

## FTIR spectra of (HF) $n$ species in solid neon

Lester Andrews, V. E. Bondybey, and J. H. English

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# FTIR spectra of $(\text{HF})_n$ species in solid neon

Lester Andrews

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

V. E. Bondybey and J. H. English

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

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Condensation of Ne/HF mixtures at 5 K produces in addition to monomer HF numerous strong, sharp infrared absorptions in the 4000–3600 and 600–300  $\text{cm}^{-1}$  regions and broader bands in the 3500–3100 and 1300–600  $\text{cm}^{-1}$  regions. The relative absorbances of these bands depend upon concentration, spray-on rate, and sample annealing, which are used to identify individual  $(\text{HF})_n$  species. Sharp bands at 3919, 3848, and 410  $\text{cm}^{-1}$  are assigned to  $(\text{HF})_2$ . Further infrared evidence is presented for an open chain  $(\text{HF})_3$  species. The broader bands assigned to cyclic- $(\text{HF})_n$  species increase at the expense of the sharper bands under conditions which favor association of HF in the matrix.

## INTRODUCTION

Liquid hydrogen fluoride is strongly hydrogen bonded as evidenced by its relatively high boiling point and high heat of vaporization. The F...H interaction represents the strongest hydrogen bond and the HF molecules are extensively associated even in the vapor phase. The  $(\text{HF})_2$  dimer and larger  $(\text{HF})_n$  clusters are simple prototype hydrogen bonded systems and they have been studied by a variety of physical methods including microwave and infrared absorption spectroscopy.<sup>1–8</sup> In particular the vibrational spectra of  $(\text{HF})_n$  clusters in solid argon have recently received considerable attention.<sup>6,7</sup>

Matrix spectroscopy has proved itself as a very useful technique for studies of both stable molecules and transient species, and it is now well established that structures and spectra of such species are typically negligibly perturbed by the solid medium. The pairwise interaction energy of Ar atoms is  $\sim 100 \text{ cm}^{-1}$ , and the interaction of an Ar atom with a typical guest molecule will in most cases be of the same order of magnitude. The entire solvation energy of the guest is therefore usually small compared with its intramolecular covalent bonding. Hydrogen bonds are, on the other hand, at least an order of magnitude weaker than conventional covalent bonds and in particular the orientational part of the potential surface is usually quite flat and shallow. Under these circumstances the effects of the solvent may be nonnegligible and one has to worry about the matrix affecting the geometry and vibrational structure of the hydrogen bonded complex. The pairwise interaction energy of neon atoms ( $\sim 29 \text{ cm}^{-1}$ ) is more than a factor of 3 weaker than that of argon, and solid neon should therefore be a much preferable medium for studies of weakly bound complexes. Very recently we have used the inert neon medium to study polymers and complexes of  $\text{SO}_3$ .<sup>9</sup> The present neon matrix study of the hydrogen bonding in various HF polymers and complexes complements and extends previous argon matrix work.

## EXPERIMENTAL

An Air Products Heli-tran system provided 5 K refrigeration for condensing Ne/HF mixtures. Fourier trans-

form infrared spectra were recorded on a Nicolet MX-1 spectrometer at  $2 \text{ cm}^{-1}$  resolution from 4400 to  $200 \text{ cm}^{-1}$  with an accuracy of better than  $1 \text{ cm}^{-1}$ . Hydrogen fluoride (Matheson) was condensed at 77 K and the volatile impurities were removed by pumping; mixtures of HF and DF were prepared by exchanging HF with the vacuum line previously treated with  $\text{D}_2\text{O}$ . Hydrogen fluoride was diluted with neon in a monel can and condensed on a 5 K CsI window at a rate of 2–3 mmol/10–15 min. Usually several aliquots were deposited and FTIR spectra were recorded before and after each deposit. Most samples were subsequently annealed at  $11 \pm 1 \text{ K}$  for 3–10 min and additional spectra were recorded to establish the effects of diffusion.

## RESULTS AND DISCUSSION

Matrix experiments were done with Ne/HF ratios ranging from 100/1–1000/1 and the spectra showed a strong concentration dependence. Dilute samples yielded rather simple spectra dominated by isolated monomer HF absorptions, but more concentrated matrices resulted in extensive complex and polymer formation. The deposition rate had a similarly strong effect upon the appearance of the spectra; during fast deposition the surface layer is being continuously annealed and aggregate formation is enhanced. The samples were usually deposited in several aliquots and spectra recorded after each deposit. Examination of such spectra shows that the annealing during deposition is a rather complex process. The first aliquot is deposited on the bare CsI substrate which dissipates efficiently the energy brought onto the surface as a kinetic and internal energy of the gaseous sample. The subsequent portions are deposited onto increasingly thick layers of rare gas which conduct the heat away much less efficiently, resulting in more aggregation. These effects can be quite pronounced. Thus for a Ne/HF = 500/1 sample, after a first 2 mmol deposit a 3992  $\text{cm}^{-1}$  monomer HF band was the strongest absorption in the spectrum. After deposition of a second aliquot, the maximum shifts to a 3848  $\text{cm}^{-1}$  band, assigned to the dimer. The spectrum after a third and final 2 mmol deposit is shown in Fig. 1(a). A band at 3706  $\text{cm}^{-1}$  labeled *T*, which is assigned

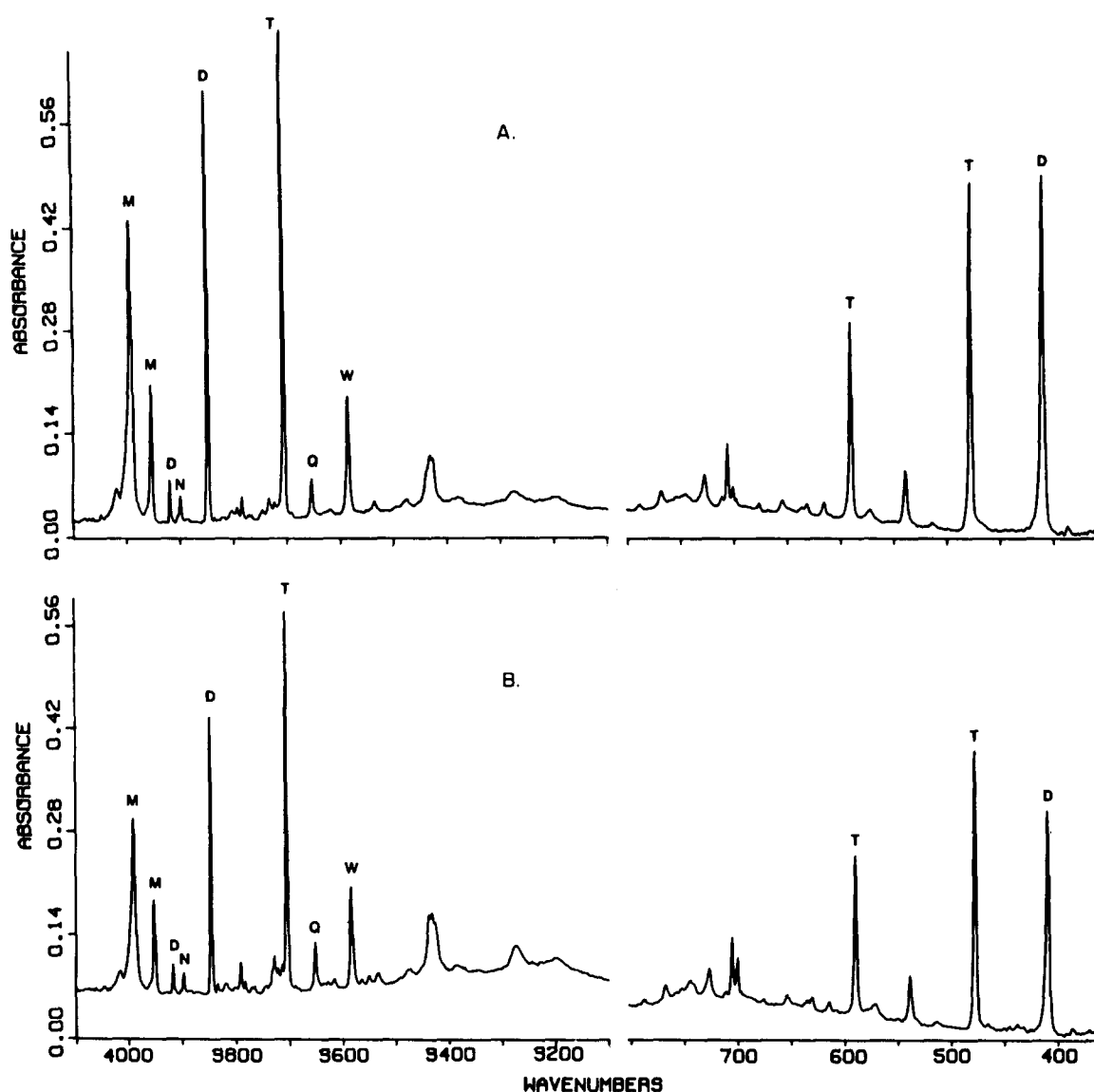


FIG. 1. FTIR spectra of 6 mmol of Ne/HF = 500/1 sample. (a) Spectrum after condensation at 5 K, (b) spectrum after warming to  $11 \pm 1$  K for 5 min and recooling to 5 K. The bands are identified by labels as follows: *M* = HF monomer, *D* =  $(\text{HF})_2$  dimer, *N* =  $\text{N}_2$ -HF complex, *T* = open- $(\text{HF})_3$  trimer, *Q* = open- $(\text{HF})_4$  tetramer, and *W* =  $\text{H}_2\text{O}$ -HF complex.

to an open chain  $(\text{HF})_3$  trimer, is now the strongest band in the spectrum. Most of the observed absorptions are summarized in Table I.

The effects of annealing of the sample for  $\sim 5$  min at  $11 \pm 1$  K can be seen in Fig. 1(b). Most of the strong sharp bands decrease by different factors while other, broader absorptions due to higher polymers grow in. The behavior of individual bands depends strongly upon initial conditions and concentration and upon the annealing temperature. For instance while in more dilute samples or at early stages of annealing the  $3706\text{ cm}^{-1}$  and other trimer bands increase, in more concentrated samples or upon more thorough annealing they decrease in favor of higher polymers.

Useful in identifying and assigning the individual polymer transitions are isotopic shifts, and several experiments were carried out with varying degrees of sample deuteration. The effects of deuteration can be seen in Figs. 2 and 3. Numerous new bands appear in the DF absorption region, which exhibit a concentration and annealing behavior simi-

lar to the HF bands and can be similarly assigned to  $(\text{DF})_n$  species. These bands are listed in the right hand column of Table I.

It is usually difficult to produce matrices completely free of impurities, with  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  being most important. Since these small molecules diffuse fairly readily through the matrix, one has to consider the likelihood of their forming complexes with HF. To identify the absorptions of such mixed aggregates, several experiments were performed with samples doped with known concentrations of these species.

Using the information from the experiments described above, one can readily identify absorptions due to HF clusters, such as  $(\text{HF})_2$  and  $(\text{HF})_3$ . Also larger species are clearly present and can be identified, although with increasing size the spectra get more complex and assignments less certain. In the following paragraphs we will describe and discuss briefly the spectra and structures of the individual species observed in the matrix.

TABLE I. Infrared absorptions (cm<sup>-1</sup>) observed following deposition of Ne/HF and Ne/(HF + DF) samples at 5 K.

(HF) <sub>n</sub>	(HF) <sub>x</sub> (DF) <sub>y</sub>	(DF)	identification
4017		2948	HF, <i>R</i> (1)
3992		2922	HF, <i>R</i> (0)
3953		2900	HF, <i>Q</i> induced
...		2889	DF, <i>P</i> (1)
3919	3915	2873	(HF) <sub>2</sub>
3898		2858	N <sub>2</sub> -HF
3848	2824	2820	(HF) <sub>2</sub>
3835		...	open-(HF) <sub>3</sub>
3792		...	N <sub>2</sub> -(HF) <sub>2</sub>
3783		2791	H <sub>2</sub> O(D <sub>2</sub> O)
3729		2763	H <sub>2</sub> O(D <sub>2</sub> O)
3706	3672, (2723)	2721	open-(HF) <sub>3</sub>
3653	3645, 3641, 2700		
	2689, 2684	2674	open-(HF) <sub>4</sub>
3586		2640	H <sub>2</sub> O-HF
3431	3485, 3388, 2566	2540	cyclic-(HF) <sub>3</sub>
3276	3273	2428	cyclic-(HF) <sub>4</sub>
3200	3187	2374	cyclic-(HF) <sub>5</sub>
3150		...	cyclic-(HF) <sub>6</sub>
1244		952	cyclic-(HF) <sub>n</sub>
857		625	cyclic-(HF) <sub>n</sub>
746,706		...	cyclic-(HF) <sub>n</sub>
653		...	cyclic-(HF) <sub>n</sub>
590	574, 533, 525, 497, 482, 472	463	open-(HF) <sub>3</sub>
539		...	...
477	428, 423, 385, 367, 363	351	open-(HF) <sub>3</sub>
410	324	306	L(HF) <sub>2</sub>

### The HF monomer

The spectra of HF in rare gas matrices have been interpreted assuming a nearly free rotation and our observations are in agreement with previous studies.<sup>10,11</sup> The *R* (0) transitions of HF and DF are prominent in dilute, unannealed matrices at 3992 and 2922 cm<sup>-1</sup>, respectively. The relative intensities of the formally forbidden, medium induced *Q* (0) transitions of HF and DF at 3953 and 2900 cm<sup>-1</sup>, respectively, increase with concentration. Transitions originating in the *J*" = 1 level are also weakly observable, particularly in the deuteride.

### Structure and spectra of (HF)<sub>2</sub>

The effects of clustering upon the HF spectrum will be twofold. The stretching vibrations of the complex will shift with respect to those of the free HF and new low frequency modes associated with relative motions of the individual HF entities can be expected in the spectrum. This is fully confirmed by the observed spectra. The dimer bands, identified as the first product bands to grow in at the expense of the monomer, appear at 3848, 3919, and 410 cm<sup>-1</sup> and are labeled *D* in the spectra. The presence of two strong HF stretching vibrations is consistent with an



open chain geometry as observed in the gas phase and eliminates centrosymmetric dimer structures. The dimer fre-

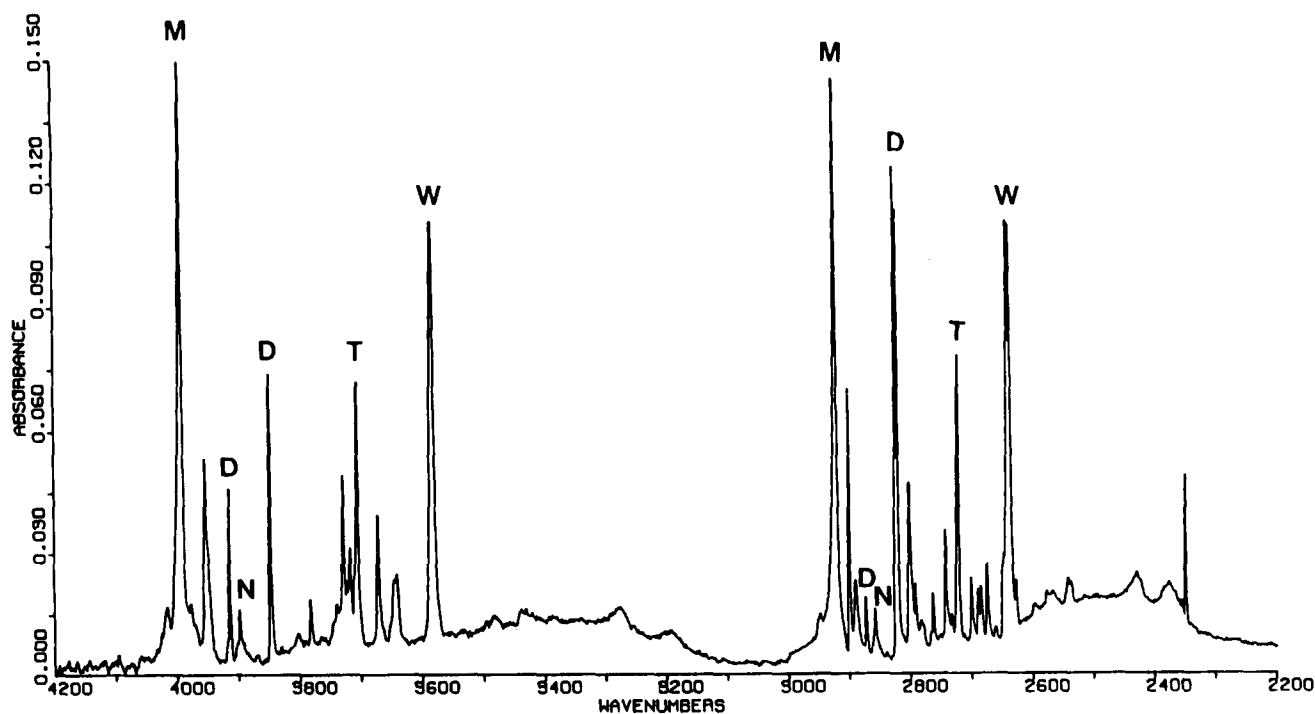


FIG. 2. FTIR spectrum of approximately 2 mmol of Ne/(HF + DF) = 300/1 in the 4200–2200 cm<sup>-1</sup> spectral region. HF/DF approximately 1/1.

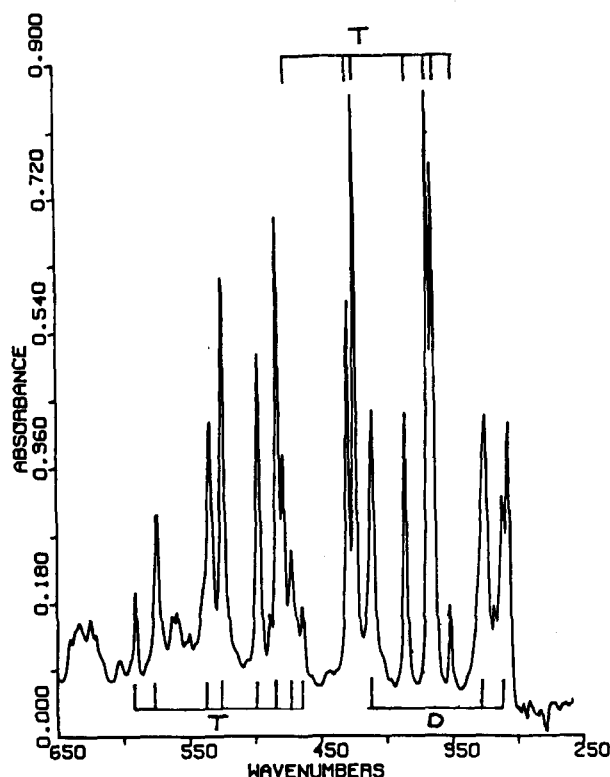


FIG. 3. FTIR spectrum of approximately 6 mmol total of the sample described in Fig. 2 in the 600–300  $\text{cm}^{-1}$  spectral region. Horizontal bars denote isotopic components of the same species.

quencies shift to 2820, 2873, and 306  $\text{cm}^{-1}$  in deuterated samples. Clearly, the lower frequency vibration at 3848  $\text{cm}^{-1}$  [2820  $\text{cm}^{-1}$  in (DF)<sub>2</sub>], involves predominantly the central, hydrogen bonded proton, and the higher frequency absorption (3919  $\text{cm}^{-1}$ ) which is closer to the monomer vibration (3953  $\text{cm}^{-1}$ ) is due to the “free” terminal proton. These neon matrix (HF)<sub>2</sub> fundamentals are displaced 20 and 10  $\text{cm}^{-1}$ , respectively, from the gas phase bandheads.<sup>8</sup> The remaining, low frequency band at 410  $\text{cm}^{-1}$  (306  $\text{cm}^{-1}$  in deuteride) is then due to a “deformation” motion associated with the central, hydrogen bonded proton. It lends support to earlier gas phase observations<sup>4,12</sup> of a weak dimer band near 380  $\text{cm}^{-1}$ . The relative intensities of the H<sub>b</sub>–F and H<sub>a</sub>–F stretching absorptions for Eq. (1) in solid neon are  $\sim 10/1$ ; this demonstrates the infrared intensity enhancement induced by hydrogen bonding.

In partially deuterated samples only three additional dimer bands appear at 2824, 3915, and 324  $\text{cm}^{-1}$ , slightly perturbed D<sub>b</sub>–F and H<sub>a</sub>–F stretching and D<sub>b</sub>–F deformation modes, suggesting that of the two possible “isomers” of the partially deuterated dimer, only the (F–D<sub>b</sub>)...(F–H<sub>a</sub>) structure appears in the matrix. This is consistent with gas phase microwave observations<sup>1</sup> and zero point energy calculations<sup>13,14</sup> and suggests an efficient isomerization of the less stable (F–H<sub>b</sub>)...(F–D<sub>a</sub>) dimer even in the 5 K matrix. Both stretching modes for (F–D<sub>b</sub>)...(F–H<sub>a</sub>) show 4  $\text{cm}^{-1}$  displacements from their values in (HF)<sub>2</sub> and (DF)<sub>2</sub>, respectively, which indicates a small amount of interaction between the two bond stretching modes.

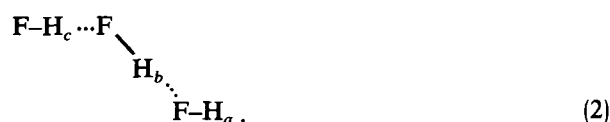
The present neon matrix observations of the two H–F

stretching fundamentals for (HF)<sub>2</sub> at 3919 and 3848  $\text{cm}^{-1}$  support assignments based on the recent high resolution<sup>8</sup> and earlier low resolution<sup>2–4</sup> infrared measurements, which stand in disagreement with assignments from vibrational predissociation<sup>5,15</sup> and very recent matrix isolation studies.<sup>16</sup> The latter study concludes that wide variations in the relative intensities of sharp 3826 and 3702  $\text{cm}^{-1}$  bands in solid argon can be accounted for by a change in matrix environment on the two H–F stretching fundamentals of (HF)<sub>2</sub> caused by different HF concentrations in the matrix. Work from these laboratories<sup>6,7</sup> concludes that this “change in matrix environment” is due to the association of another HF molecule, and that the (HF)<sub>n</sub> species and their spectral features change accordingly.

In the gas phase work of Lisy and co-workers,<sup>5,15</sup> the irradiation near 3720  $\text{cm}^{-1}$  resulted in depletion of a signal at mass 21 due to H<sub>2</sub>F<sup>+</sup> and used to monitor the dimer, while depletion due to (HF)<sub>3</sub> absorption bands was observed only at mass 41. These observations can be reconciled if their molecular beam contains some concentration of the higher energy, open-end isomer of the trimer discussed below. Unlike the cyclic trimer, where two hydrogen bonds have to be broken to accomplish fragmentation, the open chain isomer fragments effectively upon electron impact ionization, yielding mainly signal on the dimer channel. Irradiation in the intense 3720  $\text{cm}^{-1}$  open-end trimer band will then lead to depletion of the mass 21 signal, as observed.

### Open chain (HF)<sub>3</sub> trimer

The second major product to grow in relative to the monomer upon association is characterized by a strong, sharp absorption at 3706  $\text{cm}^{-1}$  and a weaker band at 3835  $\text{cm}^{-1}$ . Similar bands at 3702 and 3816  $\text{cm}^{-1}$ , respectively, in argon matrix studies<sup>6,7</sup> have been assigned to the H<sub>b</sub>–F and H<sub>c</sub>–F stretching modes of an open trimer, presumably with the *trans* structure:



The lower frequency H<sub>b</sub>–F absorption is an order of magnitude stronger, consistent with greater intensity enhancement for the more strongly hydrogen-bonded submolecule. It shifts to 2721  $\text{cm}^{-1}$  in the fully deuterated trimer. The stretching modes of Eq. (2) appear to be only relatively weakly coupled and only limited information is obtained about the isotopically mixed species.

More informative is the low frequency region where better data are obtained than in the argon studies, due to less overlapping by the dimer bands. Two prominent absorptions in the deformation region at 590 and 477  $\text{cm}^{-1}$ , respectively and a weaker one at 539  $\text{cm}^{-1}$  parallel the behavior of the 3706  $\text{cm}^{-1}$  band assigned above to the trimer and are apparently due to the same species. The HF deformation modes are more strongly coupled and extensive isotopic multiplets are observed in partially deuterated samples. The 477  $\text{cm}^{-1}$  band exhibits a 351  $\text{cm}^{-1}$  all DF counterpart ( $\bar{\nu}_{\text{HF}}/\bar{\nu}_{\text{DF}} = 1.359$ ) and five isotopically mixed components, while

the  $590\text{ cm}^{-1}$  band shifts to  $463\text{ cm}^{-1}$  upon deuteration and exhibits six intermediate isotopic bands. Assuming an open chain structure, three distinct "isomers" differing by positions of the protons are possible for  $(\text{HF})_2\text{DF}$  and three for  $\text{HF}(\text{DF})_2$ . The presence of a large number of bands attributable to isotopically mixed species would seem to suggest that most or all of these species are capable of existence in the 5 K neon matrix. This is in contrast with the dimer where the less stable mixed complex apparently readily interconverts into the more stable isomer. The reaction coordinate for isomerization of the trimer will be more complex and the respective barrier higher, since two hydrogen bonds have to be "broken" and reformed. This increased difficulty of rearranging the individual HF submolecules may explain the different behavior of the trimer.

### $(\text{HF})_4$ and higher polymers

A sharp band at  $3653\text{ cm}^{-1}$  [labeled Q in Fig. 1(a)] is in most deposits considerably weaker than the  $3706\text{ cm}^{-1}$  trimer band, but exhibits a growth rate suggestive of a higher aggregate. This band, like a similar  $3618\text{ cm}^{-1}$  argon matrix band, is tentatively assigned to an open tetramer. Consistent with this assignment, more mixed isotopic bands can be identified than for the trimer. The best explanation for the  $3653\text{ cm}^{-1}$  band is the strongest H-F stretching mode in an open tetramer.

### Cyclic $(\text{HF})_n$ polymers

Theoretical *ab initio* calculations<sup>17</sup> suggest that for all polymers larger than the dimer cyclic structures should be most stable. The argon matrix studies showed stepwise growth of broader bands at  $3404$ ,  $3244$ ,  $3186$ ,  $3118\text{ cm}^{-1}$  and suggested their assignments to cyclic- $(\text{HF})_n$  ( $n = 3, 4, 5, 6$ ) species, respectively. The bands observed at  $3431$ ,  $3276$ ,  $3200$ , and  $3150\text{ cm}^{-1}$  in neon matrices lend further support to these conclusions. The observed bands appear in good agreement with molecular beam predissociation experiments and the larger frequency shifts with respect to free HF are consistent with the expected stronger hydrogen bonding in the cyclic species. Numerous broader bands which grow in upon annealing of concentrated matrices between  $600$  and  $1300\text{ cm}^{-1}$  are probably due to "librational", deformation modes of the cyclic aggregates.

The observations by Klemperer and co-workers<sup>1</sup> that all the gaseous  $(\text{HF})_n$  polymers except dimer are nonpolar, as well as the molecular beam predissociation studies,<sup>5</sup> suggest that the cyclic species are dominant in the gas phase. On the other hand, the initial matrix deposits contain high concentrations of the open chain species. Apparently, the rigid matrix medium interferes with the high amplitude motions needed for formation of the cyclic isomers and stabilizes the initially formed open chain clusters.

### $\text{N}_2\cdots\text{HF}$ and $\text{H}_2\text{O}\cdots\text{HF}$ complexes

The observation of HF complexes with  $\text{N}_2$  and  $\text{H}_2\text{O}$  in solid neon invites comparison with recent argon matrix reports.<sup>16,17</sup> The H-F fundamental for  $\text{N}_2\cdots\text{HF}$  in solid argon at  $3881\text{ cm}^{-1}$  is shifted to  $3898\text{ cm}^{-1}$  in solid neon [labeled N

in Fig. 1(a)]. This suggests a gas phase fundamental near  $3920 \pm 20\text{ cm}^{-1}$ . The degenerate librational mode at  $262\text{ cm}^{-1}$  in solid argon<sup>18</sup> is displaced to  $288\text{ cm}^{-1}$  in the more repulsive neon cage. Since the matrix adds rigidity to the complex, the librational mode for  $\text{N}_2\cdots\text{HF}$  is predicted at  $240 \pm 20\text{ cm}^{-1}$  in the gas phase. The  $3792\text{ cm}^{-1}$  band is assigned to the  $\text{H}_a\text{F}$  stretching mode in  $\text{N}_2\cdots\text{H}_a\text{F}\cdots\text{H}_b\text{F}$  observed at  $3788\text{ cm}^{-1}$  in solid argon; a smaller neon-argon shift is noted for Eq. (2) and the  $\text{N}_2\cdots(\text{HF})_2$  complex when compared to Eq. (1) and the  $\text{N}_2\cdots\text{HF}$  complex.

The  $3586\text{ cm}^{-1}$  H-F [labeled W in Fig. 1(a)] fundamental frequency for  $\text{H}_2\text{O}\cdots\text{HF}$  is intermediate between the  $3608\text{ cm}^{-1}$  gas phase<sup>20</sup> and  $3555\text{ cm}^{-1}$  argon matrix values.<sup>19</sup> The  $758$  and  $637\text{ cm}^{-1}$  multiplets in solid neon are similar to  $753$  and  $636\text{ cm}^{-1}$  multiplets in solid argon, which have been assigned to the two librational modes of the  $\text{H}_2\text{O}\cdots\text{HF}$  complex split by inversion doubling and a small matrix effect. The observation of a similar multiplet pattern for  $\text{H}_2\text{O}\cdots\text{HF}$  with the same separation ( $\pm 1\text{ cm}^{-1}$ ) in solid neon supports the argon matrix infrared characterization of the  $\text{H}_2\text{O}\cdots\text{HF}$  complex.<sup>19</sup>

### CONCLUSIONS

Mixtures of HF in neon condensed at 5 K gave spectra whose complexity depended strongly upon spray on rate and concentration. Increased spray-on rate and sample annealing allow diffusion and association of the HF molecules. Observations of the resulting changes aid in assigning the observed absorptions to specific  $(\text{HF})_n$  ( $n = 2-6$ ) aggregates. The use of HF/DF isotopic mixtures provides supporting data. Sharp bands at  $3919$ ,  $3848$ , and  $410\text{ cm}^{-1}$  are assigned to  $(\text{HF})_2$  in solid neon in agreement with gas phase infrared spectra. The spectra of HF/DF mixtures showed  $2873$ ,  $2820$ , and  $306\text{ cm}^{-1}$  bands for  $(\text{DF})_2$  and  $3915$ ,  $2824$ , and  $324\text{ cm}^{-1}$  bands for  $(\text{H}_a\text{F})\cdots(\text{D}_b\text{F})$  without absorptions for the other, less stable, mixed dimer arrangement. Sharp bands at  $3706$ ,  $590$ , and  $477\text{ cm}^{-1}$ , which increased at the expense of HF and  $(\text{HF})_2$ , are assigned to open-chain  $(\text{HF})_3$ . The broader bands in the  $3500-3100\text{ cm}^{-1}$  region are tentatively assigned to cyclic- $(\text{HF})_n$  ( $n = 3-6$ ) species in agreement with molecular beam predissociation studies; the position of these bands indicates stronger hydrogen bonding as predicted by *ab initio* calculations. The neon matrix provides a suitable medium for controlled association of HF and gives spectroscopic data on  $(\text{HF})_n$  species which are complementary to gas phase studies.

### ACKNOWLEDGMENT

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