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Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

Codeposition of Ar/HF and Ar/N$_2$ samples at 10 K produced the N$_2$--H-F complex as evidenced by a very strong H-F stretching fundamental at 3881.4 cm^{-1} and a weak new 2332.1 cm^{-1} band assigned here to the N≡N stretching fundamental based on ^{14,15}N$_2$ and ^{15}N$_2$ substitution. A blue DF shift to 233.2 8 cm^{-1} indicates a slightly stronger deuterium bond in these floppy complexes relative to the 2327.5 cm^{-1} Raman fundamental for N$_2$ isolted in solid argon. Similar results were obtained for the weaker HCl and H$_2$O complexes. Three bond stretching modes were observed for the N$_2$--H-F--H-F complex.

INTRODUCTION

The spectroscopy of HF complexes has recently attracted a considerable amount of attention. The OC--HF complex has been characterized by microwave, tunable infrared laser, and infrared matrix spectroscopy,[1–3] while the weaker N$_2$--HF complex has been examined by microwave and matrix infrared studies.[4,5]

Molecular nitrogen, the most abundant element in our atmosphere, is almost unreactive. However, nitrogen forms a range of complexes where N$_2$ is reduced in varying degrees by bonding to transition metal atoms, and the stretching fundamental ranges from 2215 cm and 2170 cm^{-1} for the Pd and Pt complexes[6,7] and to 2101 and 2089 cm^{-1} for the Co and Ni adducts,[6,8] while further reduction in the Li$^+$ N$_2^-$ species to 1800 cm^{-1} indicates charge transfer.[9]

The weaker N$_2$--HF complex is expected to perturb the nitrogen stretching fundamental much less, but the asymmetric structure of the complex does make this fundamental infrared active. The degree to which the HF ligand can lift infrared selection rules for a homonuclear diatomic molecule is of interest here; the ν_1 mode of the CO$_2$ submolecule in the CO$_2$--HF complex and the ν_2 mode of the C$_2$H$_2$ submolecule in the C$_2$H$_2$--HF complex have been recorded as weak bands in FTIR matrix studies.[10,11] We report here infrared observation of the N≡N stretching fundamental in N$_2$ complexes with HF, HCl, and H$_2$O.

EXPERIMENTAL

The vacuum, cryogenic, and spectroscopic techniques have been described previously.[12] The spectra were obtained on a Nicolet 7199 Fourier-transform infrared spectrometer in the wavelength range 4000–400 cm^{-1} using 0.24 cm^{-1} resolution and dry nitrogen as purge gas and to operate the "air" bearings; frequency accuracy is better than ± 0.1 cm^{-1}. A background spectrum was recorded of the cold window before each experiment and all subsequent spectra, for that experiment, were ratioed against the background producing simulated double-beam spectra. The HF (Matheson) was purified by evacuating at 77 K and then at 180 K, and DF was synthesized by mixing equimolar amounts of D$_2$ (Air Products) and F$_2$ (Matheson) in a well-passivated 3 $\mathscr{L}$ stainless steel can and then outgassing the product at 77 K.

The HCl (Matheson), DCl (Merck and Co.), H$_2$O (distilled), and D$_2$O (Aldrich) were also purified by outgassing at 77 K. Two isotopic mixtures of nitrogen consisted of ^{15}N$_2$ (25% ^{14}N$_2$ impurity) (BioRad) and ^{14}N$_2$/^{14}N^{15}N/^{15}N$_2$ = 3/3/1 (Isomet).

The samples were prepared by mixing with Ar to give mole ratios (Ar/sample) of 200/1 for N$_2$ and the hydroacids (except 100/1 for DCl) and 800/1 for H$_2$O and D$_2$O. The matrices were formed by codepositing the hydrogen halides or water and the nitrogen isotopic mixture onto a CsI window at 10 K. The deposition rates were 5–9 mmol/h for each sample corresponding to a 50–60 mmol matrix for codeposition experiments. The matrix was annealed by warming to 22–25 K for 10 min and then recooling to 10 K.

RESULTS

Fourier-transform infrared spectra of nitrogen complexes with HF, HCl, and H$_2$O in solid argon will be presented.

N$_2$ + HF and DF

Codepositing samples of Ar/HF = 200/1 and Ar/^{14}N$_2$/^{14}N^{15}N/^{15}N$_2$ = 200/1 produced a very strong band at 3881.4 cm^{-1} and a band at 3787.7 cm^{-1} due to N$_2$--HF (labeled N) and N$_2$--(HF)$_2$ (labeled M), respectively, as previously reported[5]; these bands are illustrated in Fig. 1(a). Three weak bands were also observed in the nitrogen stretching region at 2332.1 (A = absorbance = 0.012), 2293.5 (A = 0.023), and 2254.2 (A = 0.07) cm^{-1}, as shown in Fig. 2(a), below the sharp CO$_2$ doublet at 2345.0 and 2339.1 cm^{-1}; the 2332 cm^{-1} band was not observed in previous studies due to interference from atmospheric CO$_2$. Upon annealing the matrix to 24 K, the three weak bands increased 50% in intensity while weak shoulder bands appeared at 2333.6, 2294.9, and 2255.7 cm^{-1} [labeled M in Fig. 2(b)]; the 3881.4 cm^{-1} band increased and the 3787.7 cm^{-1} band increased markedly [Fig. 1(b)]. In addition, sharp new bands appeared at 3816.9 cm^{-1} (marked M), 3778.6, 3774.6 cm^{-1} (labeled L) and 3717.8 cm^{-1} (indicated O). The 3825.5 cm^{-1} (HF)$_2$ (labeled D) and 3702.0 cm^{-1} (HF)$_3$ (labeled T) bands were unchanged, but new 3618 cm^{-1} and cyclic (HF)$_n$ bands were produced as reported previously [like Fig. 1(c) in Ref. 13].[13] A similar Ar/DF experiment (90% DF enrichment)
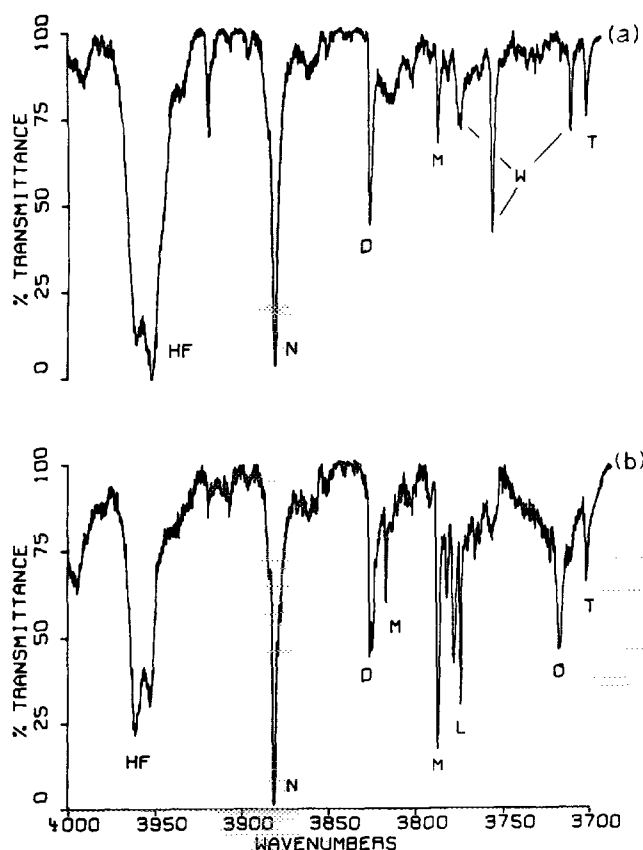
FIG. 1. (a) FTIR spectrum in the 3700–4000 cm^{-1} region for Ar/HF = 200/1 and Ar/^{14,15}N$_2$ = 200/1 samples (30 mmol each) codeposited at 10 K over a 4 h period. (b) Spectrum after annealing at 24 K for 10 min and recooling to 10 K.

was performed with the remaining ^{14,15}N$_2$ sample, and the sharp weak bands were blue shifted by 0.6–0.7 cm^{-1}, as listed in Table II. These bands increased on sample warming and new DF counterparts of the bands in Fig. 1(b) were observed and are listed in Table I. In addition, new bands were observed in the HF region, which indicates that these bands are due to mixed isotopic species, as listed in Table I. In particular the sharp doublets observed at 3807.8 and 3802.6 cm^{-1} and 2793.9 and 2791.3 cm^{-1} [shown in Fig. 1(b) of Ref. 5, but not assigned] were also markedly enhanced upon addition of nitrogen. Similar experiments were performed using ^{15}N$_2$ samples with HF, and with DF, and except for the absence of the ^{14}N^{15}N product absorption near 2294 cm^{-1}, the spectra were identical. Figure 2(c) illustrates the spectrum with this sample and DF; sample warming [Fig. 2(d)] shows the strong ^{15}N$_2$--DF product at 2254.9 cm^{-1}, with a weak ^{15}N$_2$--HF shoulder at 2254.3 cm^{-1}, and a new M band at 2256.3 cm^{-1}.

N$_2$ + HCl and DCl

Upon codeposition of Ar/HCl = 200/1 and Ar/^{15}N$_2$, ^{14}N$_2$ = 200/1 samples at 10 K, the HCl R (0) line at 2888 cm^{-1} was completely absorbing while the P (1) band at 2853 cm^{-1} had an absorbance of 0.45, and the strongest (HCl)$_2$ dimer band[14] was observed at 2817.8 cm^{-1}. The N$_2$--HCl complex[15–17] was observed at 2863.4 and 2861.3 cm^{-1}, almost completely absorbing, corresponding to the ^{35}Cl and ^{37}Cl isotopes in HCl, respectively, along with weak absorp-
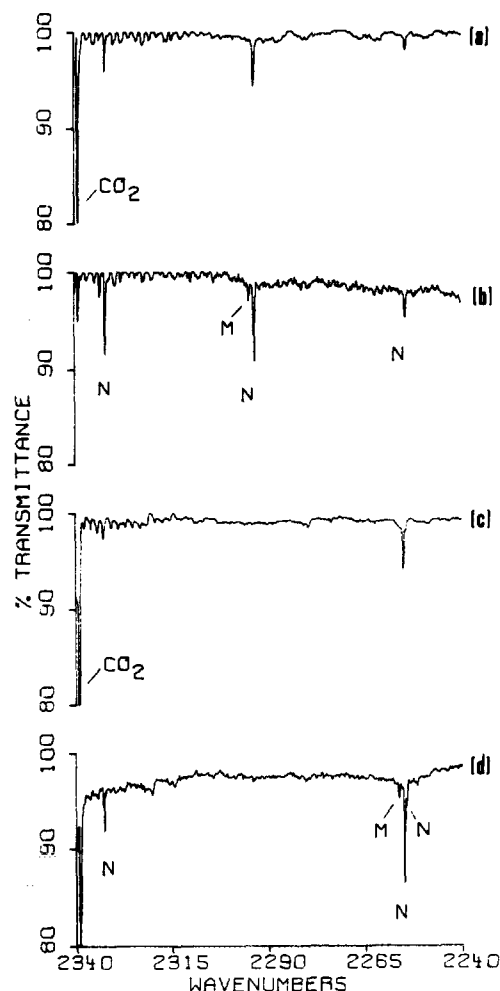

FIG. 2. FTIR spectra in 2240–2340 cm^{-1} region for isotopic samples of hydrogen fluoride and nitrogen in solid argon. (a) HF and ^{14}N$_2$, ^{14}N^{15}N, ^{15}N$_2$ after codeposition with excess argon at 10 K, (b) after annealing at 24 K for 10 min, (c) DF and ^{14}N$_2$, ^{15}N$_2$ after codeposition with excess argon at 10 K, (d) after annealing at 22 K for 10 min.

TABLE I. Isotopic absorptions (cm^{-1}) for (N$_2$)$_w$(HF)$_x$(DF)$_y$ species in solid argon at 10 K.

w	n	(N$_2$)$_w$(HF)$_n$	(N$_2$)$_w$(HF)$_x$(DF)$_y$ [a]	(N$_2$)$_w$(DF)$_n$
0	1	3919.5		2876.7
1	1	3881.4		2846.2
0	2	3825.5	2808.3	2803.6
1	2	3816.9	3807.8,2793.9	2798.7
1	2	3787.7	2791.3,3802.6	2776.5
2	2	3778.6,3774.6	3798.8,2784.5	2770.7,2767.1
1	3	3717.7	3731,2724, 2742,2737	2730.4
1[b]	1	2332.1		2332.8
1[b]	2	2333.6		(2334)
1[c]	1	2293.5		2294.2
1[c]	2	2294.9		2295.7
1[d]	1	2254.3		2254.9
1[d]	2	2255.7		2256.3

[a] $(x + y = n)$.
[b] N$_2$ = 14–14, the (2334 cm^{-1}) position was predicted from heavier nitrogen isotopes further from CO$_2$ interference.
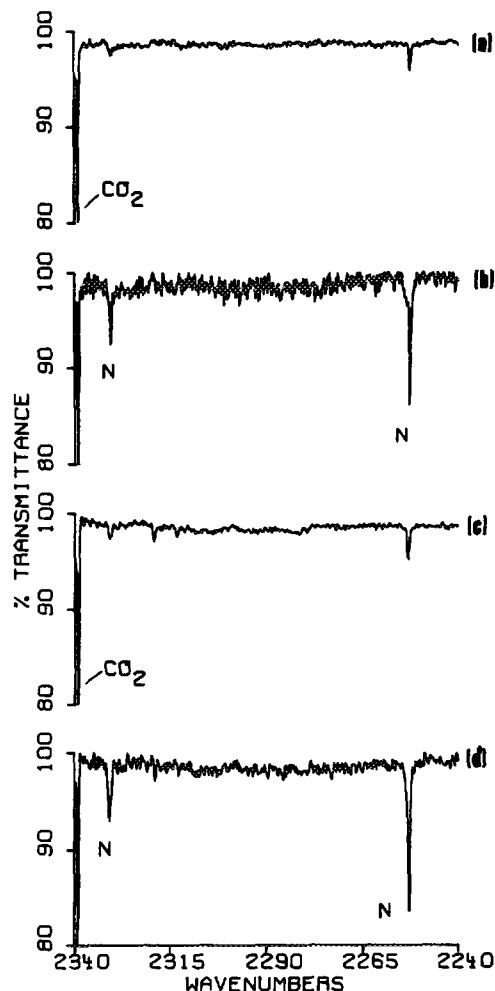[c] N$_2$ = 14–15.
[d] N$_2$ = 15–15.

FIG. 3. FTIR spectra in 2240–2340 cm^{-1} region for isotopic samples of hydrogen chloride and nitrogen in solid argon. (a) HCl and $^{14}N_2$, $^{15}N_2$ after codeposition with excess argon at 10 K, (b) after annealing at 22 K, (c) DCl (approximately 70% enrichment) and $^{14}N_2$, $^{15}N_2$ after codeposition with excess argon at 10 K, (d) after annealing at 24 K for 10 min.

tions at 2330.7 cm^{-1} ($A = 0.004$) and 2252.8 cm^{-1} ($A = 0.012$) in the N_2 stretching region [Fig. 3(a)], which are collected in Table II. A very weak triplet with major component at 2810.9 cm^{-1} and a very weak doublet with a major component at 2846.1 cm^{-1} were observed corresponding to N_2--(HCl)$_2$. Annealing the matrix to 22 K caused the two bands at 2863.4 and 2861.3 cm^{-1} to become completely absorbing, the 2330.6 and 2252.8 cm^{-1} bands to increase about five-fold in intensity, a new weak band to grow in at 2353.6 cm^{-1} ($A = 0.003$), and a high frequency shoulder to appear on the 2330.7 band at 2331.5 cm^{-1} [Fig. 3(b)]. The doublet

TABLE II. Absorptions (cm^{-1}) for isotopic nitrogen stretching fundamentals in hydrogen bonded complexes in solid argon.

Nitrogen isotope	Acid submolecules					
	HF	DF	HCl	DCl	H_2O	D_2O
14–14	2332.1	2332.8	2330.7	2331.1	2329.0	2329.6
14–15	2293.5	2294.2	2292.1	⋯	⋯	⋯
15–15	2254.3	2254.9	2252.8	2253.2	2251.2	2251.9

and triplet bands of N_2--(HCl)$_2$ grew significantly at 2846.0, 2843.3, and 2812.5, 2810.9, 2808.1 cm^{-1}, respectively, and strong (HCl)$_n$ bands appeared at 2786.9 and 2747.2 cm^{-1} as reported by Perchard et al.[16,17] A similar experiment with $^{14,15}N_2$ in the sample gave the same spectrum with the addition of a sharp 2292.1 cm^{-1} band in the nitrogen stretching region.

When Ar/DCl = 100/1 was codeposited with the $^{15}N_2$ samples, the R (0) band of D^{35}Cl at 2089 cm^{-1} was almost completely absorbing while that for D^{37}Cl, at 2086 cm^{-1}, had a correspondingly smaller absorbance. The (DCl)$_2$ dimer band at 2039.2 cm^{-1} and (HCl--DCl) mixed dimer at 2040.5 cm^{-1} were both observed as well as the N_2–DCl bands at 2073.1 and 2070.2 cm^{-1}, in agreement with the Perchard group. New weak bands were also present at 2331.1 ($A = 0.006$) and 2253.2 cm^{-1} ($A = 0.015$) in the nitrogen stretching region [Fig. 3(c)]. In the HCl region the (HCl)$_2$ band at 2817.7 cm^{-1} was observed along with the two N_2–HCl bands mentioned previously. Warming the matrix to 23 K provided growth in the 2073.1 and 2070.2 cm^{-1} bands and produced new bands including strong N_2--(DCl)$_2$ absorptions at 2060.6, 2058.1, and 2032.8 cm^{-1}, N_2--HCl--DCl bands at 2037.6, 2036.1, and 2034.6 cm^{-1}. The weak bands in the nitrogen stretching region grew five-fold in intensity with weaker bands appearing on the low frequency sides at 2330.5 and 2252.9 cm^{-1} corresponding to those observed in the HCl experiments [Fig. 3(d)]. Also, high frequency shoulders were present on each band, at 2331.7 and 2253.8 cm^{-1}, which are observed only after annealing.

N_2 + H_2O and D_2O

A matrix formed by deposition of an Ar/$^{15}N_2$, $^{14}N_2$ = 200/1 sample with trace amounts of water impurity (Ar/$H_2O \approx$ 10 000/1) contained a very weak band ($A = 0.0012$) at 2251.5 cm^{-1} in the nitrogen stretching region and weak bands at 1599.7 and 3731.8 cm^{-1} in the H_2O bending and stretching regions, respectively [Fig. 4(a)]. Warming the matrix caused these bands to increase about five-fold in intensity [Fig. 4(b)]. Deposition of a Ar/$^{14}N_2$, $^{15}N_2$/H_2O = 800/4/1 sample [Fig. 4(c)] provided two bands in the N_2 stretching region at 2251.5 cm^{-1} ($A = 0.043$) and 2329.3 cm^{-1} ($A = 0.015$) which grew 1.5-fold in intensity on warming the matrix to 22 K [Fig. 4(d)]. The sharp bands in the H_2O stretching and bending regions mentioned earlier could not be observed because of water polymer formation. Deposition of an Ar/$^{15}N_2$, $^{14}N_2$/D_2O = 800/4/1 sample provided slightly blue shifted 2329.6 and 2251.9 cm^{-1} bands with similar intensities and annealing behavior as those of the H_2O experiment.

DISCUSSION

The new infrared absorptions will be assigned to nitrogen stretching vibrations in hydrogen bonded complexes based upon a minor dependence on the acid partner and a major dependence on the nitrogen isotopic submolecule.

N_2 + HF and DF

The sharp, weak new 2332.1 cm^{-1} infrared band in the nitrogen stretching region (fwhm = 0.4 cm^{-1}) is associated
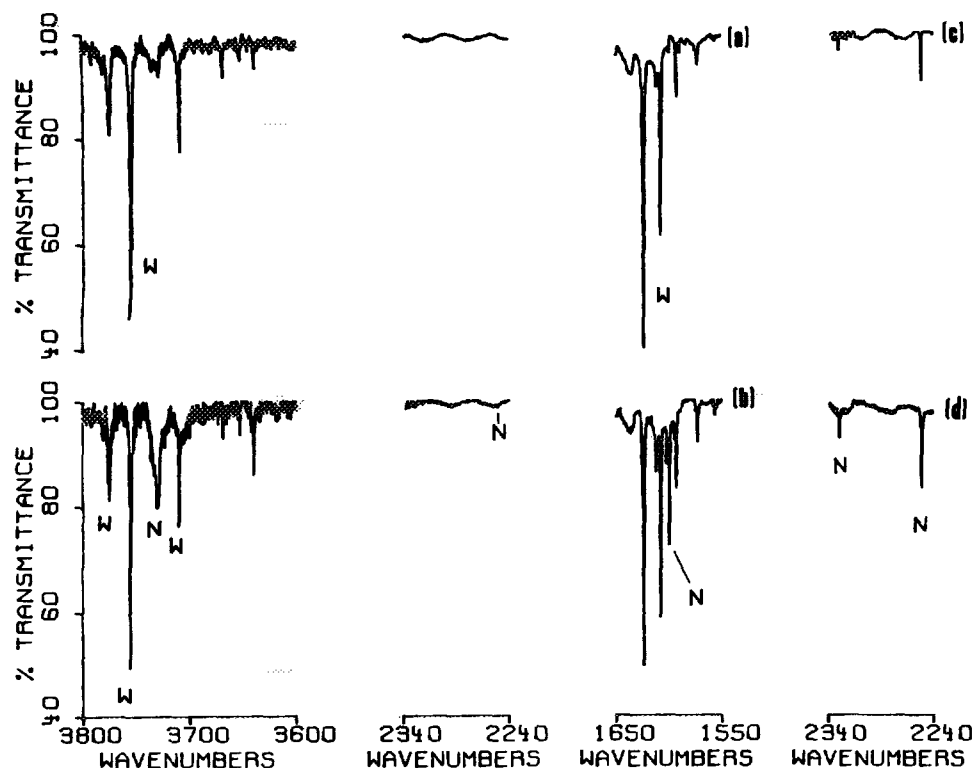
FIG. 4. FTIR spectra of Ar/$^{14}N_2$, $^{15}N_2$ = 200/1 sample with trace (Ar/$H_2O \approx 10\,000/1$) water contamination, (b) after annealing at 22 K, (c) spectra of Ar/$^{15}N_2$, $^{14}N_2/H_2O$ = 800/4/1 sample, (d) after annealing to 22 K.

with the very strong 3381.4 cm^{-1} band on sample preparation and annealing, and accordingly, the 2332.1 cm^{-1} band is associated with the N_2--HF complex (1):

$$N \equiv N\text{--}H\text{--}F. \tag{1}$$

The nitrogen isotopic behavior confirms assignment to the nitrogen stretching vibration. Simple harmonic diatomic calculations predict the 15-15 isotopic counterpart at 2253.4 cm^{-1}, just 0.9 cm^{-1} below the observed value, and predict the 14-15 species at 2293.1 cm^{-1}, only 0.4 cm^{-1} below the experimental value. These small deviations are in the direction expected for differences in anharmonicity between lighter and heavier isotopes. The small +0.7 cm^{-1} shift with DF substitution verifies that HF is the source of the perturbation. Clearly the HF ligand is responsible for infrared observation of this mode and displacement from the 2327.5 cm^{-1} Raman value for N_2 in solid argon.[17] Polarization of N_2 by HF does in fact occur to a small degree[18]; the difference in ^{14}N nuclear quadrupole coupling constants from the microwave spectrum has been interpreted to indicate transfer of 0.03e from the unbound to the bound nitrogen atom upon complex formation.[4] Hence, the $N \equiv N$ vibration should be observed in the infrared spectrum of N_2--HF.
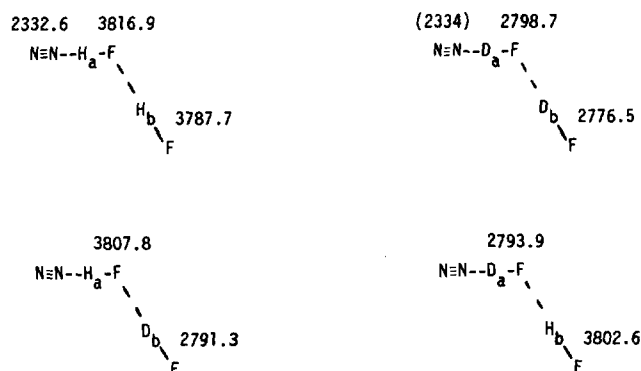
The microwave spectrum shows that the N_2--HF complex is linear, and that the two nitrogen atoms are not equivalent.[4] From a vibrational standpoint this inequivalence is too small to be resolved in the 0.48 ± 0.02 cm^{-1} bandwidth for both 14-15 isotopic absorptions at 2293.5 cm^{-1}, and the statistical weights of the two $^{14}N^{15}N$ arrangements add to give the observed spectrum. There is, however, a slight broadening of the 2293.5 cm^{-1} band as compared to the 2332.1 and 2254.3 cm^{-1} bands for the $^{14}N_2$ and $^{15}N_2$ complexes (fwhm = 0.42 ± 0.02 cm^{-1}).

Sample annealing caused diffusion and further association of HF and N_2 in the cold matrix. This produced a modest increase in absorptions due to complex (1) and an order of magnitude growth in absorptions due to a species containing 2 HF submolecules, such as complex (2) identified previously[5] by its strongest infrared band at 3787.7 cm^{-1}. Complex (2),

$$N \equiv N\text{--}H_a\text{--}F \diagdown_{H_b \diagdown_F} \tag{2}$$
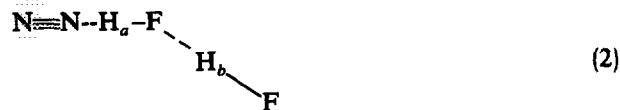
also reveals new resolved satellites 1.5 cm^{-1} above the isotopic N_2 fundamentals for complex (1) that are appropriate for the nitrogen stretching fundamental in complex (2). Here the fluoride affinity of H_b–F enables a stronger N_2--H_a hydrogen bond to be formed in complex (2) than in complex (1) which causes a larger displacement in the nitrogen fundamental from the N_2 value in solid argon.[17] The strong 3787.7 cm^{-1} band was assigned to the $\nu(H_b$–F) stretching mode and its position below the $\nu(H_b$–F) mode for (HF)$_2$ at 3825.5 cm^{-1} in solid argon was attributed to the effect of the N_2 base in complex (2), but the weaker $\nu(H_a$–F) mode was not assigned.[5] The spectra in Fig. 1 suggest that the sharp 3816.9 cm^{-1} band produced on annealing is associated with complex (2) and is due to the $\nu(H_a$–F) stretching mode. This identification is confirmed by observation of the 3816.9 cm^{-1} band in experiments involving *in situ* photolysis of N_2, H_2, F_2 samples which gave (HF)$_2$, and complexes (1) and (2) as major products without (HF)$_3$ absorptions, in accord with earlier H_2, F_2 photolysis experiments which gave (HF)$_2$ as the major product.[19] This assignment is confirmed by identifica-

tion of both mixed (HF) (DF) counterparts of complex (2). The 3807.8 and 3802.6 cm^{-1} bands maintained constant intensities relative to one another and to the 2793.9 and 2791.3 cm^{-1} bands, but the intensities of these four bands due to the two mixed isotopic (2) species relative to the 3787.7 and 2776.5 cm^{-1} bands due to the pure isotopic species depended on DF enrichment. These four mixed isotopic bands were also observed with comparable intensities after photolysis of a N_2,HD,F_2 sample. Furthermore, the mixed isotopic bands appear at almost the average of the two H–F stretching modes in complex (2), which are strongly coupled in the pure isotopic species, but not with mixed (HF) (DF). The vibrational assignments (cm^{-1}) given below form a basis for two comparisons with the (HF)$_2$ submolecule and its isotopes.

2332.6   3816.9

N≡N--H$_a$-F
            \
             \
              H$_b$ 3787.7
                 \
                  F

(2334)   2798.7

N≡N--D$_a$-F
            \
             \
              D$_b$ 2776.5
                 \
                  F

3807.8

N≡N--H$_a$-F
            \
             \
              D$_b$ 2791.3
                 \
                  F

2793.9

N≡N--D$_a$-F
            \
             \
              H$_b$ 3802.6
                 \
                  F

First, as a consequence of the N≡N--H$_a$ hydrogen bond in complex (2), the H$_a$–F and H$_b$–F stretching modes are only 29 cm^{-1} apart, whereas in (HF)$_2$ these modes are separated by 70 cm^{-1} in solid argon.[13] Accordingly, more vibrational coupling is expected in complex (2) than in (HF)$_2$, and the D$_b$–F stretching mode in the N$_2$--H$_a$–F--D$_b$–F species is 14 cm^{-1} above the N$_2$--(DF)$_2$ value, whereas the D$_b$–F mode in the H$_a$–F--D$_b$–F dimer is only 4 cm^{-1} above the (DF)$_2$ value.[13,20] Comparison of the "uncoupled" 3807.8 cm^{-1} H$_a$–F and 3802.6 cm^{-1} H$_b$–F motions in the two different mixed isotopic species suggests that the two hydrogen bonds in complex (2) are of comparable strength. The second consequence of two hydrogen bonds in complex (2) is that *both* mixed isotopic species were observed in codeposition experiments, which contrasts HF--DF where only the more stable deuterium bonded species were trapped at 10 K.[13,19,20] In a species like (2) with two hydrogen bonds of comparable strength, as determined from the vibrational spectrum, the preference of positions in the mixed isotopic species is not as critical as position is in HF--DF, which has only one "hydrogen" bond.

The sharp 3778.6 and 3774.6 cm^{-1} bands labeled L [Fig. 1(b)] increased relative to complex (2) bands on sample annealing, and they exhibit the same relationship to complex (2) bands found for the analogous HCl species assigned to N$_2$--(HCl)$_2$ and (N$_2$)$_2$--(HCl)$_2$.[17] Accordingly, the 3778.6 and 3774.6 bands are assigned to N$_2$ perturbed complex (2), i.e., (N$_2$)$_2$--(HF)$_2$. The (DF)$_2$ and mixed (HF) (DF) counterparts are similar to those for the strongest band of complex (2), which suggests a minor bonding role for the second N$_2$ sub-

molecule in the (N$_2$)$_2$--(HF)$_2$ complex. The only possible evidence for a (N$_2$)$_2$--HF species is the weak 3861 cm^{-1} shoulder on the strong 3881 cm^{-1} (1) band, but this is not a definitive identification. The 3717.7 cm^{-1} band labeled O was characterized by diffusion behavior in the earlier (HF)$_n$ study and tentatively assigned to higher open-(HF)$_n$ species.[13] The present work shows that this higher open-(HF)$_n$ species also contains one nitrogen molecule and is best identified as N$_2$--(HF)$_3$.

A similar sharp, weak 3816 cm^{-1} band was associated with (HF)$_3$ on diffusion in the previous study[13] and assigned to the weaker H$_c$–F stretching mode of trans-(HF)$_3$. This band also tracked with the 3787.7 cm^{-1} band (trace N$_2$ present), but in the present work with 0.5% N$_2$ added, the formation of (HF)$_3$ was suppressed and N$_2$--(HF)$_2$ favored, therefore the 3816.9 cm^{-1} band must be assigned to the latter species. New experiments on the HF system have failed to produce a band that can be assigned to the H$_c$–F stretching mode of trans-(HF)$_3$, which is expected to be a substantially weaker band than the H$_b$–F stretching absorption.

N$_2$ + HCl and DCl

The sharp, weak 2330.7 cm^{-1} band in the HCl experiments is due to the linear[21] N$_2$--HCl complex (3) that gives the very strong 2863.4, 2861.3 cm^{-1} chlorine isotopic doublet. The present infrared band

$$N≡N--H-Cl \qquad (3)$$

is in excellent agreement with the 2330.5 cm^{-1} Raman measurement of this fundamental in solid argon.[17] The nitrogen isotopic data in Table II confirm this assignment to the nitrogen stretching fundamental. Sample annealing produced a substantial growth in N$_2$--HCl bands, an even greater increase in bands due to N$_2$--(HCl)$_2$, and new shoulders 1 cm^{-1} above the nitrogen stretching bands for complex (3) that are assigned to N$_2$--(HCl)$_2$. The effect of DCl substitution in complex (3) is in accord with that found for DF substitution in complex (1), namely a blue shift of 0.4 cm^{-1} for the nitrogen stretching fundamental.

N$_2$ + H$_2$O and D$_2$O

The ^{15}N$_2$ sample used here exhibited a very weak 2251.5 cm^{-1} band that increased markedly when H$_2$O was doped into the sample (Fig. 4). This band and its ^{14}N$_2$ counterpart at 2329.0 cm^{-1} are appropriate for nitrogen stretching fundamentals in water complexes (4) with ^{15}N$_2$ and ^{14}N$_2$, respectively. New bands in the water absorption region

$$N≡N--H-O \atop H \qquad (4)$$

at 3731.8 and 1599.7 cm^{-1} are probably due to the H$_2$O submolecule in complex (4). These latter bands show no evidence of rotation of H$_2$O in the complex, as found for H$_2$O isolated in solid argon,[22] and the O–H stretching band is red shifted and the H–O–H bending mode is blue shifted from the monomer fundamentals ($\nu_3 = 3734.3$ cm^{-1}, $\nu_2 = 1589.1$ cm^{-1})[23] as would be expected for H$_2$O in a hydrogen bonded configuration. Finally, D$_2$O substitution results in a 0.6

cm^{-1} blue shift on the nitrogen stretching fundamental in complex (4), similar to this effect for complexes (1) and (3).

Bonding trends and comparisons

The trend of increasing nitrogen stretching fundamentals with increasing hydrogen bond strength in the series H_2O, HCl, HF, and $(HF)_2$ is illustrated in Table III. A similar trend has been reported for the analogous stronger CO complexes, which exhibit fivefold greater displacements. Intermolecular potential well depths, now available,[24] support the trend predicted from the vibrational spectra of OC--HX complexes in solid argon.[3] The hydrogen bonding interaction leads to a small (0.01e) amount of charge transfer in the OC--HF complex, although two reports disagree on its relative contribution to the bonding.[18,25] The hydrogen bonding ligand presumably interacts primarily with the nitrogen HOMO (sigma bonding) and polarizes it, and after electronic structure readjustment, the effective bonding between the nitrogen atoms is slightly enhanced. Detailed *ab initio* calculations on the N_2--HF complex show substantial polarization of both monomer electron distributions and small changes in monomer bond lengths.[18]

Although it is difficult to make a quantitative comparison, in similar experiments with similar ν(H--F) intensities the $\nu(N\equiv N)$ mode in N_2--HF exhibits about 0.05 of the infrared intensity of the $\nu(C\equiv O)$ mode in OC--HF.[3,5]

The small blue shifts in $N\equiv N$ stretching modes on substituting deuterium for hydrogen in the bonding acid are in accord with a 1.0 cm^{-1} blue shift found for the $C\equiv O$ stretching mode in the analogous carbon monoxide complexes.[3] These shifts cannot be explained by interaction between bond stretching modes in the linear complexes because the closer D--F vibration would in fact force the $N\equiv N$ stretch to lower frequency. Rather the larger perturbation by the deuterated acid is attributed to a slightly stronger deuterium bond owing to the smaller average zero point displacement of deuterium away from the equilibrium position. Microwave spectra reveal slightly shorter deuterium bonds [OC--H(D)Cl difference 0.011 Å; OC--H(D)F difference 0.0104 Å; N_2--H(D)F difference 0.014 Å][1,24,26] and a slightly deeper well depth for OC--DF (1024 cm^{-1}) as compared to OC--HF (987 cm^{-1}).[24]

The similar OC--H_a--F--H_b--F complex was identified previously,[3] but the mixed HF--DF species were not reported and assigned. Based on the above discussion of vibrational coupling for complex (2), H--F stretching modes are expected

for the two mixed isotopic species midway between the H_a--F and H_b--F stretching modes observed at 3771.7 and 3645.9 cm^{-1}, respectively, and D--F stretching modes are likewise expected for the two mixed isotopic species at a position between the D_a--F and D_b--F stretching modes at 2769.6 and 2686.4 cm^{-1}, respectively. New sharp bands were observed at 3714.6, 3697.5, 2726.0, and 2706.7 cm^{-1} in the CO experiments with HF and DF, and they again demonstrate that the two mixed isotopic arrangements are of comparable stability for the 1/2 complex involving two hydrogen bonds.

CONCLUSIONS

Argon matrix samples containing $^{14}N_2$ and HF reveal a sharp weak 2332.1 cm^{-1} band that exhibits the proper $^{14,15}N_2$ and $^{15}N_2$ isotopic behavior for the nitrogen stretching mode in the $N\equiv N$--HF complex. The blue DF shift to 2332.8 cm^{-1} indicates a slightly stronger deuterium bond in these floppy molecular complexes. Observation of the nitrogen stretching fundamental in the complex above the isolated N_2 value suggests monomer electronic structure readjustment giving a slightly stronger $N\equiv N$ bond in the complex. Weaker hydrogen bonded complexes were observed for HCl and H_2O acids with N_2. Three bond stretching modes for the $N\equiv N$--H--F--H--F complex are in accord with cooperative hydrogen bonding effects. Both mixed HF, DF isotopic arrangements have been observed for this 1/2 complex, in contrast to $(HF)_2$, which gave only the H--F--D--F arrangement on reagent cocondensation. The presence of two hydrogen bonds of comparable strength in $N\equiv N$--H--F--H--F makes arrangement of HF and DF in the two mixed isotopic dimers much less critical than in HF--DF with only one "hydrogen" bond.

Note added in proof: Normal coordinate calculations were done for N_2--HF--HF, and the mixed and fully deuterated species using the Schachtschneider FADJ program and only chemical bond stretching coordinates. The diagonal force constants, H_a--F, H_b--F interaction force constant, and potential energy distributions were not particularly sensitive to the $N\equiv N$, H_a--F interaction force constant, so the latter was fixed at zero. The simple potential function $F(N\equiv N) = 22.45$ mdyn/Å, $F(H_a$--F$) = 8.23$ mdyn/Å, $F(H_b$--F$) = 8.21$ mdyn/Å, $F(H_a$--F, H_b--F$) = 0.06$ mdyn/Å calculated H--F fundamentals about 16 cm^{-1} too high and D--F fundamentals approximately 18 cm^{-1} too low, which is the direction expected because of the cubic contribution to anharmonicity. The conclusion of substantial interaction between H_a--F and H_b--F stretching vibrations based on the appearance of mixed isotopic fundamentals intermediate between pure isotopic values is substantiated by the potential energy distributions. For N_2--$(HF)_2$, the 3816.9 cm^{-1} fundamental is 58.1% H_a--F and 41.2% H_b--F with 0.7% apportioned to the interaction, and the 3787.7 cm^{-1} fundamental is 41.9% H_a--F and 58.8% H_b--F with $-$0.7% due to the interaction force constant. An identical potential energy distribution was calculated for N_2--$(DF)_2$; however, for both mixed isotopes the three fundamentals were distributed 100% to their respective force constants. The substantial mixing of H--F modes in N_2--$(HF)_2$ and the relative intensities of the 3816.9 and 3787.7 cm^{-1} fundamentals suggests

TABLE III. Absorptions and displacements (cm^{-1}) for $N\equiv N$ and $C\equiv O$ stretching fundamentals in hydrogen bonded complexes in solid argon.

Acid	$\nu(N\equiv N)$	$\Delta\nu$	$\nu(C\equiv O)^b$	$\Delta\nu$
$(HF)_2$	2333.6	6.1	2170.5	32.2
DF	2332.8	5.3	2163.4	25.1
HF	2332.1	4.6	2162.4	24.1
HCl	2330.7	3.2	2154.3	16.0
HOH	2390.0	1.5	2149.1	10.8
$\cdots$	2327.5^a		2138.3	

^{a} Raman measurement for N_2 in solid argon, Ref. 17.
^{b} Data from Ref. 3.

that the former involves symmetric (N-phase) and the latter antisymmetric (out-of-phase) stretching of the two H–F submolecules, a point substantiated by the calculated eigenvectors.

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