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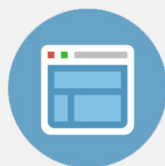
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Infrared spectra of the $\text{CO}_2\cdots\text{HF}$ and $\text{N}_2\text{O}\cdots\text{HF}$ complexes in solid argon at 12 K

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Codeposition of argon diluted samples of CO_2 and HF at 12 K produced new absorptions at 3871, 2354, 656, and 313 cm^{-1} which are assigned to the $\text{CO}_2\cdots\text{HF}$ complex. The 3871 and 313 cm^{-1} absorptions are due to the H-F stretching and librational motions of the HF submolecule in the complex, as verified by DF substitution, and the 2354 and 656 cm^{-1} bands are due to CO_2 submolecule modes. The $\text{N}_2\text{O}\cdots\text{HF}$ complex spectrum contained bands at 3851, 2250, 1306, 583, 328, and 325 cm^{-1} . The greater observed displacement in the HF submolecule modes suggests slightly stronger hydrogen bonding in the N_2O complex. The lack of splitting in the degenerate librational mode for $\text{CO}_2\cdots\text{HF}$ shows that this complex is linear, whereas the 3 cm^{-1} splitting in this mode for $\text{N}_2\text{O}\cdots\text{HF}$ is consistent with a nonlinear complex, in agreement with microwave spectra.

INTRODUCTION

A variety of weakly bound molecular complexes have been studied recently using the molecular beam electric resonance technique to obtain radiofrequency and microwave spectra. The $\text{Ar}\cdots\text{CO}_2$, $\text{CO}_2\cdots\text{HF}$, and $\text{N}_2\text{O}\cdots\text{HF}$ complexes are an interesting group of subjects owing to their different structures.¹⁻³ Complexes involving HF are particularly suitable for study by infrared matrix isolation spectroscopy, since HF serves as a probe of the hydrogen-bond strength through displacement of the H-F fundamental in the complex and through the perturbing effect of hydrogen-bonded HF on vibrations of the base submolecule in the complex. The matrix infrared spectrum of the $\text{C}_2\text{H}_2\cdots\text{HF}$ complex exhibited an H-F fundamental, displaced 208 cm^{-1} below the isolated HF value (3954 cm^{-1}), and a ν_5^c acetylene bending mode shifted 21 cm^{-1} above the isolated C_2H_2 molecule value.⁴ Similar observations on the $\text{C}_2\text{H}_4\cdots\text{HF}$ complex revealed an H-F fundamental displaced 223 cm^{-1} lower, and the ν_7^c out-of-plane ethylene bending mode shifted 25 cm^{-1} above the base molecule value without a perturbation on the in-plane bending mode, which suggested an out-of-plane position for HF in the complex.⁴ The stronger $\text{H}_3\text{N}\cdots\text{HF}$ complex displaced the H-F mode 914 cm^{-1} lower and the ν_2^c and ν_4^c ammonia bending modes 120 and 40 cm^{-1} , respectively, above ammonia values.⁵ In addition, recent studies with $\text{C}_2\text{H}_2\cdots\text{HF}$, $\text{C}_2\text{H}_4\cdots\text{HF}$, and $\text{H}_3\text{N}\cdots\text{HF}$ have shown that the librational mode of HF in the complex provides a structural probe owing to the degeneracy of this mode for C_{3v} or linear complexes.⁵⁻⁷ Accordingly, matrix infrared studies of the $\text{CO}_2\cdots\text{HF}$ and $\text{N}_2\text{O}\cdots\text{HF}$ complexes have been performed to seek additional information about these complexes and any structural difference.

EXPERIMENTAL

The vacuum and cryogenic techniques used in the present experiments have been described previously.^{8,9} Infrared spectra were recorded on a Nicolet 7199 Fourier-transform infrared spectrometer in the $400\text{--}4000\text{ cm}^{-1}$ range at 1 cm^{-1} resolution, using a germanium-coated KBr beamsplitter, a liquid-nitrogen cooled Hg-Cd-Te detector, and CsI optics for the vacuum shroud

and cold window. Useful spectra were recorded in the $130\text{--}420\text{ cm}^{-1}$ range at 2 cm^{-1} resolution, using a $6.25\text{ }\mu$ mylar beamsplitter, a deuterated triglycine sulfate detector, and polyethylene windows for the vacuum vessel and a 2 mm thick CsI plate for the cold window. The observed bands are accurate to ± 0.3 and $\pm 0.5\text{ cm}^{-1}$, respectively, in the two beamsplitter ranges.

Hydrogen fluoride with minimum water contamination was synthesized by mixing 0.2 mmol quantities of F_2 (Matheson) and H_2 (Matheson, research grade) in a well-passivated 3 l stainless steel can; DF was prepared in a similar manner using D_2 gas (Air Products). Carbon dioxide and nitrous oxide (Matheson, lecture bottle) were condensed at 77 K and vacuum distilled from Pyrex beads to remove volatile impurities. Argon mixtures of hydrogen fluoride and CO_2 or N_2O diluted to 300/1 mol ratios were used in these experiments. The gas samples were simultaneously deposited through separate tubes onto a 12 K CsI window using rates of 2.5 mmol/h for each gas mixture during 16 to 20 h periods. The sample was scanned 1000 times with signal averaging and the interferogram was converted to a single beam spectrum by a fast Fourier transform algorithm; this spectrum was ratioed with a similar spectrum of the cold window without sample to produce the double beam spectrum. In the far infrared, a factor of 4 zero filling and triangular apodization were used to best reproduce a grating spectrum.

RESULTS

Three experiments were done with the normal isotopic hydrogen fluoride-carbon dioxide system. In the first study, a $\text{Ar}/\text{HF} = 300/1$ sample was examined, and the spectrum revealed a strong HF doublet at 3962.7 , $3953.8 \pm 0.3\text{ cm}^{-1}$ and weaker bands at 3919, 3881, and 3826 cm^{-1} in the HF stretching region and trace impurities in the fluorine sample such as SiF_4 , CF_4 , and OCF_2 . In the far-infrared region of interest, bands were observed at 446, 400, and 263 cm^{-1} in the HF system; the latter band is shown in Fig. 1(a). A similar $\text{Ar}/\text{HF} = 300/1$ sample was codeposited with an $\text{Ar}/\text{CO}_2 = 300/1$ sample in the second study and the spectrum in regions of interest is shown in Fig. 1(b). New product

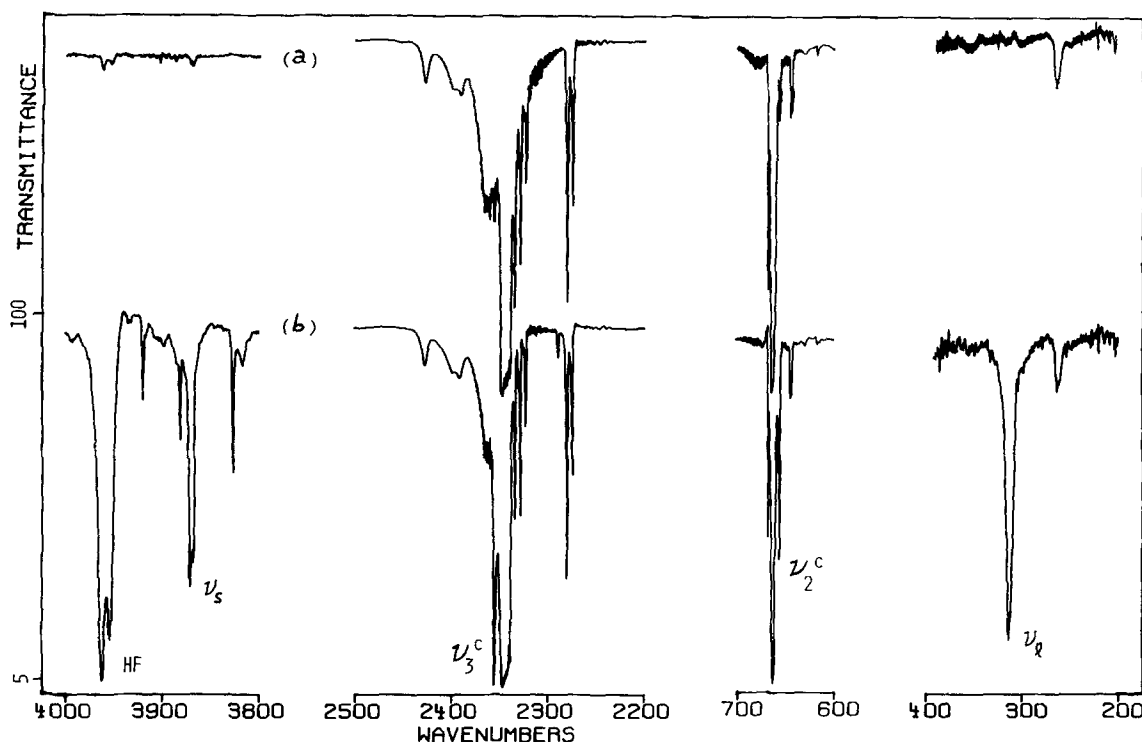


FIG. 1. Infrared spectra in selected regions for the argon/carbon dioxide/hydrogen fluoride matrix system at 12 K. (a) Ar/CO₂ = 300/1, 25 mmol deposited, trace HF impurity from system, 4000–600 cm⁻¹ region; Ar/HF = 300/1, 25 mmol deposited, 400–200 cm⁻¹ region, (b) Ar/CO₂ = 300/1 and Ar/HF = 300/1 samples codeposited. Product absorptions are labeled in accord with assignments listed in Table I.

bands were observed as follows: a doublet at 3867.7, 3870.9 cm⁻¹ in the HF stretching region, a sharp band at 2354.4 cm⁻¹, above the strong ¹²CO₂ doublet at 2344.8, 2338.4 cm⁻¹ with a natural abundance C-13 counterpart at 2289.2 cm⁻¹ above the ¹³CO₂ doublet at 2279.5, 2273.9 cm⁻¹, a sharp 656.0 cm⁻¹ band below the 663 cm⁻¹ CO₂ absorption, and a sharp band in the far infrared at 313.3 cm⁻¹; the product bands and half-widths are listed in Table I. This sample was temperature cycled to 22 K; the 3867, 3870 cm⁻¹ doublet and HF aggregate absorptions increased slightly (20%) at the expense of the HF monomer doublet. A thermal cycle to 28 K continued this trend. The final cycle to 35 K halved the 3867, 3870 cm⁻¹ doublet, reduced HF monomer to one-fourth and markedly increased HF aggregate bands. The 313 cm⁻¹ band behaved in like manner to the 3867, 3870 cm⁻¹ band upon sample warming. Although these two absorptions could not be scanned in the same experiment due to beamsplitter range limitations, their absolute intensities were comparable in several experiments. The relative intensities and positions of the 3870, 3867, 2354, and 656 cm⁻¹ bands were reproduced in another CO₂ experiment. No product bands were observed between 1200–1380 cm⁻¹; a 1383 cm⁻¹ product band increased on diffusion at 35 K when the 3867, 3870 cm⁻¹ band decreased. A third study involved an Ar/CO₂ = 300/1 sample without added HF, and the spectrum is shown in Fig. 1(a). The strong CO₂ bands were observed; a trace of HF impurity from the vacuum system and a corresponding trace of the strong product bands described above were also observed. The 200–400 cm⁻¹ region in Fig. 1(a), taken from an Ar/HF

= 300/1 experiment, shows the 263 cm⁻¹ band due to the HF system.

A 93.6% O-18 enriched CO₂ sample was codeposited with HF; the strong doublet was observed at 3867.4, 3870.5 cm⁻¹, probably within the measurement error,

TABLE I. Absorptions (cm⁻¹), full widths at half-maximum (cm⁻¹) and assignments for CO₂ and N₂O bases and their HF and DF complexes in solid argon at 12 K.

	Base ν (cm ⁻¹)	Product complexes		Product assignments
		ν (cm ⁻¹)	$\nu_{1/2}$ (cm ⁻¹)	
CO ₂		3870.9	5.8	ν_s (HF)
		2839.5	4.1	ν_s (DF)
	2344.8	2354.4	1.5	ν_3^c (C-12)
	2279.5	2289.2	1.7	ν_3^c (C-13)
	663	656.0	1.4	ν_2^c (C-12)
		313.3	6	ν_1 (HF)
		236.0	4	ν_1 (DF)
		3850.8	1.7	ν_s (HF)
		2824.8	1.3	ν_s (DF)
	3480	3528	4	$(\nu_1 + \nu_3)^c$
N ₂ O	2559	2604	4	$(2\nu_1)^c$
	2221	2250.3	1.3	ν_3^c
	1283	1306.5	1.8	ν_1^c
	588	583	a	ν_2^c
		327.9	5	ν_1 (HF)
		324.5	a	ν_1 (HF)
		250.1	3	ν_1 (DF)
		247.6	a	ν_1 (DF)

^aShoulder on more intense band.

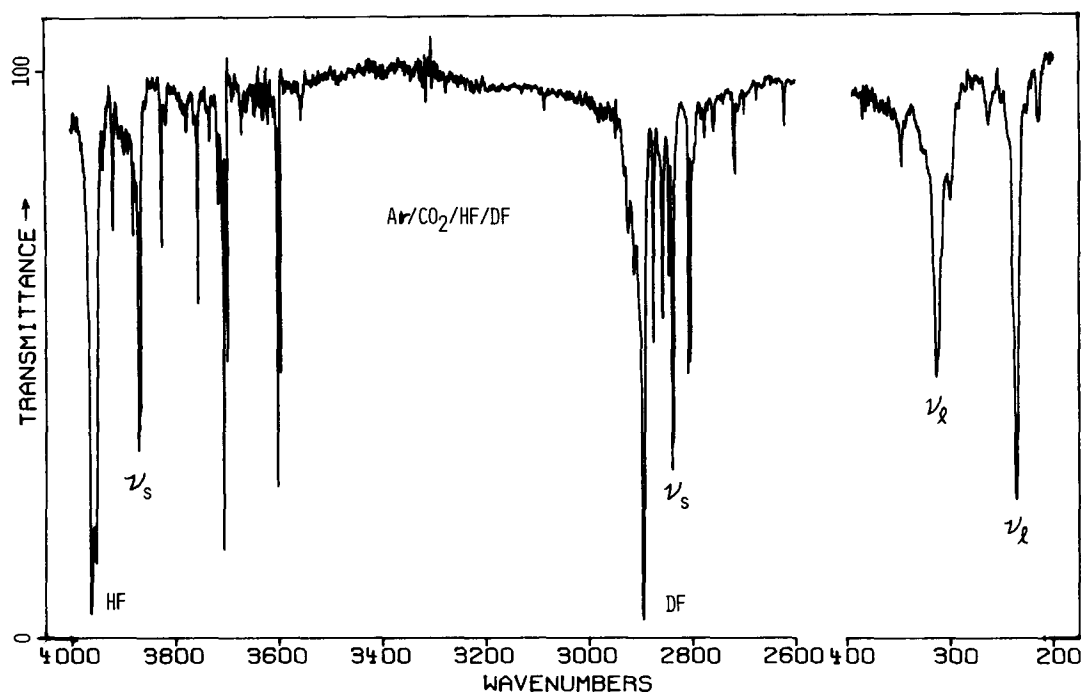


FIG. 2. Infrared spectra in 4000–2600 and 400–200 cm^{-1} regions for matrix prepared by codepositing $\text{Ar}/\text{CO}_2 = 300/1$ and $\text{Ar}/\text{HF}(\text{DF}) = 300/1$ samples. The DF enrichment was greater for sample used in far infrared.

a product band was observed at 645.9 cm^{-1} , below the ν_2 mode of C^{18}O_2 at 653 cm^{-1} , but the $2320\text{--}2350 \text{ cm}^{-1}$ region was obscured by $\text{C}^{16}\text{O}^{18}\text{O}$ in the sample.

An analogous pair of experiments was done with a DF enriched hydrogen fluoride sample, and the spectrum is shown in Fig. 2 for the HF–DF regions. The spectrum reveals DF monomer at $2895.8 \pm 0.2 \text{ cm}^{-1}$ with associated satellites, in addition to analogous HF bands. The HF product doublets were observed at 3867.7 , 3870.9 cm^{-1} and the corresponding DF product doublets were found at 2837.4 , 2839.5 cm^{-1} . The far infrared region was examined in a later experiment with a greater DF enrichment in the hydrogen fluoride sample. Two strong product bands were observed at 313.3 and 236.0 cm^{-1} above weaker bands due to hydrogen fluoride aggregates.

Three experiments were done with the nitrous oxide system. Figure 3(b) illustrates the spectrum from an $\text{Ar}/\text{N}_2\text{O} = 300/1$ sample codeposited with $\text{Ar}/\text{HF} = 300/1$. The strongest product bands appeared at 3850.8 cm^{-1} with a weaker splitting at 3847.3 cm^{-1} , at 2250.3 cm^{-1} above the N_2O band at 2221 cm^{-1} , and at 1306.5 cm^{-1} above the N_2O band at 1283 cm^{-1} . Additional weaker bands were observed at 3528 cm^{-1} above $\nu_1 + \nu_3$ of N_2O at 3480 cm^{-1} , 2602 cm^{-1} above $2\nu_1$ of N_2O at 2559 cm^{-1} , and 583 cm^{-1} below ν_2 of N_2O at 589 cm^{-1} .⁹ Figure 3(a) contrasts the spectrum of an $\text{Ar}/\text{N}_2\text{O} = 300/1$ sample with only a trace of HF as an impurity; the strong product absorptions were observed with about 10% of their intensity in the $\text{Ar}/\text{HF} = 300/1$ experiment. Another experiment was performed with a DF enriched hydrogen fluoride sample, and the spectral region involving deuterium shifts is shown in Fig. 4. The strong 2824.8 ,

2821.4 cm^{-1} and 3850.8 , 3847.3 cm^{-1} product bands were observed with greater intensity than bands due to HF (DF) species; the weak 2602 and 3528 cm^{-1} products are discernible in the figure. In the far infrared region, strong product bands were observed at 327.9 cm^{-1} with a 324.5 cm^{-1} splitting and at 250.1 cm^{-1} with a 247.6 cm^{-1} splitting. The observed product absorptions are collected in Table I.

DISCUSSION

The new product bands will be assigned to hydrogen-bonded complexes and structural implications will be considered.

Assignments

The vibrational spectrum of a hydrogen-bonded complex involving two submolecules can be described in terms of each submolecule. The spectrum of the base submolecule is expected to be perturbed slightly by the hydrogen bonding interaction, and the base submolecule modes in the complex can be assigned by comparison to the isolated basemolecule spectrum. Table I gives the assignments for the complex and compares vibrational data for the base molecules. Isotopic shifts support these assignments; the ν_3^c mode exhibits a 65 cm^{-1} C–13 shift, just as ν_3 , and the ν_2^c modes show a 10 cm^{-1} O–18 shift, just as ν_2 . It can be immediately seen that the stretching modes of N_2O are increased 29 and 23 cm^{-1} , respectively, by the hydrogen bonding interaction with N_2O , whereas ν_3^c of $\text{CO}_2 \cdots \text{HF}$ is only 10 cm^{-1} above ν_3 of CO_2 . The ν_1^c mode was not detected in the $\text{CO}_2 \cdots \text{HF}$ complex; apparently the hydrogen bonding interaction does not produce enough electrical asymmetry in the

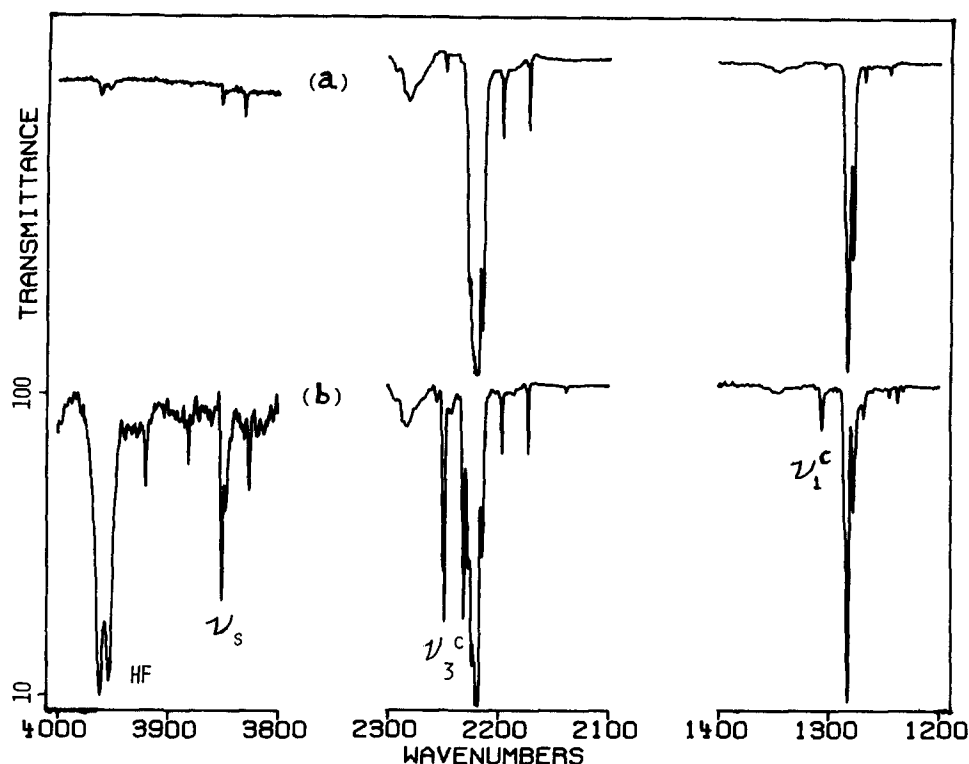


FIG. 3. Infrared spectra of the argon/nitrous oxide/hydrogen fluoride system in selected regions. (a) $\text{Ar}/\text{N}_2\text{O} = 300/1$, 20 mmol deposited with trace of HF impurity from vacuum system, (b) $\text{Ar}/\text{N}_2\text{O} = 300/1$ sample codeposited with $\text{Ar}/\text{HF} = 300/1$ sample. Product absorptions labeled as assigned in Table I.

CO_2 submolecule to give ν_1^c observable intensity.

The spectrum of the acid submolecule includes the perturbed H–F stretching mode, identified¹⁰ as ν_s , and libration of the H–F submolecule arising from the rotational degrees of freedom H–F lost in forming the

complex, which we will identify as ν_l (degenerate for linear complex), the stretching mode of the hydrogen bond itself ν_σ , and deformation of the hydrogen bond ν_δ (degenerate for linear complex). The latter two complex modes are usually quite low in frequency and probably of lower absorption cross section in comparison to

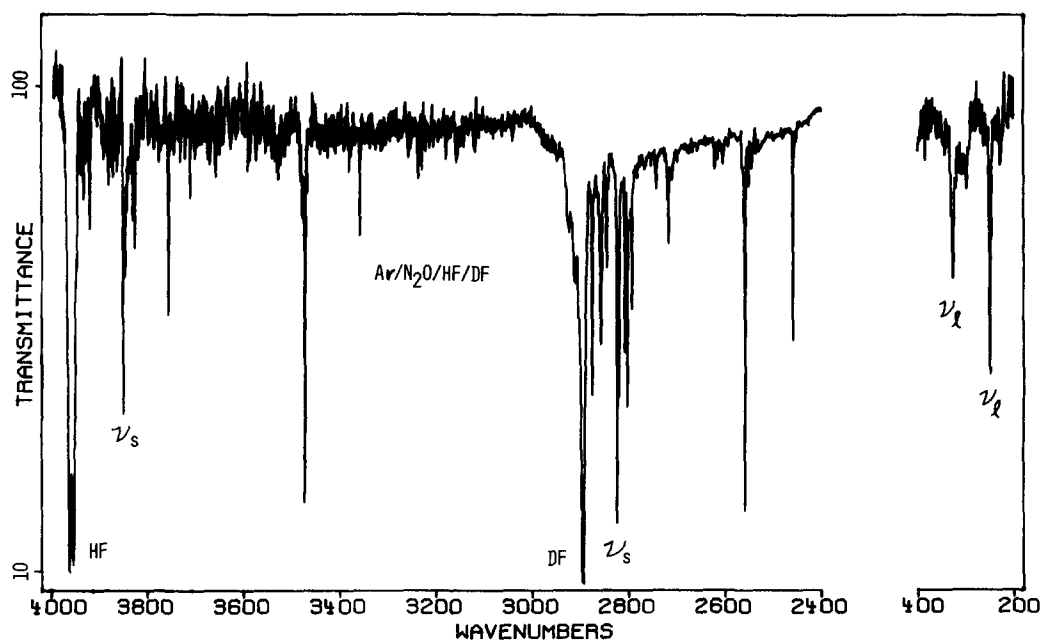


FIG. 4. Infrared spectra in 4000–2400 and 400–200 cm^{-1} regions for matrix prepared by codepositing $\text{Ar}/\text{N}_2\text{O} = 300/1$ and $\text{Ar}/\text{HF}(\text{DF}) = 300/1$ sample.

the former two complex modes, which are quite strong and observable in the infrared region.

The strong $3870.9, 3867.7 \text{ cm}^{-1}$ doublet in CO_2 , HF experiments is assigned to the ν_s mode of the $\text{OCO} \cdots \text{HF}$ complex. The band position and deuterium shift identify this absorption as an H-F vibration, which is consistent with the lack of an O-18 isotopic shift. The H/D ratio for both components is 1.3632 ± 0.0001 , just less than HF/DF ($3954/2896 = 1.365$), but greater than the H/D ratios for $\text{C}_2\text{H}_4 \cdots \text{HF}$ (1.360)⁶ and $\text{H}_3\text{N} \cdots \text{HF}$ (1.334).⁵ The analogous $3850.9, 3846.6 \text{ cm}^{-1}$ doublet in N_2O , HF experiments is likewise assigned to the ν_s mode in the $\text{N}_2\text{O} \cdots \text{HF}$ complex; the H/D ratio for both components is 1.3633 ± 0.0001 . Although the ν_s modes in the $\text{CO}_2 \cdots \text{HF}$ and $\text{N}_2\text{O} \cdots \text{HF}$ complexes have been displaced 83 and 103 cm^{-1} , respectively, from the isolated HF value, which is a relatively weak interaction for a hydrogen bonded species, the H/D ratios are little changed from the HF/DF value. The $3\text{--}4 \text{ cm}^{-1}$ splitting in the strong ν_s modes is attributed to a matrix site splitting; the ν_3 mode of CO_2 exhibits a 6 cm^{-1} matrix site splitting, although this splitting was not observed in the ν_3^c mode. The argon matrix is also expected to red shift the ν_s mode of the complex since the Q branch of HF itself is red shifted from 3958 cm^{-1} (gas)¹¹ to 3954 cm^{-1} (argon)¹² and stronger HF complexes are displaced a larger amount.⁵ It is estimated that the argon matrix may cause a $10\text{--}20 \text{ cm}^{-1}$ red shift on the ν_s modes reported here. The strong, sharp 313.3 cm^{-1} band is assigned to ν_i for the $\text{OCO} \cdots \text{HF}$ complex. The H/D ratio (1.327) is slightly greater than the $\text{H}_3\text{N} \cdots \text{HF}$ value (1.3148) and intermediate between the values for the two split components of $\text{C}_2\text{H}_4 \cdots \text{HF}$ ($423.7/322.5 = 1.3138, 396.2/296.1 = 1.3381$). The sharp doublet at $327.9, 324.9 \text{ cm}^{-1}$ in the N_2O , HF experiments is likewise assigned to ν_i of the $\text{N}_2\text{O} \cdots \text{HF}$ complex; the components of this doublet exhibit H/D ratios of 1.310 ± 0.001 .

The H/D ratios provide information about the nature of the ν_i mode in the complex. These ratios are in the range expected for the deformation mode of hydrogen in a covalent molecule. For example, the H/D ratios for the $\nu_4(e)$ hydrogen deformation modes of CHCl_3 and CHBr_3 are 1.334 and 1.352 , respectively.¹³ The 1.327 H/D ratio for $\text{CO}_2 \cdots \text{HF}$ differs substantially from the 1.5 ratio calculated from the bending modes estimated by the Harvard group² using the average angle HF makes with the molecular axis deduced from the microwave spectrum and assuming a harmonic potential. The bending frequency predicted by this model (210 cm^{-1}) is substantially lower than the observed 313 cm^{-1} matrix value. Although the argon matrix blue shifts the ν_i mode for the $\text{CH}_3\text{C}\equiv\text{N} \cdots \text{HF}$ complex from 620 to 678 cm^{-1} ,¹⁴ the weaker interaction for $\text{CO}_2 \cdots \text{HF}$ suggests a smaller matrix effect which is estimated at 5% . This estimate of the blue shift on ν_i by the solid argon matrix cage is in accord with the shift in the $J=0 \rightarrow J=1$ pure rotational transition for HF from 42 cm^{-1} (gas) to 44 cm^{-1} (solid argon).¹² Hence, we believe the matrix ν_i observation predicts a gas-phase value near 300 cm^{-1} . Finally, the H/D ratio for the ν_i mode is substantially below the ratio 1.9 for the $J=0 \rightarrow J=1$ rotational transi-

tions of HF and DF predicted from the B_e values,¹¹ and the ν_i vibrational mode at 313 cm^{-1} is substantially higher than the $J=0 \rightarrow 1$ rotational transition for HF at 42 cm^{-1} . These observations characterize the ν_i motion as a normal vibrational mode of the complex.

The full widths at half-maximum ($\nu_{1/2}$) shown in Table I, are larger for the acid submolecule modes, where the effect of hydrogen bonding is more pronounced, than for the base submolecule modes. The absorptions due to DF motions are sharper than the corresponding HF bands as might be expected from the relative vibrational amplitudes.

Finally, sample warming into the $20\text{--}30 \text{ K}$ range to allow diffusion and reaction of trapped HF produced an increase in the complex band intensities showing that the hydrogen bonding association requires little or no activation energy. Warming above 30 K leads to higher aggregation and a decrease in complex band intensities.

Structure of the complex

The present vibrational data for the $\text{CO}_2 \cdots \text{HF}$ and $\text{N}_2\text{O} \cdots \text{HF}$ complexes can provide some information on the structure of these complexes. A weak bonding association of fluorine to carbon in the $\text{HF} \cdots \text{CO}_2$ complex might be expected to produce the magnitude of shift in ν_s observed here for the base molecule vibrations ($10\text{--}30 \text{ cm}^{-1}$). However, the observation of a 83 cm^{-1} red shift in ν_s of the $\text{CO}_2 \cdots \text{HF}$ complex, relative to the HF fundamental itself, provides strong support for a bonding interaction through hydrogen rather than fluorine, as concluded from the theoretical calculations¹⁵ and microwave spectrum.²

A number of comparisons between the vibrational spectra for the $\text{CO}_2 \cdots \text{HF}$ and $\text{N}_2\text{O} \cdots \text{HF}$ complexes are of interest. The ν_s mode in the CO_2 complex is displaced 83 cm^{-1} below the H-F vibrational fundamental (3954 cm^{-1}) and the ν_s mode for the N_2O complex is displaced a larger amount (103 cm^{-1}); in like fashion, the ν_i mode for the CO_2 complex is shifted 271 cm^{-1} above the H-F rotational fundamental (42 cm^{-1}) and the split ν_i modes for the N_2O complex are displaced slightly more (283 and 286 cm^{-1}). These observations suggest slightly stronger hydrogen bonding in the N_2O complex than in the CO_2 complex. This is in apparent disagreement with the trend in O \cdots H distances of 1.91 \AA in the CO_2 complex and 1.94 \AA in the N_2O complex calculated from the microwave spectra,^{2,3} although the small differences between each determination may not be significant. Both measurements clearly show similar hydrogen bond strengths in the two complexes.

The stretching modes of N_2O are blue shifted 23 and 29 cm^{-1} in the complex, whereas ν_3^c is only 10 cm^{-1} higher than ν_3 of CO_2 . This suggests a stronger perturbation of N_2O by the hydrogen bonding interaction. One overtone and one combination band were observed for the N_2O submolecule in the complex; the values calculated from the fundamentals exceed the observed overtone by 7 cm^{-1} for the submolecule and 9 cm^{-1} for the complex and the observed combination band by 24 cm^{-1} for the submolecule and 28 cm^{-1} for the complex.

This shows a slight increase in the anharmonicity in the complexed submolecule's potential function presumably owing to asymmetric distortion by the hydrogen bonding interaction.

The most significant difference in the infrared spectra of the two complexes is found in the ν_1 modes. In the CO_2 case, a linear $\text{OCO} \cdots \text{HF}$ structure has been determined from the microwave spectrum,² and the ν_1 modes for the HF and DF species give sharp bands with no evidence of splitting which is consistent with the double degeneracy required for the linear structure. Single sharp bands have been observed for the ν_1 modes of the $\text{H}_3\text{N} \cdots \text{HF}$ and $\text{CH}_3\text{C}\equiv\text{N} \cdots \text{HF}$ complexes.^{5,14} In the N_2O case, a bent $\text{N}_2\text{O} \cdots \text{HF}$ structure has been calculated from the microwave spectrum,³ and the ν_1 modes for the HF and DF complexes with N_2O exhibit clear splittings of 3.4 and 2.5 cm^{-1} , respectively, which is consistent with splitting the degenerate ν_1 mode owing to the nonlinear structure. A larger splitting in the ν_1 mode degeneracy has been found for the $\text{C}_2\text{H}_4 \cdots \text{HF}$ and $\text{C}_2\text{H}_2 \cdots \text{HF}$ complexes, which exhibit ν_1 modes at 424, 396 cm^{-1} and 426, 382 cm^{-1} , respectively.^{6,7} Finally, the H/D ratios are 1.310 for both ν_1 modes of the N_2O complex and the ratio is 1.327 for this doubly degenerate mode in the CO_2 complex. This decrease in H/D ratio for the N_2O complex denotes an increase in cubic anharmonicity which may arise from a more asymmetric interaction required by the nonlinear structure.

Finally, any possible effect of the matrix on the structure of these complexes is not known. The interaction between CO_2 and HF is clearly stronger than the interaction of either submolecule with argon. Since the argon matrix does not distort the linear $\text{CO}_2 \cdots \text{HF}$ complex or the C_{3v} complexes $\text{CH}_3\text{CN} \cdots \text{HF}$ and $\text{H}_3\text{N} \cdots \text{HF}$, it is straightforward to attribute the 3.4 cm^{-1} splittings

in the ν_1 mode for the $\text{N}_2\text{O} \cdots \text{HF}$ complex to its nonlinear structure.

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