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Infrared spectra of HF (with DF substitution) in solid argon contain weak HF stretching–bending combination bands for N_2–HF, $(HF)_2$, and $(HF)_3$ that are higher than the sum of fundamentals. This is in accord with stronger hydrogen bonds upon vibrational excitation of the H–F stretching mode, as observed in the gas phase. Overtone bands were also observed for DF and $(DF)_2$ in solid argon. © *1999 American Institute of Physics.* [S0021-9606(99)01537-8]

I. INTRODUCTION

The low-frequency intermolecular modes of the N_2–HF complex have been measured in combination with the second overtone $(3\nu_1)$ of the H–F stretching mode recently by the Klemperer group.[1] These workers noted a striking variation in the properties of Ar–HF and N_2–HF with the H–F bond vibrational excitation, predicted that the N_2–HF bending mode observed at 328.6 cm^{-1} in combination with $3\nu_1$ would extrapolate to 259 cm^{-1} for the fundamental bending mode, and noted agreement with the direct observation of this bending mode at 262 cm^{-1} for the N_2–HF complex in solid argon.[2] This suggests that a combination band should be observable more than 262 cm^{-1} above the 3881 cm^{-1} H–F stretching fundamental for N_2–HF in solid argon.[2] Clearly, the N_2–HF hydrogen bond is strengthened upon vibrational excitation of the H–F stretching mode.[3] It will also be of interest to see if the N≡N and D–F stretching combination band can be observed in the N_2–DF complex. The N_2–HF complex has been calculated at a high level of theory and the bending mode fundamental predicted somewhat higher at 369 cm^{-1}.[4] There has been a considerable interest in the dissociation dynamics of this linear complex.[5–8] Furthermore, the increase in HF bending mode frequency in combination bands has been observed for $(HF)_2$ in the gas phase[9–13] and should apply to $(HF)_3$ and higher clusters as well. We report here an argon matrix investigation of the combination band region to examine the increase in HF bending modes in combination relative to the observed fundamental bands.

II. EXPERIMENT

Matrix isolation experiments were performed for HF and DF in argon using the same vacuum system described previously[2,14,15] with a colder 7–8 K substrate temperature for better isolation and a Nicolet 550 instrument (6000–400 cm^{-1}, 0.5 cm^{-1} resolution) with HgCdTe detector. A large number of scans (4096) was required to give good signal-to-noise at 5700 cm^{-1}. Hydrogen fluoride (Matheson) was condensed and pumped; DF was prepared by reacting D_2 with F_2 and the DF formed was condensed and evacuated to remove volatiles.[14]

III. RESULTS AND DISCUSSION

Matrix infrared spectra for HF and DF in solid argon at 7–8 K are presented in Figs. 1, 2, and 3 in the overtone and combination band regions for 1 h sample deposits, and the new absorptions are listed in Table I. Infrared spectra in the 4000–400 cm^{-1} region matched spectra recorded earlier.[14] These regions were also examined for the tracking of bands in overtone, combination band, and fundamental regions in experiments with different reagent concentrations.

A. DF

Since the DF matrix spectra always contained some HF, Fig. 1 contrasts spectra in the 5740–5420 cm^{-1} region with HF and DF; the HF experiments were performed *after* DF and also contained residual DF impurity. Figure 1(a) for 0.5% HF in argon with very little DF present shows weak bands at 5692 and 5618 cm^{-1}. Figure 1(b) with 2% HF and approximately 0.5% DF reveals stronger 5692 and 5618 cm^{-1} bands and weak new 5679 and 5607 cm^{-1} features. Figure 1(c) for 0.25% DF and 0.1% HF shows the same features. The spectrum in Fig. 1(d) for 2% DF and 0.2% HF reveals a stronger 5607 cm^{-1} band and new features at 5659, 5552, and 5435 cm^{-1}. All spectra contain a 5753 cm^{-1} band (not shown) that clearly arises from an impurity in the HF system.

In the DF spectrum, the two weak bands at 5679 and 5659 cm^{-1} (0.010 and 0.006 absorbance units, respectively) [Fig. 1(d)] are overtones of the 2896 and 2877 cm^{-1} DF $R(0)$ and impurity-induced Q bands (0.74 and 0.84 absorbance units, not shown) in solid argon.[14,15] The 5679 cm^{-1} band is stronger in the most dilute DF sample spectrum, Fig. 1(c), but the 5659 cm^{-1} band is strong at higher concentrations, Fig. 1(d); the 2896 and 2877 cm^{-1} fundamental bands follow these intensities as the Q bands exhibit intensities dependent on other molecules present. The DF overtone bands at 5679 and 5659 cm^{-1} in solid argon are each red-shifted 63 cm^{-1} from the gas phase 5742.4 and 5721.8 cm^{-1} $R(0)$ and $Q(0)$ band positions.[16] The fundamental bands at 2896 and 2877 cm^{-1} are red-shifted 32 and 30 cm^{-1}, respectively from the gas phase 2927.8 and 2906.7 cm^{-1} band positions.[16]
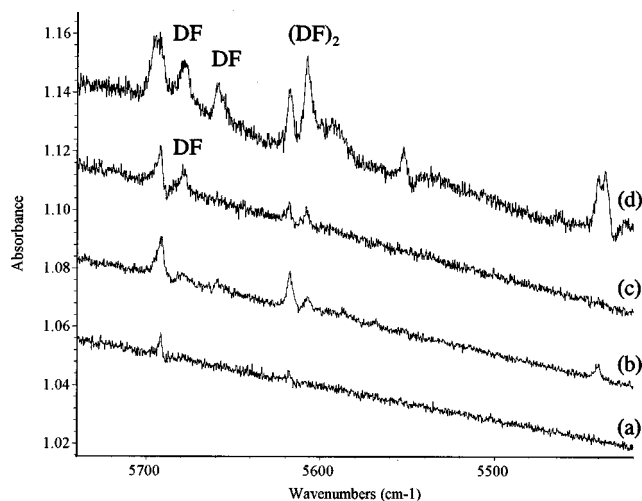
FIG. 1. Infrared spectra of HF and DF in solid argon at 7–8 K in the 5740–5420 cm^{-1} region. (a) 0.5% HF with 0.1% DF in argon, (b) 2% HF with 0.5% DF in argon, (c) 0.25% DF in argon with 0.1% HF and (d) 2% DF with 0.2% HF in argon.

B. (DF)$_2$

The most dilute DF sample also reveals a new 5607 cm^{-1} band, which increases markedly in intensity relative to DF as does the (DF)$_2$ fundamental at 2804 cm^{-1} (not shown, see Ref. 14) with increasing DF concentration. This band is due to the first DF cluster, namely (DF)$_2$. The only overtone observed to date for (HF)$_2$ in the gas phase[17] is $2\nu_{acceptor}$ at
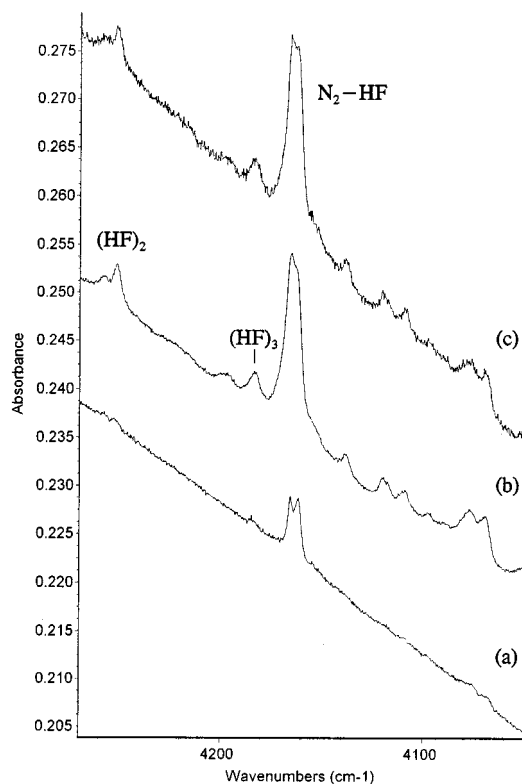

FIG. 2. Infrared spectra of HF in solid argon at 7–8 K in the 4270–4050 cm^{-1} region. (a) 0.5% HF in argon, (b) 2% HF in argon, and (c) after annealing to 25 K.
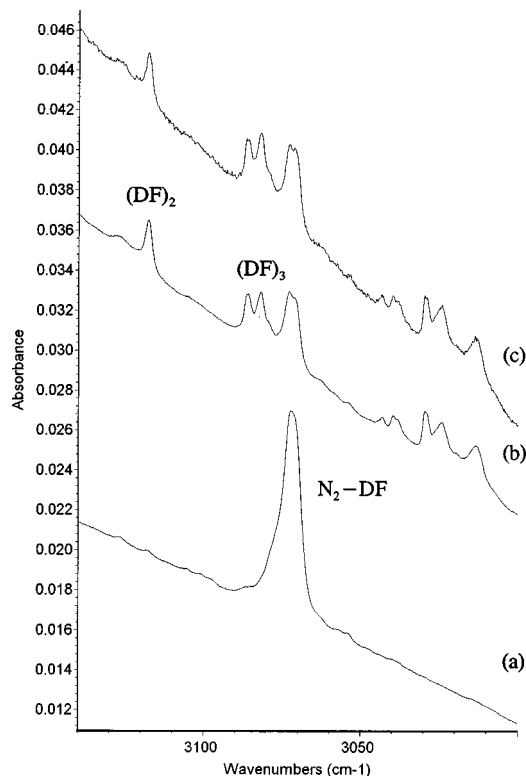

FIG. 3. Infrared spectra of DF in solid argon at 7–8 K in the 3140–3000 cm^{-1} region. (a) 1% DF plus 3% N$_2$ in argon, (b) 1% DF in argon, and (c) after annealing to 30 K.

7683 cm^{-1}. A simple prediction for $2\nu_{acceptor}$ of (DF)$_2$ is to scale 7683 cm^{-1} by the $\nu_{acceptor}$ fundamental ratio (2883/3931) for gas phase[10,11,13,18] (DF)$_2$ and (HF)$_2$, which gives 5635 cm^{-1}, but this does not account for large changes in the average angles, which will affect a simple coupled oscillator model. Jensen, et al.[19] predict the $2\nu_{acceptor}$ mode for (HF)$_2$ at 7674 cm^{-1}, near the observed value, and at 5664 cm^{-1} for (DF)$_2$. The latter value for $2\nu_{acceptor}$ of (DF)$_2$ in the gas phase is 59 cm^{-1} higher than our observed 5607 cm^{-1} band, and the 2883 cm^{-1} gas phase fundamental is 27 cm^{-1} higher than the $\nu_{acceptor}$ mode for (DF)$_2$ in solid argon.[20] Accordingly the 5607 cm^{-1} band is assigned to $2\nu_{acceptor}$ of (DF)$_2$. We cannot associate with confidence other features in the more concentrated samples with (DF)$_2$ for possible assignment to other members of the 2ν triad, which are predicted at 5723 and 5592 cm^{-1} by the *ab initio* calculations.[19]

The new 5435 cm^{-1} absorption exhibits the same profile as the 3086, 3082 cm^{-1} band, which will be assigned below to a (DF)$_3$ combination band. This 5435 cm^{-1} band is likely due to an overtone of (DF)$_3$, but we cannot make a specific assignment.

C. N$_2$–HF

Consider next the HF spectra in Fig. 2. The highest frequency band at 4252 cm^{-1} corresponds to the gas phase band[12] near 4294 cm^{-1} for the $\nu_2 + \nu_6$ (hydrogen bonded H–F stretch+out-of-plane bend) of (HF)$_2$. The strongest new band observed here at 4164 cm^{-1} is split into 4161.5 and 4165.5 cm^{-1} components. No counterpart of this band is

TABLE I. Combination bands observed for N_2–HF and $(HF)_n$ species in solid argon at 7–8 K.

HF	DF	Identification
⋯	5692	from HF sample
⋯	5679	DF, $R(0)$, 2ν
⋯	5659	DF, impurity-induced Q, 2ν
⋯	5618	from HF sample
⋯	5607	$(DF)_2$, $2\nu_1$
⋯	5552	enhanced by N_2
⋯	5435	$(DF)_3$, overtone
⋯	5178	N_2–DF, ν_1(D–F stretch)+ν_2(N≡N stretch)
4252	3118	$(HF)_2$, $\nu_2+\nu_6$
4184	3086, 3082	$(HF)_3$, ν(H–F stretch)+ν(H–F bend)
4164	3072	N_2–HF, ν_1(H–F stretch)+ν(H–F bend)
4143	3040	$(HF)_n$
4119	3029	$(HF)_n$
4109	3024	$(HF)_n$
4098	3014	$(HF)_n$
4077	⋯	$(HF)_2$?
4069	⋯	$(HF)_2$?
3963	2896	HF, $R(0)$
3920	2877	HF, impurity induced Q
3881	2846	N_2–HF, ν_1(H–F stretch)
3826	2804	$(HF)_2$, ν_2(bound H–F stretch)
3702	2717	$(HF)_3$, cyclic, $\nu_{donor}(e)$
2332	2333	N_2–HF, ν_2(N≡N stretch)
262	214	N_2–HF, ν(H–F bend)

observed up to 4200 cm^{-1} in the gas phase $(HF)_2$ dimer spectrum.[12] Doping the Ar/HF sample with 1% N_2 *increased* the 4164 cm^{-1} combination band and the 3881 cm^{-1} fundamental N_2–HF band[2] by 4× and *decreased* the 4252 cm^{-1} combination and 3826 cm^{-1} fundamental $(HF)_2$ bands[14] by an order-of-magnitude. Figure 3 illustrates spectra for Ar/DF/N_2 and Ar/DF samples, which reveal the new combination band at 3072 cm^{-1}. The 5930±20 cm^{-1} region revealed no absorption above the noise level.

On the basis of the above evidence, the 4164 cm^{-1} band is assigned to the H–F stretching and bending combination band of the N_2–HF complex and the deuterium counterpart at 3072 cm^{-1}, which has the same behavior, to the analogous mode for the N_2–DF complex. The differences 4164−3881 =283 cm^{-1} for N_2–HF and 3072−2846=226 cm^{-1} for N_2–DF correspond to the HF(DF) bending modes in combination with ν_1 and are higher than the bending mode fundamentals observed at 262 and 214 cm^{-1}, respectively, in solid argon.[2] This follows from the Klemperer group observation of the H–F bending mode 329 cm^{-1} above 3ν_1 in the combination band and suggests that in combination with 2ν_1, the H–F bending mode should be near 305 cm^{-1}.

A very weak 5178 cm^{-1} band ($A=0.002$) appears with added N_2 and tracks with the 2333 cm^{-1} N≡N fundamental ($A=0.116$) and very strong 2846 cm^{-1} D–F fundamental ($A=5.7$) of the N_2–DF complex. The 5178 cm^{-1} band is assigned to the $\nu_{NN}+\nu_{DF}$ combination band for N_2–DF and appears just 1 cm^{-1} below the sum of fundamentals. The DF interaction with N_2 is weak and the D–F, N≡N vibrational coupling is small; hence, a small difference is observed for this mode in N_2–DF (2332.8 cm^{-1}) and N_2–HF (2332.1 cm^{-1}).[2] These complex modes are blue-shifted only 2.1–2.8

cm^{-1} from the nitrogen fundamental (2330.0 cm^{-1}) in the gas phase.[21]

The extrapolation[1] of the bending mode from the 328.6 cm^{-1} value in combination with 3ν_1 to 259 cm^{-1} suggests that the argon matrix[2] has only a small effect on this 262 cm^{-1} direct observation. Furthermore, this near agreement between gas phase and argon matrix measurements shows that the high level calculation[4] does not adequately describe this intermolecular motion. The intramolecular H–F stretching mode observed at 3918.5 cm^{-1} in the gas phase N_2–HF complex red shifts 36.7 to 3881.5 cm^{-1} in solid argon, which is slightly less than the 41.9 cm^{-1} red shift in H–F fundamental itself in the gas phase (3961.4 cm^{-1}) to the argon matrix (3919.5 cm^{-1}).[6,14] The increase in H/D isotopic frequency ratio for the fundamental bending mode, 262/214 =1.224, and this bending mode in combination, 283/226 =1.252, further illustrates the bending mode dependence on HF (or DF) quantum number in the combination mode where the hydrogen bond is stronger and stiffer. Finally, the low H/D ratio for the HF bending fundamental suggests that this large amplitude mode may also involve some N_2–HF stretching character as the H/D ratio for this bending mode in Ar–HF is also low (1.164).[22]

D. $(HF)_2$

Comparison with the gas phase[12] bands at 4294 cm^{-1} for $\nu_2+\nu_6$, and at 3868 cm^{-1} for ν_2 of $(HF)_2$ with the ν_2 band for $(HF)_2$ in solid argon,[14,15] indicates this combination band assignment for the 4252 cm^{-1} solid argon band. Interestingly, the differences 4294−3868=426 cm^{-1} for the gas phase and 4252−3826=426 cm^{-1} for the argon matrix give the same value for ν_6 in combination with ν_2. The ν_6 out-of-plane bending mode has been observed at 400 cm^{-1} in solid argon, and the $K=1$ state observed in the gas phase near 400 cm^{-1} with an estimated 380 cm^{-1} fundamental band origin.[23,24] For $(DF)_2$ the 3118 cm^{-1} argon matrix band is red-shifted from the gas phase[13] $\nu_2+\nu_6$ band at 3152 cm^{-1}. The differences, 3152−2835=317 cm^{-1} for the gas phase and 3118−2804=314 cm^{-1} for the argon matrix, are nearly the same and the fundamental band is observed at 300 cm^{-1} in solid argon.[14,15] So we see that the argon matrix has little effect on the enhanced strength and rigidity of the hydrogen bond in HF–HF with excitation of ν_2, the hydrogen-bonded H–F stretching fundamental. Note also that the H/D ratio for the bending mode in combination, 426/314 =1.357, is higher than for the fundamental bending mode, 400/300=1.333.

E. $(HF)_3$

The 3702 cm^{-1} $(HF)_3$ band is favored relative to the 3826 cm^{-1} $(HF)_2$ band on increasing HF concentration in argon and on annealing.[14,15] Likewise the 4184 cm^{-1} combination band is favored over the 4252 cm^{-1} $(HF)_2$ band so the 4184 cm^{-1} band must be considered for $(HF)_3$. The difference 4184−3702=482 cm^{-1} is again just above the bending mode observed in solid argon, at 446 cm^{-1} for the degenerate in-plane mode of the trigonal-ring $(HF)_3$ complex.[14,15,25] Similarly, for the deuterium counterpart at
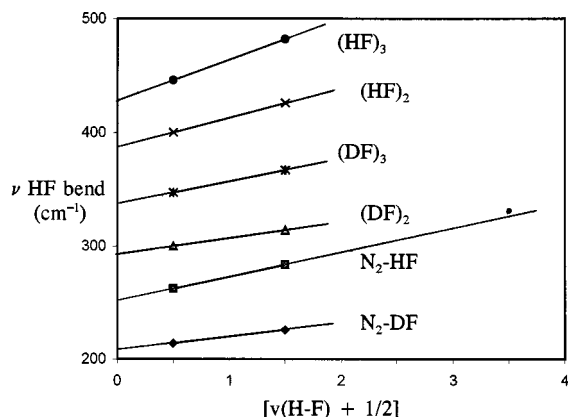
FIG. 4. Plot of HF intermolecular bending modes for N_2–HF, $(HF)_2$, and $(HF)_3$ complexes in solid argon as a function of effective H–F intramolecular quantum number $[\nu(H–F)+1/2]$. The $\nu=3$ point is for the gas phase N_2–HF complex, Ref. 1.

3084 cm^{-1} (average of split band), the difference 3084 $-$ 2717 $=$ 367 cm^{-1} is just above the 347 cm^{-1} value for this mode measured in solid argon at 347 cm^{-1}. The H/D ratios for the fundamental bending mode, 446/347 $=$ 1.285, and for this bending mode in combination, 482/367 $=$ 1.313, again show the increase with intramolecular quantum number for this bending mode in the combination band where the hydrogen bond is strengthened.

The weaker absorptions at 4143–4098 cm^{-1} are probably due to combination bands in higher clusters, most likely $(HF)_4$, but we cannot be more definite.

F. Bending mode correlations

The HF (and DF) intermolecular bending modes in combination bands observed here in solid argon are plotted with their fundamental bands observed earlier in solid argon[2,14,15] against effective intramolecular HF (and DF) quantum number for N_2–HF, $(HF)_2$, and $(HF)_3$ in Fig. 4. The mass dependent relationship with quantum number is clearly seen from the increased slopes in each H/D pair. The gas phase value for N_2–HF, 328.6 cm^{-1} at $\nu=3$ from the Klemperer group,[1] is only 3 cm^{-1} above our linear extrapolation (325.5 cm^{-1}), which suggests that the matrix has only a small effect on this intermolecular bending mode and that the dependence on intramolecular quantum number is nearly linear. We note that the square roots of the slopes of these plots (1.323, 1.363, 1.342, respectively, for N_2–HF, $(HF)_2$, $(HF)_3$) approach the square root of the HF/DF reduced mass ratio (1.379) more closely than the equilibrium (intercept) ratios (1.212, 1.321, 1.270). This suggests that these modes attain more pure HF bending character with increasing intramolecular HF stretching quantum number in the combination bands.

IV. CONCLUSIONS

The ''stiffening'' of the hydrogen bond in N_2–HF and HF–HF with bonded-HF vibrational excitation observed in the gas phase[1,4,11–13] occurs equally for the argon matrix isolated species and for the cyclic-$(HF)_3$ trimer as determined from increase in HF bending frequencies from fundamental to combination bands. This increase in combination with the hydrogen-bonded H–F stretching fundamental is 21 cm^{-1} for the 262 cm^{-1} bending fundamental in N_2–HF, 26 cm^{-1} for the 400 cm^{-1} out-of-plane bending mode in $(HF)_2$, and 36 cm^{-1} for the 446 cm^{-1} in-plane bending mode in $(HF)_3$. The increased bending modes in the combination bands have higher H/D isotopic ratios than the corresponding fundamental bands in the bending potential for the stronger hydrogen bond in the combination mode, which follows from the effective intermolecular quantum number dependence for the intermolecular bending mode.

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