IMPROVED SYNTHESIS AND REACTION CHEMISTRY OF FN_3

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14. ABSTRACT

FN3 was first prepared by J. F. Haller at Cornell University in 1942. Very little work was done with FN3 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 FN3 was mandatory for studying its reaction chemistry.

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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

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

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

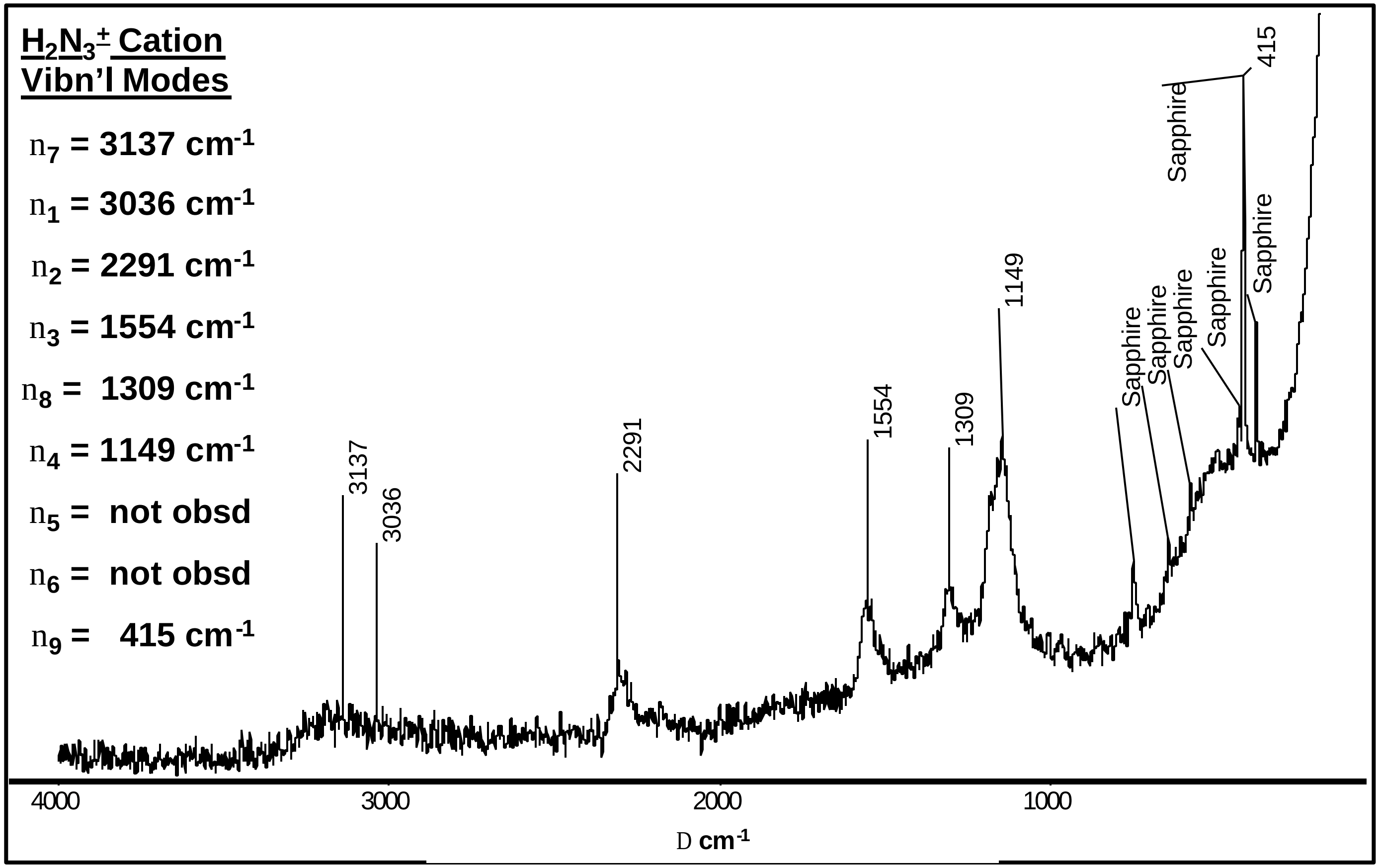
New Results

- 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

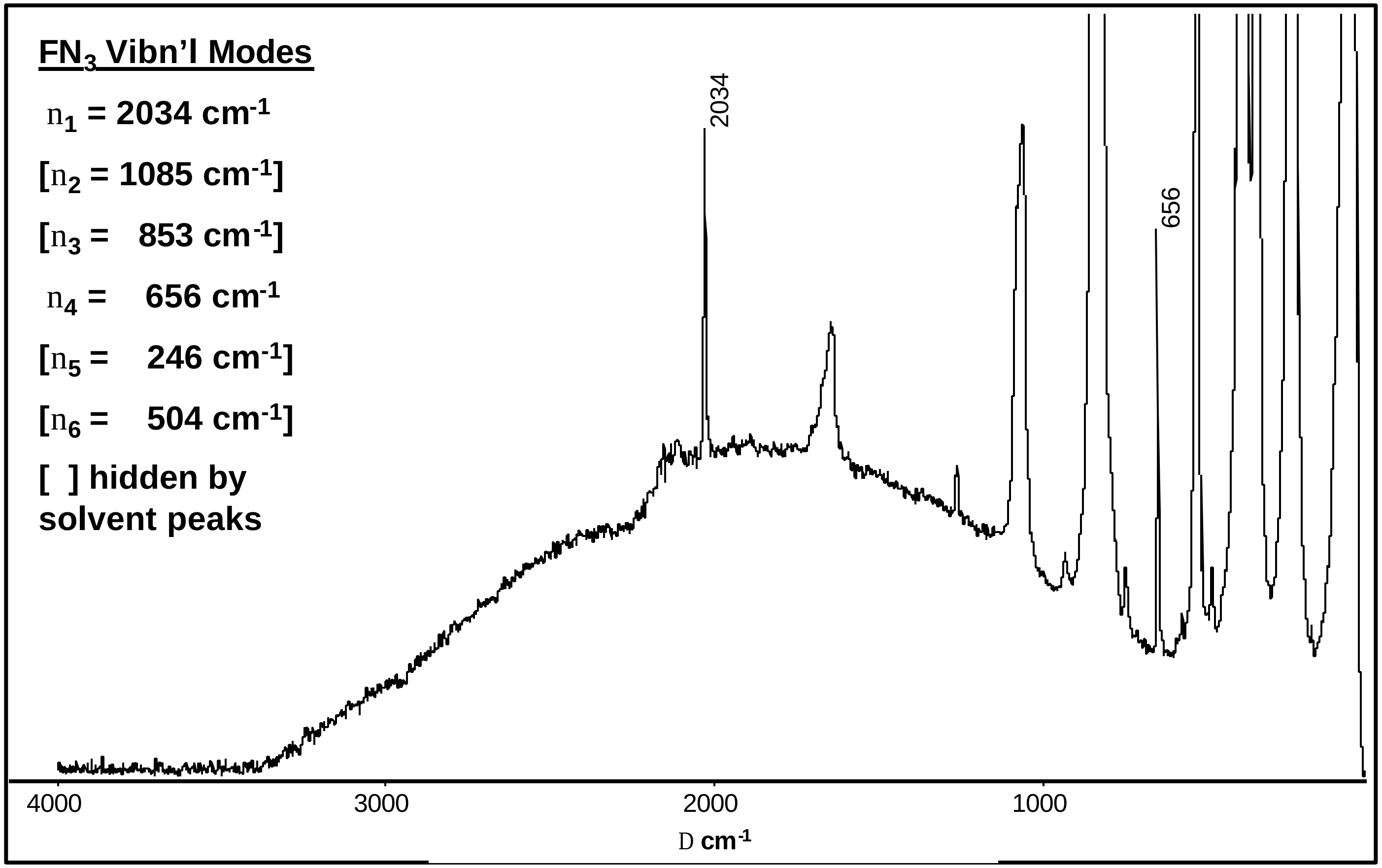
n_6 = not obsd

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}]

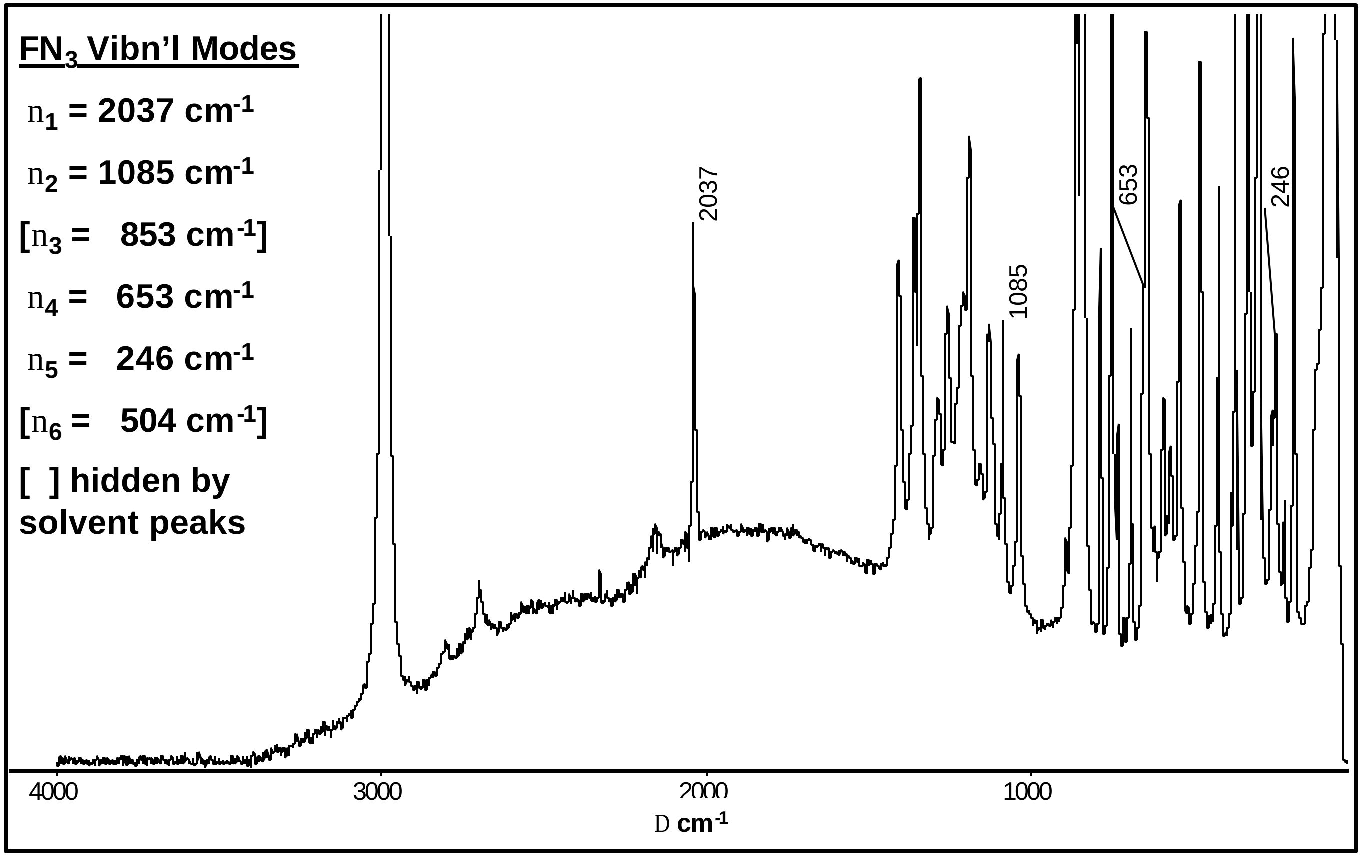
n_4 = 656 cm^{-1}

[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 $(CH_3)_3SiN_3$

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

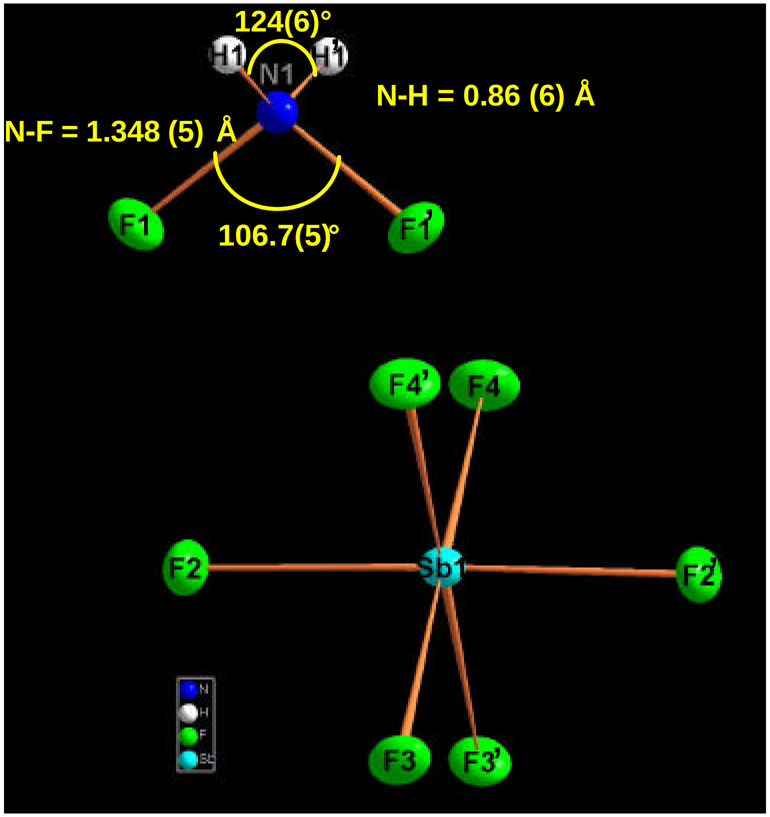
- FN_3 was also produced in quantitative yield and high purity

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*

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

$\beta = 91.366(8)°$

Volume ($Å^3$) = 295.4(2)

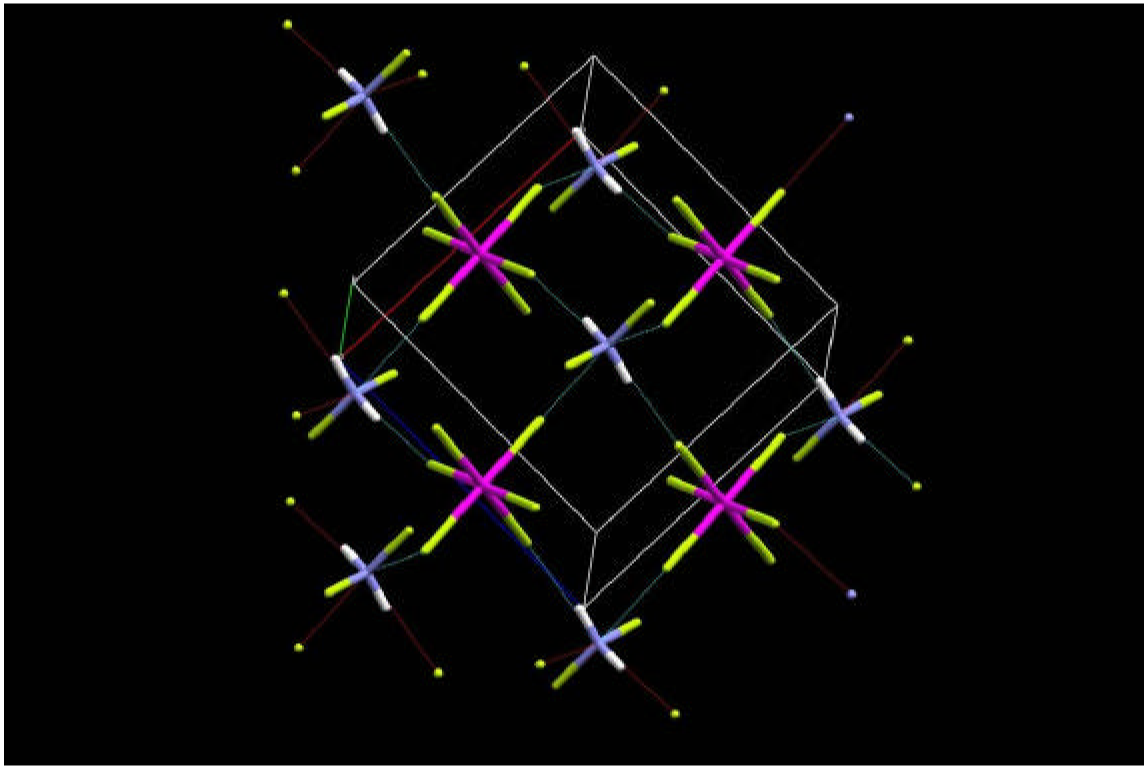
$Z = 2$; $T = 173$ K; D_{calc} ($g\ cc^{-1}$) = 3.258

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

Sb-F Distances (Å) & Angles (°)

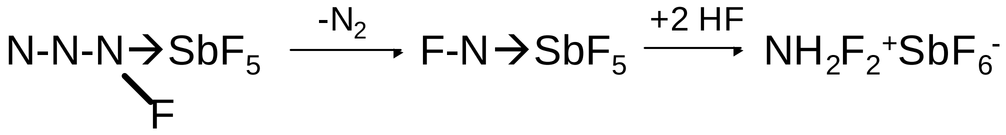
Sb1-F2 = 1.861(4); Sb1-F3 = 1.887(3)
Sb1-F4 = 1.857(3)
F2-Sb1-F2’ = 178.2(1); F3-Sb1-F4 = 177.5(1)
F2-Sb1-F4 = 90.9(2)

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



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

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 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