suggests alternative interpretations of many reactions (gasification, cyclization, hydrogenation, etc.) that involve conformational conversion.

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Infrared Spectra of the NH_3–F_2 and NH_2F–HF Complexes in Solid Argon

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Abstract: Cocondensation of Ar/NH_3 and Ar/F_2 samples at 12 K produced a weak NH_3–F_2 complex, which photolyzed to give several NH_2F–HF complexes, based on matrix infrared spectra. The major product contained HF hydrogen bonded to the nitrogen lone pair of NH_2F and exhibited $\nu_s(HF) = 3389$ cm^{-1} and $\nu_l(HF) = 750$ and 723 cm^{-1}; these observations characterize a weaker H_2FN–HF interaction than the H_3N–HF interaction and indicate weaker basicity for NH_2F than NH_3. Four NH_2F submolecule modes observed for the complex provide the first direct spectroscopic evidence for the highly reactive NH_2F molecule. The minor product exhibited HF bonded to a fluorine lone pair with $\nu_s(HF) = 3722$ cm^{-1} and $\nu_l(HF) = 596$ and 515 cm^{-1}; this spectrum characterizes a stronger interaction for NH_2F–HF than for CH_3F–HF.

Fluoramide is the simplest and perhaps the most elusive substituted amine owing to extremely high reactivity. Although there is no report of isolation or characterization of NH_2F in the literature, NH_2F has been generated from various media and postulated as a reaction intermediate[1-5] and subjected to theoretical calculations of structure,[6-8] infrared spectra,[9] inversion barrier,[10-12] and proton affinity.[13,14] In the most recent study $(NH_3F^+)(HF_2^-)(HF)_n$ salts were sublimed under vacuum, and 16-eV electron impact produced a strong mass 35 peak, which provides evidence for the evaporation of NH_2F molecules.[5] Fluorimide (NHF_2), however, is relatively stable in the gas phase, and its infrared spectrum has been recorded,[16] but under certain conditions it can be a vicious explosive.[17] Matrix photochemical reaction of the CH_4–F_2 dimer produced the CH_3F–HF complex,[18] and the analogous NH_3–F_2 matrix photochemical reaction was performed in an attempt to stabilize and characterize fluoramide in the NH_2F–HF complex. This complex follows a series of HF complexes with NH_3, alkylamines, and hydroxylamine studied in this laboratory[19-21] and compares the effect of a fluorine substituent on the spectrum of the HF complex.

Table I. New Absorptions (cm^{-1}) Observed on Cocondensation, Photolysis, and Annealing of Ar/NH_3 and Ar/F_2 Samples at 12 K[a]

$NH_3 + F_2$	$^{15}NH_3 + F_2$	NHD_2	$ND_3 + F_2$	ident.
3722	3722	3718	2735	ν_s(F) (**2**)
3626	3626	3611	2652	ν_s (**3**)
3450	3448	3452	2548	site of **1**
3389	3388	3384	2505	ν_s (**1**)
3269	3264		2399	ν_1 (**1**)
3063	3063			NH_2–HF
1568.1	1565.9	1428.9[b]	1151.4	ν_2 (**1**)
1314	1314	1312	998	$2\nu_1$ (**1**)
1243.7	1238.0	979.7	968.1	ν_2 (**1**)
966.2	962.2		748.3	NH_3–F_2
933.7	916.2	933.4	923.7	ν_3 (**1**)
781.0	781.0	obscured		NH_3–F_2
750.3	750.3	738.8[c]	560.9[d]	ν_l (in-plane) (**1**)
723.0	723.0	725.0	539.9	ν_l (out-plane) (**1**)
596.7	597.0	596	441	ν_l(F) (**2**)
514.7	514.6	515	381	ν_l(F) (**2**)

[a] Very weak bands for NH_3–HF (ref 17) are not included. [b] Absorption for NHDF–HF; other sharp bands for this mixed isotopic species appeared at 1209.2 and 1015.3 cm^{-1}. [c] Due to ν_l(HF) in ND_2F–HF. [d] Shoulder at 567.0 cm^{-1} due to ν_l(DF) in NHDF–DF.

Experimental Section

The matrix photolysis experiments involved a combination of techniques applied in other studies.[18,19] Ammonia (Matheson) and ND_3 and $^{15}NH_3$ (MSD isotopes) were diluted with argon to 200/1 or 400/1 ratios. Fluorine (Matheson) was mixed with argon to 100/1 or 200/1 ratios in a passivated stainless-steel system, and in some experiments, this sample was passed through a U-tube immersed in liquid nitrogen to remove HF before deposition. Samples were codeposited at 3–4 mmol/h each for

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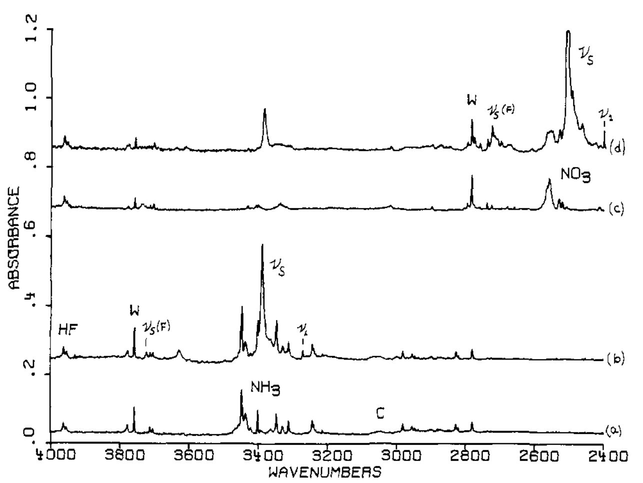

Figure 1. Infrared spectra in the 4000–2400-cm^{-1} region for fluorine and ammonia samples codeposited at 12 K: (a) Ar/NH$_3$ = 400/1 and Ar/F$_2$ = 200/1; (b) after photolysis for 30 min; (c) Ar/ND$_3$ = 200/1 and Ar/F$_2$ = 200/1; (d) after photolysis for 60 min.

4-5 h on a 12 K CsI window. Infrared spectra were recorded on a Nicolet 7199 or Perkin-Elmer 983 spectrometer both before and after mercury arc photolysis (BH-6-1) through a water filter and sample annealing to 28 ± 2 K.

Results

New infrared absorptions produced in NH$_3$/F$_2$ photolysis experiments are listed in Table I. Figure 1 illustrates spectra in the 4000–2400-cm^{-1} region before and after photolysis of F$_2$ and NH$_3$ or ND$_3$ samples. Note the trace of HF, water (labeled W), NH$_3$–HF complex (labeled C),[19] ammonia, and ammonia dimer[22,23] present in the original NH$_3$ spectrum. Photolysis produced a strong new band at 3389 cm^{-1} (labeled ν_s in Figure 1b), a sharp 3722-cm^{-1} band (ν_s(F)), and several weaker bands given in the table. The original ND$_3$ spectrum revealed D$_2$O used to exchange the vacuum manifold, a trace of DF (A = absorbance = 0.01) formed by reaction of ND$_3$ and F$_2$ during sample condensation, ND$_3$ and NHD$_2$ bands, and ND$_3$–DF (A = 0.002 not shown).[19] Photolysis produced a strong ν_s band at 2505 cm^{-1}, several nearby weaker bands, and new weak bands in the HF region that were slightly shifted from their positions in the NH$_3$ experiment. Figure 2 shows expanded scale spectra in the 1100–700-cm^{-1} region. The original NH$_3$ spectrum exhibited strong NH$_3$ monomer and dimer bands. The original NH$_3$ spectrum exhibited strong NH$_3$ monomer bands, a weak ammonia dimer band at 999.8 cm^{-1} (labeled D), a new resolved 966.2-cm^{-1} band, and a weak 781.0-cm^{-1} absorption labeled PC; sample warming to 27 ± 2 K markedly increased the 966.2- and 781.0-cm^{-1} bands and slightly reduced NH$_3$ monomer and dimer bands. The best indication of the relative population of (NH$_3$)$_2$ in these experiments can be obtained from the spectrum in Figure 2a for a final Ar/NH$_3$/F$_2$ = 800/1/2 matrix; the sharp D (dimer) band at 999.8 cm^{-1} is a very small fraction of the total absorption from 950 to 1020 cm^{-1}, which except for the sharp PC band at 966.2 cm^{-1} is all due to NH$_3$ monomer.[22] Photolysis virtually destroyed the PC bands and produced a new 933.7-cm^{-1} band (ν_4) in this region. In the larger 1700–500-cm^{-1} region, shown in Figure 3, a strong 750.3, 723.0 cm^{-1} doublet (labeled ν_1), a weak ν_1(F) doublet, and four sharp weaker bands labeled ν_2, $2\nu_1$, ν_3, and ν_4 were produced. Prolonged photolysis destroyed the ν_s(F) and ν_1(F) bands and slightly increased the other new bands.

The original ND$_3$ spectrum, shown in Figure 3c, revealed a new resolved 748.3-cm^{-1} PC band and about 25% NHD$_2$, HOD, and D$_2$O from isotopic exchange in the deuteriation process. Photolysis reduced the 748.3-cm^{-1} band and produced a ν_1 doublet at 560.9 and 539.9 cm^{-1} and ND$_3$ counterparts for the sharp bands observed in this region from NH$_3$. In addition 4 sharp weak bands were observed at 1429, 1209, 1015, and 933 cm^{-1} (labeled ν'). In the low-frequency region, a ν_1(F) doublet was observed at 443 and 380 cm^{-1}. Again prolonged photolysis decreased the ν_s(F) and ν_1(F) bands and slightly increased the other product absorptions. In these three experiments with varying degrees of deuterium enrichment, absorptions of the NH$_3$ product, one mixed H–D product, and one fully deuteriated product tracked together as 3 units, but the relative populations of the isotopic products varied with precursor deuterium enrichment.

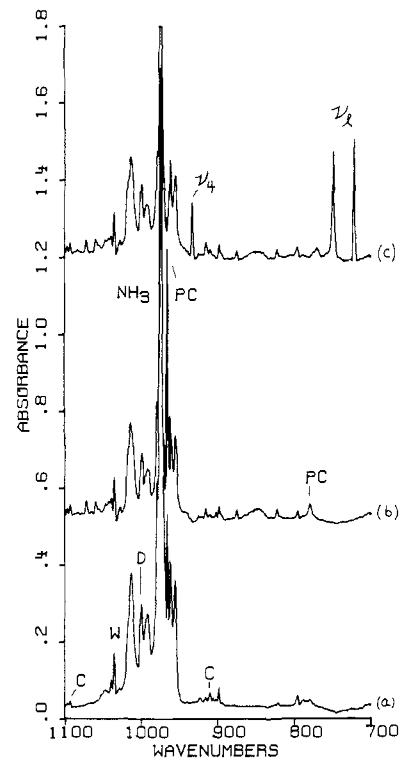

Figure 2. Expanded scale infrared spectra in the 1100–700-cm^{-1} region for fluorine and ammonia samples: (a) Ar/NH$_3$ = 400/1 and Ar/F$_2$ = 200/1 codeposited at 12 K; (b) after temperature cycling to 27 ± 2 K; (c) after photolysis for 30 min.

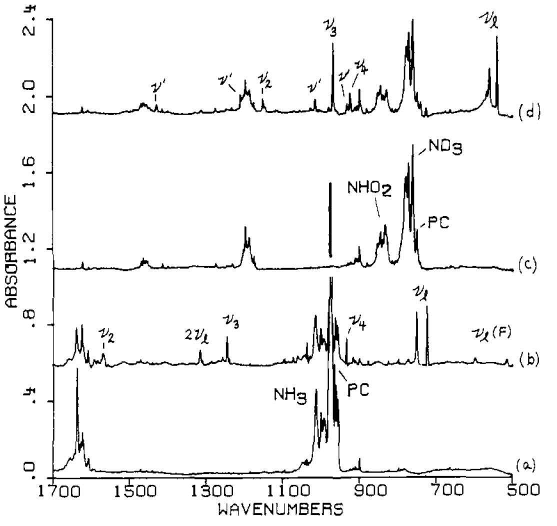

Figure 3. Infrared spectra in the 1700–500-cm^{-1} region for the same samples as Figure 1.

Similar experiments with more concentrated 200/1 NH$_3$ and ND$_3$ samples gave the same but more intense product bands. Sample annealing after photolysis produced a sharp 3063-cm^{-1} band and FO$_2$ absorption[24] at 1489 cm^{-1} and left the other product

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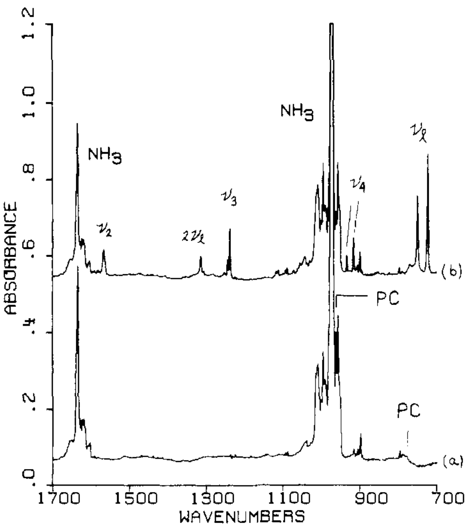

Figure 4. Infrared spectra in the 1700–700-cm^{-1} region for fluorine and ammonia samples codeposited at 12 K: (a) Ar/$^{15}NH_3$ = 400/1 approximately 70% ^{15}N enrichment; (b) after photolysis for 60 min.

absorptions unchanged. Sample annealing before photolysis increased the 966- and 781-cm^{-1} bands and the very weak NH_3–HF bands and decreased NH_3 monomer and dimer absorptions, as illustrated in Figure 2.

Three experiments were performed with $^{15}NH_3$; owing to residual $^{14}NH_3$ adsorbed on the walls of the vacuum system, these samples contained successive stages of $^{15}NH_3$ substitution and the final sample was only 70% ^{15}N enriched. Figure 4 illustrates a representative spectrum. The ν_l doublets and $2\nu_l$ exhibited no $^{15}NH_3$ shift, but the ν_1, ν_2, ν_3, and ν_4 product bands were shifted and the latter two were resolved into ^{14}N and ^{15}N doublets.

Concern for the potential role of ammonia dimer in the ammonia–F_2 reaction and the desire to synthesize NH_2F directly prompted experiments with hydrazine. Anhydrous hydrazine was studied alone, with F_2 and with HF in solid argon, and no absorptions are common to bands reported above. The strongest hydrazine fundamental at 954 cm^{-1} was not observed on the NH_3 band at 956 cm^{-1}, and strong N_2H_4 bands at 811 and 1084 cm^{-1} are not detected in any of the spectra. The N_2H_4–F_2 matrix reaction gave a N_2H_3F–HF complex with no evidence for NH_2F. The N_2H_4–HF complex exhibited a strong ν_s fundamental at 2928 cm^{-1}, which will be described fully in a later report.[25]

Discussion

The new precursor complex and photochemical products will be identified from their infrared absorptions, vibrational assignments will be made, and structure and bonding comparisons will be given for related amine and fluoride complexes.

Identification. Infrared spectra of samples prepared by codeposition of ammonia and fluorine in excess argon revealed absorptions due to the ammonia system[22,23] and the trace impurities in commercial fluorine. The strongest NH_3 mode ν_2 is complicated by inversion splitting, rotation, and the presence of weak ammonia dimer and water complex bands. However, extra absorptions that grow on annealing before photolysis and are markedly decreased by photolysis are candidates for the NH_3–F_2 precursor complex (see Figure 2). The presence of excess F_2 in these experiments retards the formation of $(NH_3)_2$ in favor of the heterodimer NH_3–F_2. The sharp band at 966.2 cm^{-1} resolved from the strongest NH_3 band at 974 cm^{-1} is assigned to the precursor complex; the ND_3 counterpart was observed at 748.3 cm^{-1}. The fluorine molecule is, of course, not infrared active, but the fluorine fundamental has been observed at 892 cm^{-1} in solid argon by matrix Raman techniques.[26] In a complex, however, the fluorine fundamental is allowed by symmetry but it is weak in infrared intensity. The weak 781-cm^{-1} band is appropriate for the F_2 fundamental in the precursor complex. The red shift in the F_2 fundamental suggests charge transfer into the unfilled fluorine σ^* antibonding molecular orbital in the ground state of the complex.

Table II. Comparison of Hydrogen Fluoride Stretching and Librational Modes (cm^{-1}) in Base–HF Complexes

base	ν_s	ν_l	ref
CH_2CHF	3805	421, 384	*a*
CH_3F	3774	453, 435	18
NH_2F	3722	596, 515	this work
NH_2F (cyclic)	3626		this work
NH_2F	3389	750, 723	this work
NH_2Cl	3311		36
NH_2OH (cyclic)	3042	885, 780	21
NH_3	3041	916	19
NH_2CH_3	2816	1036, 869	20

[a] Andrews, L.; Johnson, G. L.; Kelsall, B. L. *J. Am. Chem. Soc.* **1982**, *104*, 6180.

The four NH_3–F_2 photochemical product bands at 3722, 3626, 3450, and 3389 cm^{-1} in the H–F stretching region exhibit ND_3-substituted counterparts and H/D ratios between 1.353 and 1.367, which are appropriate for H–F and D–F stretching modes in hydrogen-bonded complexes. The major product band at 3389 cm^{-1} is due to the primary photolysis product, and the weaker

$$NH_3\text{–}F_2 + h\nu \rightarrow NH_2F\text{–}HF$$

satellite band at 3450 cm^{-1}, which was destroyed on prolonged photolysis in favor of the 3389-cm^{-1} band, is attributed to a different matrix environment for this species. Fluorine is known to photolyze efficiently with short wavelength mercury arc radiation,[18] and F atoms react rapidly[27] with NH_3 to give HF. The remaining F atom and NH_2 radical combine in the matrix cage, dissipate energy to the matrix, and form the complex product NH_2F–HF. The analogous CH_4–F_2 reaction gave CH_3F–HF as the major photoproduct. The weaker sharp 3722-cm^{-1} and broader 3626-cm^{-1} bands are assigned to primary complexes of the same formula but with different structural arrangements; the former was reduced by prolonged photolysis. The small but distinct deuterium shifts for these H–F vibrations with NHD_2 substitution and the D–F counterparts with ND_3 substitution demonstrate that ammonia is involved in the photolysis product. No evidence was found for the photochemical reaction between F_2 and the small amount of $(NH_3)_2$ in these samples; the large exothermicity of the reaction of F_2 with one submolecule in the dimer may expell the other submolecule from the matrix cage.

A fluoramide complex with HF bonded to the nitrogen lone pair is expected to follow the spectrum[19] of NH_3–HF with important differences. The inductive effect in the fluorine substituent reduces the basicity of the lone pair, decreases the shift in the ν_s and ν_l modes, and splits the latter owing to removal of degeneracy, which is in accord with the observed spectrum. Table II compares spectra for several relevant complexes and shows that the major product is the nitrogen lone pair bonded complex **1**; assignment of 4 base submolecule modes to the complex in the next section confirms this identification. A fluoramide complex with HF bonded to a fluorine lone pair should follow CH_3F–HF as a model;[18] the latter complex exhibited ν_s at 3774 cm^{-1} and ν_l at 453 and 435 cm^{-1}, which are near the present ν_s(F) and ν_l(F) bands. We, however, expect the fluorine in NH_2F to be more basic than the fluorine in CH_3F owing to the greater electron donating ability of the NH_2 group, and this gives rise to a larger shift in ν_s from the isolated HF value (3919 cm^{-1})[28] and higher ν_l modes for the NH_2F–HF complex **2**. A similar effect has been found for the nitrile complexes CH_3CN–HF and NH_2CN–HF.[29,30]

The ν_s (3389 cm^{-1}) and ν_s (3722 cm^{-1}) bands for HF modes in fluoramide complexes show small (4–5 cm^{-1}) shifts with deu-

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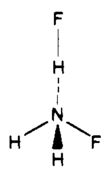
terium substitution in the fluoramide base. The weaker, broader 3626-cm^{-1} band, however, shows a much larger (15 cm^{-1}) shift for the ND_2F complex. This infers a direct involvement of HF with the base deuterium and the greater displacement in ν_s suggests a cyclic complex **3** like that proposed for hydroxylamine–HF.[21] This species was produced in low yield and only a weak ν_s mode was observed.



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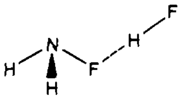

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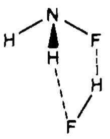

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Finally, the role of single F atom reactions and a possible NH_2–HF radical complex must be considered. In the CH_4–F_2 experiments, sample warming promoted diffusion of photochemically produced F atoms and the formation of O_2F and the CH_3–HF radical complex.[18] This radical complex was the major product in a matrix study of the CH_4 + F atom reaction.[31] Photolysis produced a shoulder at 3063 cm^{-1} on a weak NH_3–HF band[19] at 3040 cm^{-1}; sample warming increased the 3063-cm^{-1} band several-fold and produced O_2F. the 3063-cm^{-1} band is tentatively assigned to the NH_2–HF radical complex produced by the NH_3 + F atom reaction in the cold matrix cage. It is interesting to note the close agreement with NH_3–HF and to infer more repulsion from the free radical electron for HF than from a third hydrogen. This can explain the slightly smaller displacement in ν_s(HF) for the radical complex.

Vibrational Assignments. The major product **1** has the most complete spectrum and its vibrational assignments will now be considered. The strong ν_s band at 3389 cm^{-1} is clearly the H–F stretching fundamental in **1**; this mode shifts to 2505 cm^{-1} in ND_3 experiments, giving a $\nu_s(HF)/\nu_s(DF)$ = 1.353 ratio. The sharp 750.3, 723.0 cm^{-1} ν_l doublet is due to the H–F librational fundamentals in **1**; the fully deuteriated counterparts appeared at 560.9 and 539.9 cm^{-1}, giving $\nu_l(HF)/\nu_l(DF)$ ratios of 1.338 and 1.339 cm^{-1}. Just as ν_s(HF) showed a small shift (5 cm^{-1}) in the ND_2F complex, ν_l(HF) decreased 11.5 cm^{-1} for the upper mode and increased 2.0 cm^{-1} for the lower librational mode. One overtone was observed at 1314 cm^{-1}; the absence of a $^{15}NH_3$ shift in this region demonstrates that the 1314-cm^{-1} band is an acid submolecule mode. Ratios $2\nu_l/\nu_l$ = 1314/723 = 1.817 and 1314/750 = 1.752 offer a preference for the former pairing; the ND_3–F_2 experiments provided a weak 998-cm^{-1} band for $2\nu_l$ and a 998/540 = 1.848 ratio. The NH_3–HF and NH_3–DF complexes exhibited $2\nu_l/\nu_l$ = 1679/916 = 1.833 and 1316/697 = 1.888 ratios[19] demonstrating more anharmonic character for the less rigid NH_2F–HF and ND_2F–DF complexes.

One of the above librational modes is in the symmetry plane of the complex (and base submolecule) and the other is perpendicular to this plane. The two lowest base submolecule modes to be assigned next are symmetric modes that will interact slightly with the ν_l(sym) mode. Thus the effect of partial deuteriation, i.e., the ν_l(HF) modes for ND_2F–HF, reveals −11.5 and +2.0 cm^{-1} displacements from the NH_2F–HF ν_l(HF) values. The 750.3-cm^{-1} band is therefore ν_l(sym) for NH_2F–HF and its displacement to 738.8 cm^{-1} for ND_2F–HF is due to interaction with the now closer ND_2 wag (979.7 cm^{-1}) which must therefore shift in the opposite direction from the ND_2F–DF value (968.1 cm^{-1}). A resolved shoulder at 567.0 cm^{-1} on the stronger 560.9-cm^{-1} ν_l(sym) band for ND_2F–DF is assigned to this motion for NHDF–DF which is also present in the sample.

Table III. Fluoramide (NH_2F) Base Submolecule Vibrational Modes (cm^{-1})

	NH_2F–HF (**1**)	NH_2F predicted[a]	NH_2F ab initio[b]
ν_1 (sym NH_2 str)	3269	3270 ± 10	3101
ν_2 (sym NH_2 bend)	1568	1565 ± 5	1607
ν_3 (sym NH_2 wag)	1244	1160 ± 20	1224
ν_4 (sym N–F str)	934	920 ± 10	900

[a] This work. [b] Reference 9.

Four base submolecule modes observed for **1**, which are labeled ν_1, ν_2, ν_3, ν_4 in Figures 1b and 2b, can be assigned on the basis of the isotopic data. The ν_2 band at 1568.1 cm^{-1} is just below the NH_2 scissors mode for ammonia, and it shifted 2.2 cm^{-1} lower with the $^{15}NH_3$ reagent. Experiments with ND_3 provided a fully deuteriated counterpart at 1151.4 cm^{-1} and one intermediate mixed H–D species at 1428.9 cm^{-1}. These observations substantiate assignment of the 1568.1-cm^{-1} band to ν_2, the symmetric H–N–H valence angle bending mode in NH_2F in the **1** complex. The H/D ratio 1.362 is near the ammonia value (1.377).[23]

The strongest base submolecule band at 1243.7 cm^{-1} exhibits a small $^{15}NH_3$ shift to 1238.0 cm^{-1} and a large ND_3 shift to 968.1 cm^{-1}. These isotopic shifts identify the symmetric NH_2 wagging motion of NH_2F in the **1** complex (ratios 1.0046 and 1.285 for complex and 1.0043 and 1.282 for ammonia).[23] The 1243.7-cm^{-1} wagging mode in the complex is obviously blue shifted from the unknown NH_2F value owing to repulsive interaction with the HF submolecule. Two intermediate mixed H–D isotopic bands were observed at 1209.2 and 1015.3 cm^{-1}. It must be remembered that the NHDF species does not have a plane of symmetry and the symmetric wag and antisymmetric rock in this region[9,16] now mix in C_s symmetry giving in-phase and out-of-phase combinations of the H–N–F and D–N–F internal coordinate angle changes. The two mixed NHDF bands are assigned accordingly.

The above model requires an N–F stretching fundamental that is expected in the congested 900-cm^{-1} region. Fortunately, cold trap removal of HF from the Ar/F_2 sample during matrix condensation allowed observation of the new ν_3 band at 933.7 cm^{-1}. The critical experiment required $^{15}NH_3$, and the spectrum in Figure 4b revealed a new ^{15}N component at 916.2 cm^{-1}. This ^{15}N shift is slightly less than the 915.6-cm^{-1} value predicted for a harmonic N–F oscillator owing to a slight amount of NH_2 wagging character in the N–F stretching mode. This point is substantiated in the ND_3 spectrum of Figure 3d, which contains no detectable ND_3–HF. The N–F stretching mode is red-shifted to 923.7 cm^{-1} by interaction with the ND_2 wag at 968.1 cm^{-1} in ND_2F–DF, but the N–F stretching mode in NHDF–DF is red-shifted only 0.4 cm^{-1} owing to less interaction with the 1209.2- and 1015.3-cm^{-1} bending modes described above.

Finally, the new 3269-cm^{-1} band exhibited a 5-cm^{-1} $^{15}NH_3$ shift, which characterizes an N–H and not an F–H stretching mode. Although the 3269-cm^{-1} band is below the 3345-cm^{-1} ν_1 band for NH_3 monomer in solid argon,[23] the ν_1 band[16] for NHF_2 is lower still at 3193 cm^{-1} and this red shift can be attributed to the inductive effect of fluorine substituents. The sharp ND_2F–DF counterpart at 2399 cm^{-1} defines an H/D isotopic ratio of 1.363, which is appropriate for N–H vibrations.

Bonding and Structure Comparisons. Since NH_2F is an elusive species[25,32] it is worthwhile to predict NH_2F fundamentals from those of the base submolecule in the complex. Our predictions, based on considerable experience with HF complexes and perturbed base submolecule modes,[18-21,28] are compared in Table III with the results of ab initio calculations.[9] This is, however, the first complex prepared with a base submolecule that has not itself been characterized. The perturbations on ν_1 and ν_2 are each expected to be small as there is little interaction owing to little change in the amide hydrogen–acid hydrogen distance during the vibration. The symmetric NH_2 wag, however, involves a larger displacement and a larger interaction is expected. Hydroxylamine and NH_2OH–HF provide one model, and these values are 1118 and 1163 cm^{-1}, respectively.[21] Ammonia and NH_3–HF offer 974- and 1094-cm^{-1} values, respectively, for this system with 3 H atoms

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(31) Jacox, M. E. *Chem. Phys.* **1979**, *42*, 133.

(32) Withnall, R.; Andrews, L., unpublished results. Numerous attempts to prepare NH_2F by 254-, 184-, and 107-nm photolysis of NH_3 and F_2 mixtures during codeposition produced no new absorptions. Matrix reactions of discharged F_2 and NH_3 under various conditions produced NF, NF_2, HNF_2, and a new weak 1147-cm^{-1} band. The latter could be ν_3 of NH_2F, but isotopic data are needed for confirmation.

in the wagging mode.[19,23] Finally, the N–F stretching mode is not expected to undergo much shift in the complex; the major effect of HF in the complex is to blue shift ν_3 and thereby decrease interaction with ν_4, which results in a small blue shift in ν_4 for the complex from the isolated molecule.

As has been offered for identification of the product complexes, comparison with the acid submolecule modes of other similar complexes characterizes the local structure of complexes **1**, **2**, and **3**. The major photolysis product clearly has the nitrogen lone pair bonded structure **1** as comparison with the spectra of NH_3–HF and NH_2OH–HF indicates.[19,21] The small separation between the two ν_l modes (750.3 and 723.0 cm^{-1}) reveals asymmetry in the librational potential due to distortion of the nitrogen lone pair by the fluorine substituent. Recall that ν_l was a single, very sharp 916.0-cm^{-1} band for the C_{3v} NH_3–HF complex. The inductive effect of the fluorine substituent is responsible for a major decrease in basicity and decrease in the vibrational perturbation of the base (NH_2F) on the acid (HF) as compared to the NH_3–HF complex.[19] The minor photolysis product has the fluorine lone pair structure NH_2F–HF. The large separation between these two ν_l modes (596 and 515 cm^{-1}) characterizes substantially more asymmetry in the potential due to the fluorine lone pair involved in the **2** complex. This is much more asymmetry than in CH_3F–HF (18 cm^{-1} difference between ν_l modes)[9] as is expected owing to more asymmetry contribution from the NH_2 group than the CH_3 group. Additional lowering of the ν_s(HF) mode in **2** from 3722 to 3626 cm^{-1} provides evidence for another weak interaction, and a simple possibility is the cyclic structure **3**. The weak chelating N–H- -F interaction weakens the H–F bond slightly and lowers the ν_s(HF) vibration from the **2** value. A similar effect was found in the cyclic NH_2OH–HF complex.[21]

The displacement of ν_s(HF) from the isolated HF fundamental in similar complexes is generally taken as a measure of the base–HF interaction. Clearly, the larger $\Delta\nu_s$ for the nitrogen lone pair complex **1** (530 cm^{-1}) as compared to the fluorine lone pair complex **2** (197 cm^{-1}) indicates a stronger interaction and basicity for the nitrogen lone pair. This is consistent with the results of ab initio calculations of proton affinities for each site, which give 40–60 kcal/mol higher values for the nitrogen lone pair site.[13,14]

Finally, what can be said about the weak precursor complex NH_3–F_2 from two infrared absorptions? First, the 966 cm^{-1} perturbed ν_2 mode for NH_3 in NH_3–F_2 is precisely (± 1 cm^{-1}) intermediate between the inversion doublet components for isolated ammonia[22] and no splitting was observed; this indicates that the F_2 adduct prevents inversion of the NH_3 submolecule just as HF does in the NH_3–HF complex,[19,28] and that there is no significant shift of the ν_2 mode from the median of the inversion doublet by interaction with F_2 in the argon matrix cage. Second, the observation of a weak F–F stretching mode suggests axial attachment of F_2 to the nitrogen lone pair as this arrangement would provide more asymmetry and infrared intensity, and a more favorable overlap with the $\sigma^*(2p)$ molecular orbital of fluorine. Third, the NH_3–Cl_2 complex has been prepared,[33,34] and the perturbed ν_2 ammonia mode at 988 cm^{-1} demonstrates a stronger interaction than that found for NH_3–F_2, which is in agreement with SCF calculations.[35] The perturbed Cl_2 fundamental at 479 cm^{-1} was considerably stronger relative to the 988-cm^{-1} band than the perturbed F_2 fundamental in NH_3–F_2 relative to the 966-cm^{-1} band. This is expected owing to the greater polarizability of Cl_2 than F_2.[36]

The axial structure deduced from the infrared spectrum for NH_3–F_2 is in accord with earlier SCF calculations, which assumed fixed submolecule structural parameters from the isolated submolecules.[35] These calculations revealed a small (0.04e) polarization in the F_2 submolecule that helps account for the weak infrared absorption intensity. The 111-cm^{-1} red shift in the F–F fundamental in the complex can be interpreted by charge transfer into the fluorine $\sigma^*(2p)$ molecular orbital, but the calculations showed no ($\pm$0.01e) charge transfer $NH_3 \rightarrow F_2$ assuming a F–F distance fixed at the diatomic molecule value. Multistructure valence-bond calculations[37] have revealed a substantial increase in bond length ($\sim$0.3 Å) on the addition of an electron to F_2 to form F_2^-. Although the 111-cm^{-1} reduction in the F_2 fundamental in the precursor complex is less than the 530 ± 20 cm^{-1} reduction[26] for F_2^-, some increase in F–F bond length in the complex is indicated. More recent ab initio calculations[38] have provided evidence for a weak charge-transfer interaction in the linear NH_3–F_2 complex. We suggest that a fully optimized geometry ab initio calculation for NH_3–F_2 will reveal a slight increase in F–F distance and a small amount of charge transfer to the fluorine submolecule.

Conclusions

Codeposition of Ar/NH_3 and Ar/F_2 samples at 12 K provided evidence for a weak NH_3–F_2 complex, which photolyzed by mercury arc radiation to give NH_2F–HF complexes with different structural arrangements. The NH_3–F_2 precursor complex exhibited one perturbed $\nu_2(NH_3)$ mode intermediate between the inversion components of the isolated molecule and a weakly activated F_2 fundamental. The major photolysis product involved HF binding to the nitrogen lone pair and exhibited ν_s(HF) at 3389 cm^{-1} and a split ν_l(HF) doublet at 750 and 723 cm^{-1}; these observations characterize a weaker interaction than that found for NH_3–HF owing to the inductive effect of fluorine and the reduced basicity of NH_2F compared to NH_3. Perturbed NH_2F base submolecule modes were observed at 3269, 1568, 1244, and 934 cm^{-1}; these observations for NH_2F in the HF complex provide the first infrared evidence for the highly reactive NH_2F species and an estimate of vibrational modes for the as yet uncharacterized free NH_2F molecule. The minor product complex had HF binding to a fluorine lone pair with ν_s(HF) at 3722 cm^{-1} and a ν_l(HF) doublet at 596 and 515 cm^{-1}; these observations indicate a stronger interaction for NH_2F–HF than in CH_3F–HF owing to the greater electron donating ability of the NH_2 group as compared to CH_3. The matrix cage plays an important role in relaxing the newly formed NH_2F submolecule in these complexes before it can decompose by eliminating HF.

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(36) Similar experiments with NH_3 and ClF gave a much stronger complex with bands at 1054 and 599 cm^{-1} for the respective submolecules, which is in agreement with calculations.[35] Photolysis reduced these bands slightly and produced a new weak 3311-cm^{-1} band. Two analogous ND_3 experiments gave 817 and 599-cm^{-1} complex bands and 2457-cm^{-1} (A = 0.06) photolysis products. The photolysis products are believed to be NH_2Cl–HF and ND_2-Cl–DF, and the two bands are due to the ν_s(HF) and ν_s(DF) modes, respectively.

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