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FTIR spectra of water–hydrogen fluoride complexes in solid argon. Evidence for inversion doubling in the HF librational modes of H_2O- -HF

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Co-condensation of dilute Ar/HF and Ar/H_2O samples at 12 K produces a number of sharp new infrared absorptions. The major species, which exhibits a strong 3554.7 cm^{-1} band and two quartets beginning at 753.1 and 635.6 cm^{-1}, is identified as H_2O- -HF. Isotopic substitution in the base submolecule changes the splitting in the latter multiplets and provides evidence for inversion doubling of the H–F librational modes in the H_2O- -HF complex. The reverse complex HF- -HOH, identified at 3915.5 cm^{-1}, exhibits a stronger interaction when HOH is replaced by DOD. Two H–F stretching fundamentals, which show small D_2O shifts, increased markedly on sample warming and are assigned to the 1:2 complex H_2O- -HF- -HF with an open structure.

INTRODUCTION

The H_2O--HF heterodimer is of fundamental importance because of the role each submolecule plays in the study of hydrogen bonding. In particular, the structure of H_2O--HF is of chemical interest because conventional valence theory gives two bonded electron pairs and two nonbonded electron pairs tetrahedrally arranged about oxygen so a pyramidal structure might be expected if HF is attached to one nonbonded pair. The H_2O--HF complex was first observed by gas phase infrared spectroscopy which characterized the ν_s mode and two poorly resolved ν_l modes and suggested that the complex is planar.[1] Later microwave studies of the ground state complex were unable to discriminate between planar and pyramidal with a low barrier,[2] but spectra of excited vibrational states have conclusively established a pyramidal structure ($\phi = 46 \pm 8°$) with a 126 ± 70 cm^{-1} barrier to inversion.[3] These studies also showed a substantial perturbation for the lower frequency bending mode of the hydrogen bond that follows the inversion motion. *Ab initio* molecular orbital calculations with geometry optimization for the H_2O--HF complex are consistent with the microwave structure, and similar calculations predict the reverse complex HF--HOH to be less stable.[4]

Fourier-transform infrared spectra of HF complexes in solid argon have revealed very strong, sharp H–F stretching (ν_s) and H–F librational (ν_l) motions for the HF submolecule in the complexes which are diagnostic of the hydrogen bonding and structure in the complexes.[5–8] Although the higher frequency ν_l mode in the mirror plane of the pyramidal complex does not duplicate the inversion motion, inversion doubling of the ν_l levels might be expected. The argon matrix spectrum of H_2O--HF gives sharp ν_l bands with evidence for inversion doubling which will be described here.

EXPERIMENTAL

The apparatus and techniques have been described previously.[5–8] All spectra were recorded using a Nicolet 7199 FTIR spectrometer between 4000 and 400 cm^{-1} at 1.0 cm^{-1} resolution with ± 0.2 cm^{-1} accuracy and reproducibility for sharp bands. Hydrogen and deuterium fluoride were prepared in m mol quantities by reaction of F_2 (Matheson) and H_2 (Matheson) or D_2 (Air Products) in a 3 ℓ stainless-steel can and diluted with argon to Ar/HF = 200/1 to 600/1 mixtures. Distilled water, D_2O (Aldrich) and $H_2{}^{18}O$, $HD^{18}O$, $D_2{}^{18}O$ (97% ^{18}O enriched; 15% H_2O, 40% HOD, 45% D_2O as observed; Oak Ridge National Lab) were used after outgassing; the Ar/H_2O dilutions are approximate because of adsorption on the surface of the vacuum system. Argon mixtures of HF and water were simultaneously condensed on a 12 ± 1 K CsI window at 2 m mol/h rates for up to 18 h, and a spectrum was recorded. The matrix was warmed to 20–22 K for 10 min, recooled to 12 K and another spectrum was recorded to monitor the diffusion and association of molecular species.

RESULTS

Experiments for different isotopic submolecules will be described in turn.

H_2O + HF

Four experiments were done with H_2O and HF in solid argon with approximate Ar/H_2O concentrations ranging from 300/1 to 3600/1 and Ar/HF ratios of 300/1 and 600/1. Spectra of the more concentrated H_2O samples were complicated by water polymer absorptions, which increased significantly in absorbance after temperature cycling. Trace (a) in Figs. 1 and 2 illustrates the two product regions in the spectrum recorded after co-deposition of Ar/HF = 600/1 and Ar/H_2O = 3600/1 samples. This spectrum, where the most dilute water sample was used, shows water bands[9] (labeled *W*) and product absorptions that were stronger in more concentrated experiments, which include a strong, sharp band at 3554.7 cm^{-1} (labeled ν_s) and two quartets beginning at 753.1 and 635.6 cm^{-1} (labeled ν_l and listed in Table I). In addition, sharp HF absorptions were observed at 3962.3 and 3953.8 cm^{-1} and new bands due, respectively, to $(HF)_2$ and N_2--HF species were observed at 3825.5

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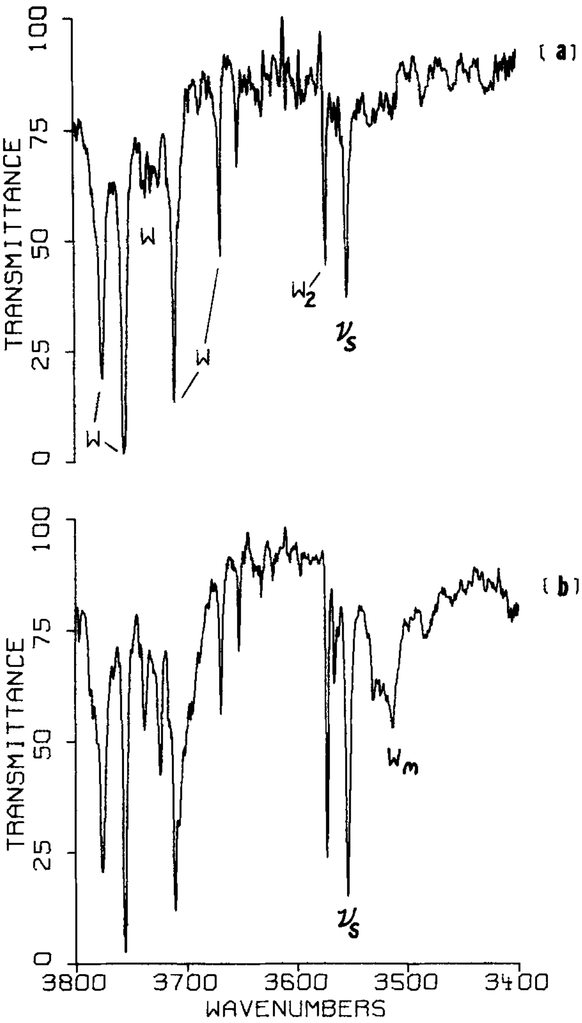


FIG. 1. FTIR spectrum in the 3800–3400 cm^{-1} region for sample prepared by co-condensing approximately equal amounts of Ar/H_2O = 3600/1 and Ar/HF = 600/1 mixtures. (a) Original sample condensed at 12 ± 1 K, (b) after warming to 19 K for 10 min and recooling to 12 K.

and 3881.5 cm^{-1}.[10,11] The relative absorbances of the components of each quartet, the quartets, and the 3554 cm^{-1} band remained constant in all of the H_2O + HF experiments and on temperature cycling the sample. Trace (b) in Figs. 1 and 2 shows the spectrum after warming the sample to 19 K for 10 min and recooling to 12 K. Several absorptions[12,13] due to $(H_2O)_2$ and $(H_2O)_n$ increased in absorbance, the ν_s and ν_l product absorptions of interest doubled in absorbance (the 753, 746 cm^{-1} doublet reached $A = 0.045$ and the 3554 cm^{-1} band reached $A = 0.74$), and weak absorptions increased at 3690 (shoulder) and 3272 cm^{-1}.

In the more concentrated sample prepared from 300/1 mixtures of each reagent, a sharp new band (subsequently identified as R) was observed at 3915.5 cm^{-1}, next to the induced Q branch of HF at 3919.5 cm^{-1}, which is listed in Table II. Temperature cycling this sample to 20 K for 10 min destoyed the 3915.5 cm^{-1} band, decreased the ν_s and ν_l absorptions by 40%, increased 3690 and 3272 cm^{-1} bands about 50%, and increased shoulders at 765 and 652 cm^{-1}, which are col-

TABLE I. New absorptions (cm^{-1}) produced upon co-condensation of water and hydrogen fluoride in solid argon at 12 K which are assigned to the 1 : 1 H_2O—HF complex.

H_2O + HF	$(\Delta\nu_l)$[a]	HOD + HF	$(\Delta\nu_l)$	D_2O + HF	$(\Delta\nu_l)$
3554.7		3551 ± 1		3549.0	
753.1		737.2		723.0	
746.8		731.4		716.4	
721.1	(32.0)	716.2	(21.0)	707.2	(15.8)
715.3				702	
635.6		629.4		625.3	
629.8		623.3		619.1	
614.3	(21.3)	613.7	(15.7)	613.1	(12.2)
608.6				607.5	
H_2O + DF				D_2O + DF	
2621.1				2613.4	
593.5				553.6	
588.0				547.4	
561.7	(31.8)			537.9	(15.7)
555.9				532.0	
487.2				467.6	
482.8				461.7	
468.6	(18.6)			455.6	(12.0)
462.9				450.5	

[a] The $(\Delta\nu_l)$ value given is the separation between the first and third bands in the librational mode multiplet.

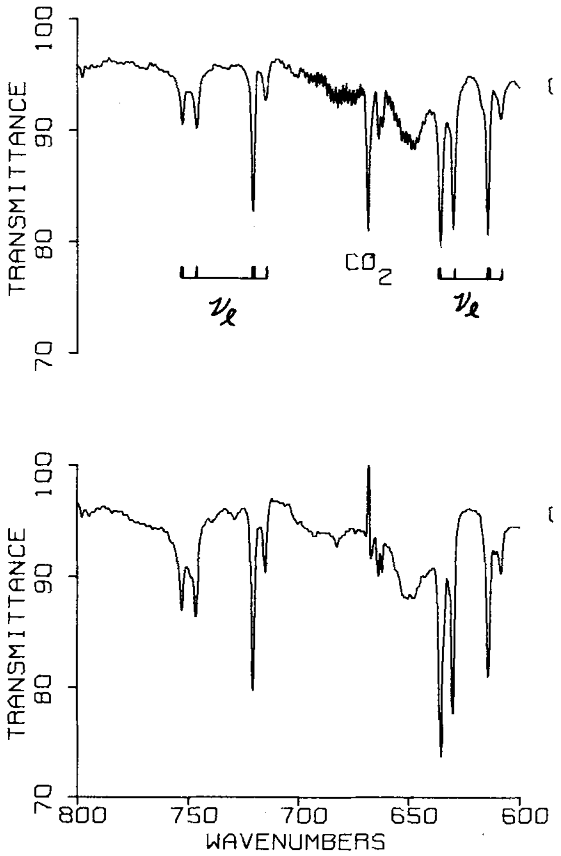


FIG. 2. Infrared spectrum in the 800–600 cm^{-1} region for sample described in Fig. 1 caption.

TABLE II. New absorptions (cm^{-1}) produced by association of water and hydrogen fluoride in solid noble gases at 12 K, which are assigned to the reverse HF—HOH complex.

Solid argon		Solid krypton
HF—HOH	DF—HOH	HF—HOH
3915.5	2873.1	3905.9
HF—DOD	DF—DOD	DF—HOH
3914.6	2872.5	2865.8

lected in Table III. The 3915.5 cm^{-1} band absorbance in this series of experiments was related to the H_2O concentration with approximately Ar/$H_2O \approx 1000/1$ required for observation; the 3915.5 cm^{-1} band decreased markedly on sample warming in all experiments.

The most dilute water experiments were Ar/HF studies with water present as a trace contaminant at the $10^4/1$ level. These experiments[10] gave weaker sharp ν_s and ν_l bands, like those in Figs. 1 and 2, free of any weak satellite sbsorptions that appeared in some of the more concentrated water experiments. Three Ar/H_2O samples without HF were examined during the course of these studies; the above product absorptions were absent from these samples.

Several experiments were done in solid krypton at 12 K to compare matrix effects. In a Kr/H_2O = 1000/1 and Kr/HF = 400/1 experiment, the sharp ν_s band was observed at 3542.5 cm^{-1}, the *R* band appeared at 3905.9 cm^{-1}, and sharp bands were observed at 755.0, 721.8, 636.3, and 615.2 cm^{-1} with weaker partially resolved shoulders at 750.3, 719.6, 633.5, and 608.9 cm^{-1} in the ν_l region. One of these experiments contained sufficient DF impurity to observe the sharp ν_s and *R* counterparts at 2612.0 and 2865.8 cm^{-1}, respectively. These product bands were not observed in a similar krypton–hydrogen fluoride experiment without water.

H_2O + DF and HF

Three experiments were done with 70% DF enriched hydrogen fluoride. The strong 3554.7 cm^{-1} band exhibited a DF counterpart at 2621.1 cm^{-1} (labeled ν_s) and the sharp 3915.5 cm^{-1} band showed a DF counterpart at 2873.1 cm^{-1} (labeled *R*), which are illustrated in Fig. 3. New product bands were also observed at 2697 2437 cm^{-1} [labeled (3)]. The lower frequency region is illustrated in Fig. 4; the quartets at 753.1 and 635.6 cm^{-1} exhibited similar DF counterparts beginning at 593.5 and 487.2 cm^{-1} (Table I). An Ar/H_2O = 1000/1 and Ar/(DF + HF) = 300/1 experiment gave similar weaker absorptions; sample warming to 16 K for 10 min and back to 12 K destroyed the *R* bands, doubled the ν_s and ν_l bands and produced a weak set of (3) bands (Table III).

D_2O + DF and HF

Two runs were carried out with D_2O and 70% DF. The sharp ν_s bands were observed at 3549.0 and 2613.4 cm^{-1}, and the ν_l multiplets were displaced 30–40 cm^{-1} as given in Table I. The infrared spectrum in Fig. 5(a) also shows a strong sharp 3914.6 cm^{-1} band (labeled *R*), 3881.5, and 3825.5 cm^{-1} bands due to N_2--HF and $(HF)_2$ (labeled *N* and *D*, respectively) and new product bands at 3667 and 3259 cm^{-1} [labeled (3)]; new DF counterparts at 2872.5, 2686, and 2417 cm^{-1} are not shown. The infrared spectrum in Fig. 6(a) shows the ν_l multiplets and new bands at 750.5, 635(sh), 561.7, and 475 cm^{-1}(sh) [labeled (3)]. This sample was warmed to 22 K for 10 min, recooled to 12 K and another spectrum shown in Figs. 5(b) and 6(b) was recorded; a considerable increase in intensity was observed for D_2O polymer bands, the ν_s and ν_l bands decreased 40%, the *R* bands decreased 20%, and

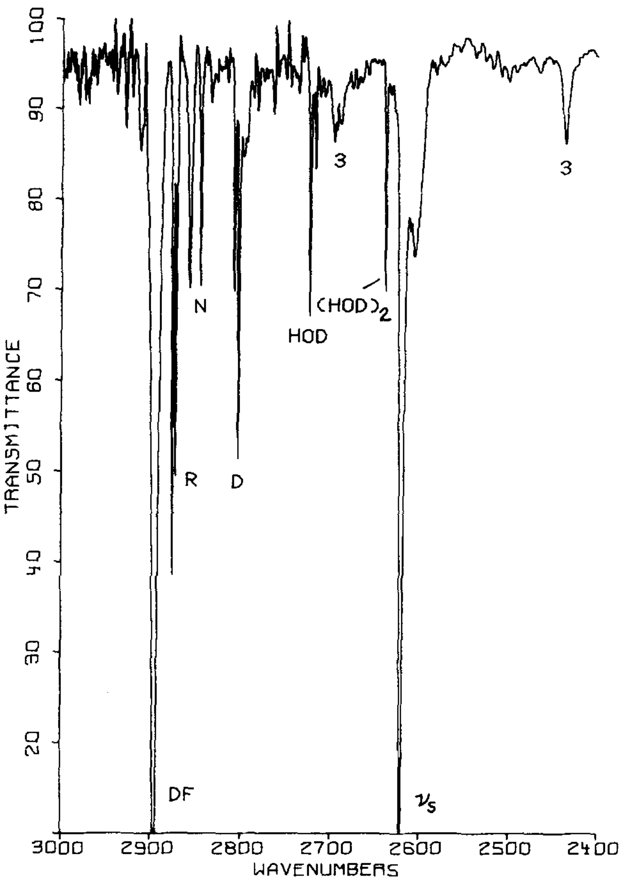


FIG. 3. FTIR spectrum in the 3000–2400 cm^{-1} region for sample formed by co-depositing Ar/H_2O = 400/1 and Ar/(DF + HF) = 200/1 (approximately 70% DF) sample at 12 K.

TABLE III. New absorptions (cm^{-1}) produced by co-deposition of water and hydrogen fluoride in solid argon at 12 K, which are assigned to the 1 : 2 H_2O—$(HF)_2$ complex.

H_2O—$(HF)_2$	H_2O—$(DF)_2$	D_2O—$(HF)_2$	D_2O—$(DF)_2$
3690	2697	3667	2686
3272	2437	3259	2417
(765sh)[a]	(576)	750.5	561.7
(652sh)	(492sh)	635sh	475sh

[a] Tentative band positions; sh denotes shoulder.

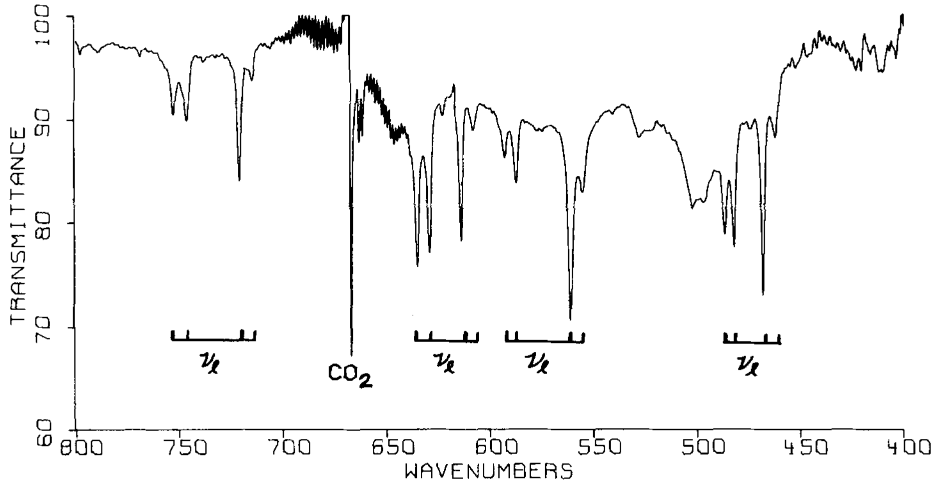


FIG. 4. Infrared spectrum in the 800–400 cm^{-1} region for sample described in Fig. 3 caption.

the complex (3) bands increased approximately 60%. None of these product bands appeared in a separate Ar/D$_2$O experiment. An analogous Ar/D$_2$O = 400/1 study gave weaker product bands in the same positions.

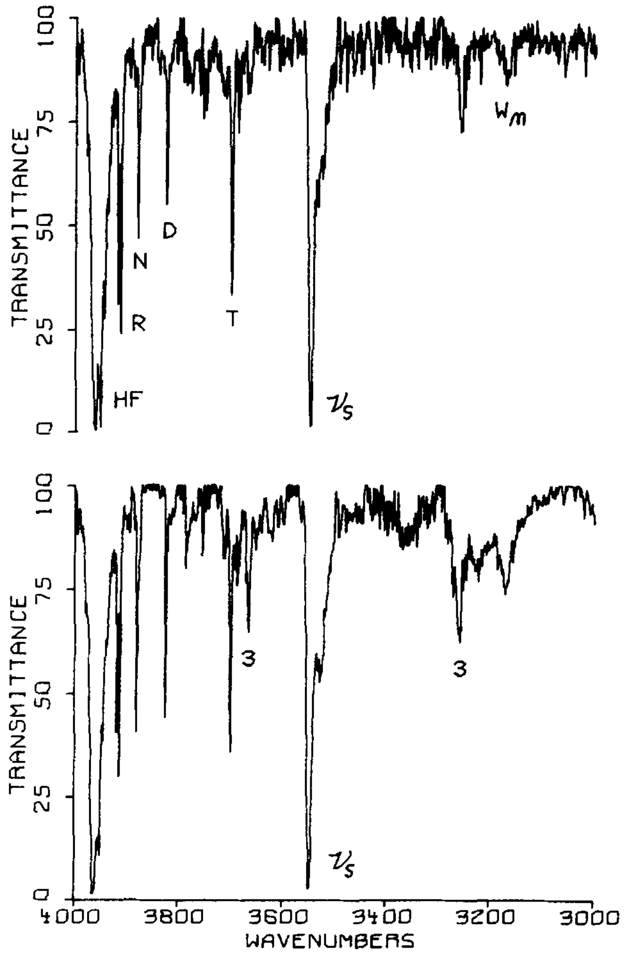


FIG. 5. FTIR spectrum in the 4000–3000 cm^{-1} region for sample prepared by co-condensing Ar/D$_2$O = 200/1 (>90% D$_2$O reached the matrix) and Ar/(DF + HF) = 200/1 (70% DF) mixtures. (a) Original sample condensed at 12 ± 1 K, (b) after warming to 19 K for 10 min and recooling to 12 K.

^{18}OHD and ^{18}OD$_2$ + HF

One experiment done with a multiple isotopic water sample gave a slightly broader ν_s band at 3551 cm^{-1}. Since the ν_l product bands are very sharp (FWHM < 2 cm^{-1}), the bands arising from H$_2$O and D$_2$O complexes were identified, unshifted by oxygen-18 substitution, and new multiplets for the HOD complex were observed beginning at 737.2 and 629.4 cm^{-1} as given in Table I.

DISCUSSION

The products of the H$_2$O and HF co-condensation reaction will be identified from the spectra, assignments

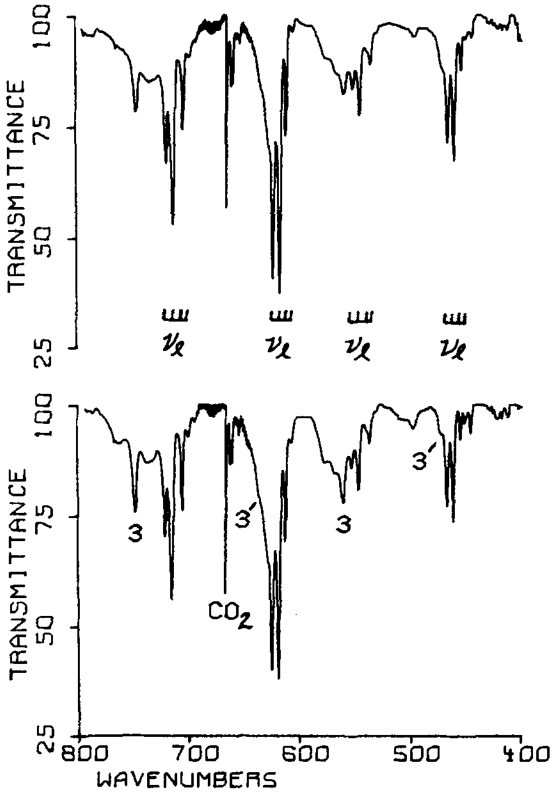
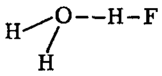


FIG. 6. Infrared spectrum in the 800–400 cm^{-1} region for sample described in Fig. 5 caption.

will be given, and spectral information on bonding and structure in the product complexes will be presented.

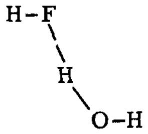
Identification

The sharp, strong 3554.7 cm^{-1} band labeled ν_s is the major product of the H_2O and HF co-condensation reaction using an extreme range of reagent concentrations, including trace H_2O contamination in other HF experiments,[5-8,10] which is appropriate for a 1:1 complex. The ν_s band increased on warming the more dilute samples, but it decreased slightly on warming more concentrated samples. This absorption is clearly due to an H–F stretching fundamental based on the 3554.7/2621.1 = 1.3562 ratio, and the small dependence of the ν_s bands on D_2O substitution shows that H_2O is involved in the complex. The position of the 3554.7 cm^{-1} band below the strong 3608 cm^{-1} absorption for the H_2O--HF complex in the gas phase[1] confirms this identification for the sharp argon matrix band. The ν_l quartets display constant absorbances relative to the 3554 cm^{-1} band upon sample warming and they are associated with the H_2O--HF species (1) as well.



(1)

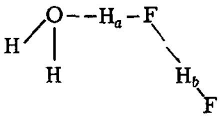
The sharp 3915.5 cm^{-1} band was observed only with H_2O concentrations greater than about 0.1% in the sample, and it is also due to an H–F stretching fundamental based on the HF/DF ratio 3915.5/2873.1 = 1.3628. The small shifts in these bands when H_2O is replaced by D_2O (Table II) verify that water is a part of this species. Sample warming demonstrates that the 3915.5 cm^{-1} band is due to a less stable species than the 3554.7 cm^{-1} ν_s band. The sharp 3915.5 cm^{-1} band is therefore assigned to the reverse HF--HOH complex (2),



(2)

which has been determined from *ab initio* calculations to be less stable than the H_2O--HF complex. Presumably, the warmer matrix cage allows rearrangement of (2) to the more stable (1) structure. A 3915.5 cm^{-1} band was observed by Bowers, *et al.*[15] and recognized as HF with a foreign molecule nearest neighbor, but substantial water impurity was present in their samples. The 3915.5 cm^{-1} band is reminiscent of the sharp 3891.8 cm^{-1} HF--HCN product of the HCN and HF co-condensation reaction, which decreased on sample warming while HCN--HF absorptions increased.[14]

The more concentrated experiments produced another set of product bands (Table III) that increased on sample warming while the H_2O--HF bands decreased slightly. These bands exhibited a dependence on DF and D_2O isotopic substitution and are assigned to the 1:2 complex (3) based upon the observation of two ν_s(H–F) modes,



(3)

one displaced more and one displaced less than ν_s of complex (1). Complexes of formula $(H_2O)_2(HF)$ were likely produced in the present experiments, but strong $(H_2O)_2$ absorptions probably mask absorptions for the latter 2:1 complex. Weak bands at 902 and 876 cm^{-1} in H_2O and D_2O experiments increased on sample warming and are probably due to an unidentified $(H_2O)_n(HF)_m$ species.

H_2O--HF assignments

The strong, sharp 3554.7 cm^{-1} absorption is assigned to the ν_s (H–F stretching) fundamental in complex (1) based on near agreement of the HF/DF = 1.3562 ratio with the diatomic ratio of 1.3654 in solid argon.[10] The argon matrix band is displaced 53 cm^{-1} below the gas phase absorption, which indicates a relatively small matrix interaction between argon and H_2O--HF. Earlier work[15] with HF in solid neon revealed a strong, sharp band at 3586 cm^{-1}, which is assigned here to ν_s of H_2O--HF in solid neon; the complex sustains a smaller 22 cm^{-1} displacement in the less polarizable matrix. The small further displacement for ν_s to 3542.5 cm^{-1} in solid krypton with the same HF/DF = 1.3562 ratio again verifies a small matrix interaction for H_2O--HF.

No base submolecule modes were observed for the H_2O--HF complex owing to the complicated matrix spectrum for rotating H_2O and $(H_2O)_n$ species. The 3700–3750 cm^{-1} region where the ν_3^c mode is expected is unfortunately obscured by $(H_2O)_n$ species which exhibit changes on sample warming.

The quartets beginning at 753.1 and 635.6 cm^{-1} are assigned to librational modes of the H–F submolecule in H_2O--HF. The relative intensities of the components of each quartet were unchanged on temperature cycling the sample (Fig. 2) so the components are due to the same complex. These bands are in general agreement with a broad 650 cm^{-1} absorption for the gaseous complex,[1] although analysis of the latter was hampered by lack of experimental resolution, anharmonicity, and in retrospect, inversion doubling. The pyramidal complex has one plane of symmetry, but previous discussions[3] of the librational modes referred to the plane the complex passes through on inversion. We, however, in the following discussion will refer to the mirror plane that bisects the H–O–H angle of the pyramidal complex. Now, the complex has two H–F librational modes, one in the miror plane and one perpendicular to the mirror plane. The bands in the 753.1 cm^{-1} quartet exhibit an average HF/DF ratio of 1.277 whereas the average ratio for the 635.6 cm^{-1} quartet is 1.309. Since the in-mirror-plane librational mode might be expected to couple more effectively with the inversion motion causing an increase in anharmonicity, the 753.1 cm^{-1} quartet is attributed to the in-mirror-plane librational mode and the 635.6 cm^{-1} quartet is assigned to the corresponding out-of-plane mode.

The HF/DF ratio for the 753.1 and 746.8 cm^{-1} bands (1.270 ± 0.001) is slightly different from the ratio (1.286 ± 0.002) for the 721.1 and 715.3 cm^{-1} bands in the upper quartet for the H_2O complex. Likewise, the components of the higher doublet in the lower quartet exhibit a slightly different ratio (1.304 ± 0.001) from the lower doublet components (1.313 ± 0.002). A similar HF/DF ratio relationship was found for the upper and lower doublets (1.307 ± 0.001 and 1.317 ± 0.003) for the 723.0 cm^{-1} quartet and the upper and lower doublets (1.339 ± 0.002 and 1.347 ± 0.002) for the 625.3 cm^{-1} quartet of the D_2O complex. This suggests that the components in each doublet are due to the same librational motion of the complex in two different matrix environments, but that each doublet is due to a slightly different librational motion in the complex as a consequence of another interaction within the complex, which is proposed to be inversion doubling. This explanation is supported by the krypton matrix spectrum of H_2O--HF, which exhibits four similar strong bands in the librational mode region, each with a minor shoulder due to a matrix site splitting.

The quartets beginning at 723.0 and 625.3 cm^{-1} for D_2O--HF show slightly different relative intensities than the components of the analogous H_2O--HF quartets, and the DF quartet components are similar to the HF components for each isotopic water complex. The interval ($\Delta\nu_l$) between the first and third components in each ν_l quartet, however, exhibits a large dependence on the water isotope and a very small dependence on the hydrogen fluoride isotope, which must arise from interaction with a base molecular motion. On the other hand, the doublet splittings are 1.0 ± 0.2% without clear isotopic dependence, which is in accord with a matrix site splitting. It is proposed that the intervals ($\Delta\nu_l$) given in Table I are due to inversion splitting of the librational levels. Since the inversion motion involves only the H_2O submolecule exchanging lone pairs with the acid, inversion splitting depends on water and not acid isotopic submolecules, as observed in the spectra. The in-mirror-plane librational motion will alter the height of the pyramid formed by the complex more than the out-of-mirror-plane libration, and the larger inversion splitting ($\Delta\nu_l$) observed for the former (32.0 cm^{-1}) as compared to the latter (21.3 cm^{-1}) supports the above librational mode descriptions based upon anharmonicity.

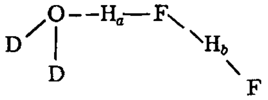
Although the inversion splitting of 32 cm^{-1} in the in-mirror-plane librational mode in the H_2O--HF complex is near the 36 cm^{-1} inversion splitting observed for the symmetric bending (ν_2) mode of ammonia,[16] the two cases are otherwise substantially different. In the H_2O--HF complex, inversion splitting has been described for a normal mode similar but not identical to the inversion motion, and the subject normal mode is substantially above the inversion barrier, whereas in the well-known NH_3 case, the ν_2 mode follows the inversion motion but the ν_2 fundamental is below the barrier to inversion.[16] Finally, the ν_l modes and inversion splittings for H_2O--HF in solid argon are within 2 cm^{-1} of the solid krypton values, which is consistent with a small guest–host interaction as deduced from the small displacements of ν_s for H_2O--HF in these matrices.

HF--HOH assignments

The 3915.5 cm^{-1} band is due to the H–F stretching fundamental in complex (2) owing to the large HF/DF ratio (1.3628) and the small (0.9–0.6 cm^{-1}) D_2O shifts (Table II). It is interesting to note that D_2O has a slightly greater perturbation on the H–F fundamental in the reverse complex than does H_2O. No other fundamentals were observed for the reverse complex owing to the presence of strong H_2O and $(H_2O)_2$ absorptions.

H_2O--$(HF)_2$ assignments

The H_2O--$(HF)_2$ complex (3) exhibits two ν_s modes and a single sharp ν_l mode for one acid submolecule, as listed in Table III. The ν_s modes for complex (3) exhibit similar small H_2O–D_2O shifts in complex (4) as observed for the 1 : 1 complex (1). The HF/DF ratios are more accurate for the D_2O species (4) produced in larger yield (3667/2686 = 1.365 and 3259/3417 = 1.348); these ratios bracket the 1.3562 value for ν_s of complex (1) as the observed



(4)

bands bracket the 3554.7 cm^{-1} ν_s value. The 3667 and 3259 cm^{-1} bands are assigned, respectively, to the H_b–F and H_a–F stretching modes in complex (4). It is readily seen that the H_a–F stretching mode of complex (4) [and complex (3)] is reduced from the H_a–F value in complex (1) owing to the fluoride ion affinity of the H_b–F submolecule. Likewise, the H_b–F mode in complex (4) [and complex (3)] is reduced from the H_b–F value in $(HF)_2$ owing to the cooperative effect of the water base at proton H_a in the water complex. Splittings for the mixed (HF) (DF) isotopomer of complex (4) [and complex (3)] were not resolved owing to the larger 8 cm^{-1} bandwidth of the former, in contrast to the 4.5 cm^{-1} separation between the sharp D_b–F modes for (HF) (DF) and $(DF)_2$.[10]

The 1 : 2 complexes with D_2O were produced in larger yield than the H_2O species presumably owing to less diffusion and aggregation of D_2O in contrast to H_2O, and the librational modes of D_2O--$(HF)_2$ and D_2O--$(DF)_2$ can be compared to the librational modes of D_2O--HF and D_2O--DF [Fig. 6(b)]. The 750.5 and 561.7 cm^{-1} bands (HF/DF = 1.3361) are assigned to the in-mirror-plane librational modes, respectively, of the H_a–F submolecule in D_2O--$(HF)_2$ and the D_a–F submolecule in D_2O--$(DF)_2$. The out-of-mirror-plane librational modes for these species are probably responsible for the unresolved shoulder absorptions at 635 and 475 cm^{-1} on the 1 : 1 complex absorptions. These librational modes are higher than for the 1 : 1 complex owing to the stronger base--H_a hydrogen bond in the 1 : 2 complex. The hydrogen fluoride submolecule modes for 1 : 2 complex isotopomers are summarized in Table III; water submolecule modes for the 1 : 2 complex were not resolved from $(H_2O)_n$ bands in these experiments.

Bonding and structure

The vibrational spectrum of H_2O--HF in solid argon is in general agreement with the gas-phase spectrum,[1] and the anharmonicity and inversion doubling found in the H–F librational modes are consistent with the pyramidal structure having a low inversion barrier deduced from the microwave spectrum.[3] In contrast, the more strongly bound $(CH_3)_2O$--HF complex in solid argon[17] exhibits a ν_s mode at 3349.4 cm^{-1} (HF/DF $=1.3495$) and only two librational bands at 801.3 and 687.3 cm^{-1} with almost identical HF/DF ratios (1.3545 ± 0.0012). The dimethyl ether–HF complex shows no evidence of inversion doubling.

The matrix spectrum of H_2O--$(HF)_2$ exhibits two H–F stretching fundamentals, one displaced more and one displaced less than ν_s for H_2O--HF, which indicates an open structure (3) for the 1 : 2 complex. The effect of H_b–F is to increase the H_2O--H_a–F hydrogen bond strength in complex (3) as compared to complex (1), which gives a lower H_a–F fundamental and higher H_a–F librational modes. The in-mirror-plane H_a–F librational mode in complex (4) is broader than its complex (1) counterpart, and there is no evidence for inversion splitting in the ν_l modes for the 1 : 2 complex. Furthermore, the larger HF/DF ratio (1.336) is indicative of a smaller amplitude, less anharmonic motion for H_a–F in complex (4) as compared to the D_2O--H_a–F species (HF/DF $=1.307$). This is perhaps a consequence of the stronger base--H_a–F hydrogen bond in the 1 : 2 complex, which is expected to increase the inversion barrier.

The open structure for H_2O--$(HF)_2$ is different from the bifid structure observed for the H_2O--$(HCl)_2$ species,[18] which of course can be explained by the relative electronegativities of Cl, O, and F. The most electronegative site in complex (1) for attachment of H_b–F is at fluorine, but the most electronegative site in H_2O--HCl for attachment of a second HCl is the other lone pair of the oxygen atom.

Although only the H–F fundamental was observed for the reverse complex (2), the position of this fundamental at 3915.5 cm^{-1} indicates a very weak perturbation of HF, which must therefore involve the fluorine end of the H–F molecule. The small shift in the sharp H–F fundamental of the reverse complex when D_2O is substituted for H_2O (Table II) identifies H_2O as the source of the perturbation. Three complexes with HF serving as a base have been characterized in recent matrix studies, and the displacement of the H–F fundamental increases with increasing strength of the acid. For the present reverse HF--HOH complex, the displacement from the diatomic HF fundamental (3953.8 cm^{-1}) is $\Delta\nu$(H–F) $=38$ cm^{-1}, for HF--HCN[14] the $\Delta\nu$ is 62 cm^{-1}, and for H_a–F--H_b–F the $\Delta\nu(H_a\text{–}F)$ is 77 cm^{-1}.[10]

Finally, the slightly greater perturbation exerted by D_2O in the reverse complex as compared to H_2O suggests that D_2O forms a slightly stronger deuterium bond than the analogous hydrogen bond with H_2O. This can also be inferred from the observation of only deuterium bonded DOH in mixed isotopic water dimers[13] and only the HF--DF mixed isotopic hydrogen fluoride dimer.[10] The observation of stronger vibrational perturbations by DF than HF in the CO complexes[19] and by DCl compared to HCl in dimers[20] is consistent with this suggestion.

CONCLUSIONS

The slow condensation of dilute Ar/HF and Ar/H_2O samples at 12 K provides controlled diffusion and association of H_2O and HF submolecules and sharp infrared absorptions for three different hydrogen bonded complexes. The isotopic dependence of the sharp matrix absorptions provides evidence for inversion doubling in the H–F librational modes for H_2O--HF, which is not found for the more strongly bound H_2O--$(HF)_2$ complex, and provides a basis for identification of the less stable reverse HF--HOH complex. These argon matrix studies are complementary to gas phase investigations and provide more information on the important water–hydrogen fluoride system.

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