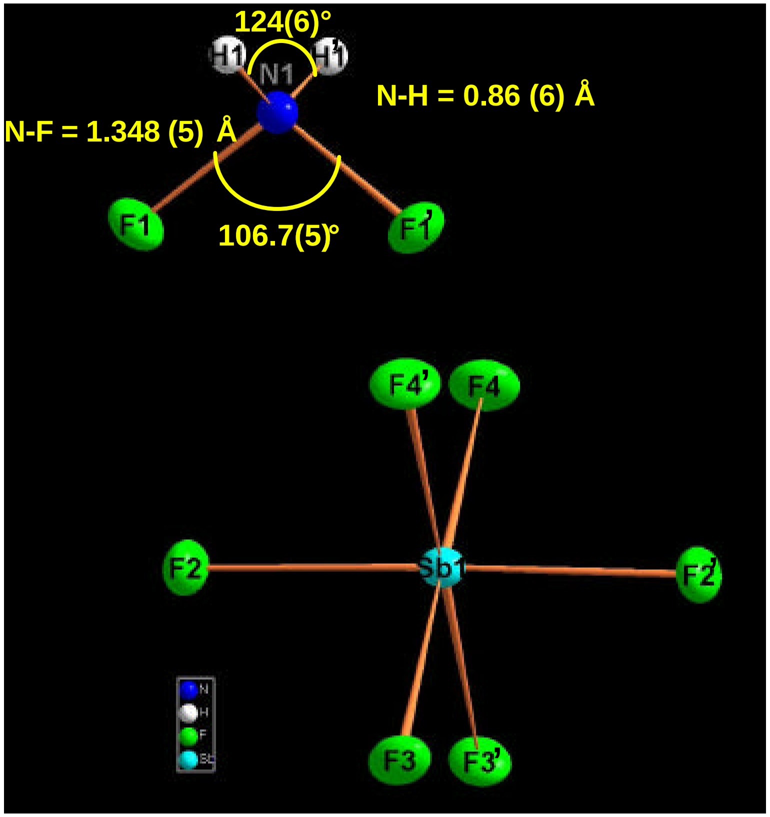
- FN_3 was also produced in quantitative yield and high purity

Solutions of FN_3 in CF_3CHFCF_3

Reaction Chemistry of FN_3

- 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

$NH_2F_2SbF_6$ Crystal Structure



Unit cell dimensions (Å)

Monoclinic (twinned)

Space Group: *P2/n*

a = 7.078(3); b = 5.678(2); c = 7.353(3)

ß = 91.366(8)°

Volume ($Å^3$) = 295.4(2)

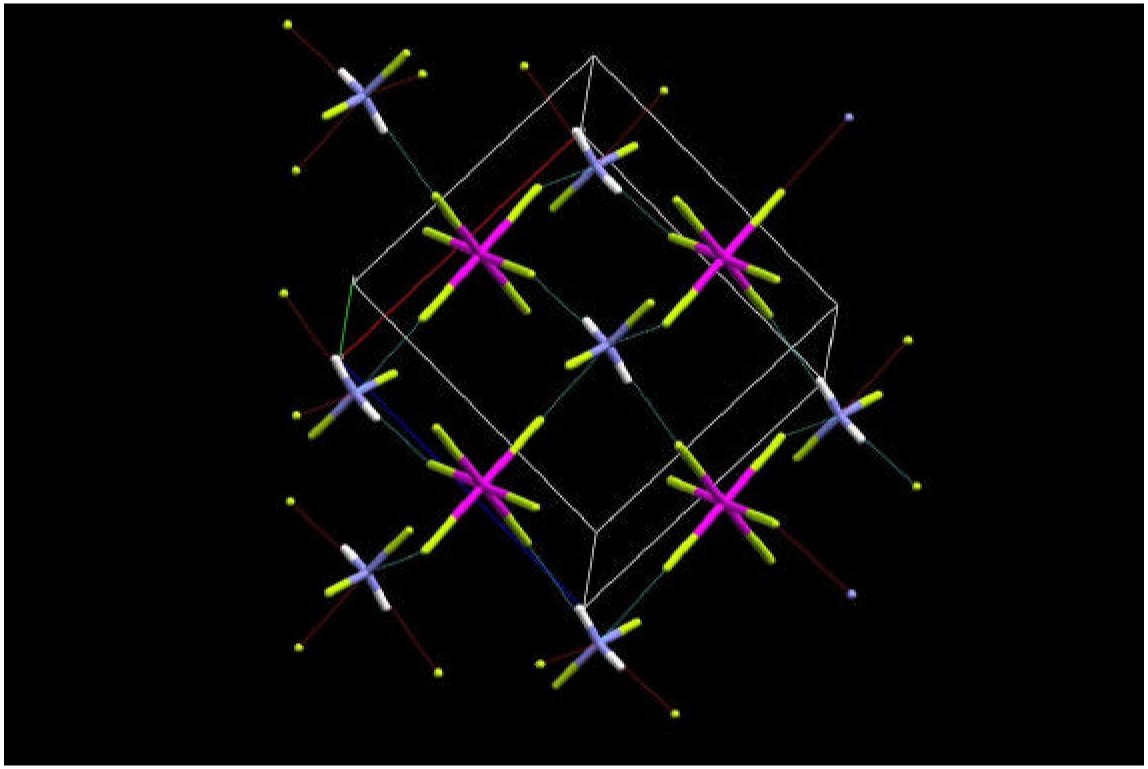
Z = 2; T = 173 K; D_{calc} ($g\ cc^{-1}$) = 3.258

$R1$ = 0.0321; $wR2$=0.0898; S = 1.04

Sb-F Distances (Å) & Angles (°)

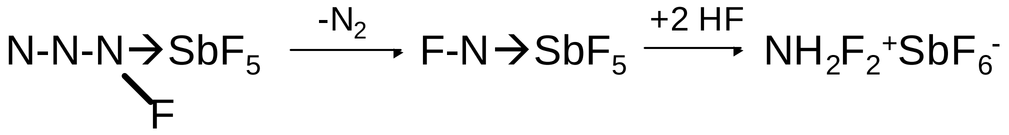
Sb1-F2 = 1.861(4); Sb1-F3 = 1.887(3)
Sb1-F4 = 1.857(3)
F2-Sb1-F2' = 178.2(1); F3-Sb1-F4 = 177.5(1)
F2-Sb1-F4 = 90.9(2)

Packing Diagram for $NH_2F_2SbF_6$



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



$$\mathrm{N\text{-}N\text{-}\underset{F}{N}} \rightarrow \mathrm{SbF_5} \xrightarrow{-N_2} \mathrm{F\text{-}N} \rightarrow \mathrm{SbF_5} \xrightarrow{+2\ HF} \mathrm{NH_2F_2^+SbF_6^-}$$

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 and no bands due to N_3-groups

Addition of FN_3 across Double Bonds

- Addition reactions of FN_3 were studied using the following substrates
  - *trans*-stilbene
  - perfluoropropene
  - chlorotrifluoroethylene

Reaction of FN_3 with trans-Stilbene

- FN_3 was generated from $(CH_3)_3SiN_3$ and F_2 in solution and mixed with $C_6H_5CH{=}CHC_6H_5$ in CF_3Cl at -78C
  - ➢ Yellow-orange powder
  - ➢ FT Raman spectra reveal no N_3 bands
  - ➢ Evidence suggests cyclization and formation of a triazole

Reactions of FN_3 with $CFCl{=}CF_2$ and $CF_2{=}CFCF_3$

- Reactions of FN_3 were conducted using fluorinated olefins
  - ➢ FN_3 with $CFCl{=}CF_2$ gave an addition product that was characterized by ^{19}F NMR, FT Raman spectroscopy and FTIR
  - ➢ The reaction of FN_3 with $CF_2{=}CFCF_3$ similarly yielded products that indicated an addition product

Summary

- A scalable method for the safe production and handling of FN_3 was developed by direct fluorination of either HN_3 or $(CH_3)_3SiN_3$ in solution
- HF can protonate HN_3 to give $H_2N_3^+HF_2^-$
- SbF_5 undergoes rapid F/Cl exchange with $CFCl_3$ to give $SbCl_4^+$ antimonates
- In the presence of HF, FN_3 forms with SbF_5 the $NH_2F_2^+SbF_6^-$ salt
- SbF_5 forms an adduct with $(CH_3)_3SiF$
- Addition reactions of FN_3 across double bonds were studied

Joshua Trees in the Mojave Desert

Blooms in the Mojave Desert

Sunset in the Mojave Desert near the Air Force Research Laboratory