with that of an authentic sample. (A single strong absorption was observed at 1890 cm^{-1} in $CHCl_3$.) The monophosphine complex was conveniently isolated after a mixture of 0.32 mmol of $(CO)_4W(MeCN)_2$ and 0.32 mmol of triphenylphosphine was electrolyzed for 600 s at 1 mA. The yield of *cis*-$(MeCN)(PPh_3)W(CO)_4$ was 102% by IR analysis. The product precipitated as yellow microcrystals upon the addition of deoxygenated water (0.16 g, 84% yield). It was recrystallized from a mixture of CH_2Cl_2 and hexane to afford 0.12 g of lustrous needles. The IR and ^1H NMR spectra were in agreement with the published spectra.[74]

The reaction between equimolar amounts (0.16 mmol) of *cis*-$(py)_2W(CO)_4$ and PPh_3 was performed similarly. It afforded a 98% yield of *cis*-$(py)(PPh_3)W(CO)_4$ by IR analysis. Precipitation with water gave a bright yellow product in 68% yield. It was characterized by its IR spectrum.[30c] The reaction of *cis*-$(py)_2W(CO)_4$ (66 mg, 0.14 mmol) with excess PPh_3 (79 mg, 0.3 mmol) gave *cis*-$(py)(PPh_3)W(CO)_4$ quantitatively after electrolysis for 1200 s at 1 mA. The IR spectrum showed that no further substitution occurred after 4200 s of additional oxidation. No $(PPh_3)_2W(CO)_4$ was formed.

Reactions of *cis*-$(CO)_4W(MeCN)_2$, *fac*-$(CO)_3W(MeCN)_3$, and *cis*-$(CO)_4Mo(py)_2$ with *t*-BuNC. The reaction of *cis*-$(CO)_4W(MeCN)_2$ (53 mg, 0.14 mmol) with excess *t*-BuNC (29 mg, 0.35 mmol) required electrolysis for 1800 s at 1 mA. It afforded, after precipitation with water, 53 mg (84% yield) of *cis*-$(t\text{-}BuNC)_2W(CO)_4$ as a cream-colored solid. The IR spectrum of the product was identical with that of the authentic compound prepared independently.

Excess *t*-BuNC (80 mg, 0.96 mmol) and *fac*-$(CO)_3W(MeCN)_3$ (61 mg, 0.16 mmol) reacted with complete substitution of the acetonitrile ligand (87%, IR yield). The substitution required oxidation for 2000 s at 0.5 mA. The product *fac*-$(CO)_3W(t\text{-}BuNC)_3$ was isolated in 68% yield by precipitation with water as a yellow solid. The IR spectrum was identical with that reported previously.[9]

Reaction of *cis*-$(py)_2Mo(CO)_4$ (51 mg, 0.14 mmol) and *t*-BuNC (46 mg, 0.55 mmol) afforded an 80% yield by IR analysis of *cis*-$(t\text{-}BuNC)_2Mo(CO)_4$. The electrolysis required 2600 s at 1 mA. The product was isolated (35 mg, 67%) by precipitation with water and identified by comparison of the IR spectrum with the published spectrum.[9]

Reaction of *fac*-$(CO)_3Mo(MeCN)_3$ with PPh_3. Triphenylphosphine (300 mg, 1.1 mmol) was added, under an argon backflush, to a solution of the subject molybdenum carbonyl (42 mg, 0.14 mmol) in 10 mL of MeCN containing 0.1 M TEAP which was "stabilized" with a reducing current. No reaction was apparent after 1 h. This system could not be monitored readily by IR analysis since the substitution occurred readily in the solution cell. A short application of an oxidizing current (120 s at 1 mA) induced the complete precipitation of the product which is quite insoluble in MeCN. Anal. Calcd for $(CH_3CN)_{1.5}[(C_6H_5)_3P]_{1.5}Mo(CO)_3$: C, 62.4; H, 4.3; P, 7.3. Found: C, 61.5; H, 4.5; P, 7.2.

Acknowledgment. We wish to thank the National Science Foundation for support of this research.

Registry No. *fac*-$(MeCN)_3W(CO)_3$, 30958-95-3; *fac*-$(MeCN)_3Mo(CO)_3$, 17731-95-2; *cis*-$(py)_2Mo(CO)_4$, 16742-99-7; *cis*-$(py)_2W(CO)_4$, 16743-01-4; *cis*-$(MeCN)_2W(CO)_4$, 29890-10-6; $(MeCN)W(CO)_5$, 15096-68-1; $(py)W(CO)_5$, 14586-49-3; $(MeCN)_cr(CO)_5$, 15228-38-3; $(py)Cr(CO)_5$, 14740-77-3; $(Ph_3P)Cr(CO)_5$, 14917-12-5; *trans*-$(Ph_3P)_2Cr(CO)_4$, 38800-75-8; *cis*-$(MeCN)_2Cr(CO)_4$, 29890-09-3; *cis*-$(py)_2Cr(CO)_4$, 24354-36-7; *fac*-$(MeCN)_3Cr(CO)_3$, 22736-49-8; *cis*-$(t\text{-}BuNC)_2W(CO)_4$, 42401-92-3; *fac*-$(t\text{-}BuNC)_3W(CO)_3$, 42401-95-6; $(Ph_3P)W(CO)_5$, 15444-65-2; $(t\text{-}BuNC)W(CO)_5$, 42401-89-8; *trans*-$(Ph_3P)_2W(CO)_4$, 16743-03-6; *cis*-$(Ph_3P)(py)W(CO)_4$, 38496-28-5; *cis*-$(Ph_3P)(MeCN)W(CO)_4$, 18078-18-7; *cis*-$(t\text{-}BuNC)_2Mo(CO)_4$, 37584-08-0.

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Matrix Infrared Spectrum of the H_3N--HF Hydrogen-Bonded Complex

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Abstract: Codeposition of Ar/NH_3 and Ar/HF samples at 12 K produced new absorptions at 3401, 1920, 1679, 1093, and 916 cm^{-1}, which are due to reaction products. Concentration studies and evaporation from solid NH_4HF_2 identify the 1920-cm^{-1} absorption as due to a 1:2 complex ammonium bifluoride species and the other four product bands as the 1:1 hydrogen-bonded complex. Isotopic substitution (DF, $^{15}NH_3$, ND_3) supports assignment of the 3041- and 916-cm^{-1} bands to the ν_s stretching and ν_l librational motions of the HF submolecule in the complex and the 1679- and 1093-cm^{-1} bands to the $\nu_4{}^c$ and $\nu_2{}^c$ vibrations of the NH_3 submolecule in the complex, respectively. The argon-to-nitrogen matrix shift in ν_s for the H_3N--HF complex shows that the complex is relatively polar, in agreement with theoretical calculations.

Hydrogen bonding is an important phenomenon in many biological and chemical systems and has been studied a great deal by experimental and theoretical methods.[1,2] Hydrogen fluoride is useful in the study of hydrogen bonding because it forms strong hydrogen bonds and HF and DF are straightforward to synthesize; in addition HF complexes give simple vibrational spectra and are light enough for meaningful theoretical work. Studies of HF complexes with the π systems of acetylene and ethylene in solid argon have produced strong stretching modes at 3747 and 3732 cm^{-1} for the HF submolecule in the complex (ν_s).[3] The shift in ν_s from the H–F value, $\Delta\nu_s$, is a useful indicator of the strength of the hydrogen bond, and a study of complexes between HF and methyl-substituted amines has demonstrated a linear correlation between the proton affinity of the base and the shift of the HF stretching fundamental for these complexes.[4]

The purpose of this study is to characterize the 1:1 complex between hydrogen fluoride and ammonia in solid argon by its infrared spectrum. Infrared spectra of ammonia in inert gas matrices have been thoroughly investigated,[5,6] and a complex between ammonia and hydrogen chloride has been identified in solid nitrogen.[7] The ammonia–hydrogen fluoride complex has

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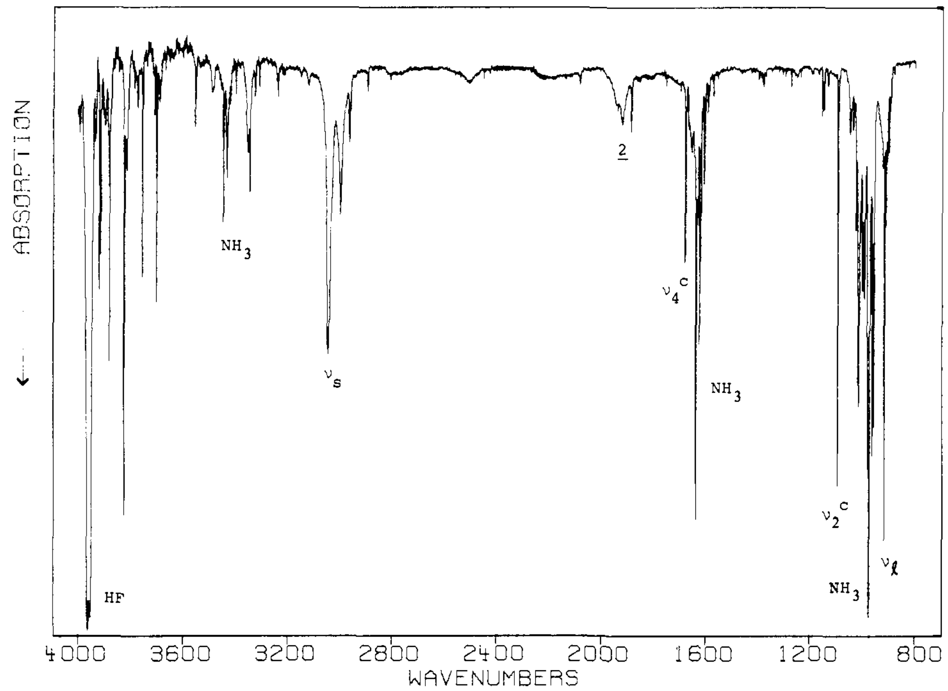

Figure 1. Infrared spectrum of sample prepared by codepositing Ar:NH_3 = 300:1 and Ar:HF = 300:1 mixtures onto a CsI window at 12 K.

been the subject of extensive theoretical work,[8-10] and molecular beam electric resonance and infrared spectra in the high frequency region have been obtained very recently for the vapor species.[11,12] The complex has a significant dipole moment (4.448 D) and a shorter hydrogen bond (N-HF = 2.66 Å) than predicted by theoretical calculations.[11] The complementary matrix infrared spectrum of the H_3N--HF complex will be discussed below.

Experimental Section

The vacuum and cryogenic techniques used have been described previously.[13] All spectra were recorded with a Nicolet 7199 Fourier transform infrared spectrometer in the 4000–400 cm^{-1} range at 1-cm^{-1} resolution. The ammonia (Matheson), ND_3 (Merck, Sharp and Dohme), and $^{15}NH_3$ (Merck, Sharp and Dohme) were purified by condensing at 77 K into a glass column loosely packed with Pyrex beads and allowing the condensate to distill off the glass beads. Solid $NH_4^+HF_2^-$ (Mallinckrodt), argon gas (Burdett, 99.995%), and nitrogen gas (Air Products) were used as supplied with no further purification. Hydrogen fluoride was synthesized by mixing equimolar amounts of F_2 (Matheson) and H_2 (Matheson, research grade) sufficient to make about 1 mmol of HF gas in a well-passivated 3-L stainless steel can; DF was prepared in a similar manner with D_2 gas (Air Products).

Argon solutions of hydrogen fluroide and ammonia diluted to 300:1 mol ratios were used in most of these studies. Concentration effects were examined by using HF dilutions ranging from 50:1 to 800:1 with ammonia dilutions ranging from 800:1 to 200:1 mol ratio, respectively. The gas samples were simultaneously deposited through twin jets onto a CsI window held at 12 K by using rates of 2 mmol/h for each gas mixture during 16- to 20-h periods (higher substrate temperatures gave poor isolation of HF). The resulting matrix was scanned 1000 times by the interferometer, and the signal-averaged interferogram was converted to a single-beam spectrum by a fast Fourier transform algorithm and ratioed with a single-beam spectrum of the cold window to produce the working spectrum.

Matrix experiments with solid ammonium bifluoride ($NH_4 \cdot HF_2$) were performed with the following procedure: About 0.2 g of ammonium bifluoride flakes (as supplied) was placed in a 12-mm o.d. Pyrex tube with a 1-mm orifice mated by an o-ring seal to the vacuum vessel. A heating coil was placed around the end of the tube covering the ammonium bifluoride, and a thermocouple was inserted between the tube and the heater to monitor the temperature. The cryostat head was rotated so that the cold window faced the 1-mm opening of the tube, and argon was flowed through the tube at about 2 mmol/h. Three experiments were performed, one with the ammonium bifluoride heated to 35 °C and another at 24 °C. For determination of the effects of HF enrichment, an argon:HF = 100:1 mixture was sprayed onto the cold window as the ammonium bifluoride was simultaneously deposited.

Table I. Major Product Absorptions (cm^{-1}) in Cocondensation Reactions of Ammonia and Hydrogen Fluoride

NH_3 + HF	$^{15}NH_3$ + HF	NH_3 + DF	$^{15}NH_3$ + DF	ND_3 + HF	ND_3 + DF	assign[a]
3041	3042	2278	2277	3017	2269	ν_s (1)
1679.4	1678.3	1679.5	1677.8	1272	1272	ν_4^c (1)
1093.5	1087.3	1093.9	1087.7	849	849.2	ν_2^c (1)
916.0	915.0	696.7	695.2	906.0	674.5	ν_l (1)
1920	1919	1536, 1909	1531, 1909	1862	1484	ν_s (2)
1154.8	1147.5	1152.1	1144.5			ν_2^c (2)

[a] Assignments described in text for 1:1 complex (**1**) and 1:2 complex (**2**). ν_s and ν_l denote acid submolecule vibrations and ν_2^c and ν_4^c denote base submolecule vibrations in the complex.

Results

Twenty-five cocondensation experiments were performed with isotopic argon/ammonia and argon/hydrogen fluoride samples, and three experiments were done with ammonium bifluoride vapor; observations from these studies will be presented in turn.

NH_3 + HF. Figure 1 shows the infrared spectrum of a typical experiment codepositing Ar:NH_3 = 300:1 and Ar:HF = 300:1 samples at 12 K for 16 h. Several prominent new bands appearing in the product spectrum were not observed in separate matrix spectra of NH_3 or HF recorded in this laboratory; these bands include a new product absorption at 3041 cm^{-1} (A = 0.32) with full width at half-maximum (fwhm) = 16 cm^{-1}, and weaker satellites at 2999 and 2964 cm^{-1}, a new 1920-cm^{-1} band (A = 0.04, fwhm = 30 cm^{-1}) with weaker satellites at 1888 and 1856 cm^{-1}, a sharp new absorption at 1679.4 cm^{-1} (A = 0.17, fwhm = 2.8 cm^{-1}) above the ν_4 mode of NH_3 at 1639 cm^{-1}, a sharp band at 1154.8 (A = 0.04), a strong, sharp new band at 1093.5 cm^{-1} (A = 0.61, fwhm = 1.4 cm^{-1}) above the ν_2 mode of NH_3 at 974 cm^{-1}, and a strong, sharp new absorption at 916.0 cm^{-1} (A = 0.84, fwhm = 2.2 cm^{-1}). The new bands are collected in Table I. The sample was subjected to full high-pressure mercury arc photolysis in one experiment; no change was observed in the product spectrum.

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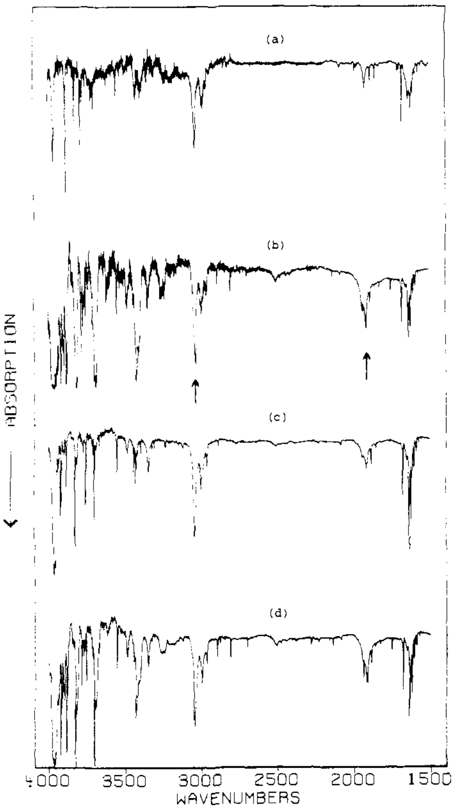


Figure 2. Concentration study of the effects of varying $HF:NH_3$ ratios upon relative yields of products: (a) $Ar:NH_3$ = 200:1 codeposited with Ar:HF = 800:1 at 12 K; (b) $Ar:NH_3$ = 400:1 codeposited with Ar:HF = 100:1; (c) Ammonium bifluoride sublimed at 24 °C and trapped in solid Ar at 12 K; (d) Ammonium bifluoride sublimed at 24 °C and codeposited with Ar:HF = 100:1 mixture.

This experiment was repeated with a wide range of reagent concentrations. The new product bands at 3041, 1679, 1093, and 916 cm^{-1} did not change relative intensities; however, the 1920-cm^{-1} band and its satellites, the 1154-cm^{-1} absorption, and new bands at 1347 and 1250 cm^{-1} were favored in the HF-rich experiments. Figure 2 summarizes these concentration studies by contrasting experiments with (a) $Ar:NH_3$ = 200:1 and Ar:HF = 800:1 and (b) $Ar:NH_3$ = 400:1 and Ar:HF = 100:1, which clearly shows that the 1920-cm^{-1} band (noted with an arrow) is increased relative to the 3041-cm^{-1} band (noted with an arrow) at higher $HF:NH_3$ concentration ratios.

One experiment was done with $N_2:NH_3$ = 300:1 and N_2:HF = 300:1 samples. The major new product bands were observed at 2778 cm^{-1} (A = 0.24, fwhm = 50 cm^{-1}) with a 2645-cm^{-1} satellite, 1109.6 cm^{-1} (A = 0.32), and 1023.3 cm^{-1} (A = 0.48).

NH_3 + DF. Although the vacuum system was exchanged with DF with heating for several days, experiments with DF were still contaminated by HF from exchange with the vacuum system. Figure 3 illustrates the spectrum from an experiment with $Ar:NH_3$ = 200:1 and Ar:DF:HF = 500:2:1 samples. New product bands were observed at 3042 cm^{-1} (A = 0.07, fwhm = 15 cm^{-1}), 2278 cm^{-1} (A = 0.40, fwhm = 4 cm^{-1}) with a satellite at 2266 cm^{-1}, 1679.4 cm^{-1} (A = 0.04), 1536 cm^{-1} (A = 0.03, fwhm = 10 cm^{-1}) with a satellite at 1510 cm^{-1}, 1152.1 cm^{-1}, 1093 cm^{-1} (A = 0.47, fwhm = 1.5 cm^{-1}), 916.0 cm^{-1} (A = 0.19), and 696.7 cm^{-1} (A = 0.31, fwhm = 1.8 cm^{-1}). The NH_3 + DF experiment was repeated at a later date with 200:1 samples, and the product spectrum was reproduced with a 50% higher yield. This sample was thermal cycled 12–24–12 K over a 15-m period, and the spectrum revealed a *50% growth* in the 3042, 2278 (and satellites), 1679-, 1093-, 916-, and 696-cm^{-1} bands and a *threefold* growth in the 1536-cm^{-1} band (and 1510-cm^{-1} satellite), the 1152-cm^{-1} band, and 1920- and 1909-cm^{-1} absorptions (and 1888- and 1856-cm^{-1} satellites). This operation also *decreased* HF and DF monomer absorptions by 20%, *decreased* ammonia absorptions slightly, and *increased* hydrogen fluoride and deuterium fluoride dimer absorptions.

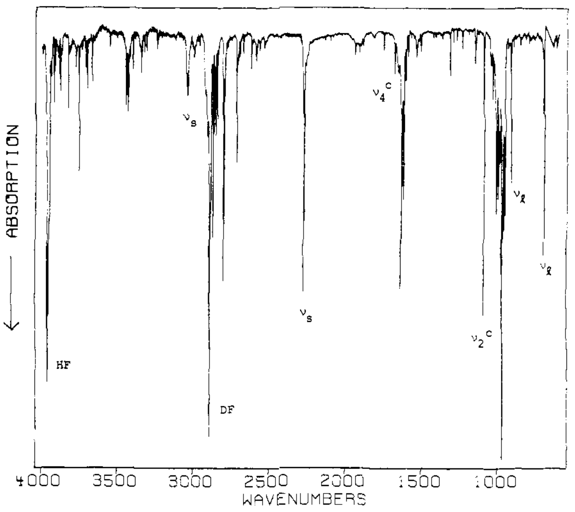


Figure 3. Infrared spectrum of matrix formed by codeposition of $Ar:NH_3$ = 200:1 and Ar:DF:HF = 500:2:1 samples at 12 K.

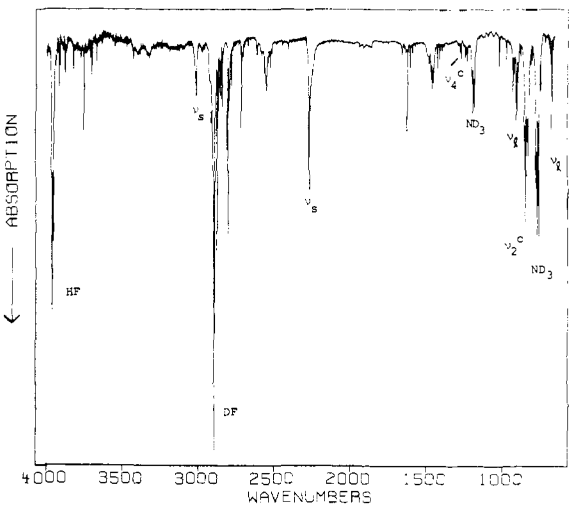


Figure 4. Infrared spectrum of sample prepared by codepositing $Ar:ND_3$ = 200:1 and Ar:DF:HF = 500:2:1 samples onto a CsI window at 12 K.

A similar experiment was performed with $N_2:NH_3$ = 200:1 and N_2:DF = 200:1 samples. The major product band was displaced to 2102 cm^{-1} (A = 0.16, fwhm = 22 cm^{-1}), the 1109.6- and 1023.3-cm^{-1} bands were again observed (A = 0.30 and 0.18, respectively), and a new band was found at 774.6 cm^{-1} (A = 0.32). Sample warming to 20 K virtually eliminated these absorptions and produced substantial DF polymer bands.

ND_3 + DF and HF. Samples of ammonia-d_3 ($Ar:ND_3$ = 200:1) and deuterium fluoride (Ar:DF = 150:1) were codeposited; the infrared spectrum is illustrated in Figure 4. Small quantities of NHD_2, NH_2D, and NH_3 were observed in the spectrum owing to exchange in the ammonia vacuum line; likewise exchange contamination of DF with a small amount of HF was noted. A similar sample of ND_3 was examined with HF for comparison. New product bands in Figure 4 at 2269 (fwhm = 7 cm^{-1}), 1484, 1272, 849.1, and 674.5 cm^{-1} (fwhm = 2.5 cm^{-1}) are attributed to the reaction of DF and ND_3, and weaker bands at 3017 (fwhm = 11 cm^{-1}) 1862 and 906 cm^{-1} (fwhm = 2.7 cm^{-1}) are due to species produced by the reaction of HF and ND_3. The sharp new 932-cm^{-1} band is probably due to reaction of DF (and HF) with NHD_2. Two separate experiments were performed with HF and ND_3, and the 3017-, 1862-, 1272-, 906-, and 849-cm^{-1} bands were observed with increased intensity and no 2269- and 675-cm^{-1} absorption.

$^{15}NH_3$ + HF and DF. Samples of $^{15}NH_3$ and HF in argon (300:1) were codeposited at 12 K; new product bands not in a similar sample of $^{15}NH_3$ are listed in Table I. The same $^{15}NH_3$–argon sample was codeposited with a more dilute DF sample (Ar:DF = 500:1) to repeat the above operation; new absorption in the DF reaction with $^{15}NH_3$ are also given in Table I.

$NH_4 \cdot HF_2$. The experiments with ammonium bifluoride were performed to augment the data obtained from the concentration studies and aid identification of absorptions due to 1:2 ammonia:HF complexes. Trace c of Figure 2 shows the spectrum of the matrix obtained by deposition of room temperature ammonium bifluoride in the 4000–1500-cm^{-1} region. The spectrum is similar to trace a in the relative yields of the major product bands at 3041 and 1920 cm^{-1}. The HF monomer absorption at 3962 cm^{-1} and ammonia absorptions at 1639 and 974 cm^{-1} are attributed to decomposition of NH_4HF_2 during evaporation. When the solid NH_4HF_2 was evaporated at 24 °C and the matrix was enriched with HF, the intensity of the 1920-cm^{-1} band increased significantly relative to the intensities of the 3041-, 1679-, 1093-, and 916-cm^{-1} bands, as shown in trace d. Absorptions below 1500 cm^{-1} that also show this growth are the bands centered at 1347, 1250, 1155, and 1008 cm^{-1}. These latter bands and the strong 1920-cm^{-1} feature increased markedly in another experiment involving evaporation of the solid at 35 °C and condensation of the vapors in argon.

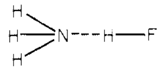
Discussion

The new product absorptions will be identified, vibrational assignments will be made, and bonding in the complex will be discussed.

Identification. The new product absorptions listed in Table I were not observed in ammonia or hydrogen fluoride/argon samples; these new bands were, however, produced in large yield when the two reagents were mixed during condensation. This information indicates that the new bands are due to ammonia–hydrogen fluoride complexes, a point substantiated by isotopic substitution in both the ammonia and hydrogen fluoride submolecules.

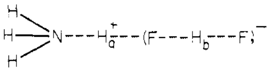
The 3041-, 1679-, 1093-, and 916-cm^{-1} bands maintained approximately constant relative intensities when the HF:NH_3 ratio was changed from 1:2 to 8:1; however, the 1920- and 1154-cm^{-1} bands increased relative to the above four bands with increasing HF concentration. In the DF (30% HF) experiments, a new 1909-cm^{-1} band appeared on sample warming, which is most likely due to a mixed HF–DF complex species. This indicates that the 1920- and 1154-cm^{-1} bands are due to a complex containing more HF submolecules than the complex responsible for the above four bands. Evaporation and decomposition of NH_4HF_2 at room temperature followed by condensation of the vapors in argon at 12 K produced the same six product bands (Figure 2c); however, condensing the effusing vapors with an Ar:HF = 100:1 sample increased the relative yield of the 1920- and 1154-cm^{-1} bands (Figure 2d).

The matrix observations under a wide range of concentration conditions indicate that the 3041-, 1679-, 1093-, and 916-cm^{-1} absorptions are due to the 1:1 ammonia–hydrogen fluoride complex, and the 1920- and 1154-cm^{-1} bands are due to a 1:2 complex involving an ammonium bifluoride type species. Theoretical calculations of Kollman and Allen show that the most stable geometry for the 1:1 complex is the C_{3v} species (**1**) with the acid



1

hydrogen bonded to the lone pair of the ammonia base.[8] The molecular beam electric deflection results[11] and the vibrational assignments to be described below support this model. Since the H_3N- -HF complex was formed upon diffusion in a 24-K solid argon matrix at the expense of HF and NH_3, practically no activation energy is required for its formation. The broad 1920-cm^{-1} absorption is in the region for shared proton vibrations in hydrogen fluoride systems, just above a 1740-cm^{-1} measurement for asymmetric bifluoride ion[14] and the 1377-cm^{-1} value for symmetric, isolated bifluoride ion,[15] which suggests that this 1:2 species might be a hydrogen-bonded complex involving a bifluoride anion (**2**). The present concentration and sample warming studies



2

show that **2** is a secondary reaction product involving **1** and another HF molecule.

Assignments. Given a C_{3v} geometry, the 1:1 complex (**1**) has 12 infrared-active modes of vibration with four doubly degenerate (e) modes and four (a_1) modes. The vibrational modes of the complex may be divided into two groups: vibrations of the ammonia submolecule perturbed by the interaction, which include symmetric and antisymmetric N–H stretching modes, $\nu_1{}^c(a_1)$ and $\nu_3{}^c(e)$, and symmetric and antisymmetric N–H deformations, $\nu_2{}^c(a_1)$ and $\nu_4{}^c(e)$, respectively, and vibrations of the HF complex, which include the perturbed H–F stretch, called[1] $\nu_s(a_1)$, libration of the H–F submolecule, which we will call $\nu_l(e)$ to avoid confusion with torsional modes in other systems,[1] the H_3N–HF stretch, $\nu_\sigma(a_1)$, and deformation of the H_3N–HF bond, $\nu_\beta(e)$.

The strong, broad 3041-cm^{-1} absorption and the strong, sharp 916-cm^{-1} band are assigned to the ν_s and ν_l vibrations for the HF complex on the basis of large shifts upon substitution of DF for HF (3041:2278 = 1.334; 916.0:696.7 = 1.315). These HF complex vibrations were relatively insensitive to $^{15}NH_3$ substitution in the ammonia submolecule, although substitution of ND_3 caused small decreases in the ν_s and ν_l modes. The sharp 1093- and 1679-cm^{-1} bands are assigned to the $\nu_2{}^c$ and $\nu_4{}^c$ vibrations of the ammonia submolecule in the complex on the basis of their proximity to the ν_2 and ν_4 absorptions of isolated ammonia and their isotopic behavior. The ammonia submolecule vibrations were insensitive to substitution of DF for HF, but exhibited shifts on $^{15}NH_3$ and ND_3 substitution similar to the parent molecule. ($^{15}NH_3$ shifts for ν_2 and ν_4 are 4.3 and 2.6 cm^{-1}, respectively; ND_3 shifts for ν_2 and ν_4 are 216 and 446 cm^{-1}, respectively.) The weaker $\nu_1{}^c$ and $\nu_3{}^c$ modes were not observed in the spectrum; these bands are probably lost in the complicated structure of the parent absorptions, since significant changes between these modes for the parent and complex are not expected. The far-infrared was searched unsuccessfully down to 130 cm^{-1} for the low-frequency complex modes ν_σ and ν_β. Excluding masking by $(HF)_n$ bands at 401, 263, and 190 cm^{-1}, the ν_σ and ν_β complex modes are either too weak to be observed here or these modes absorb below 130 cm^{-1}.

The observation of sharp doubly degenerate $\nu_4{}^c(e)$ and ν_l (e) vibrations for the ammonia and hydrogen fluoride submolecules in the H_3N- -HF complex without splitting indicates that threefold symmetry in the complex is preserved in the solid argon matrix.

As mentioned above, the new species **2** band at 1920 cm^{-1}, which exhibits a deuterium counterpart at 1536 cm^{-1}, is in the region for shared proton vibrations in hydrogen fluoride systems. This absorption falls between ν_s for strong type I hydrogen-bonded species like H_3N- -HF and the ν_3 mode for the equally shared proton in the type II species $HF_2{}^-$ at 1377 cm^{-1}.[15] The 1920-cm^{-1} absorption could be due to the stretching vibration of H_a and/or H_b in species **2**. With a reasonable value (339 ± 10 kcal/mol) for the proton affinity of $HF_2{}^-$, the vibrational correlation diagram of Ault et al. shows that the 1920-cm^{-1} absorption could be due to vibration of the proton H_a shared between H_3N and $HF_2{}^-$ in a type II species.[16] On the other hand, the bifluoride subunit of **2** is probably distorted by the asymmetric environment,[17] and asymmetric bifluoride modes have been reported in the 1740-cm^{-1} range,[14] which suggests that the 1920-cm^{-1} band could be due to

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Table II. H-F Stretching Fundamental (ν_s) and H-F Librational Motion (ν_l) in Several Hydrogen Fluoride-Base Complexes in the Gas Phase and in Solid Argon

	ν_s, cm^{-1}			ν_l, cm^{-1}	
complexes	gas	solid argon	R(B-F), Å gas	gas	solid argon
CO_2-HF		3871[a]	2.83[b]		313[a]
C_2H_2-HF		3747[c]			426, 382[c]
C_2H_4-HF		3732[c]			424, 396[c]
CH_3CN-HF	3627[d]	3482[c]	2.76[e]	620 ± 3[d]	681
H_2O-HF	3608[f]	3549[c]	2.66[g]	696, 666 ± 30[f]	716, 629[c]
H_3N-HF	3215[h]	3041	2.66[i]		916

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the stretching vibration of H_b in an asymmetric bifluoride subunit of a complex like **2**. The 1-cm^{-1} ^{15}N shift in the 1920-cm^{-1} band and the 5-cm^{-1} ^{15}N shift in the 1536-cm^{-1} DF couterpart band verify vibration of H_a against nitrogen; possible ND_3 counterparts at 1862 and 1484 cm^{-1} for the HF and DF species also support slight NH_3 involvement in the vibration. Substantial asymmetry in the potential function for this vibration is indicated by the HF:DF = 1920:1536 = 1.25 ratio, which is less than the 1.34 H:D ratio for the analogous $(CH_3)_3N$-$(HF)_2$ complex[4] and the 1.42 ratio for the isolated symmetric HF_2^- species.[15] Since H_a would be expected to vibrate in a more asymmetric potential in a type II species than H_b would feel in a bifluoride subunit, the low H:D ratio suggests a type II complex. The observation of a 1909-cm^{-1} band in the HF/DF experiment, not present in the HF studies, which may be identified as the mixed species H_3N-H^+-(F-D-F)$^-$, shows that some mixing of H_a and H_b motions occurs in the 1920-cm^{-1} normal vibration. To summarize, the above evidence suggests that the 1920-cm^{-1} absorption involves H_a to a greater degree than H_b, which supports assignment of the 1920-cm^{-1} band to a ν_s mode and characterizes **2** as a type II hydrogen-bonded complex.

The sharp 1154-cm^{-1} band exhibits the proper ^{15}N shift for a $\nu_2{}^c$ type mode of the ammonia submolecule in **2**. The further increase in $\nu_2{}^c$ of **2** as compared to **1** and ν_2 of NH_3 provides additional evidence for the stronger hydrogen bond in **2** as compared to **1**. A 3-cm^{-1} shift in this mode was found for deuterium substitution at the hydrogen-bonded position, which provides additional evidence for a strong N-H_a interaction. The ND_3 counterpart of $\nu_2{}^c$ was not observed owing to the lower yield of **2** and isotopic contamination in ND_3 experiments. Three other weaker bands at 1345, 1250, and 1008 cm^{-1} increased with the stronger 1920- and 1154-cm^{-1} bands in the most productive ammonium bifluoride experiments; the 1345-cm^{-1} absorption could be due to the "HF_2^-" proton H_b, but without isotopic data, definitive vibrational assignments for these bands cannot be made.

Bonding. Three bonding trends are of interest: the effect of a second HF molecule on the first hydrogen fluoride molecule in the complex, different acid molecules binding to a common base, and the effect of different base molecules binding to a single hydrogen fluoride molecule.

In 1:2 base-hydrogen fluoride complexes, the first HF submolecule is more acidic owing to the fluoride affinity of the second HF molecule. This trend is substantiated by the spectra of 1:2 ether-HF complexes F-H-F-H-B, which show that the ν(FH)B value is lower than the ν_s value for the corresponding 1:1 complex.[18] Hence, a greater degree of proton transfer to NH_3 is expected in the present **2** species than in **1**, which is verified by greater displacements in ν_s and $\nu_2{}^c$ for the former species. With the increase in proton affinity of NH_3 compared to ethers,[19] more proton sharing with NH_3 is expected in the 1:2 ammonia—HF species than in the 1:2 ether-HF complexes. Accordingly, H_3H-HF is a strong type I hydrogen-bonded species, and H_3N-H^+-(F-H-F)$^-$ provides another example of the asymmetric type II species.

For the HF, HCl, and HBr complexes with ammonia,[7,16] the decrease in proton affinity of the corresponding halide anion[19] allows the proton to be transfered successively more to the NH_3 base. As illustrated by a vibrational correlation using normalized proton affinities,[16] this series provides examples of the three hydrogen-bond types I, II, and III for the complexes H_3N- -HF, H_3N- -H- -Cl, and H_3N-H^+- -Br^-, respectively.

Just as the base strength has a marked effect on the bonding in the $(HF)_2$ submolecule in **2**, base strength affects the hydrogen-bond strength in 1:1 complexes. The characteristic ν_s values of several hydrogen fluoride-base complexes are compared in Table II. Although ν_s is more generally used as a measure of hydrogen bond strength, the ν_l value is an equally good indicator, as is shown in Table II; in addition, the ν_l mode provides structural information owing to degeneracy in a C_{3v} or linear complex.

The hydrogen fluoride-ammonia complex exhibits an unusually strong hydrogen bond for a neutral complex. This is attested by the relatively short N-H-F distance (2.66 Å) from the microwave spectrum, the relatively large $\Delta\nu_s$ from the vapor species (745 cm^{-1})[12] and the argon matrix-isolated species (921 cm^{-1}), the large ν_l value (916 cm^{-1}), and the calculated hydrogen-bond energy (12 kcal/mol).[8] SCF-MO calculations[10] show that the strong electrostatic contribution to the hydrogen bond in this system is supplemented by a substantial charge-transfer contribution from NH_3 σ to HF σ^*. Further 6-31G* calculations[9] predict a charge transfer of 0.033 electron and a dipole moment of 4.7 D, about 0.8 D in excess of sum of calculated values for NH_3 and HF. The measured dipole moment for the complex 4.448 D[11] exceeds the sum of experimental NH_3 and HF values by an even larger 1.2 D.

Matrix infrared spectra of the H_3N- -HF complex are consistent with significant charge transfer and a large dipole moment. Matrix shifts from the gas phase are known to be larger for polar molecules with large dipole moments than for covalent molecules. Lithium fluoride, with a dipole moment of 6.32 D,[20] is a case in point. The gas-phase fundamental (894 cm^{-1}) shifts to 842 cm^{-1} in solid argon and 776 cm^{-1} in solid nitrogen.[21,22] The solid nitrogen matrix interacts particularly strongly with ionic molecules, as has been described for the LiO molecule.[23] The matrix shifts for ν_s of H_3N- -HF from the vapor phase (3215 cm^{-1}) to solid argon (3041 cm^{-1}) to solid nitrogen (2775 cm^{-1}) are 5.4% and 13.7%, respectively, as compared to 5.8% and 13.2%, respectively, for LiF. The increase in ν_l from 916 to 1023 cm^{-1} on going from solid argon to nitrogen parallels the decrease in ν_s from 3041 to 2778 cm^{-1}; interaction with the nitrogen matrix apparently gives a stronger, more rigid H_3N- -HF complex. The observation of similar gas-to-argon matrix and gas-to-nitrogen matrix shifts for ν_s in the H_3N- -HF complex and the polar LiF molecule correlates the gas and matrix spectra for H_3N- -HF and demonstrates the substantial polar character of this strong hydrogen-bonded complex.

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