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FTIR Spectra of Hydroxylamine–Hydrogen Fluoride Complexes in Solid Argon

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Abstract: Codeposition of Ar/HF and Ar/NH_2OH samples at 12 K produced strong new absorptions at 3612, 3042, 1385, 885, and 780 cm^{-1} and a weak 1928-cm^{-1} band. Annealing and concentration studies indicate that the 1928-cm^{-1} band is due to a 1:2 hydroxylamine–hydrogen fluoride species, while the others are due to the 1:1 complex. Isotopic shifts support assignment of the 3042-, 885-, and 780-cm^{-1} bands to the ν_s, ν_l(s), and ν_l(a) motions of the HF submolecule, while the 3612- and 1385-cm^{-1} bands can be attributed to the $\nu_1{}^c$ and $\nu_4{}^c$ OH group vibrations, respectively, of the hydroxylamine submolecule. Comparison of the ν_s, $\nu_1{}^c$, and $\nu_4{}^c$ values with those expected for a hydrogen-bonded interaction with the amine group suggests the formation of a primary hydrogen bond to the amine and a secondary chelating hydrogen bond between the fluorine and the hydroxyl hydrogen.

Unlike many of the base complexes studied in this laboratory,[1-3] the hydrogen bonding of hydroxylamine, NH_2OH, has received little treatment in the literature.[4-7] Although it is a likely candidate for hydrogen bonding due to lone pairs of electrons on both the nitrogen and oxygen atoms, it has been relatively ignored because it is unstable with respect to decomposition into water and ammonia. This ready decomposition makes gas-phase experiments difficult, explaining the paucity of data; however, matrix isolation experiments can trap the molecule and provide some added stability.

The study of hydroxylamine hydrogen bonding is attractive because of the variety of possible products. Both the nitrogen and oxygen atoms are basic sites, and while the nitrogen might initially be considered the preferred site because of high amine basicity, the electron-withdrawing effect of the hydroxyl group must be considered. If sufficient electron density is withdrawn from nitrogen, oxygen could become the preferred site. This has already been observed with H_2N–CN- -HF, where the cyano substituent is sufficiently electron-withdrawing so that the amine is no longer the more basic site.[8]

In this series of experiments, the matrix-phase fundamental vibrations of hydroxylamine were observed, as were absorptions attributable to 1:1 and 1:2 hydroxylamine–hydrogen fluoride complexes. Additionally, both DF and ND_2OD experiments were performed to characterize certain absorptions. From these data, a novel structure for the hydrogen-bonded product is proposed.

Experimental Section

The apparatus and techniques used have been described previously.[9,10] Spectra were recorded either with a Nicolet 7199 Fourier Transform infrared spectrometer in the 4000–400-cm^{-1} range at 1-cm^{-1} resolution or with a Nicolet 5DXB FT-IR spectrometer in the 4000–250-cm^{-1} range, at 2-cm^{-1} resolution. Hydroxylamine was produced by heating solid hydroxylamine phosphate [$(NH_2OH)_3H_3PO_4$] (Fluka A.G.) 10–30 °C above room temperature in a glass tube, while passing argon carrier gas (Air Products) over the sample. Deuteriated hydroxylamine was prepared by refluxing the salt with D_2O and a trace of NaOH for several minutes. The hydrogen fluoride gas (Matheson) was diluted with argon to concentrations ranging from 50:1 to 300:1 (Ar:HF). Deuterium fluoride was synthesized by mixing equimolar amounts of F_2 (Matheson) and D_2 (Air Products) sufficient to make about 1 mmol of gas in a well-passivated stainless steel can. The DF was then diluted with argon in the same manner as HF.

The argon mixtures of the HF and NH_2OH were deposited onto a 12 K CsI window from separate tubes into a 10^{-7}-Torr vacuum in which the cold window was suspended. Deposition continued at a rate of 4–6 mmol/h for 5–7 h, and a spectrum was recorded. The sample was annealed by heat cycling from 12–26–12 K, and another spectrum was taken to determine the diffusion and association of the reagent species.

Results

An extensive study of HF and NH_2OH was performed, involving 12 codeposition experiments. A typical experiment, which had an Ar/HF ratio of 100:1 and a NH_2OH temperature of 50 °C, is shown in Figure 1. Characteristic HF system absorptions were observed and are labeled in the following manner: D, $(HF)_2$; T, $(HF)_3$; C, $(HF)_n$; W, H_2O; W^c, H_2O—HF; N, N_2—HF.[11]

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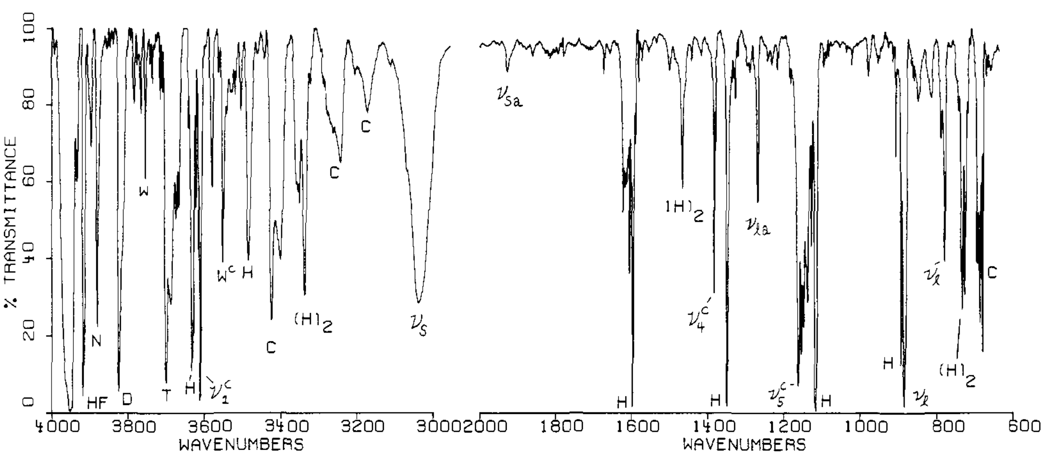

Figure 1. Infrared spectrum of sample prepared by codepositing Ar:NH_2OH [$(NH_2OH)_3H_3PO_4$ salt heated to 55 °C] and Ar:HF = 300:1 mixtures onto a CsI window at 12 K. ν_1^c, ν_s, ν_4^c, ν_5^c, ν_6^c, and ν_l are due to the 1:1 complex; ν_{sa} and ν_{la} are due to the 1:2 complex.

Table I. Observed Vibrational Frequencies (cm^{-1}) of Hydroxylamine and Complexes with Hydrogen Fluoride

assgn[a]	NH_2OH	ND_2OD	NH_2OH–HF	ND_2OD–HF	NH_2OH–DF	ND_2OD–DF
ν_1	3635	2686	3612	2669	3613	2670
ν_4	1351	1035	1385	1057	1385	1055
ν_5	1118	915	1163	949	1159	942
ν_6	896	818	865	851	869	866
ν_s			3042	3026	2280	2274
ν_l(s)			885	784	684	659
ν_l(a)			780	730	660	655
ν_{sa}			1928	1897		
ν_{la}			1270	938		

[a] All product bands are due to the 1:1 complex except ν_{sa} and ν_{la} which are due to the 1:2 complex.

Absorptions corresponding to NH_2OH, labeled H, were observed when NH_2OH was deposited alone into the matrix.

A number of absorptions appeared only on codeposition of NH_2OH and HF. Bands not located adjacent to NH_2OH absorptions include a medium-intensity, broad band at 3042 cm^{-1} (A = 0.54; full-width half-maximum (fwhm) = 50 cm^{-1}) (labeled ν_s), a strong, sharp band at 885 cm^{-1} (ν_l(s)), a sharp but weaker band at 780 cm^{-1} (ν_l(a)), and a peak at 1928 cm^{-1} (A = 0.05, fwhm = 10 cm^{-1}) (ν_{sa}). The 3042-, 885-, and 780-cm^{-1} bands all exhibited similar annealing behavior, while the 1928-cm^{-1} band showed a consistently greater increase than the trio. Among absorptions located near NH_2OH fundamental bands are sharp peaks at 3612 cm^{-1} (ν_1^c), and 1385 cm^{-1} (ν_4^c), and 1163 cm^{-1} (ν_5^c), all of which follow the annealing behavior of ν_s, ν_l(s), and ν_l(a). Table I contains a complete listing of these and other associated absorptions.

Separate experiments were done with samples with less HF relative to NH_2OH; the spectra of these samples revealed stronger $(NH_2OH)_2$ bands and weaker $(HF)_n$ absorptions, but the seven new product bands given in the above paragraph maintained constant relative intensity except for the ν_{sa} band which decreased. Additional weaker bands observed at 3583 and 3507 cm^{-1} in Figure 1 were not observed with reduced HF concentration; these bands are probably due to higher HF cluster complexes that are not of interest here.

In addition, two experiments were conducted by substituting DF for HF. Due to some HF impurity, the bands mentioned above were seen again. New absorptions observed include a broad band at 2280 cm^{-1} (labeled ν_s in Figure 2), sharp peaks at 684 and 660 cm^{-1} (ν_l(s) and ν_l(a)), and bands at 3613, and 1385, and 1159 cm^{-1} (ν_1^c, ν_4^c, and ν_5^c). Additional weaker bands at 2642, 2589, and 2577 cm^{-1} show a higher order DF dependence and are not due to the primary complex.

Also, six experiments employed deuteriated hydroxylamine, mostly ND_2OD, but some mixed isomers were observed as well. Bands attributable to an ND_2OD–HF product formation include 3026 cm^{-1} (ν_s), 2269 cm^{-1} (ν_1^c), and 1057 cm^{-1} (ν_4^c). Major ND_2OD–DF absorptions include bands at 2274 cm^{-1} (ν_s), 2670 cm^{-1} (ν_1^c), and 1055 cm^{-1} (ν_4^c), which are listed in Table I.

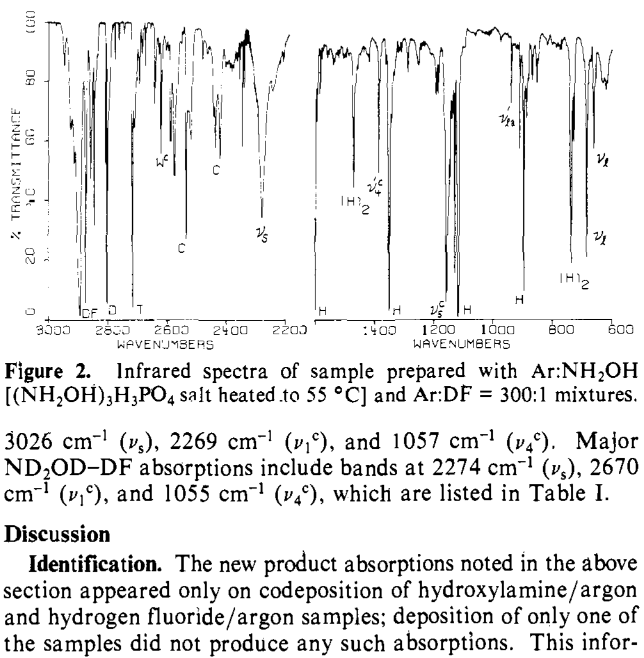

Figure 2. Infrared spectra of sample prepared with Ar:NH_2OH [$(NH_2OH)_3H_3PO_4$ salt heated to 55 °C] and Ar:DF = 300:1 mixtures.

Discussion

Identification. The new product absorptions noted in the above section appeared only on codeposition of hydroxylamine/argon and hydrogen fluoride/argon samples; deposition of only one of the samples did not produce any such absorptions. This information indicates that the new bands are due to hydroxylamine–hydrogen fluoride complexes, a point substantiated by predictable frequency shifts upon isotopic substitution in either reagent molecule.

Demarcation of the new product absorptions into 1:1 and 1:2 complex categories can be done by considering annealing behavior and changes in relative band intensities with changes in reagent concentration. With HF/NH_2OH ratios of 1 to 3, the 3612-, 3042-, 1385-, 885-, and 780-cm^{-1} bands maintained constant relative intensities, while the 1928-cm^{-1} band increased compared to the other bands with increasing amounts of HF. This indicates that the 1928-cm^{-1} band is due to a complex with multiple HF submolecules. Similarly, while warming the matrix often decreased the intensity of the five bands grouped above, the 1928-

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cm^{-1} band always grew. When annealing caused an increase in intensities for those five bands, the 1928-cm^{-1} band consistently increased more substantially, often several times greater. These observations lead to the identification of the 3612-, 3042-, 1385-, 885-, and 780-cm^{-1} bands as belonging to the 1:1 hydroxylamine–hydrogen fluoride complex and the 1928-cm^{-1} band as belonging to the 1:2 complex.

Assignment. Product bands can be divided into perturbations of either the hydroxylamine or hydrogen fluoride submolecule vibrations. The spectrum of NH_2OH in an argon matrix has been studied extensively in this laboratory.[12] Perturbed hydroxylamine submolecule vibrations include ν_1^c and ν_6^c, the O–H and N–O stretching modes; ν_3^c and ν_5^c, the "scissors" and "wagging" motions of the NH_2 group; and ν_4^c, the NOH bending vibration. HF vibrations include ν_s, the HF stretching mode, and $\nu_{l(s)}$ and $\nu_{l(a)}$, the HF librational modes. The (s) and (a) subscripts denote motion in or out of the plane of symmetry of the hydroxylamine molecule.

On the basis of large shifts upon substitution of DF for HF, the 3042-, 885-, and 780-cm^{-1} absorptions are assigned respectively to the ν_s, ν_l(s), and ν_l(a) motions of the HF submolecule (3042/2280 = 1.334; 885/684 = 1.290; 780/660 = 1.182). Deuteriation of hydroxylamine caused small decreases in the ν_s absorptions and moderate decreases in the ν_l bands, while preserving nearly the same HF/DF ratios as found for ammonia complexes.[1] This demonstrates that a complex is formed between HF and NH_2OH.

The HF librational mode, ν_l(s), is noteworthy, as it is more intense than its isotopically substituted counterparts relative to ν_l(a) and has a HF/DF ratio significantly greater than those for other librational bands in both NH_2OH and ND_2OD. The reason for this is a coupling between the ν_l(s) (885 cm^{-1}), ν_5^c (1163 cm^{-1}), and ν_6^c (865 cm^{-1}) modes. They all lie in the molecular plane of symmetry and have similar frequencies, making them good candidates for such an interaction. The ν_l(s) mode is thus blue-shifted slightly, explaining the HF/DF ratio anomaly, and borrows intensity from the ν_6^c mode, explaining its greater strength relative to the ν_l(a) mode. This is substantiated by DF substitution, which shifts ν_l(s) to 684 cm^{-1}, significantly reducing the coupling and allowing ν_5^c and ν_6^c to relax to 1159 and 869 cm^{-1}, respectively.

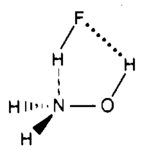
A perturbed torsional mode, ν_9^c, proved difficult to observe. On codeposition of hydroxylamine and hydrogen fluoride, a weak shoulder appeared at 368 cm^{-1}, red shifted from the 375-cm^{-1} fundamental band. However, we expect ν_9^c to shift above ν_9 owing to the effect of the hydrogen bonding. It is possible that the product band is coincident with a strong $(HF)_2$ band at 401 cm^{-1}, but evidence for a concrete assignment does not exist.

Deuteriation of the hydroxylamine submolecule provides some interesting spectroscopic observations. The NH_2 wagging, NOH bending, and NO stretching motions all may interact since they are symmetric with respect to the molecular plane of symmetry. In NH_2OH, such coupling is minimal, since the frequencies of motion are not close enough to allow significant mode mixing. However, considerable coupling between these modes occurs in ND_2OD. This results in an almost arbitrary labeling scheme, as for example the wagging motion has considerable stretching character. It also results in an otherwise anomalous shift for the ν_6^c absorption, which falls at 851 cm^{-1}. In NH_2OH, the shift from fundamental frequency to product frequency is $\Delta\nu_6 = -41$ cm^{-1}, while for the deuteriated species the sign is changed and $\Delta\nu_6 = +33$ cm^{-1}. This unusual result can be attributed to mode mixing, so that the tendency of the product wagging mode to increase in frequency is more important than the tendency of the product NO stretching mode to decrease. This is also reflected in a smaller blue shift for ν_5^c, compared to the hydrogenated species ($\Delta\nu_5(NH_2OH) = +45$ cm^{-1}, $\Delta\nu_5(ND_2OD) = +35$ cm^{-1}).

Bonding and Structure. There are two possible models for the NH_2OH–HF complex structure: a hydrogen bond between the HF hydrogen and a lone pair on the nitrogen or oxygen atom. While bonding to the nitrogen might be expected, in a fashion similar to the ammonia–HF complex,[1] the electron-withdrawing capability of the hydroxyl group reduces the amine basicity and suggests the possibility of a methanol–HF or water–HF type structure.[2,13] However, comparison of the ν_s and ν_l frequencies obtained to those observed for the NH_3–NF, CH_3OH–HF, and H_2O–HF complexes shows that the NH_2OH–HF complex forms at the nitrogen lone pair. The ν_s absorption for the ammonia complex appears at 3041 cm^{-1}, while those of methanol and water appear at 3438 and 3555 cm^{-1}, respectively, and the corresponding ν_l values are 916, 747 and 656, and 716 and 629 cm^{-1}.[1,2,13] The proximity of the hydroxylamine product bands to the ammonia product bands indicates a complex structure similar to that of the ammonia complex, and the NH_2 wagging mode, ν_5, is blue-shifted 45 cm^{-1} in the complex, indicating that hydrogen bonding is occurring at the nitrogen atom.

One would expect the hydroxyl substituent to withdraw electron density from the nitrogen lone pair, reducing its basicity and therefore reducing the shift of the ν_s vibration, as compared to NH_3–HF. Thus, the appearance of the band at nearly the same frequency suggests either that the OH group is not electron withdrawing or that a second interaction with the fluorine further decreases the ν_s frequency. As the first alternative is unlikely, the second solution will be accepted. This spectrum cannot be rationalized by formation of a NH_2OH–$(HF)_2$ complex, as that would cause too large of a frequency decrease (see ν_{sa} below). Another explanation, suggested as the model for the complex, is a chelating hydrogen bond between the hydroxyl hydrogen and the fluorine, producing the model shown in **1**.

If the N–HF hydrogen bond length is 1.7 Å, near that found for NH_3–HF,[14] an F–H—N hydrogen bond angle of 160° with an FH—N–O bond angle of 90° allows an F–HO distance of 2.1 Å with use of the equilibrium structure for hydroxylamine.[15] The latter is slightly longer than the 1.9 Å HF–HF distance in $(HF)_2$,[16] which shows that the molecular dimensions are reasonable for a cyclic complex involving two hydrogen bonds.



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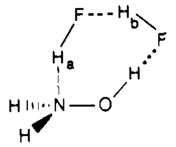

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Ample spectroscopic evidence exists to support this structure. The product band at 3612 cm^{-1} is assigned to ν_1^c, the perturbed O–H stretching mode. The shift of −23 cm^{-1} from the fundamental frequency of 3635 cm^{-1} is characteristic of the behavior of stretching modes when one of the atoms is involved in hydrogen bonding.[17] However, this is a relatively small red shift indicating a very weak hydrogen bonding interaction, and it should not be confused with $(NH_2OH)_2$, which exhibits a strongly perturbed OH stretching mode at 3340 cm^{-1}.[12] A simple ammonia-like structure with only an amine–HF primary hydrogen bond cannot explain this shift, and the tracking of this band with other 1:1 absorptions rules out any interactions with a second HF molecule. Thus, this shift must be due to the HF submolecule already in the complex.

Similarly, the band at 1385 cm^{-1} is assigned to ν_4^c, the perturbation of the NOH bending mode. Bending modes are generally blue-shifted upon hydrogen bonding,[17] and the frequency shift $\Delta\nu_4 = +44$ cm^{-1} ($\nu_4 = 1351$ cm^{-1}) suggests this interaction. Again, this blue shift is much smaller than that found for $(NH_2OH)_2$ absorbing at 1469 cm^{-1} and is indicative of a weak secondary hydrogen bonding interaction with the OH group. Once more, no such interaction would be expected with the ammonia-like complex. The chelated structure offered as the explanation for

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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.

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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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