the behavior of $\nu_1{}^c$ also explains the shift in the $\nu_4{}^c$ band.

Addition of another HF submolecule to NH_2OH–HF produces a 1:2 complex similar to the ammonia–$(HF)_2$ 1:2 complex.[1,18] The observed frequency for ν_{sa}, the stretching mode of the interior H_a–F submolecule, at 1928 cm^{-1} is very close to the ammonia–$(HF)_2$ mode at 1920 cm^{-1}. This occurs because, in the 1:1 complex, the fluorine atom is the most basic site and is preferentially attacked by the second HF molecule. The large decrease in the H_a–F stretching frequency characterizes a very strong primary hydrogen bond in the 1:2 complex. The structure of the 1:2 complex cannot be determined from the present infrared spectrum since no perturbed base submolecule modes were detected. However, the cyclic nature of the 1:1 complex and hydrogen fluoride trimer[19,20] and the results of recent ab initio calculations on NH_3–$(HF)_2$[21] invite consideration of a cyclic structure for NH_2OH–$(HF)_2$. If the base submolecule has acid and base strengths at opposite ends exceeding that for HF a cyclic structure is likely. Such is probably the case for **2** since **1** is clearly cyclic; however, vibrational spectroscopic observations for N_2–$(HF)_2$ and OC–$(HF)_2$ characterize open structures[21,22] in accord with the weak acid and base character for N_2 and CO.

The proximity of the ν_s band to that of the ammonia–HF complex may cause some concern that the band is actually due to the presence of ammonia. When it is realized that hydroxylamine decomposes readily into NH_3 and H_2O in air at room temperature, this concern becomes stronger. Fortunately, these fears are dismissable on two grounds.

First, the band at 3042 cm^{-1} is very broad (fwhm = 50 cm^{-1}), compared with a sharper band for NH_3–HF (fwhm = 16 cm^{-1}). By virtue of shape, the two bands are quite different. The reason for the broadness of the NH_2OH band lies in the very weak chelating hydrogen bond. This bond is not in the most favorable position sterically. Therefore, given the librational motion of the HF submolecule and the torsional motion of the OH bond, the strength of the HOH_2N–HF interaction is variable, thus altering the frequency of the ν_s(HF) mode over the bandwidth.

Second, there is little evidence for hydroxylamine decomposition into ammonia and water. Coles et al. reported that storing hydroxylamine under argon at −5 °C prevented any decomposition.[24] In this experiment, argon was passed over a heated hydroxylamine salt, meaning the liberated hydroxylamine experienced only an argon medium. Although the temperatures were nearly 60 deg warmer, the molecule was in the gas phase for only a brief period before being trapped in the cold matrix. This supposition is supported by a lack of spectroscopic evidence for the presence of NH_3 (ν_2 = 974 cm^{-1})[25] or the product (916 cm^{-1} for NH_3–HF).

Conclusions

In summary, codeposition of HF and NH_2OH in excess argon produced new infrared absorptions corresponding to perturbed acid and base submolecule vibrations for a 1:1 complex. The position and breadth of the ν_s(HF) mode and the large blue shift on the NH_2 wagging mode indicate that hydrogen fluoride is bonded to the hydroxylamine nitrogen rather than to the oxygen, a model consistent with theoretical calculations of proton affinities.[26] The large blue shift on the NOH bending motion and the large red shift on the O–H stretching vibration both indicate weak hydrogen bonding at the hydroxyl hydrogen. These findings lead to the novel cyclic hydrogen-bonded structure with the primary hydrogen bond to the amine group and a secondary hydrogen bond between the fluorine and OH group. Isotopic substitution of both submolecules verifies that such a complex is formed. Hydrogen fluoride complexes with large base submolecules containing atoms of different polarity can be expected to form similar cyclic hydrogen-bonded complexes involving interactions with both the hydrogen and fluorine of the acid submolecule. At higher HF concentration and on sample annealing a 1:2 complex is formed with a low H–F stretching fundamental characteristic of 1:2 amine–$(HF)_2$ complexes.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation under Grant CHE 85-16611 and preparation of ND_2OD samples by B. Pitts.

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Infrared Spectra and ab Initio SCF Calculations for Alkane–Hydrogen Fluoride Complexes

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Abstract: The complexes formed between HF and a series of five alkanes, methane to isobutane, were studied by matrix isolation FTIR spectroscopy and ab initio Hartree–Fock SCF calculations. A comparison of the HF stretching and librational fundamentals shows that these complexes are weak and reveals a reverse geometry for the H_3CH–FH complex with HF assuming the base role while ethane–, propane–, and butane–HF complexes involve hydrogen bonding of HF as an acid to the C–C single bond. The decrease in C–H bond polarity with increasing hydrocarbon chain length and the availability of a C–C bond contribute to this change in structure. Both types of complexes appear to be trapped with isobutane and HF. Complexes with a 1:2 (alkane–HF) stoichiometry were also formed and support the structure of the 1:1 complex (normal or reverse) formed with each hydrocarbon.

Hydrogen bonding between molecules can greatly affect the physical and chemical properties of a vast array of compounds. Furthermore, hydrogen bonding between moieties of the same molecule can determine the conformation and properties of many biologically important molecules. The use of HF as a model to study the hydrogen-bonding phenomenon has several advantages. Hydrogen fluoride forms strong hydrogen bonds and HF complexes give simple vibrational spectra and are useful as models

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for more complicated systems. Many HF complexes are small enough for meaningful theoretical work and calculated properties can compare favorably to those determined experimentally.

Matrix isolation infrared spectroscopy is a useful tool for studying these complexes. Because of the cryogenic temperatures and minimal interaction between the matrix and the complex, information not readily available in the gas phase can be extracted. Small perturbations observed in the HF and in particular the base submolecule spectra yield information concerning the structure and bonding of the complexes. Furthermore, matrix studies provide a starting point for band searching with high-resolution laser spectrometers.

Hydrogen fluoride can assume a dual role in forming hydrogen-bonded complexes: the hydrogen atom is acidic in nature and forms strong bonds with electron-rich sites such as nonbonded electrons and multiple bonds, and the fluorine atom is basic in nature and can interact with electron-deficient sites such as atoms with a partial positive charge. The former is denoted as a normal hydrogen-bonded complex while the latter is termed a reverse complex. The simplest example of these two types of complexes is the H_aF–H_bF dimer[1,2] in which H_aF acts as a base and H_bF as an acid. Of the HF complexes studied thus far, the normal type are by far the most common and are the only type observed in the gas phase (except for HF clusters). Examples of reverse HF complexes observed in a solid argon matrix are those involving water,[3] hydrogen cyanide,[4] and diacetylene.[5]

Most of the HF complexes studied to date involve strong base submolecules, but by determining the structure and bonding of weak HF complexes much information relevant to hydrogen bonding can be obtained. A companion paper[6] focuses on the HF complexes with three group IV hydrides while this paper deals with the HF complexes involving a series of five alkanes.

Experimental Section

The vacuum and cryogenic techniques used in these experiments have been described previously.[7,8] The neon matrix experiments, however, were performed with use of an Air Products Heliplex 4 closed cycle helium refrigerator. Infrared spectra were recorded on a Nicolet 7199 Fourier-transform infrared spectrometer at 0.24- and 1.0-cm^{-1} resolution in the 4000–400-cm^{-1} region and 2-cm^{-1} resolution for the 425–40-cm^{-1} region. The mid-IR spectra were obtained with use of a KBr beamsplitter and a nitrogen cooled Hg–Cd–Te detector; in the far-IR region (<425 cm^{-1}) mylar beamsplitters and a DTGS detector were used.

The HF (Matheson) was purified by outgassing at 77 and then 178 K. The DF was prepared by mixing D_2 (Air Products) and F_2 (Matheson) in a well-passivated 3-L stainless-steel can and outgassed at 77 K. The hydrocarbon samples were all obtained from Matheson except for C_2D_6 (Merck, Sharpe and Dohme). The methane (M) and ethane (E) samples were used without further purification, while the propane (P), butane (B), and isobutane (I) samples were outgassed at 77 K. The reagents were diluted in argon or neon to give mole ratios (Ar/reagent) between 500/1 and 50/1. The gas mixtures (Ar/HF and Ar/alkane) were codeposited through separate stainless-steel lines onto a CsI window held at 12 K for argon experiments and 5 K for neon. About 15–70 mmol of total gas were condensed on the cold window at a rate of 15–20 mmol/h. To allow migration of the HF within the matrix, the cold window was warmed to 18–35 K for argon and 11 K for neon matrices and recooled for more spectra.

The ab initio Hartree–Fock SCF calculations were performed on a CDC 855 computer, at the University of Virginia, using QCPE program No. 401, HONDO5.[9] The familiar 6-31G[10] and 6-31G**[11] atomic basis sets were used for the calculations. Correction for electron correlation was not included in the calculations, and similar studies on hydrogen-bonded complexes that included correlation correction did not affect bonding energies more than 20%.[12]

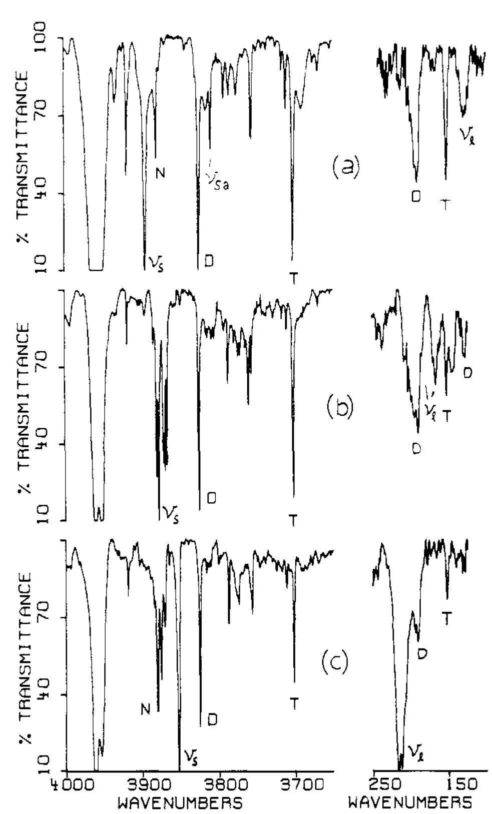

Figure 1. FTIR spectra of matrices formed by codeposition of between 20 and 40 mmol each of Ar/alkane = 300/1 to 100/1 and Ar/HF = 400/1 to 100/1 samples at 12 K: (a) methane + HF in argon; (b) ethane + HF in argon; (c) propane + HF in argon.

Table I. Methane–Hydrogen Fluoride Submolecule Fundamentals (cm^{-1}) for 1:1 and 1:2 (CH_4–HF) Complexes in Solid Argon[a]

reagents	CH_4 + HF	CH_4 + DF	CD_4 + HF	CF_4 + DF	$^{13}CH_4$ + HF	assign
3919, 2877	3896.2	2856	3894.7	2856	3896.1	ν_s
	2914		2098.2	2098		ν_1^c
	130	103				ν_l
	3810	2792	3908.7	2792		ν_{sa}(1:2)

[a] In solid neon ν_s = 3911 cm^{-1} while the HF(Q) = 3953 cm^{-1}; $\nu_1{}^c$ was observed at 2907 cm^{-1}.

Results

Infrared spectra of argon and neon matrix samples containing simple alkanes plus HF and DF along with Hartree–Fock SCF calculations on the methane, ethane, and propane complexes with HF will be presented.

Methane. Methane complexes with HF have been reported elsewhere[6] and these observations are summarized here for comparison to the other hydrocarbons, along with new results for the methane + HF complexes in a solid neon matrix. When samples of CH_4 and HF in argon were condensed at 12 K, a strong new band appeared at 3896 cm^{-1} along with a sharp less intense absorption at 3810 cm^{-1}; these bands are contrasted in Figure 1 with the products of similar ethane and propane studies. A very weak band at 2914 cm^{-1} in the region of the IR inactive symmetric C–H stretching mode, ν_1, of methane[13] was not present in a similar CH_4 sample. Upon warming the matrix to 22 K, the intensity of the 3896-cm^{-1} band did not change appreciably, but the sharp 3810-cm^{-1} band increased 2-fold. Substituting DF for HF in the codeposition experiments provided a new strong absorption at 2856

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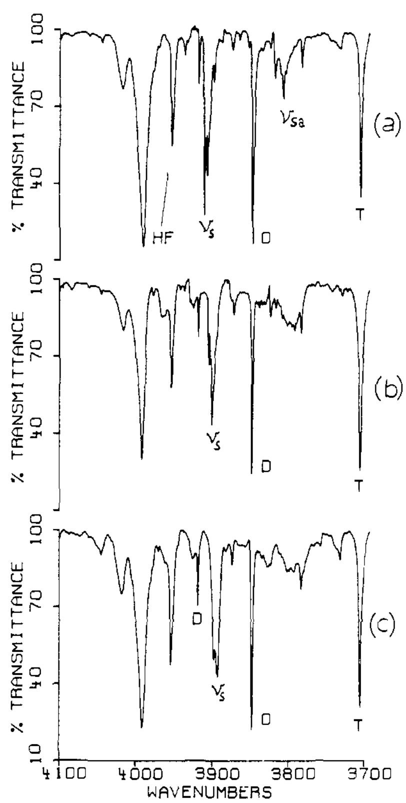

Figure 2. FTIR spectra of matrices formed by codeposition of 11 to 16 mmol each of Ne/alkane = 200/1 and Ne/HF = 200/1 samples at 5 K: (a) methane + HF in neon; (b) ethane + HF in neon; (c) propane + HF in neon.

cm^{-1} with a weaker sharp band at 2792 cm^{-1}. In the far-infrared region several experiments were performed with methane + HF and HF alone and a new band was observed at 130 cm^{-1} in the HF experiments, in addition to $(HF)_2$ and $(HF)_3$ bands labeled D and T in Figure 1a. A new band was observed at 103 cm^{-1} for methane + DF. Product bands from methane experiments are listed in Table I.

Similar experiments employed methane, HF, and DF in a neon matrix. When Ne/CH_4 = 200/1 and Ne/HF = 200/1 samples were codeposited at 5 K, a strong band was observed at 3911 cm^{-1} (labeled ν_s) with a weaker satellite at 3907 cm^{-1}, which are shown in Figure 2. A moderately strong doublet was observed at 3819 and 3808 cm^{-1} (ν_{sa}) plus bands due to $(HF)_2$ dimer at 3919 and 3848 cm^{-1} and $(HF)_3$ trimer at 3706 cm^{-1}.[14] Weak bands were present at 3898 cm^{-1} due to the N_2–HF species[14] and at 2907 cm^{-1} in the ν_1 symmetric C–H stretching region. Warming the matrix to 11 K provided moderate growth in the doublet band while the 3911-, 3907-, and 2907-cm^{-1} bands remained relatively unchanged. When a HF/DF mixture was deposited with methane in a neon matrix, the absorptions mentioned above were all present plus a new weak band at 3822 cm^{-1}. In the DF region, new bands were observed at 2867 cm^{-1} (ν_s) with a shoulder at 2864 cm^{-1}, while a moderately strong doublet appeared at 2799 and 2791 cm^{-1} (ν_{sa}).

Ethane. When a matrix was formed with Ar/ethane = 300/1 and Ar/HF = 300/1 samples, substantially different results were obtained than in the methane experiments as illustrated in Figures 1 and 3. A strong sharp new band was observed at 3879 cm^{-1} (labeled ν_s) with two weaker satellites at 3871 and 3868 cm^{-1} plus weak bands at 3816, 3809, 3775, and 3765 cm^{-1} (labeled ν_{sa} and ν_{sb}). Also present are bands at 3881 and 3787 cm^{-1} due to the N_2 1:1 and 1:2 complexes with HF (labeled N and M)[15] and the 3825-cm^{-1} $(HF)_2$ and 3702-cm^{-1} $(HF)_3$ absorptions (labeled D and T).[16] In the lower frequency region a weak band was observed at 846 cm^{-1} (labeled $\nu_9{}^c$) near the ν_9 C–C–H bending mode for ethane[17] at 822 cm^{-1} in argon as shown in Figure 3. Warming the matrix to 32 K halved the 3879-cm^{-1} band, tripled absorbance of the sharp bands at 3871 and 3868 cm^{-1}, and increased the 846-cm^{-1} band on top of $(HF)_n$ librational absorptions in this region.[16] Bands that increased an order of magnitude in intensity included 3816 and 3809 cm^{-1} (ν_{sa}), 3775 and 3763 cm^{-1} (ν_{sb}), and 3693 cm^{-1} (T^c) near $(HF)_3$.

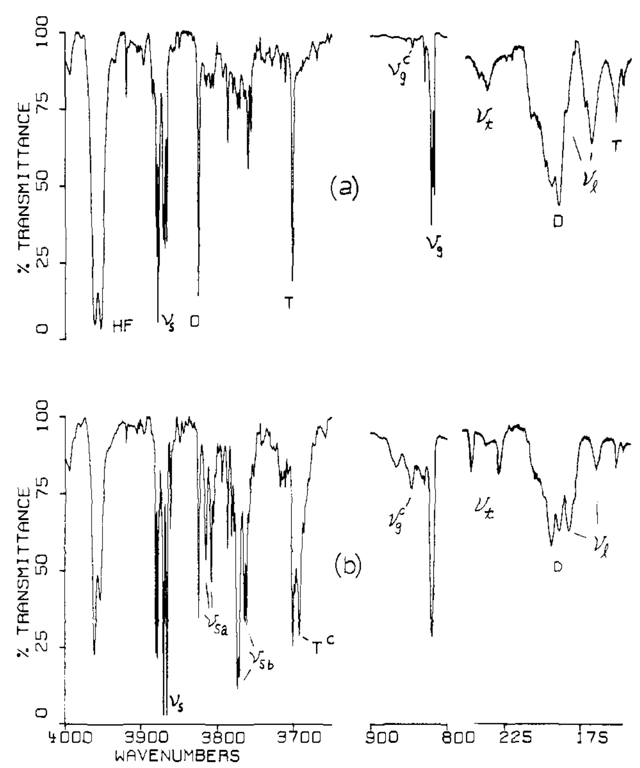

Figure 3. FTIR spectra of matrices formed by codeposition of 23 mmol of Ar/ethane = 300/1 and 27 mmol of Ar/HF = 300/1, for the regions 4000–3650 and 900–800 cm^{-1}, and 20 mmol of Ar/ethane = 100/1 and 19 mmol of Ar/HF = 150/1, for the region 225–175 cm^{-1}: (a) after deposition at 12 K; (b) after warming to 30 K for 10 min and recooling to 12 K.

Table II. Submolecular Fundamentals for the 1:1 and 1:2 Ethane–HF Complexes in Solid Argon

reagents	C_2H_6 + HF	C_2H_6 + DF	C_2D_6 + HF	assign
3919, 2877	3879	2843	3879	ν_s
	3871, 3868	2836	3870	ν_s (site)
3953, 2900	3901	2860		ν_s (neon)^a
	3816, 3809	2793	3809	ν_{sa}
	3795^b	2784^b		$(\nu_{sa})^a$
	3775, 3765	2758	3773	ν_{sb}
	3788^b	2768^b		$(\nu_{sb})^b$
3702, 2717	3693	2712	3693	$(T^c)^c$
822, 594	846	846	614	ν_9
446, 347	443	342		$(T^c)^c$
	422	317		ν_{lb}
	247, 228	246, 227		ν_t
	183	151		ν_l

[a] Neon matrix values. [b] Mixed (HF, DF) 1:2 complex. [c] Trimer complex E–$(HF)_3$.

When ethane and HF/DF mixtures were codeposited in argon, new bands were observed in the DF region plus some of the HF bands, reported above, were shifted. The two ν_{sa} and ν_{sb} bands gave three almost equal intensity bands at 3795, 3788, and 3775 cm^{-1}. In the DF region two strong bands were present upon codeposition at 2843 and 2836 cm^{-1} (ν_s) plus weak ν_{sa} and ν_{sb} bands at 2793, 2784, 2768, and 2758 cm^{-1}. A new band was also observed near the ν_9 fundamental at 846 cm^{-1}. Upon warming the matrix, the 2843-cm^{-1} band decreased in intensity while the 2836-cm^{-1} band grew and another band appeared at 2832 cm^{-1}. The four ν_{sa} and ν_{sb} bands mentioned above all increased in in-

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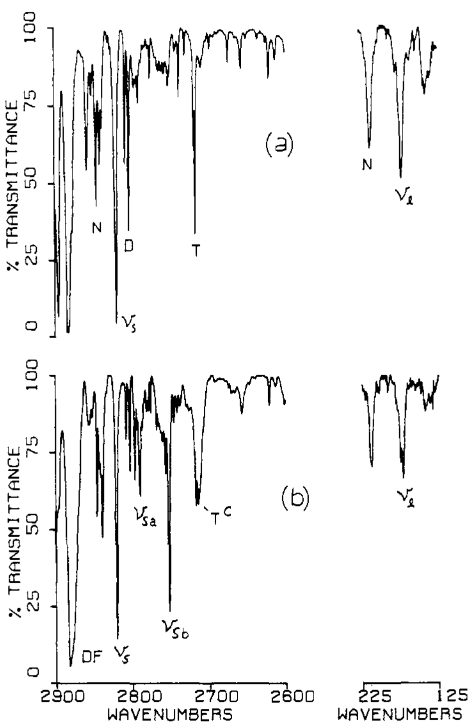

Figure 4. FTIR spectra of a matrix formed by codeposition of 26 mmol of Ar/propane = 300/1 and 29 mmol of Ar/DF/HF = 600/3/1 samples, for the region 2900–2650 cm^{-1}, and 27 mmol of Ar/propane = 100/1 and 32 mmol of Ar/DF = 100/1 samples, for the region 225–125 cm^{-1}: (a) after deposition at 12 K; (b) after warming to 30 K for 10 min and recooling to 12 K.

tensity with the two middle bands growing the most. A band at 2712 cm^{-1} appeared below $(DF)_3$.

When ethane-d_6 was codeposited with HF similar results were obtained, and the bands are listed in Table II. The major difference involved the ν_9 C–C–D bending mode,[17] which shifted to 594 cm^{-1} and exhibited a weak satellite product at 614 cm^{-1}.

Seven experiments were performed in the far-infrared region down to 125 cm^{-1} at varying concentrations of ethane, HF, and DF. For the HF experiments a new band was observed at 166 cm^{-1} near a $(HF)_2$ absorption at 189 cm^{-1}; upon annealing the 166-cm^{-1} band decreased, a 183-cm^{-1} band increased from a shoulder on the $(HF)_2$ band, and 422-, 247-, and 228-cm^{-1} bands increased markedly. For DF, this region was complicated by $(DF)_2$ at 162 cm^{-1} and $(DF)_3$ at 155 cm^{-1}, but a new band appeared at 151 cm^{-1} that was not present with DF in argon, and 317-, 246-, and 227-cm^{-1} bands increased markedly on sample warming.

Cocondensation reactions with ethane, HF, and DF were also performed in a neon matrix. In the HF region a strong band was observed at 3901 cm^{-1} (labeled ν_s) with a less intense satellite at 3905 cm^{-1} as compared with methane in Figure 2. A broad absorption was also present at 3792 cm^{-1}. In the DF region a strong band appeared at 2860 cm^{-1} (ν_s) with a broad absorption at 2785 cm^{-1}.

Propane. Codeposited samples of Ar/propane = 200/1 and Ar/HF = 400/1 gave a strong band at 3854 cm^{-1} (ν_s) along with weaker satellites at 3878 and 3872 cm^{-1} as shown in Figure 1. Upon warming the matrix to 32 K, the 3854-cm^{-1} band decreased slightly while ν_{sa} and ν_{sb} bands at 3814 and 3760 and a new band at 3698 cm^{-1} appeared. DF counterparts for each of these bands were observed in a mixed DF/HF experiment, illustrated in Figure 4, and include a strong peak at 2821 cm^{-1} (ν_s) with a weaker band at 2840 cm^{-1}. Warming the matrix provided new ν_{sa} and ν_{sb} bands that are given in Table III.

In the far-infrared region a strong, sharp doublet was observed at 216 and 212 cm^{-1} in HF experiments with a much weaker band due to $(HF)_3$ at 153 cm^{-1}. Upon annealing, the matrix bands at 417, 256, and 247 cm^{-1} increased markedly. When DF was substituted for HF, a sharp band appeared at 173 cm^{-1} with a 176-cm^{-1} satellite, while annealing produced bands at 313 cm^{-1} above the $(DF)_2$ dimer band and at 247 cm^{-1}. The propane results with HF and DF are reported in Table III.

Table III. Submolecule Fundamentals for the 1:1 and 1:2 Propane–HF and Butane–HF Complexes in Solid Argon

reagents	C_3H_8 + HF	C_3H_8 + DF	C_4H_{10} + HF	C_4H_{10} + DF	assign
3919, 2877	3854	2821	3859, 3853	2825, 2820	ν_s
	3872	2840	3877, 3870	2837, 2831	ν_s (site)
	3814	2797	3816	2798	ν_{sa}
	3803	2790	3806	2793	ν_{sa}[a]
	3760	2753	3765	2757	ν_{sb}
	3767	2757	3772	2763	ν_{sb}[a]
	3698	2714	3696	2713	(T^c)[b]
	436	340	438	341	(T^c)[b]
	417	313	414	311	ν_{lb}
251[c]	247	247	252	252	ν_t
	256		216		ν_{la}
	216, 212	176, 173	202	164	ν_l

[a] Mixed (HF, DF) 1:2 complex; ν_{sa}, ν_{sb}, and ν_{lb} are for 1:2 complex. [b] Trimer complex with hydrocarbon. [c] Weak band observed for butane in solid argon and presumed to be due to a methyl twisting mode designated ν_t.

Table IV. Submolecule Fundamentals for the 1:1 and 1:2 Isobutane–HF Complexes in Solid Argon

reagents	$(CH_3)_3CH$ + HF	$(CH_3)_3CH$ + DF	assign
3919, 2877	3911	2871	ν_s (R)[a]
3919, 2877	3895	2852	ν_s (site N)
	3868	2833	ν_s (N)[a]
	3814	2795	ν_{sa} (R)
	3781	2771	ν_{sb} (N)
	3792[b]	2777[b]	ν_{sb} (N)[b]
	3694	2711	T^c

[a] (R) = reverse complex; (N) = normal hydrogen-bonded complex. [b] Mixed (HF, DF) 1:2 complex.

Butane. The spectra obtained for butane were very similar to those of propane described above and are listed in Table III. Codeposition of butane and HF in an argon matrix produced a strong absorption at 3859 cm^{-1} along with weaker satellites. Other bands include ν_{sa} at 3816 cm^{-1} and ν_{sb} at 3765 cm^{-1}. Warming the matrix to 35 K produced growth in the 3859-cm^{-1} band, substantial growth in the 3816- and 3765-cm^{-1} bands, and the appearance of a new band at 3696 cm^{-1} near $(HF)_3$. DF and butane experiments produced DF counterparts for each of the HF bands listed above, which are given in Table III. In the low-frequency region, HF experiments gave bands at 202 cm^{-1} plus a 216-cm^{-1} band that substantially increased in intensity upon annealing. Two other bands appeared at 414 and 252 ± 2 cm^{-1} only after annealing the matrix. With DF and butane a new band appeared at 164 cm^{-1}, and upon annealing bands increased at 341, 311, and 252 ± 2 cm^{-1}.

Isobutane. Experiments with isobutane and HF gave results similar to both methane and butane. New products listed in Table IV include a sharp band at 3911 cm^{-1}, a group between 3895 and 3868 cm^{-1}, and a weak band at 3781 cm^{-1}. Upon warming the matrix to 30 K the 3911-cm^{-1} band doubled while the other bands listed above decreased slightly in intensity. The 3781-cm^{-1} band increased 8-fold while new bands appeared at 3814 cm^{-1} near $(HF)_2$ and at 3694 cm^{-1}. A similar experiment was also performed with DF and isobutane and the analogous set of bands is given in Table IV. An experiment was performed in the far-infrared, but due to the low yield of products no fundamentals for the isobutane–$(HF)_n$ complexes were observed.

Calculations. Hartree–Fock SCF calculations were performed on CH_4, C_2H_6, and C_3H_8 complexes with HF. Several geometries were considered and optimized for each structure. Possible structures for the methane complex included each end of the HF molecule interacting with a hydrogen atom, an edge, and a face of the tetrahedron. Those considered for ethane include the fluorine of HF interacting with a hydrogen and the hydrogen of

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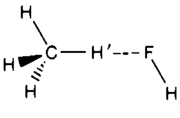
Table V. Optimized Geometry Parameters and Binding Energies for the Methane and Ethane Complexes with HF

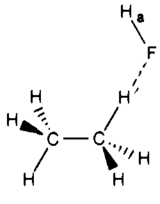
complex	basis	E_b (kcal/mol)[a]	$R(H'-F)$[b]	$R(C_1-H_a)$[b]	$R(C_2-H_a)$[b]
1	6-31G**//6-31G**	0.92[c]	2.67		
2	6-31G	0.82	2.65		
2	6-31G**//6-31G	0.86	2.65		
3	6-31G	1.12	2.65	2.85	2.55
3	6-31G**//6-31G	0.85	2.65	2.85	2.55
P–HF (**2**)	6-31G	0.91	2.70		
P–HF (**3**)	6-31G	1.22	2.61	2.84	2.54

[a] $E_b = E_T(\text{submolecules}) - E_T(\text{complex})$. [b] Distance in Å. [c] Similar calculations with the GAUSSIAN 82 program gave an 0.93-kcal/mol binding energy and a 2.60-Å hydrogen bond distance for **1**.

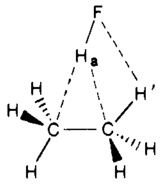
HF interacting with the C–C bond. Each geometry was optimized and the lowest energy structures are shown below. Propane–HF structures followed the ethane analoguges. Complex **1** was calculated with use of the 6-31G**//6-31G** basis while **2**, **3**, and propane analogues were calculated with use of 6-31G and 6-31G**//6-31G basis sets. The binding energies of each complex are given in Table V along with optimized geometry parameters. It should be noted that **1** is 0.43 kcal/mol more stable for the $H'FH_a$ angle of 110° than for a 180° angle, which follows the isoelectronic $(HF)_2$ dimer structure.[1] The same was found for **2**; the structure with an $H'FH_a$ angle of 110° is 0.4 kcal/mol more stable than the linear model previously calculated.[18] Geometry optimization for **3** was started with HF at a number of different intermediate positions until the given structure was obtained. The HF submolecule is in the plane of symmetry of the staggered ethane submolecule. In this process, a 6-31G optimized structure was found with HF nearly perpendicular to the C–C bond and fluorine 3.70 Å from each carbon, but this structure had a binding energy of only 0.66 kcal/mol. Rocking the C_2 methyl group back 15°, twisting the C_1 methyl group 15°, and rotating the HF submolecule 15° and 30° around the C–C axis all decreased the binding energy. It should be noted that **3** contains some of the attractive F–H interaction of **2** although a less optimum angle is required in order to place H_a at the most favorable distance from the carbon–carbon bond. Mulliken populations for atoms in the complexes were computed; for both **1** and **2** a small amount of electron density is donated from FH_a to the alkane, and H′ is polarized more positively than the other alkane hydrogens. In complex **3**, however, there is essentially no charge transfer. The fluorine atom in **3** is essentially on the bisector of the C–C bond while H_a is closer to C_2 than C_1 in order to minimize repulsion between H′ and H_a. The optimum geometry for C_3H_8–HF is similar to **3** with the acid submolecule one hundreth of an Å closer to the C–C bond.



1



2



3

Discussion

Hydrocarbon complexes with HF and DF will be identified and structure and electronic properties of the complexes considered.

Identification. The new product absorptions reported here were not present with the two reagents deposited separately. The IR product absorptions will be assigned to specific hydrogen-bonded complexes, involving both reagents, on the basis of their frequency and annealing behavior, which promotes diffusion and further association of HF.

Methane. Methane and HF in solid argon provided a sharp new band at 3896 cm^{-1}, red shifted 23 cm^{-1} from free HF in argon, giving evidence of the formation of a weak complex between methane and HF. The 3896-cm^{-1} absorption is assigned to the HF stretching fundamental (ν_s) in the hydrogen-bonded complex; the DF counterpart in the complex appeared at 2856 cm^{-1}, giving a $\nu_s(HF)/\nu_s(DF) = 3896/2856 = 1.355$ ratio, consistent with a HF vibration in a hydrogen-bonded complex. The weak absorption at 2914 cm^{-1} is assigned to the symmetric C–H stretch, ν_1, of methane in the complex. This mode is IR inactive in methane, but the HF ligand induces enough asymmetry in the methane submolecule to make the ν_1 fundamental weakly active. This observation greatly supports the case for a methane–FH complex. A DF counterpart for the ν_1 mode was not observed due to the strong DF absorption at 2896 cm^{-1}; however, the ν_1 mode in the CD_4 complex with DF was observed at 2098 cm^{-1}, coincident with that for the CD_4 + HF complex.[6]

The band present at 3810 cm^{-1} in the methane + HF experiments is assigned to the H_aF stretch ν_{sa} in the 1:2 H_3CH–FH_a–FH_b complex. This band increased substantially in intensity upon annealing the matrix while the 3896-cm^{-1} band remained unchanged, showing that these two bands belong to different species. The 3810-cm^{-1} vibration is red shifted 15 cm^{-1} from the corresponding $(HF)_2$ dimer band at 3825 cm^{-1}. This is consistent with a structure having methane attached to the terminal fluorine in $(HF)_2$ which will slightly weaken the adjacent HF bond relative to that in $(HF)_2$ alone. The H_bF mode is expected to be close to the free H–F mode in the $(HF)_2$ dimer and very weak in intensity. The D_aF counterpart in the 1:2 complex appeared at 2793 cm^{-1}, giving a $\nu_{sa}(H_aF)/\nu_{sa}(D_aF) = 1.365$ ratio, again consistent with an HF vibration in a hydrogen-bonded complex.

The far-infrared region was investigated down to 40 cm^{-1}, and a new band was observed at 130 cm^{-1}, which is assigned to the HF libration in the CH_4–FH complex. The DF counterpart is assigned to the absorption at 103 cm^{-1}, giving an $\nu_l(HF)/\nu_l(DF) = 130/103 = 1.262$ ratio. The only other example of a librational mode in a reverse-type complex is the stronger $(HF)_2$ dimer at 189 cm^{-1} in solid argon.[16]

In a neon matrix, the band at 3911 cm^{-1} is assigned to the HF stretch, ν_s, in the methane–FH complex; the weaker band at 3907 cm^{-1} is most likely due to a matrix site-splitting. The ν_s(DF) counterpart was observed at 2867 cm^{-1} with a slightly weaker band at 2864 cm^{-1}, giving an $\nu_s(HF)/\nu_s(DF) = 3911/2867 = 1.364$ ratio in solid neon. The ν_s mode in neon is 15 cm^{-1} higher in energy than that in argon. The neon–argon shift of ν_s in the N_2–HF complex is also of this magnitude.[14] The absorption at 3809 cm^{-1} is assigned to the H_aF stretch in the CH_4–$(FH)_2$ 1:2 complex with a D_aF counterpart at 2791 cm^{-1}. In mixed HF/DF experiments with methane in neon, the 3809 and 2791-cm^{-1} bands are again present, but two new bands are observed at 3821 and 2800 cm^{-1} and are assigned to the H_aF and D_aF stretches in the mixed 1:2 CH_4–H_aF–D_bF and CH_4–D_aF–H_bF complexes, respectively.

Ethane. The strong band at 3879 cm^{-1} present upon codeposition in ethane and HF experiments is assigned to the HF stretch, ν_s, in the C_2H_6–HF complex. The $\nu_s(HF)/\nu_s(DF) = 3879/2845 = 1.363$ ratio is consistent with other hydrogen-bonded complexes. The two weaker bands at 3871 and 3867 cm^{-1} are also assigned to this complex with slightly different relative submolecule configurations, a point inferred from their growth on sample warming (Figure 3). The weak band at 846 cm^{-1} is assigned to the perturbed $\nu_9{}^c$ C–C–H bending mode of ethane in the 1:1 complex, which is blue shifted 24 cm^{-1} relative to ν_9 in ethane alone. In

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(18) Sapse, A. M.; Jain, D. C. *J. Phys. Chem.* **1984**, *88*, 4970.
(19) Liu, S.-Y.; Dykstra, C. E. *J. Phys. Chem.* **1986**, *90*, 3097.

the far-infrared region, the band at 183 cm^{-1}, partially resolved from the $(HF)_2$ dimer absorption at 189 cm^{-1}, is assigned to the HF libration in the E–HF complex. The DF counterpart was observed at 151 cm^{-1}, giving a $\nu_l(HF)/\nu_l(DF) = 183/151 = 1.212$ ratio. The bands at 247 and 228 cm^{-1} showed little DF shift, grew markedly on sample warming, and exhibited no methane counterparts. These bands are in the region expected for the inactive torsional mode of the ethane submolecule[20] and are tentatively assigned to the torsional mode of the E submolecule in the 1:1 and 1:2 complexes.

The strong bands at 3816 and 3809 cm^{-1}, noted ν_{sa}, that grew markedly upon annealing the matrix are assigned to the H_aF stretch in the C_2H_6–H_aF–H_bF 1:2 complex, and the bands at 3772 and 3765 cm^{-1} noted ν_{sb} are assigned to the H_bF stretch. The 1:2 complex bands compare closely to those of the N_2–$(HF)_2$ complex where H_aF is observed at 3817 and H_bF at 3788 cm^{-1}.[15] The band observed at 3691 cm^{-1} is assigned to the C_2H_6–$(HF)_3$ complex and is probably due to an ethane molecule perturbing the cyclic $(HF)_3$ trimer normally absorbing at 3702 cm^{-1}. DF counterparts and assignments are given in Table II. The 846-cm^{-1} band for the perturbed ν_9 bend in the 1:1 DF complex is again blue-shifted 24 cm^{-1} from ethane. With a HF/DF mixture, new 1:2 complex bands were observed at 2784 and 2768 cm^{-1} and at 3795 and 3775 cm^{-1}. These four new bands are assigned to HF or DF stretches in the mixed 1:2 complexes. In one, the bands at 3795 and 2768 cm^{-1} are the H_aF and D_bF stretches, respectively, while in the other mixed 1:2 complex the bands at 2784 and 3775 cm^{-1} are the D_aF and H_bF stretches, respectively. In the two mixed 1:2 complexes, the H_aF mode shifts 14 cm^{-1} to lower energy, while H_bF shifts 13 cm^{-1} to higher energy. This mixing of modes involving the two HF or DF stretches was also seen in the methane 1:2 complex.

For the ethane-d_6 experiment with HF, the bands observed with ethane were also present as listed in Table II. In contrast the ν_9 mode of ethane-d_6 is at 592 cm^{-1}, and the new band at 612 cm^{-1} is assigned to the perturbed $\nu_9{}^c$ mode of the C_2D_6–HF complex.

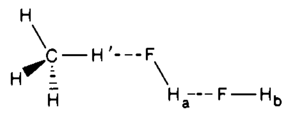
Propane and Butane. The experimental results obtained for propane and butane with HF are very similar to each other and also to the ethane results. The observed absorptions due to the P and B complexes with HF are listed and identified in Table III. Points of particular interest are that the ν_s modes for the P–HF and B–HF complexes are slightly lower than that of E–HF and the librational modes are correspondingly slightly higher. Absorptions due to the H_aF and H_bF modes in the 1:2 (Alkane: HF) complexes were also present, after annealing the matrix, and compare favorably to the E–$(HF)_2$ complex as do those for the two mixed HF/DF 1:2 complexes. One major difference is that the librational modes are more intense for P and B complexes with HF and the H_aF and H_bF librational modes were detected and have been assigned to bands at 417 and 256 cm^{-1}, respectively, for the P–H_aF–H_bF complex and at 414 and 217 cm^{-1} for the B–H_aF–H_bF complex. DF counterparts are observed for the HF complex bands listed above and give HF/DF ratios consistent with the E complexes. Finally, the bands near 250 cm^{-1} grew on annealing, showed no DF shift, and are tentatively assigned to methyl twisting motions in the 1:1 and 1:2 complexes.

Isobutane. The results for ethane, propane, and butane are each similar but contrast those for methane. The isobutane spectra, however, appear to be a mixture of the two sets of data. Similar to methane, the isobutane–HF complex has a strong sharp band at very high frequency and the band present at 3911 cm^{-1} is assigned to the HF stretch in the reverse-type isobutane–FH complex, resembling a structure like methane–FH. Also, the sharp band at 3814 cm^{-1} is assigned to the H_aF stretch in the reverse isobutane–$(FH)_2$ complex. The weak band at 3868 cm^{-1}, and weaker site-splittings at slightly higher frequency, are assigned to the HF stretch in the normal-type isobutane–HF complex, while the absorption at 3781 cm^{-1} is assigned to the H_bF stretch in the isobutane–$(HF)_2$ 1:2 complex. In a mixed HF/DF experiment, the 3781-cm^{-1} band is blue-shifted to 3792 cm^{-1}, while the 3814-cm^{-1} band observed in HF expriments was not present at even a shifted frequency. This shows that the 3814- and 3781-cm^{-1} bands must belong to different complexes. The 3911-cm^{-1} band was present, however, unshifted in frequency. DF counterparts were observed for the bands mentioned above and are listed in Table IV.

Structure and Bonding. The proposed structure for the methane–FH complex is given in **1**, and both the infrared spectra and SCF calculations support this reverse structure. The HF stretching frequency in the 1:1 complex is substantially higher than normal hydrogen-bonded complexes and compares favorably to the free H–F mode in $(HF)_2$ at 3896 cm^{-1} and that for the HF–HCN reverse complex[4] at 3892 cm^{-1}. The high HF stretching frequency in reverse-type complexes is easily explained. In normal hydrogen-bonded complexes with HF, it is the hydrogen atom of the acid that interacts with the base. The HF stretch is predominantly a motion of the hydrogen atom due to the disparity in masses of hydrogen and fluorine. When the hydrogen atom participates in a weak bond, the HF stretching frequency is going to be affected much more than if the fluorine atom were the participant. Both types of complexes can be affected by electrostatic interactions perturbing the HF vibrational potential and weakening of the HF bond due to hydrogen bonding with the other submolecule.[19] The higher than normal HF stretch in the methane–FH complex is consistent with the fluorine atom being bound to CH_4.

The HF librational frequency also indicates a reverse-type complex. The two librational fundamentals of HF in a hydrogen-bonded complex, arising from the two rotational degrees of freedom in free HF, are hindered rotations of the HF submolecule. The librational motion occurs about the center of mass of HF, essentially the fluorine atom, so it is a motion composed primarily of the hydrogen atom. In a normal-type complex, the hydrogen atom is interacting with the base and there is a substantial hindrance to rotation of the HF, markedly raising the librational frequency. In a reverse complex, the fluorine is participating in the interaction while the hydrogen atom is free to undergo a hindered rotation giving a lower librational frequency. In the methane–FH complex, the very low librational frequency (130 cm^{-1}) is consistent with a reverse complex.

The 1:2 methane–$(FH)_2$ complex **4** also provides evidence for a reverse-type geometry. Since the HF stretch in the 1:1 complex is perturbed only slightly compared to free HF, the HF stretches in the 1:2 complex should be only slightly perturbed from that of $(HF)_2$ dimer. The sharp band at 3810 cm^{-1} is consistent with a slightly perturbed H_aF mode from that of the $(HF)_2$ dimer at 3825 cm^{-1}. The fact that a second band attributable to the H_bF stretch in the 1:2 complex was not observed is also consistent with the reverse-type structure. In the free $(HF)_2$ dimer, the H_bF stretch is very weak at 3896 cm^{-1}, coincident with the 1:1 complex HF stretch. Other weak complexes of the normal type, such as SiH_4–HF[6] and N_2–HF,[15] have two bands in the spectra due to the HF stretches in their respective 1:2 complexes.



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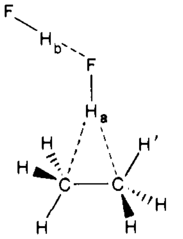

5

Ab initio calculations at the SCF level also support a reverse-type geometry, and a binding energy of 0.92 kcal/mol is found in the 6-31G** basis. The C–H bond of methane is polarized such that the carbon is partially negative and the hydrogens are partially positive in charge. The partially negative fluorine atom interacts electrostatically with a hydrogen of methane, and this hydrogen is subsequently polarized more positively, by about 0.02 e, than the other three. HF in turn is slightly more positive,

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[20] Herzberg, G. *Molecular Spectra and Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; D. Van Nostrand Co., Inc.: Princeton, NJ, 1962.

by 0.01 e, than free HF in this basis, with 0.01 e donated from HF to methane.

On the other hand, the structures of the ethane, propane, and butane 1:1 complexes with HF are proposed to be more of a normal hydrogen-bonded complex with the hydrogen atom of HF interacting with the carbon–carbon single bond. The HF stretching frequencies are displaced more than that of the methane–FH complex and are consistent with other weak normal-type HF complexes such as N_2–HF.[15] The lower frequency HF stretch supports an interaction between the hydrogen atom of HF and the hydrocarbon. The HF librational fundamentals for E (183 cm^{-1}), P (216 cm^{-1}), and B (202 cm^{-1}) are substantially higher than that for M (130 cm^{-1}) and suggest a greater hindrance to rotation of HF, consistent with the hydrogen atom interacting with the C–C bond in a structure like **3**. Finally, the $\nu_9{}^c$ base submolecule mode in the E–HF complex is blue-shifted 24 cm^{-1} by the HF ligand in the complex. This motion is predominantly a C–C–H bend involving tilting of the methyl groups into each other.[20] The large blue shift in the complex mode supports a structure where hydrogen of HF is interacting with the C–C bond and in a position to exert repulsive forces between the acid hydrogen and the partially positive hydrogens of ethane. In the ethylene–HF complex with HF centered over the π bond, the out-of-plane C–H_2 deformation was blue-shifted by 26 cm^{-1} while the in-plane C–H_2 bend was not perturbed.[21]

The 1:2 complexes for E, P, B, and HF, depicted in **5**, are different from **4** for M in that two strong HF stretches were present in the spectra, one corresponding to H_aF and the other to H_bF, whereas in the latter only one was observed. The presence of both HF stretches in the 1:2 complex is consistent with the 1:1 complex **3** where the F–H′ bond is replaced by a stronger F–H_b bond involving H_bF. As H_bF bonds to H_aF of the 1:1 complex, the H_aF mode is further perturbed and red shifts from the value in the 1:1 complex. The H_bF bond is weakened due to its interaction with H_aF, and since the fluorine atom of H_aF is a stronger base than the hydrocarbon, H_bF is at a lower frequency than H_aF, similar to that seen in the N_2–$(HF)_2$ complex.[15]

The 1:3 (alkane:HF) complexes observed with each hydrocarbon are proposed to be perturbed $(HF)_3$, cyclic trimers. The new 1:3 complex bands were all observed slightly red-shifted from the $(HF)_3$ band. Open base–$(HF)_3$ complexes have been observed, most notably in several methyl-substituted acetonitrile complexes with HF.[22] The original base–HF interaction was much stronger than in the alkane–HF complexes and stabilized the open 1:3 complex with three distinct HF stretches observed in the spectrum. However, the weak alkane complexes with HF do not have this stabilizing effect and the cyclic $(HF)_3$ complex is produced.

The Hartree–Fock SCF calculations on the E–HF structure (6-31G basis) predict that the reverse C_2H_6–FH complex **2**, analogous to CH_4–FH, is bound by 0.82 kcal/mol, while the more normal-type C_2H_6–HF complex **3** is bound by 1.12 kcal/mol; however, 6-31G**//6-31G calculations predict nearly identical binding energies for each structure. The 6-31G calculations support the experimental conclusions that the larger ethane–HF complexes have structures like **3**.

HF complexes with unsaturated hydrocarbons involve HF bonded to the electron-rich multiple bond,[12,18,21,23,24] and it is perhaps surprising that the acid hydrogen is directed toward the C–C single bond in these alkanes. The C–H bonds are polarized so that the H atoms are partially positive and the C atoms slightly negative. In ethane, there is approximately 0.67 e^- of extra charge between the two carbons[25] obtained at the expense of the hydrogens. This is much less than the four or six electrons in C=C and C≡C bonds, respectively, but the alkane complexes are much weaker than the alkene and alkyne complexes with HF. The calculated hydrogen bond length in the E–HF complex is also longer (2.5 Å from the C–C bond) than that observed for the ethylene complex (2.2 Å).[19] This must also be due in part to repulsions between the hydrogens of ethane and the H atom of HF.

The P–HF complex is expected to be similar to the E–HF complex except for the extra CH_3 group. The HF stretch is lower in frequency in the P–HF than the E–HF complex and this is attributed to the electron-donating properties of the methyl group which makes the C–C bond slightly more basic in P than in E. This behavior is clearly seen for unsaturated hydrocarbons in which substitution of a methyl group for a hydrogen in ethylene or acetylene substantially increases the basicity of the multiple bond.[26,27] The ν_l mode is higher in P–HF, indicating a more rigid orientation of the acid submolecule, again pointing to a stronger complex, which is substantiated by the SCF calculations.

The B–HF complex is also expected to follow after the E and P complexes, but in this case there are two different bonds available, to the HF: one interior and two terminal C–C bonds. On the basis of the electron-donating property of the methyl groups, the interior C–C bond should be the most basic, but it is the most sterically hindered. The terminal C–C bonds should be more accessable but slightly less basic. In the IR spectra of the B–HF complex there are two HF stretching bands, one slightly above that of the P–HF complex and one slightly below. It is possible that the upper band corresponds to a HF bound to a terminal C–C bond while the lower one is due to a HF interacting with the more basic interior C–C bond; however, the possibility cannot be ruled out that the two bands are due to a matrix site-splitting. It is of interest to note than an HF complex with cyclobutane produced nearly the same ν_s mode, but the cyclopropane–HF complex exhibited a substantially lower ν_s mode (3753 cm^{-1}) than the present propane–HF complex.[28] This contrasts the π-like nature of cyclopropane owing to the ring strain.

The spectra of the isobutane complexes with HF contain absorptions common to both the M– and E–, P–, and B–HF complexes, and it is not easily placed in the normal- or reverse-type complex category. Several weak bands in the 3860–3890-cm^{-1} region suggest a weak normal complex while the absorption at 3911 cm^{-1} points to a reverse complex, and both are believed to form upon codeposition in an argon matrix. Warming the matrix produced a band at 3814 cm^{-1}, which is attributed to the H_aF mode in the reverse 1:2 complex, and at 3781 cm^{-1}, which is to be due to the H_bF stretch in the normal 1:2 complex. The reduced yield of product bands is probably due to the large amount of steric hindrance in isobutane where the C–C bonds are much less accessable to HF than in E, P, or B. For this reason it is believed that a reverse complex is favored, but it is not possible to tell whether the unique hydrogen or one of the methyl hydrogens is complexed with the fluorine atom. The HF stretch of the reverse 1:1 complex is 14 cm^{-1} higher in energy than that for the M–FH complex. This is attributed to the decreased positive charge on the hydrogen atoms in I than in M,[29] making for a weaker interaction with less perturbation of the HF submolecule.

Conclusions

Upon codeposition of HF with methane, ethane, propane, butane, and isobutane in a noble gas matrix, two types of weak complexes were formed: a reverse complex with the fluorine of HF weakly bonded to a hydrogen atom of the alkane, and a normal complex with the hydrogen of HF interacting with a C–C bond of the alkane. The CH_4–FH complex exhibits the reverse geometry while the ethane–, propane–, and butane–HF complexes have a normal acid structure. Both normal and reverse complexes were

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apparently formed with isobutane–HF, but the yield of the normal complex was much less than that with ethane, propane, and butane. The reverse complex is characterized by a small red shift in the H–F fundamental (23 cm^{-1} in the case of CH_4–FH) and a very low H–F librational mode (130 cm^{-1} for CH_4–FH) and the normal complexes by larger red shifts in the H–F mode (65 cm^{-1} for C_3H_8–HF) and a higher H–F librational frequency (216 cm^{-1} for C_3H_8–HF). The ethane–HF complex also exhibits a blue-shifted methyl-tilting mode, which is indicative of repulsions for a ligand positioned over the C–C bond. Complexes with a 1:2 alkane–HF stoichiometry were formed on diffusion of HF and support the structure of the different 1:1 complexes with each hydrocarbon.

There are at least two factors at work that favor the switch from a reverse to normal complex in the alkane series CH_4 to C_4H_{10}. The hydrogen becomes progressively less positively charged as the chain length increases,[29] reducing the dipole interaction between the alkane hydrogen and the fluorine atom of HF, and the available C–C bond with a slight excess of negative charge becomes more polarizable with substitution of electron-donating methyl groups. If these complexes were all of the reverse structure, the HF fundamental shift would decrease with decreasing hydrocarbon acidity, which is not the case. The electron-donating property of the methyl group is clearly seen in the alkane complexes where the HF stretch shifts 24 cm^{-1} more in the propane–HF complex relative to the ethane–HF complex, indicating an increased interaction with HF. Accordingly, the C–C bond is the preferred site of attachment for the acid HF.

The ab initio calculations presented show that methane forms a reverse HF complex with a small amount of charge density donated from HF to methane and that the ethane–HF complex involves a primary interaction between the acid hydrogen and the C–C bond and a secondary interaction between fluorine and one ethane hydrogen. The hydrogen bond lengths for the weak alkane complexes are longer than other stronger complexes; the CH_4–HF length is 2.67 Å while the two C–HF distances are 2.55 and 2.85 Å in the ethane complex. The relatively long hydrogen bond length in the latter complex is a result of repulsion between the alkane hydrogens and the hydrogen of HF, and at a distance of 2.3 Å, the complex is not bound.[30] The matrix infrared spectra and ab initio calculations show that definite long-range forces operate between alkanes and HF, which lead to weak complexes with defined structures. These studies provide a useful starting point for more accurate spectroscopic measurements, structure determinations, and theoretical calculations.

The HF absorptions due to the 1:1 complexes in a neon matrix are all higher than those in an argon matrix and frequency differences (argon to neon) range from 15 cm^{-1} for the M–HF complex to 47 cm^{-1} for the P–HF complex. This difference is due to the increased polarizability of argon compared to neon as the gas-to-matrix shift is due in part to dipole–induced dipole interactions. From this information and neon and gas-phase data on N_2–HF,[14,15,31] we predict the gas-phase HF stretches in the simple alkane complexes to be between 3900 and 3930 cm^{-1}.

Acknowledgment. Financial support from N.S.F. Grant CHE 85-16611 and the Academic Computing Center of the University of Virginia and helpful consultations with C. Trindle are gratefully acknowledged.

Registry No. HF, 7664-39-3; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; *n*-butane, 106-97-8; isobutane, 75-28-5.

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Infrared Spectroscopy and Photochemistry of Iron–Ethylene Oxide in Cryogenic Matrices. The FTIR Spectrum of Vinyliron Hydroxide

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Abstract: The mechanism of the cryogenic reaction between an iron atom and an ethylene oxide molecule has been delineated. Iron spontaneously inserted into the carbon–oxygen bond of the cyclic molecule and formed the first unligated metallaoxetane. Upon visible photolysis of ferraoxetane, a metathesis reaction was observed where cleavage occurred through the iron–carbon and the carbon–oxygen bonds of the metallacycle. UV photolysis of the reaction intermediate, an iron oxide π-complexed to ethylene, led to the activation of one of the C–H bonds of ethylene and the formation of the final product, vinyliron hydroxide. Similar reaction pathways were observed for the diiron molecule reaction with ethylene oxide. Evidence for the double insertion of two iron atoms into the C–O bonds of ethylene oxide and the subsequent formation of a five-membered oxametallacycle ring has been seen through the detection of frequencies characteristic of an Fe–O–Fe stretching mode and a carbon–carbon stretching mode in the case of the perdeuterio product.

I. Introduction

The interactions or the reactions between metal atoms and organic molecules in cryogenic matrices may lead to species that are similar to the reaction intermediates that occur in biological systems. The identification of the vibrational spectra of these transient species via FTIR matrix isolation spectroscopy will help delineate reaction mechanisms where the formation of such intermediates has been proposed. For instance, the mechanism of the oxygen transfer event in the catalytic cycle of cytochrome P-450 has been the subject of many studies. In an effort to study the intermediates proposed or speculated to be formed in such reactions, Groves and co-workers[1–3] used substrate molecules to

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(1) Groves, John T.; Haushalter, Robert C.; Nakamura, Mikio; Nemo, Thomas E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.

(2) *Cytochrome P-450. Structure, Mechanism and Biochemistry*; Ortiz de Montellano, Paul R., Ed.; Plenum: New York, 1986.

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