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Lester Andrews, Gary L. Johnson, and Benuel J. Kelsall

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Infrared spectra of the hydrogen-bonded pi complex C$_2$H$_4$–HF in solid argon

Lester Andrews, Gary L. Johnson, and Benuel J. Kelsall

Chemistry Department, University of Virginia, Charlottesville, Virginia 22901
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The hydrogen-bonded pi complex C$_2$H$_4$--HF has been prepared by codeposition of C$_2$H$_4$ and HF with excess argon at 12 K. Isotopic substitution in both submolecules identified the complex and provided assignments to v_s at 3731 cm^{-1}, v_l at 424 and 396 cm^{-1}, and v_7^c at 973 cm^{-1}. The observation of a substantial perturbation on the out-of-plane bending mode of the C$_2$H$_4$ submolecule in the complex without a perturbation on the in-plane bending mode indicates that H–F is bonded to the pi electron system perpendicular to the plane of the molecule. The positions of v_s and v_l indicate a hydrogen bond of intermediate strength and the splitting in v_l is characteristic of the anisotropy in the hydrogen bonding interaction with a π system.

INTRODUCTION

The hydrogen bonding phenomenon is of considerable interest and importance. Although σ-electron donor hydrogen-bonded complexes have received wide attention,[1–14] several matrix isolation investigations,[15–17] microwave studies,[18,19] and theoretical calculations[20,21] have been performed on simple olefin–hydrogen halide pi complexes. A recent study from this laboratory presented vibrational spectroscopic evidence for a "T-shaped" complex with hydrogen halides and acetylene.[17] The present investigation with isotopic ethylene species was designed to explore vibrations of the C$_2$H$_4$ and HF submolecules in the hydrogen-bonded pi complex. This system is of particular interest owing to the geometry of the complex and because meaningful theoretical calculations should be possible for this first-row complex.

EXPERIMENTAL

Ethylene–hydrogen fluoride complexes were prepared by codepositing Ar/C$_2$H$_4$ = 300/1 and Ar/HF = 300/1 samples from separate manifolds at about 2 mM/h onto a 12 K CsI plate.[22,23] Ethylene samples C$_2$H$_4$ (Matheson), CH$_2$CD$_2$, C$_2$D$_4$, and ^{13}C$_2$H$_4$ (Merck, Sharpe, and Dohme) were condensed at 77 K to remove any traces of volatile impurities. Hydrogen fluoride was prepared by react-

ing equimolar quantities of the elements at low pressure (~ 2 Torr each) in a well-passivated stainless steel vacuum system. Enriched deuterium fluoride was prepared in like manner using deuterium gas and fluorine; after exchanging the system with fresh DF samples for 3 days, the DF enrichment was about 75%.

Infrared spectra were recorded on a Nicolet 7199A FT-IR using 0.1, 0.5, and 1.0 cm^{-1} resolution in the 400–4000 cm^{-1} region (KBr beam splitter) for experiments with about 20–30 mmol of each gas mixture deposited over a 10–15 h period. Similar experiments were done and spectra were recorded with 2 cm^{-1} resolution in the 125–425 cm^{-1} region (6.25 μ mylar beam splitter) using polyethylene vacuum windows.[10]

RESULTS

Isotopic ethylene studies with HF and DF will be described first followed by experiments with chlorine and bromine species.

C$_2$H$_4$ + HF

Several experiments were done with the normal isotopic system. The full spectrum recorded at 1.0 cm^{-1} resolution is illustrated in Fig. 1 for codeposited samples of Ar/C$_2$H$_4$ = 300/1 and Ar/HF = 300/1. Compari-
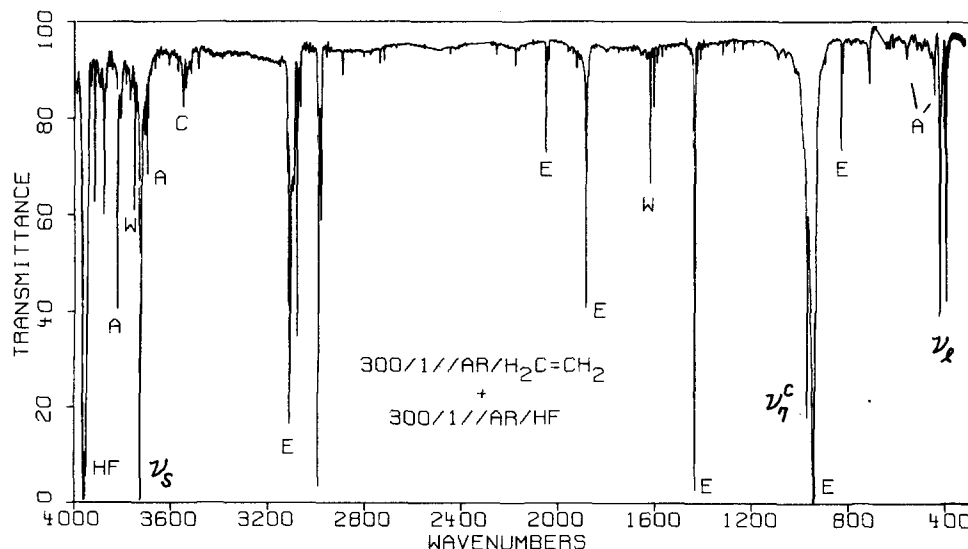
FIG. 1. Infrared spectrum in the 4000–400 cm^{-1} region for a matrix prepared by codepositing Ar/C$_2$H$_4$ = 300/1 and Ar/HF = 300/1 samples at 12 K. The symbols v_s, v_7^c, and v_l identify absorptions due to the C$_2$H$_4$–HF complex. A denotes HF aggregate, W bands are due to H$_2$O, the C band arises from H$_2$O–HF, and E bands are due to ethylene. CO$_2$ has been removed in processing the data.

TABLE I. Product absorptions (cm^{-1}) of ethylene–hydrogen fluoride cocondensation reactions in solid argon (or nitrogen) at 12 K.

| (Argon) | | (Nitrogen) | | (Argon) | | |
HF+C$_2$H$_4$ (A)[a]	HF+^{13}C$_2$H$_4$	DF(HF)+C$_2$H$_4$ (A)	FWHM[b]	DF(HF)+C$_2$H$_4$ (A)	FWHM[b]	Assign
3730.7 (1.80)	3730.7	3664.3 (0.6)	2.1	3730.9 (0.4)	2.4	ν_s (HF)
⋯	⋯	2696.5 (0.9)	1.6	2742.0 (0.9)	1.4	ν_s (DF)
1926.6 (0.02)	1909.0	⋯		1928.0 (0.03)	1.2	$(\nu_7 + \nu_8)^c$
973.0 (0.55)	963.2	975.6 (0.5)	1.5	973.4 (0.70)	1.2	ν_7^c
715.3 (0.05)	715.2	860.0 (0.03)	5.0	714.8 (0.02)	6.0	$[2\nu_l (HF)]^d$
⋯	⋯	⋯		558.2 (0.04)	4.0	$[2\nu_l (DF)]^d$
423.7 (0.35)	423.3	485.5 (0.12)	3.0	423.8 (0.08)	2.0	ν_l (HF)
396.2 (0.30)		464.4 (0.12)	3.0			ν_l (HF)
				423.8 (0.14)^c	3.7	ν_l (HF)
				396.1 (0.12)^c	4.8	ν_l (HF)
				322.4 (0.29)^c	2.8	ν_l (DF)
				296.2 (0.24)^c	3.3	ν_l (DF)

[a]Band absorbances given parenthetically.
[b]Full width at half maximum, cm^{-1}.
[c]Measurements from separate far–infrared experiment.
[d]Tentative assignment.

son with spectra from each reagent sample deposited separately identifies sharp new bands at 3730.7, 1926.6, 973.0, 423.7, and 396.2 ± 0.2 cm^{-1} as products of the ethylene–HF reaction. These bands are labeled in Fig. 1 and listed in Table I with absorbances. A slightly broader new band was observed at 715.3 cm^{-1}.

^{13}C$_2$H$_4$ + HF

The spectrum recorded after cocondensation of Ar/^{13}C$_2$H$_4$ = 300/1 and Ar/HF = 300/1 samples revealed sharp new bands at 3730.7, 1909, 963.2, and 423.3 ± 0.2 cm^{-1}. The broader feature was also observed at 715.2 cm^{-1}. This sample was temperature cycled 12–22–12 K, and all of the above product absorbances increased by 50%, an HF aggregate band at 446 cm^{-1} doubled, and HF monomer at 3962 cm^{-1} decreased.

CH$_2$CD$_2$ and C$_2$D$_4$

Deuterated ethylenes were codeposited with HF samples and DF/HF mixtures; spectra were recorded on 0.1 cm^{-1} resolution to examine the effect of isotopic

substitution in one submolecule on the vibration of the other submolecule in the complex. Under the high resolution conditions, the two strongest product bands in the HF/C$_2$H$_4$ system were measured at 3730.7 ± 0.1 cm^{-1} (full width at half maximum = FWHM = 2.4 cm^{-1}) and 973.0 ± 0.1 cm^{-1}, the error limits encompass the reproducibility of several measurements in different experiments. The out-of-plane bending region 700–1000 cm^{-1} for HF cocondensed with the CH$_2$CH$_2$, CH$_2$CD$_2$, and CD$_2$CD$_2$ isotopic compounds is contrasted in Fig. 2. These product bands are listed in Table II. For the lower symmetry species CH$_2$CD$_2$, two out-of-plane bending modes are infrared active and two product bands were observed.

C$_2$H$_4$ + DF

Another series of experiments was done with DF enriched hydrogen fluoride. The strongest product bands were shifted to 2742.0 ± 0.1 (FWHM = 1.4 cm^{-1}) and 973.4 ± 0.1 cm^{-1} (FWHM = 1.2 cm^{-1}), as measured from 0.1 cm^{-1} resolution spectra; these bands are compared

TABLE II. Strongest isotopic product absorptions (cm^{-1}) from 0.1 cm^{-1} resolution spectra for HF and C$_2$H$_4$ submolecules in C$_2$H$_4\cdots$HF complexes in solid argon at 12 K.

| HF | | | DF(HF) | | | |
C$_2$H$_4$	CH$_2$CD$_2$	C$_2$D$_4$	C$_2$H$_4$	CH$_2$CD$_2$	C$_2$D$_4$	Assign
3730.3[a]	3728.9	3727.2	3730.7	2729.4	3727.8	ν_s(HF)
			2742.0[b]	2741.0	2739.9	ν_s(DF)
973.0[b]			973.4			ν_7^c
	961.6[c]			962.5		ν_{7a}^c
	763.2[c]			763.7		ν_{7b}^c
		738.0[c]			738.6	ν_7^c

[a]Full width at half maximum = FWHM = 2.4 cm^{-1}.
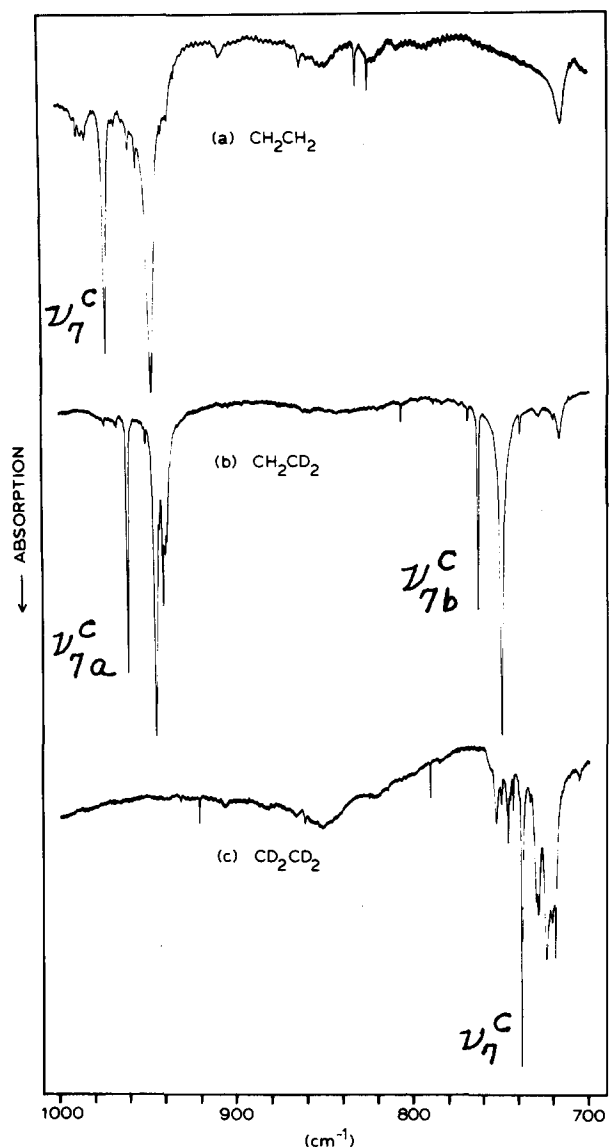[b]FWHM = 1.4 cm^{-1}.
[c]FWHM = 0.5 cm^{-1}.

FIG. 2. Infrared spectra of isotopic ethylene–hydrogen fluoride complexes in the out-of-plane bending region 700–1000 cm^{-1}. (a) C_2H_4, (b) CH_2CD_2, (c) C_2D_4.

with HF product absorptions in Table II. Another experiment was performed with Ar/C_2H_4 = 300/1 and Ar/DF/HF ≈ 900/2/1 samples; the spectrum, recorded at 0.5 cm^{-1} resolution, is illustrated in Fig. 3 and the bands and absorbances are listed in Table I. The strong 2742 cm^{-1} band is the obvious deuterium counterpart of the 3731 cm^{-1} band, and the weaker 558.2 cm^{-1} band is likewise related to the 715 cm^{-1} band. The 423.8 cm^{-1} band is substantially reduced in intensity, compared to Fig. 1, but its intensity relative to the 3731 cm^{-1} band has remained constant. Another product band and the deuterium counterparts were found in the far infrared: two experiments were performed, the first with a modest DF enrichment gave four product bands at 423.7, 396.2, 322.5, and 296.1 ± 0.2 cm^{-1}, and the second with increased effort to exchange deuterate the system gave product bands at 423.8, 396.1, 322.4, and 296.2 ± 0.2 cm^{-1}, which are also shown in Fig. 3 and listed in Table I. These latter bands were not observed in an Ar/DF/HF experiment without ethylene.

Nitrogen matrix

One experiment was performed with a N_2/C_2H_4 = 300/1 and N_2/DF/HF ≈ 900/2/1 samples and the spectrum is shown in Fig. 4. The HF and DF monomer fundamentals were shifted to 3880.6 and 2845.4 cm^{-1} from their 3953.8 and 2895.8 cm^{-1} positions in solid argon. The major product absorptions were observed at 3664.3 and 2696.5 cm^{-1} in solid nitrogen. Another product absorption was observed at 975.6 cm^{-1}, above the 946.8 cm^{-1} C_2H_4 absorption, a new band at 860 cm^{-1} and a sharp product doublet were observed at 485.5 and 464.4 cm^{-1}. The far infrared was not scanned.

C_2H_4 + HCl

Although this system has been investigated previously,[15,16] it was re-examined here and the spectral region was extended into the far infrared. Codeposition of Ar/C_2H_4 = 200/1 and Ar/HCl = 100/1 mixtures produced bands at 2751 cm^{-1} (A = 0.19) and at 957.5 cm^{-1} (A = 0.05).

FIG. 3. Infrared spectrum in the 4000–2500 and 1050–150 cm^{-1} regions for a matrix prepared by codepositing Ar/C_2H_4 = 300/1 and Ar/DF/HF = 900/2/1 samples at 12 K.
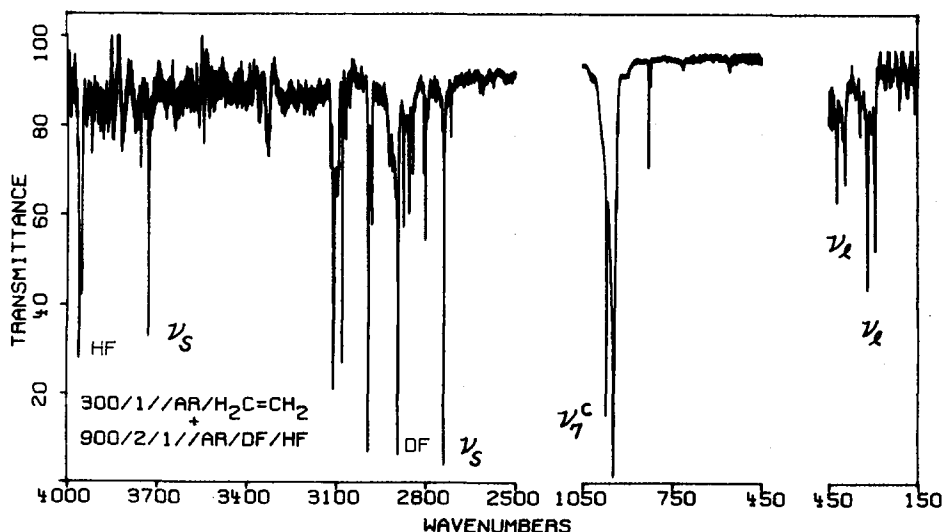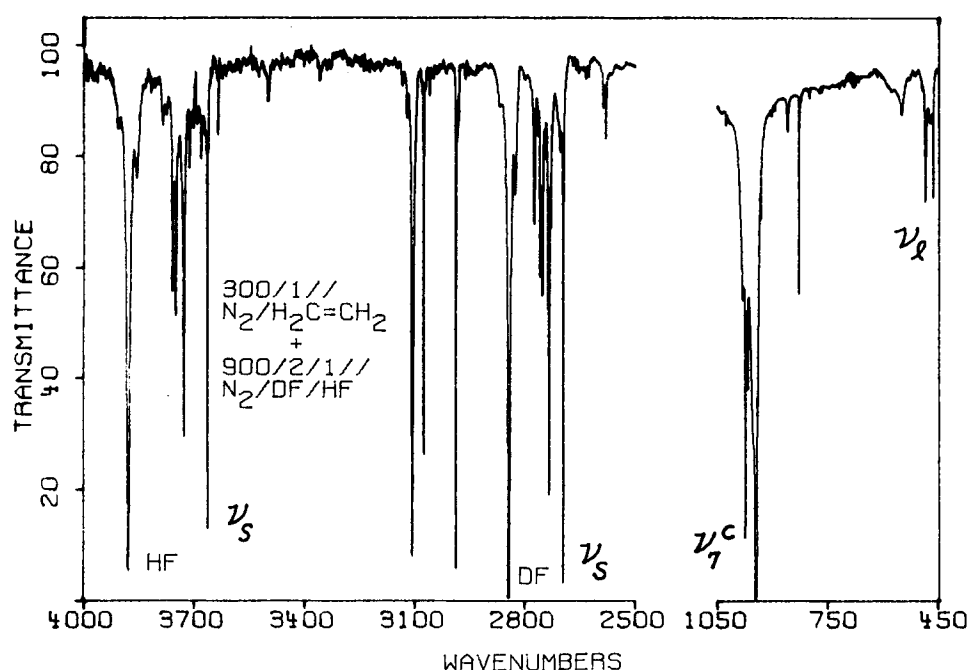
FIG. 4. Infrared spectrum in the 4000–2500 and 1050–450 cm^{-1} regions for a matrix prepared by codepositing $N_2/C_2H_4 = 300/1$ and $N_2/DF/HF = 900/2/1$ samples at 12 K.

No product absorption was observed near the 1440 cm^{-1} C_2H_4 band or in the 200–400 cm^{-1} region.

CH_3CH_2Cl photolysis

One experiment was performed subjecting an $Ar/CH_3CH_2Cl = 200/1$ sample to argon resonance photolysis for HCl photoelimination as described previously for CH_2CHCl.[17] A new band at 2765 cm^{-1} ($A = 0.09$) is in agreement with the band assigned earlier to the C_2H_2--HCl complex[17]; an additional new band was observed at 2748.0 cm^{-1} ($A = 0.08$). Vinyl chloride and chloracetylene absorptions were also observed in this experiment.

CH_3CH_2Br photolysis

One photolysis experiment was performed with ethyl bromide; a product band at 2467 cm^{-1} ($A = 0.19$) is in agreement with the previous assignment to the C_2H_2--HBr complex.[17] In addition, a new band was observed at 2453 cm^{-1} ($A = 0.10$) along with weak C_2H_4 and CH_2CHBr bands.

DISCUSSION

The new product species will be identified, vibrational assignments will be given, and structure and bonding will be considered.

Identification

The product absorptions listed in Tables I and II provide a basis for identification of the 1:1 ethylene–hydrogen fluoride hydrogen-bonded pi complex for the following reasons. (1) The product absorptions were not observed in separate C_2H_4 and HF experiments; the codeposition of both reagents was required. (2) The bands all increased by 50% on temperature cycling the sample 12–22–12 K while HF monomer decreased and HF dimer absorptions doubled in intensity. (3) The strongest absorptions for each submolecule (Table II) show a small but definite shift in the vibration of one submolecule with isotopic substitution in the other submolecule; this confirms a moderate interaction between the two submolecules. (4) The strongest absorption for the complexes is 12–15 cm^{-1} below this band in the analogous $C_2H_2 \cdots HX$ complexes.[17] The latter species were formed by cocondensation of the submolecules *and* vacuum ultraviolet photolysis of vinyl halides, which trapped the C_2H_2 and HX photolysis products in the same matrix cage.[17] (5) Counterparts for the strongest modes were observed for the analogous HCl and HBr complexes, which are listed in Table III.

Assignments

When a hydrogen halide molecule forms a hydrogen-bonded complex, three translational and two rotational

TABLE III. Absorptions (cm^{-1}) assigned to HX acid and C_2H_4 base submolecules and $C_2H_4 \cdots HX$ complexes in solid argon.

X	$\nu(HX)$	ν_s	$(\nu_7 + \nu_8)^c$	$(\nu_7 + \nu_8)$	ν_7^c	ν_7	ν_l
F	3954	3731	1927	1889	973.0	947.4	424, 396
Cl	2888	2751	...	1889	957.5	947.4	... ...
Br	2569	2453	...	1889	...	947.4	... ...

TABLE IV. H—F stretching fundamental (ν_s) and H—F librational motion (ν_l) in several hydrogen fluoride base complexes in the gas phase and in solid argon.

Complexes	ν_s (cm^{-1}) Gas	ν_s (cm^{-1}) Solid argon	ν_l (cm^{-1}) Gas	ν_l (cm^{-1}) Solid argon
CO_2–HF	$\cdots$	3871[a]	$\cdots$	313[a]
C_2H_2–HF	$\cdots$	3746[b]	$\cdots$	426, 382[b]
C_2H_4–HF	$\cdots$	3731	$\cdots$	424, 396
CH_3CN–HF	3627[c]	3482[d]	620 ± 3[c]	681[d]
H_2O–HF	3608[e]	3549[b]	$696, 666 \pm 30$[e]	716, 629[b]
H_3N–HF	3215[f]	3041[g]	$\cdots$	916[g]

[a]Reference 10.
[b]L. Andrews, G. L. Johnson, and B. J. Kelsall, J. Phys. Chem. (to be published).
[c]Reference 4.
[d]Reference 26.
[e]Reference 5.
[f]R. K. Thomas (to be published).
[g]Reference 11.

degrees of freedom become vibrational degrees of freedom of the complex. The two strongest absorptions in the infrared spectrum are ν_s, the perturbed H—X stretching vibration in the complex and ν_l, the librational motion of H—X in the complex, which is doubly degenerate for a symmetric top base molecule. The three translational modes of H—X become ν_σ and ν_B (also doubly degenerate for a symmetric top base); these important characteristics of the hydrogen bond are difficult to study, due to their low intensity and low frequency. Since application of the standard mode designations for hydrogen bonds in RAH---B systems[1] to the X—H case results in confusion between the ν_t (out-of-plane torsion of R—A—H bond) and the ν_b (in-plane bending of R—A—A bond) modes on going to the diatomic aid (for which does not exist), we will use the symbol ν_l to denote the intense librational motion of H—X in the complex. The vibrational modes of the base submolecule should be only slightly affected by the hydrogen bonding interaction, depending upon the structure of the complex. Accordingly, the spectrum of the base molecule provides a model for the spectrum of the base submolecule in the complex.

The strong, sharp 3731 cm^{-1} absorption is assigned to the ν_s mode for $C_2H_4\cdots$HF based upon its position and HF/DF ratio, $3730.7/2742.0 = 1.3606$, which is near the isolated diatomic molecule fundamental[24] ratio $3953.8/2895.8 = 1.3654$. Similar HF/DF ratios were observed for the $CH_2CD_2\cdots$HF, $3728.9/2741.0 = 1.3604$, and $C_2D_4\cdots$HF complexes, $3727.2/2739.9 = 1.3603$. The ν_s mode for $C_2H_4\cdots$HF is intermediate between ν_s values for the weaker $CO_2\cdots$HF and stronger $CH_3CN\cdots$HF complexes,[10,26] as summarized in Table IV.

The 2751 and 2453 cm^{-1} absorptions in HCl and HBr photoelimination experiments are assigned to the ν_s modes of the $C_2H_4\cdots$HCl and $C_2H_4\cdots$HBr complexes. The HX fundamentals decrease by 223, 137, and 116 cm^{-1}, respectively, in the HF, HCl, and HBr complexes,

which are 5.6%, 4.7%, and 4.5% decreases in the HX fundamental upon hydrogen bonding. The decrease in relative displacement of the HX fundamental reflects the weaker hydrogen bond formed by the heavier hydrogen halide.

The 423.8, 396.1 cm^{-1} doublet is assigned to the two components of the HF librational mode ν_l, one in the xy plane (the x axis lies along the C—C bond and the z axis is perpendicular to the molecular plane)[25] and the other in the yz plane. These ν_l modes are intermediate between values for the CO_2 and CH_3CN complexes, as Table IV indicates. The two ν_l modes exhibit similar HF/DF ratios: $423.7/322.5 = 1.314$ and $396.2/296.1 = 1.338$. The bending angles θ_b and θ_c determined from the microwave spectrum of $C_2H_4\cdots$HCl suggest that the motion of the hydrogen atom is only slightly less constrained in the yz plane than in the xz plane and that the motion is very nearly isotropic.[19] Accordingly, the lower wavenumber component may be assigned to libration in the yz plane $\nu_l(yz)$ and the higher component to libration in the xz plane $\nu_l(xz)$. The 715 cm^{-1} band appears to be due to the complex, and it could be the overtone of one of the ν_l modes. It is puzzling for only one overtone to be observed for the two ν_l fundamentals; however, it is possible for one of these motions to be enough more anharmonic than the other to give only one observable overtone. From the HF/DF ratios, the higher ν_l fundamental is more anharmonic, but the overtone/fundamental ratio (1.688) is smaller than the ratio (1.751) for the lower ν_l fundamental. Unfortunately, this possible overtone cannot be identified with a specific one of the librational planes. The lower HF/DF ratio $714.8/588.2 = 1.281$ for the overtone indicates more anharmonicity in the overtone than in the fundamental. Bending modes in hydrogen-bonded complexes are often sufficiently anharmonic to give appreciable intensity in the overtone.[27,28]

The ν_l modes for the $C_2H_4\cdots$HCl complex were not observed between 200 and 400 cm^{-1}. These bands are expected to be broader than the HF counterparts and the yield of HCl complex was substantially less, which prevented their detection.

The sharp 973.0 cm^{-1} band is 25.5 cm^{-1} above the $\nu_7(b_{1u})$ out-of-plane bending mode of the precursor molecule[25] at 947.5 cm^{-1}; the product band shifts 4.8 cm^{-1} upon $^{13}C_2H_4$ substitution while the intense precursor mode shifts 5.1 cm^{-1}. Accordingly, the 973.9 cm^{-1} band is assigned to ν_7^c representing the ν_7 mode of the C_2H_4 submolecule in the $C_2H_4\cdots$HF complex. A similar product at 738 cm^{-1} in C_2D_4 experiments, 19 cm^{-1} above ν_7 for C_2D_4 at 719 cm^{-1}, is assigned to ν_7^c for the $C_2D_4\cdots$HF complex. The ν_7^c modes exhibit essentially the same H/D ratio (1.318) as the ν_7 modes (1.317). In the case of CH_2CD_2, two out-of-plane bending modes are infrared active, and two ν_{7a}^c and ν_{7b}^c bands were observed for the $CH_2CD_2\cdots$HF complex at 962 and 763 cm^{-1}, displaced 17 and 14 cm^{-1}, respectively, above the precursor absorptions.

A sufficient concentration of the $C_2H_4\cdots$HCl complex was formed to observe the ν_7^c mode at 957.5 cm^{-1}, dis-

placed 10.1 cm^{-1} above the ν_7 mode of ethylene. Just as the displacement in ν_8 was less for the HCl complex, the displacement of ν_7^c above ν_7 is less owing to the weaker hydrogen bond formed by HCl.

A weak product band was observed at 1927 cm^{-1}, above the precursor $(\nu_7 + \nu_8)$ mode[25] at 1889 cm^{-1}. A similar band was observed at 1909 cm^{-1}, above the $(\nu_7 + \nu_8)$ mode for $^{13}C_2H_4$ at 1872 cm^{-1}. These product bands are assigned to the combination band of the ethylene submolecule in the complex $(\nu_7 + \nu_8)^c$. The 38 cm^{-1} displacement on complex formation can be attributed to perturbations in each fundamental where a 26 cm^{-1} displacement was observed for ν_7^c, and by difference, a 12 cm^{-1} displacement can be attributed to the $\nu_8(b_{2g})$ fundamental, not observed in the infrared. From the atomic displacements in these two normal modes,[25] it is reasonable for HF in an out-of-plane position to exert more perturbation on ν_7 than on ν_8. No complex counterpart was observed for the strong in-plane bending mode $\nu_{12}(b_{3u})$ at 1440 cm^{-1}; it is presumed that ν_{12}^c is not shifted and therefore obscured by ν_{12}. No complex counterparts were observed for any of the forbidden infrared bands; unfortunately, the most interesting of these, the C=C stretching mode $\nu_2(a_g)$, appears[25] at 1623 cm^{-1} in the water region where a weak product might be obscured. Even though the overall symmetry of the complex is C_{2v}, the local symmetry of the C_2H_4 submolecule remains approximately D_{2h} as far as vibrational selection rules are concerned.

Structure

Two of the observed fundamentals are relevant to the structure of the complex: ν_7^c, and $\nu_l(xz)$ and $\nu_l(yz)$. The observation of a significant perturbation for ν_7^c and no perturbed ν_{12}^c mode indicates that the electrophilic proton of HF is bonded to the C_2H_4 pi electron system in an out-of-plane (z axis) position, as proposed from an early $C_2H_4 \cdots HF$ experiment reported in the analogous $C_2H_2 \cdots HF$ study.[17] An interaction involving fluorine would probably not cause nearly as large a displacement in ν_8 as observed here (223 cm^{-1}). This out-of-plane ligand structure is in agreement with a recent microwave study of the $C_2H_4 \cdots HCl$ complex.[19]

The observation of two separated ν_l bands shows that there is enough x, y asymmetry in the librational potential function to split this mode into two components; a slightly larger splitting was observed for the ν_l modes of the $C_2H_2 \cdots HF$ complex (Table IV). The ν_l modes for the linear σ-complexes $CO_2 \cdots HF$ and $CH_3CN \cdots HF$ are single bands, as given in Table IV, whereas the ν_l modes for the nonlinear σ-complex $H_2O \cdots HF$ are split at 629 and 716 cm^{-1}. The ν_l mode, therefore, provides information on the symmetry of the hydrogen-bonded complex.

Bonding

The hydrogen bond strength in the ethylene–hydrogen fluoride π-complex is intermediate between the linear σ-complexes with CO_2 and CH_3CN bases[10,26] as characterized by the position of ν_8 and ν_l in Table IV. The interaction between C_2H_4 and HF submolecules in the

complex is sufficient for isotopic substitution in one submolecule to cause a small shift in the most intense vibrational modes of the other submolecule.

A nitrogen matrix is known to interact more strongly with polar molecules.[29] Accordingly, comparison of the vibrational spectrum of $C_2H_4 \cdots HF$ in solid argon and nitrogen may provide information about the degree of charge transfer in the bonding interaction. The HF fundamental is displaced from 3954 cm^{-1} in solid argon to 3881 cm^{-1} in solid nitrogen. The strong ν_8 mode is shifted 67 cm^{-1} lower and the ν_l modes are shifted about 65 cm^{-1} higher in solid nitrogen as compared to argon (Table I); in addition ν_7^c is displaced 3 cm^{-1} higher above ν_7 in solid nitrogen. These shifts denote a stronger complex in the nitrogen host and suggest that nitrogen may stabilize the complex through a guest–host interaction arising from a small amount of polar character owing to $C_2H_4(\pi) \rightarrow HF(\sigma^*)$ charge transfer in the complex. Considerably more polar character is predicted for the $H_3N \cdots HF$ complex from the much larger displacements in solid nitrogen as compared to argon.[11] The combined argon and nitrogen matrix observations suggest that ν_8 and ν_l will absorb at about 3770 ± 30 and 390 ± 30 cm^{-1}, respectively, for the $C_2H_4 \cdots HF$ complex in the gas phase.

CONCLUSIONS

The hydrogen-bonded pi complex $C_2H_4 \cdots HF$ has been formed by cocondensation of C_2H_4 and HF with excess argon at 12 K. The complexes were characterized by a strong H–F fundamental at 3731 cm^{-1}, ν_8, split H–F librational fundamentals at 424 and 396 cm^{-1}, ν_l, and a strong out-of-plane bending fundamental of the C_2H_4 submolecule in the complex ν_7^c. The HF/DF ratio for ν_8 was essentially identical to the HF monomer value. The split librational mode demonstrates x, y asymmetry in the potential function governing the hydrogen-bonding interaction. The observation of a substantial perturbation in the out-of-plane bending mode of C_2H_4 in the complex without a perturbation on the strong in-plane bending mode indicates that H–F is bonded to the pi electron system perpendicular to the plane of the molecule. The positions of ν_8 and ν_l show that the $C_2H_4 \cdots HF$ hydrogen bond strength is intermediate between $CO_2 \cdots HF$ and $CH_3CN \cdots HF$ values.

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