Infrared Spectra of Two 1:1 Complexes between HCN and HF in Solid Argon at 12 K

Gary L. Johnson and Lester Andrews*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received June 14, 1982

Abstract: The cocondensation reaction between HF and HCN produced two 1:1 hydrogen-bonded complexes in an Ar matrix at 12 K of the form HF--H–C≡N (I) and HC≡N--HF (II). The concentration of I decreased upon warming the matrix above 20 K, while the amount of II in the matrix increased, indicating that II is the more stable complex formed either by reaction between HCN and HF or by rearrangement of I. The HF stretching frequency of the complex was observed at 3891.8 cm^{-1} for I and 3625.6 cm^{-1} for II. Complex II displayed a single degenerate librational mode at 585.8 cm^{-1}, indicating a linear skeletal structure; however, the C–H bending mode of I gave rise to a doublet at 761.3 and 758.4 cm^{-1}, which provides evidence for a nonlinear structure. The reaction between HCl and HCN yielded the complex HC≡N--HCl with little evidence for a complex analogous to I. The HCl stretching frequency in the complex was observed at 2703 cm^{-1}, and a single absorption for the librational mode of HCl in the complex was observed at 375 cm^{-1}, indicating a linear structure.

Introduction

Hydrogen-bonded compounds are of interest from theoretical and practical standpoints and have been subjected to considerable spectroscopic analysis. A great deal of study has been devoted to inter- and intramolecular hydrogen bonded compounds in solution, but of more theoretical interest are those systems simple enough for study in the gas phase or a solid noble gas matrix. Hydrogen fluoride is a very useful proton donor for this application, and several infrared studies of B–HF type systems in both gas and matrix phase complement each other. A gas phase study of the HCN–HF and CH_3CN–HF systems[1] has provided information on the vibrational modes of the HF moiety of the complex and modes that primarily involve motions of the hydrogen bond. However, the spectra were complicated by rotational fine structure of the species and the presence of hot bands, and information on modes of the basic moiety of the complex was not obtained. These complications do not occur in low-temperature matrix studies; therefore it is possible to obtain complementary spectroscopic information about these complexes from low-temperature matrix spectra.

Experimental Section

The stainless steel vacuum system, CsI cold window, and closed cycle cryogenic refrigeration system have been described previously.[2] All spectra for the HF and DF experiments were recorded with a Nicolet 7199 FTIR spectrometer equipped with a cooled (77 K) Hg–Cd–Te detector and a KBr beamsplitter at 1 cm^{-1} resolution between 4000 and 400 cm^{-1}. Each matrix was scanned 1000 times with signal averaging and the resulting interferogram was converted to a phase-corrected single-beam spectrum using Nicolet FFT software. The single-beam spectrum was ratioed with a similar spectrum of the cold CsI window to produce the equivalent of a double-beam spectrum. The spectra for the HCl and DCl experiments were recorded to the nearest 1 cm^{-1} (calibrated) on a Beckman IR-12 between 200 and 4000 cm^{-1}.

The HF was produced by mixing 0.2 mmol of H_2 (Matheson, research grade) with an equimolar amount of F_2 (Matheson) in a well-passivated 3-L stainless steel can. DF was produced in a similar manner using D_2 (Air Products) after the stainless steel can was treated while hot with DF and excess F_2 for 48 h. The HCl (Matheson) and DCl (Merck, Sharp and Dohme) were used without further purification. HCN was synthesized by adding concentrated aqueous HCl dropwise to solid KCN. The vapor produced by the reaction was swept with dry nitrogen through a trap immersed in a dry ice–acetone bath. The HCN produced in this manner was condensed at 77 K and vacuum-distilled off of Pyrex beads before use. DCN was produced by dropwise addition of D_2O to an equimolar mixture of KCN and P_2O_{10}.[3] The vapor produced was swept through a cold trap with dry nitrogen as before, and the resulting DCN was used in the same manner as the HCN. This method produced

cyanide with approximately 50% deuteration, as determined by the spectrum.

Most of the cyanide samples were diluted either 200/1 or 300/1 (mole ratio) with argon (Air Products, 99.995%) by standard manometric techniques. The HF and DF samples were diluted to either 150/1 or 300/1, and the HCl and DCl samples were diluted wither 100/1 or 200/1. The samples in the HF–cyanide experiments were simultaneously sprayed onto a 12 K CsI window at a rate of 2–3 mmol/h each for 18–22 h before final spectra were recorded. The matrix was then annealed at 20–24 K for 5–10 min and more spectra were recorded. The window temperature was held at 20 K and annealed at 30–40 K for the HCl–cyanide experiments.

There were 13 experiments performed in this study: two using HF + HCN, four using DF + HCN, four using DF + DCN, two using HCl + HCN, and one using DCl + HCN. The results given are representative of the data collected in all of the experiments.

Results

HF + HCN. A spectrum of a matrix formed by deposition of 42 mmol of an Ar/HCN = 300/1 sample was recorded and compared to matrix spectra of HCN found in the literature;[3,4] besides the absorptions due to isolated HCN there were absorption bands of $(HCN)_2$ and $(HCN)_x$ in the spectrum. The matrix was also contaminated with small amounts of water and CO_2, and a trace of HF in the system gave rise to absorption of the HCN–HF complex with intensities less than 7% of the product absorptions in a matrix containing equimolar amounts of HF and HCN. The matrix was warmed to 22 K to allow diffusion, cooled back to 12 K, and another spectrum was recorded. The HCN dimer and polymer absorptions at 3200, 3180, 2105, 1498, 798, and 733 cm^{-1} increased in intensity by about a factor of 2 after the first diffusion, and another increase in the intensity of these bands by about a factor of 1.3 was observed after temperature cycling the matrix to 26 K.

Samples of HCN (Ar/HCN = 200/1) and HF (Ar/HF = 200/1) were simultaneously deposited onto a cold CsI window and an infrared spectrum was recorded. Comparison of the spectrum with spectra of isolated HCN and HF showed several new product absorptions: a sharp new band at 3891.7 cm^{-1} (integrated absorbance = IA = 1.58 absorbance units × cm^{-1}) near the HF monomer absorption at 3954 cm^{-1}, a sharp band at 3625.6 cm^{-1} (IA = 2.30), a band at 3453.3 cm^{-1} (IA = 0.436), a weak doublet at 3372.3 and 3358.5 cm^{-1} (combined IA = 1.00), a sharp band at 3271.0 cm^{-1} (IA = 1.08) near the ν_3 fundamental of HCN at 3304.1 cm^{-1}, three weak bands at 2118.9, 2122.7, and 2130.6 cm^{-1} (proximity to absorptions assigned to HCN polymer prevented accurate IA measurement) near the ν_1 fundamental of HCN at 2093 cm^{-1}, a broad, weak band at 1497.9 cm^{-1} (IA = 0.233) near the $2\nu_2$ overtone of HCN at 1425.8 cm^{-1}, a broad weak

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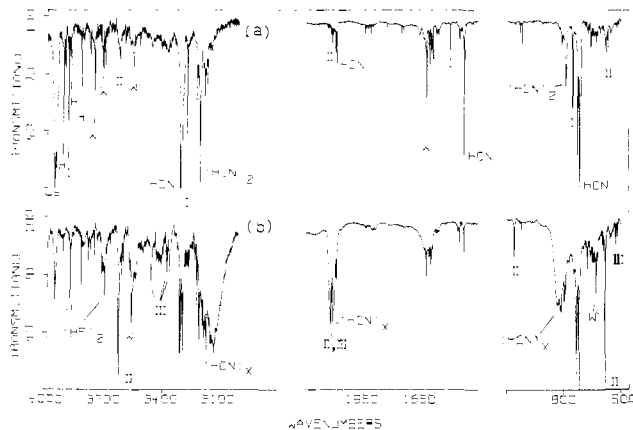(4) Pacansky, J.; Calder, G. V. *J. Mol. Struct.* **1972**, *14*, 363.

Figure 1. (a) Spectrum of matrix formed by codeposition of 33 mmol each of Ar/HCN = 200/1 and Ar/HF = 400/1 at 12 K. (b) Spectrum recorded after warming to 21 K for 10 min and recooling to 12 K. The bands labeled W are due to water, while those labeled W^c are absorptions of the H$_2$O—HF complex. The bands due to HF-related species are labeled H.

band at 1063.2 cm^{-1} (IA = 0.0767), a doublet at 761.4 and 758.3 cm^{-1} (IA = 1.16) near the ν_2 fundmental of HCN at 721.6 cm^{-1}, a strong absorption at 585.7 cm^{-1} (IA = 0.535), and two sharp bands at 529.1 and 519.5 cm^{-1} (combined IA = 0.228) were observed. The matrix was temperature cycled through 22 K and another spectrum was recorded after cooling back to 12 K. No new product absorptions other than the ones present in the previously recorded spectrum were observed, although several shifts in intensity were noted upon examination of the integrated absorbances of the new bands before and after temperature cycling. The bands at 3891.7, 3271.0, and 1497.9 cm^{-1} and the doublet at 761.4 and 758.3 cm^{-1} decreased in integrated absorbance by factors of 0.79, 0.82, 0.89, and 0.81, respectively. These bands were the only product absorptions to show a decrease in intensity, and the magnitude of the change for each absorption suggests that they are all due to a single well-defined product species between HF and HCN, hereinafter designated as I. The absorptions at 3625.6 and 585.7 cm^{-1} increased in integrated absorbance by factors of 1.75 and 1.91, respectively; the band at 1061.7 cm^{-1} increased, but its intensity before annealing was too low to allow an accurate measurement of the growth; the band at 2118.5 cm^{-1} increased, but an accurate measure of the amount could not be determined due to the close proximity of the HCN polymer absorptions. These bands are due to another reaction product between HCN and HF, designated II. The absorptions at 3453.3 cm^{-1}, the pair at 3372.3 and 3358.5 cm^{-1}, and the pair at 529.1 and 519.5 cm^{-1} grew upon diffusion by factors of 2.4, 2.6, and 2.3, respectively, indicating another species, labeled III, that increased after annealing the matrix.

In order to study the effect of concentration changes upon the formation of HF–HCN complexes, the previous experiment was repeated with samples of HCN and HF in argon diluted to 200/1 and 400/1, respectively. The spectrum recorded after about 33 mmol of each sample were deposited is shown in Figure 1a. The same product bands that were observed in the previously described experiment were also seen in the present spectrum and are listed in Table I. The matrix was warmed to 21 K for 10 min and another spectrum was recorded at 12 K (Figure 1b). The results of the temperature cycle on the integrated absorbances of the product bands are shown in Table I. The most notable feature is the apparent disappearance of the bands at 3891.8, 3271.3, 1498.0, 761.3, and 758.4 cm^{-1} after sample warming. This indicates that product species I is either diffusion or temperature sensitive. The increase in intensity of the bands at 3625.6, 1061.7, and 584.8 cm^{-1} shows that species II is the more stable of the two reaction products between HF and HCN. The low intensities and small growth after diffusion for the bands at 3457.9, 3375.0, 3360.9, 528.9, and 519.7 cm^{-1} using a low concentration of HF suggest that species III is an aggregate complex. Although the

Table I. Frequencies, Full Widths at Half Maximum (fwhm), and Integrated Absorbances (IA) of Product Absorptions Observed after 35 mmol of Ar/HCN = 200/1 and 31 mmol of Ar/HF = 400/1 Were Condensed onto a CsI Window at 12 K and after Annealing at 21 K

species	ν, cm^{-1}	fwhm, cm^{-1}	IA, $A \times$ cm^{-1}	IA after annealing, $A \times$ cm^{-1}	change in IA, %
I	3891.8	1.7	1.04	b	-
	3271.3	1.2	1.57	0.21	−87
	1498.0	2.0	0.17	b	-
	761.3	-		b	-
	758.4	-	0.94		-
II	3625.6	4.1	0.818	4.27	422^a
	2118.5	-	-	-	–
	1061.7	3.7	b	0.457	-
	585.8	2.1	0.665	2.71	307
III	3457.9	5.8	0.229	0.748	227
	3375.0	-	0.412	1.75	325^c
	3360.9	-			
	529.0	2.1	0.110	0.350	217
	519.5	1.7			

^{a} Extra growth in 3625.6-cm^{-1} band not reflected in 585.8-cm^{-1} band may be due to proximity of HF + H$_2$O) reaction product absorption. ^{b} The absorption band was too low in intensity to obtain an accurate integrated absorbance measurement. ^{c} Extra increase in integrated absorbance due to HF polymer band in immediate proximity which also increased after annealing.
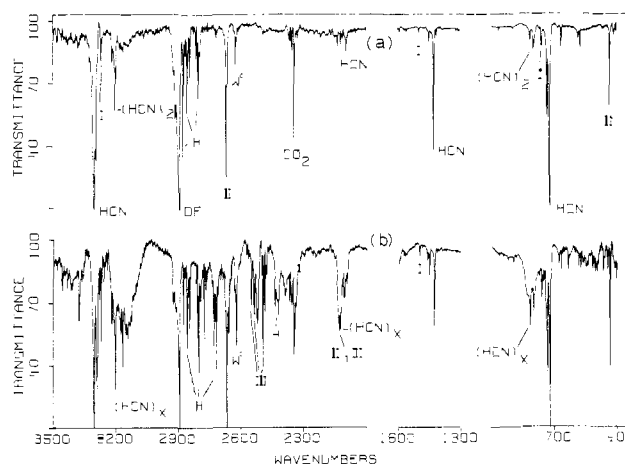

Figure 2. (a) Spectrum of matrix formed by codeposition of Ar/HCN = 300/1 (49 mmol) and Ar/DF = 300/1 (57 mmol) at 12 K. (b) Spectrum recorded after warming to 24 K for 10 min and recooling to 12 K.

change in integrated absorbance for the bands assigned to species II and III do not show a large difference in their growth after annealing the matrix, the difference is more apparent in the previously described experiment with HF, as well as in the DF experiments with the deuterium counterparts of the absorptions. It is also noteworthy that the increase in the intensity of these bands was smaller for the lower concentration of HF.

DF + HCN. The spectrum of a matrix formed by cocondensation of 57 mmol of a DF sample (Ar/DF = 300/1) and 49 mmol of an HCN sample (Ar/HCN = 300/1) was recorded and compared to separate matrix spectra of DF and HCN. The spectrum for the regions of interest is shown in Figure 2a. The DF sample was contaminated by a small amount of HF (<30%), due to incomplete exchange in the vaccum system, and trace amounts of water and carbon dioxide. The trace of HF in the matrix gave rise to absorptions at 3892, 3626, and 585 cm^{-1} from the HF reaction. New bands were also observed at 3271.5 (IA = 0.466), 2668.6 (IA = 2.63), 2138.4, 2123.2 (due to proximity of HCN polymer bands an accurate integrated absorbance was not measurable), 1497.8, a doublet at 761.2 and 758.0 (combined IA

= 0.184), and 434.3 cm^{-1} (IA = 0.599). A deuterium counterpart of the band at 3892 cm^{-1} due to product species I was not observed in the present experiment, or in succeeding DF experiments with HCN or DCN, probably because of masking by DF species absorptions in the 2847–2878-cm^{-1} region. The matrix was warmed to 24 K for 10 min to allow diffusion and another spectrum was recorded and compared to the previous one. The absorptions of isolated DF and HCN decreased in intensity while the bands due to (DF)$_x$ and (HCN)$_x$ species increased substantially as shown in Figure 2b. New product bands not present before the diffusion were observed at 2550.0, 2495.4, and 2485.0 cm^{-1}, and the integrated absorbances of all the product bands observed in the previous spectrum increased after the diffusion with the largest increase seen in the bands at 2668.6, 2131.3, 2123.3, and 434.3 cm^{-1}. The matrix was warmed a second time to 27 K and another spectrum was recorded; however, no significant changes from the previous spectrum were observed.

The previous experiment was repeated using gas mixtures of Ar/HCN = 200/1 and Ar/DF = 400/1 to study any concentration effects. The most notable effect observed was the low intensity of the bands at 2550, 2495, and 2485 cm^{-1} after the matrix was annealed at 19 K.

DF + DCN. A matrix was formed by codeposition of 41 mmol of DCN sample (Ar/DCN = 100/1) and 47 mmol of DF sample (Ar/DF = 200/1) over a 20-h period, and a spectrum was recorded and compared to matrix spectra of DCN and DF. The DF sample was contaminated with HF (<30%), and the DCN sample contained a large amount (~50%) of HCN; thus the spectrum also showed the previously reported absorptions of the HCN + HF and HCN + DF products. Other product bands are attributed to the DF + DCN reaction: 2669.1 cm^{-1} (IA = 3.52), 2606.9 cm^{-1} (IA = 0.406), a triplet at 1943.9, 1939.5, and 1936.1 cm^{-1} (no accurate integrated absorption was obtained due to the proximity of DCN polymer absorptions), a doublet at 1195.3 and 1190.3 cm^{-1} (combined IA = 0.127), 602.1 cm^{-1} (IA = 0205), and 433.9 cm^{-1} (IA = 1.78). Two successive warmups of the matrix were performed with a spectrum recorded after each; the first warmup was to 21 K for 5 min, and in the second, the matrix was warmed to 25 K for 5 min. The absorptions at 2669.1, 1943.9, 1939.5, 1936.1, and 433.9 cm^{-1} increased in integrated absorbance after each warmup and are due to product II, while the bands at 2606.9, 1195.3, 1190.3, and 602.1 decreased in integrated absorbance after diffusion and are attributed to product I.

The experiment was repeated with the DCN and DF samples diluted to 200/1 and 400/1 in argon, respectively, in order to determine the effects of concentration changes. Except for a decrease in the yield of the reaction products, the results were the same as in the previous experiment.

HCl + HCN. A matrix formed by codeposition of 27 mmol of an HCl sample (Ar/HCl = 100/1) and 38 mmol of an HCN sample (Ar/HCN = 200/1) at 20 K was scanned with a Beckman IR-12 recording spectrophotometer and the product regions of the spectrum are shown in Figure 3a. Product bands were observed at 375.4 (absorbance units = A = 0.14), 422.5 (A = 0.02), 750.2 (A = 0.15), 2632.2 (A = 0.18), 2664.0 (A = 0.05), 2687.0 (A = 0.23), and 2703.3 cm^{-1} (A = 0.47). The weak absorption at 750.2 cm^{-1} was the only evidence observed for a complex between HCl and HCN analogous to I. The matrix was warmed to approximately 40 K for 5 min and another spectrum was recorded (Figure 3b). The product band at 750.2 cm^{-1} decreased markedly in intensity after annealing the matrix (factor of 0.32 decrease), while the product absorptions at 375.4, 2664.0, 2687.0, and 2703.0 cm^{-1} decreased slightly in intensity. The product bands at 422.5 and 2632.2 cm^{-1} increased in intensity after annealing and new absorptions grew in at 2590.2, 2616.2, 2757.0, and 2770.0 cm^{-1}.

DCl + HCN. A matrix was formed by codeposition of 44 mmol of HCN sample (Ar/HCN = 200/1) and 40 mmol of DCl sample (Ar/DCl = 150/1) at 20 K, and a spectrum was recorded (Figure 3c). The DCl sample also contained a small amount (<30%) of HCl; consequently, the product bands observed in the previous experiment are present in the spectrum. New absorptions assigned
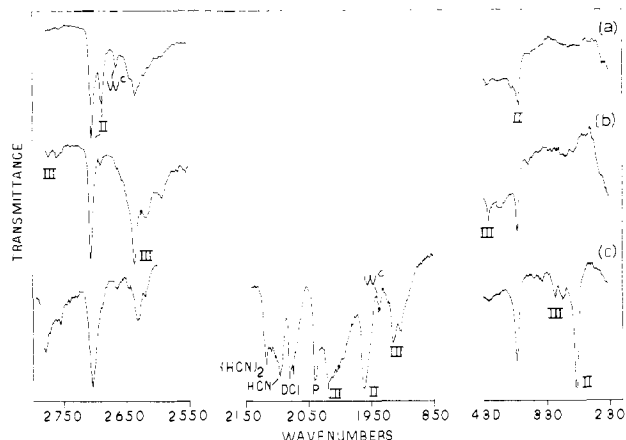

Figure 3. (a) Spectrum of matrix formed by codeposition of Ar/HCN = 200/1 (38 mmol) and Ar/HCl = 100/1 (27 mmol) at 20 K. (b) Spectrum recorded after warming to 40 K for 5 min and recooling to 20 K. (c) Spectrum of matrix formed by codeposition of Ar/HCN = 200/1 (44 mmol) and Ar/DCl = 150/1 (40 mmol) at 20 K.

to the DCl + HCN product were observed at 281.0 (A = 1.2), 750.5 (A = 0.11), 1901.5 (A = 0.28), 1912.7 (A = 0.34), 2019.5 (A = 0.83, and 1961 cm^{-1} (A = 1.1). The matrix was warmed to 40 K, recooled, and another spectrum was recorded. After the diffusion cycle the matrix was considerably more scattering, especially in the high-frequency region of the spectrum; therefore the spectrum only yielded useful information below 1000 cm^{-1}. New product bands not present before the diffusion cycle were observed at 248.5 (A = 0.13), 304.0 (A = 0.10), 314.6 (A = 0.61), and 342.0 cm^{-1} (A = 0.17), while the product bands at 281.0 and 750.0 cm^{-1} increased by a factor of 1.2 and 1.7, respectively.

Discussion

The cocondensation reaction products of HCN + HF (and HCl) will be identified from their infrared absorption spectra, and their structure and bonding will be characterized.

Identification. As discussed previously, the changes in the spectrum of a matrix containing both HF and HCN upon annealing suggests the presence of three separate reaction products. Since the two sets of intense bands (products I and II) were present during all of the concentration studies, it is reasonable to assign them to 1:1 complexes between HF and HCN. In general, HF has been observed in both gas and matrix phases to form complexes of the type B--HF, where B is an electron-donor molecule. However, since HCN is itself weakly acidic, it could conceivably be attracted to the electron-rich fluorine end of the HF species, giving rise to the following possible forms for a 1:1 complex.

$$\text{HF--H--C}\equiv\text{N} \qquad \text{HC}\equiv\text{N--HF}$$
$$\text{I} \qquad\qquad \text{II}$$

The third set of bands (product III) appeared most intense after annealing and was concentration dependent, suggesting the possibility of a polymeric or aggregated complex of the form

$$\text{HC}\equiv\text{N--H}_a\text{--F--H}_b\text{--F}$$
$$\text{III}$$
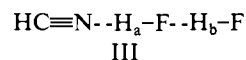
A product of this type has been observed for acetonitrile + HF in both the gas phase[5] and in the matrix,[6] and an H$_3$N--(HF)$_2$ product has been observed in the matrix.[7] The product identifications are verified by their infrared spectra.

Spectral Assignments. The product frequencies for representative isotopic substitution experiments, given in Table II, are grouped according to the different product species postulated from the changes observed in the spectrum after annealing the matrix. Most of the new absorptions present in the spectra of a matrix

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Table II. Observed Product Frequencies in the Spectra of HCN + HF or HCl in Ar

species	HF + HCN	DF + HCN	DF + DCN	HCl + HCN	DCl + HCN	assignments
I	3891.8	-	-			ν_{HF}^c
	3271.3	3271.5	2606.9			ν_3^c
			1195.3			
	1498.0	1497.8	1190.3			$2\nu_2^c$
	761.3	761.2				
			602.1	750.5 ?	750.5 ?	ν_2^c
	758.4	758.0				
II	3625.6	2668.6	2669.1	2703.0^a	1961.0	
				2687.0		
						ν_s
	2118.5	2123.2	1936.1			ν_1^c
	1061.7	-	-			$2\nu_1$
	585.8	434.3	433.9	375.4	281.0	ν_1
III^b	3457.9	2550.0	-	2770.0	1912.7^a	
				2957.0	1901.5	
	3375.0^a	2495.4	-	2632.2^a	2019.5	
				2616.2		ν_s
	3360.9	2485.0	-	2590.2		
	529.0	-	-		342.0	
				422.5	314.6^a	ν_1
	519.5	-	-		304.0	
					248.5	

^{a} Most intense band of the system. ^{b} The other ν_s and ν_1 type modes expected for the 2:1 complex were not seen due to their low intensities and the presence of absorptions of the parent compounds in the region of the spectra where these modes should absorb.

containing both HCN and HF are assigned to the two 1:1 hydrogen bonded complexes, HF--HCN (I) and HCN--HF (II). The observed product bands for both complexes may be described by considering absorptions of the perturbed HCN submolecule of the complex and absorptions of the perturbed H–F submolecule. Classification of the product bands in this way is useful because the hydrogen-bonding interaction is weak compared to the covalent bonds in the two submolecules so that a given vibration of one of the submolecules will still have the same character as the corresponding vibration of the isolated molecule, except for the low-frequency vibrations that directly involve the hydrogen bond.

HF--HCN (I). The bands listed in Table I and II under species I are assigned to vibrations of the HF--HC≡N complex. These bands appear strongly in the first matrix spectrum and decrease in integrated intensity upon annealing the matrix. The assignment of these bands to species I is made on the basis of the perturbation of the HCN submolecule vibration, specifically the hydrogen motion of the HCN submolecule in the complex. In general, one expects to see distinct perturbations on the C–H modes of HCN in cases where the cyanide hydrogen is involved in a hydrogen bond, as was observed in the $(CH_3)_2O$--HCN complex by Steel and Sheppard,[8] but there should be little or no perturbation of these modes if the HCN molecule is weakly bound at the nitrogen. The doublet at 761.3 and 758.4 cm^{-1} may be seen to belong to the perturbed bending mode (ν_2^c) of the cyanide hydrogen in the complex. As can be determined from the data in Table II, the band shows an H/D ratio of 1.262 for the DF–DCN complex while the deuterium shift for the DF–HCN complex is zero within experimental error, indicating that the mode is primarily an H–C bending vibration in the complex. The doublet is blue shifted an average of 38.2 cm^{-1} from the ν_2 fundamental of HCN at 721.6 cm^{-1} in comparison to an average shift of 74.2 cm^{-1} for the $(HCN)_2$ absorptions[3] at 798.2 and 793.4 cm^{-1}, indicating a weaker association between the base HF and the acid HCN than between two HCN molecules. The relative hydrogen bond strengths of the HF–HCN complex and the HCN dimer are reflected by their relative proton affinities: 113 kcal/mol for HF[9] and 170 kcal/mol for HCN.[10] The doublet nature of the absorption means that the degeneracy of the ν_2 mode has been broken, indicating a bent structure for the complex. Curtiss and Pople[11] have calculated

a bond angle of 140° between HF and HCN, which would be consistent with a nondegenerate F--H–C bend with in-plane and out-of-plane components. These results are in direct contradiction of the geometry predicted for species I by a semiempirical calculation which gave a bond angle of 180° for the heterodimer.[12] The band at 1498.0 cm^{-1} is assigned to the $2\nu_2^c$ mode of the complex. Although the ν_2^c mode is a doublet, a small difference in the anharmonicity for the in-plane and out-of-plane motions could cause the overtones of each to overlap, resulting in the single band observed at 1498.0 cm^{-1}. In the DF–DCN complex the $2\nu_2^c$ mode does show a splitting while the ν_2^c mode gives rise to a singlet (Table II). This is probably due to the isotope effect shifting the anharmonicities of the in-plane and out-of-plane vibrations. The H/D ratio for the $2\nu_2^c$ mode is 1.256 (calculated using an average frequency for doublets), which is in agreement with the ratio for the ν_2^c fundamental. The sharp band at 3271.3 cm^{-1} is assigned to the ν_3^c mode of the complex, which is the C–H stretching motion. The band shows an H/D ratio of 1.255 for the DF–DCN complex, while the deuterium shift for the DF–HCN complex is zero within experimental error, demonstrating that the mode is primarily a C–H stretch in the complex. This band is shifted −33 cm^{-1} from the ν_3 mode of HCN in argon in comparison to a shift of −104 cm^{-1} and the C–H stretch of $(HCN)_2$. In hydrogen bonds of the type B--HA the H–A stretching frequency is generally used as a measure of the strength of the hydrogen bond,[13] and on this basis the HF--HCN complex is a much weaker one than the $(HCN)_2$ association. This is in agreement with the evidence cited previously for the ν_2^c mode of the complex. The C–H/C–D ratio for the DF–DCN complex is 1.255 which is also in agreement with the ν_2^c ratio. The band at 3891.8 cm^{-1} is assigned to the H–F stretch, $\nu_{H–F}$, of complex I. Unfortunately, the DF counterpart was not observed due to the presence of DF species absorptions. The small shift of ν_{HF}^c (−62 cm^{-1}) in I from the stretching frequency of HF in solid argon shows that the association is a weak one compared to complexes where the HF is bound at the hydrogen atom; in complexes of the type B--HF the shift in ν_{HF} is usually between 100 and 900 cm^{-1}, indicating a greater weakening of the H–F bond. A large decrease in the HF bond strength and a concurrent shift in the stretching frequency is to be expected when the hydrogen is bonded since the σ^* orbital of HF accepts electron density from the base, while in the case of I, the orbital donating

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electron density is a nonbonding p orbital on the fluorine and a change in electron density in this orbital would have a smaller effect on the H–F bond.

HCN--HF (II). The frequencies and assignments for the absorptions of the HCN--HF (species II) complex are given in Tables I and II. There are three vibrational modes of the complex assigned to the HF submolecule: the perturbed H–F stretching mode, ν_s, which is seen at lower frequencies than the HF monomer stretch because of weakening of the HF bond due to partial proton transfer in the complex, the librational mode, ν_l, which is the librational motion of HF bound in the complex, and the overtone of the librational mode, $2\nu_l$. The 3625.6-cm^{-1} band is assigned to the ν_s mode of the complex on the basis of its deuterium shift when the complex is formed with DF (H/D = 1.359) and proximity to the stretching frequency of monomeric HF in the matrix (ν_{HF} = 3954 cm^{-1}). The band observed at 585.8 cm^{-1} is assigned to the librational ν_l mode on the basis of its DF shift (HF/DF = 1.347). Further evidence for the assignment of the ν_s and ν_l absorptions is their agreement with gas phase spectra of II. Thomas has assigned absorptions at 3710 and 555 cm^{-1} in gas phase mixtures of HCN and HF to the ν_s and ν_l modes of II, respectively.[1] These modes exhibit argon matrix shifts of –84 and +31 cm^{-1}, respectively, suggesting that a small amount of charge transfer has taken place, since the matrix tends to perturb ionic bonds to a greater degree than covalent species. In comparison, the H$_3$N--HF complex,[7] known to be a strong hydrogen bonded species, shows a matrix shift of –174 cm^{-1} for the ν_s mode, indicative of a larger degree of charge transfer from the base submolecule. The CH$_3$CN--HF complex in argon[6] is slightly stronger than II, with ν_s = 3482 cm^{-1}, and it shows a matrix shift of –145 cm^{-1}, consistent with more charge transfer than II.

The weak absorption at 1064 cm^{-1} is assigned to the first overtone of the HF libration, $2\nu_l$. The DF counterpart of $2\nu_l$ was expected to be near 790 cm^{-1}, but this region of the spectrum was obscured by HCN polymer absorption and no extra band was observed. The ratio between the frequencies of $2\nu_l$ and ν_l ($2\nu_l/\nu_l$ = 1.816) indicates a large anharmonicity for this vibration, expected for large amplitude librational motion.

The product absorptions at 2118.5, 2122.4, and 2130.5 cm^{-1} are assigned to the C–N stretching, ν_1^c, mode of the HCN submolecule on the basis of the proximity of the ν_1 mode of HCN at 2093 cm^{-1}. The band is a multiplet, probably due to matrix interactions as well as a counterpart of ν_1^c for species III (see next section); the 2118.5-cm^{-1} band increased the most in intensity after diffusion and is considered the main ν_1^c product absorption. Since the hydrogen in HCN is not involved in bonding to HF in complex II, the ν_2^c and ν_3^c modes are not displaced enough to be resolved from the precursor absorptions in the present experiments.

On the basis of the data collected herein, the HCN–HF complex has the linear structure. The ν_l mode for the complex gives rise to a single intense absorption, indicative of the degeneracy expected for this vibration in a band with local $C_{\infty v}$ symmetry, as opposed to the case of the "T-shaped" complexes C$_2$H$_2$ + HF and C$_2$H$_4$ + HF where the ν_l absorption is split by 42 and 28 cm^{-1}, respectively.[14,15] Although the HC≡N species possesses π-bonding system which could form an association with HF (as in the C$_2$H$_2$--HF complex), the linear structure indicates that the acidic hydrogen interacts with the lone pair of electron present at the nitrogen end of the base submolecule. One would expect the lone-pair interaction, with its increased s character, to be stronger than a π-bonded association; this assumption is consistent with existing data if one considers the ν_l mode as an indicator of the strength of the association. The ν_s band for HC≡N--HF is shifted –328 cm^{-1} from the stretching frequency, ν_s, in solid argon, while the ν_s modes for C$_2$H$_2$--HF and C$_2$H$_4$--HF are shifted 206 and 221 cm^{-1}, respectively. Gas-phase microwave spectra of II by Legon et al.[16] have also shown the complex to be linear. The

LCAO–SCF calculations of Curtiss and Pople support this geometry and they conclude that II is more stable than I by 3.8 kcal/mol.[11] This result for the geometries of I and II is contradicted by the semiempirical calculation of Kollman,[12] indicating that more exact calculations are necessary for weakly bound systems.

HCN--(HF)$_x$ (III). The absorptions listed in Table II for species III showed an increase in intensity after annealing the matrix with some HF concentration dependence indicating they belong to a product that is formed by a diffusion process in the matrix. The 3457.9-, 3375.0-, and 3360.9-cm^{-1} bands are in the same frequency range as absorptions of HF polymers formed after diffusion, and they show HF/DF ratios of 1.356, 1.352, and 1.352, respectively. The bands at 529.0 and 519.5 cm^{-1} as well as the absorptions previously mentioned are reproducible and well defined, indicating a stable species with a single stoichiometry. Although these bands appear in the same regions of the spectrum as the absorptions of II, the concentration dependence and intensity changes after annealing suggest that a higher order complex may be formed. The H/D ratios with DF show that the absorptions are due to hydrogen motions in an HF submolecule, and the red shift of the high-frequency bands from the ν_s band of II indicates a stronger perturbation of an HF bond than is seen in II. On this basis the bands are assigned to the HC≡N--H$_a$–F--H$_b$–F complex, where the high-frequency absorptions are ν_s vibrations shifted from complex II values, and the low low-frequency features probably belong to the ν_l mode of the H$_b$–F submolecule. Complexes with HF of this type have been observed for other strong bases such as NH$_3$ in argon,[6] (CH$_3$)$_2$CO in argon,[17] and (CH$_3$)$_2$CO in the gas phase.[5] In species III the observed ν_s frequencies are red-shifted from the ν_{HF} absorption at 3954 cm^{-1} an average of 556 cm^{-1}, showing that the H$_a$–F bond has been weakened even more than in species II owing to the stronger hydrogen bond HCN--H$_a$ because of the fluoride ion affinity of the H$_b$–F molecule. Some of the splittings of the ν_3^c mode of II may actually be due to a ν_3 mode of III; it was difficult to obtain an accurate integrated absorbance measurement due to (HCN)$_2$; however, the band seemed to grow more than would be expected for a mode of II after annealing the matrix, and III would be expected to exhibit a ν_3 mode in this region.

HCl + HCN. The product frequencies and assignments for the HCl + HCN complexes are given in Table II. It may be seen from the data that HCl and HCN form reaction products analogous to species II and III, with evidence for an analogue to species I. The bands at 2703 and 2687 cm^{-1} show respective H/D ratios of 1.378 and 1.388, and the 375.4-cm^{-1} band shows an H/D ratio of 1.336 with DCl substitution. These bands correspond to the ν_s and ν_l modes of the HCN--HCl complex where the single sharp ν_l mode indicates that the heterodimer is linear, as in the case of II. The results of an FT microwave study of pulsed molecular beams of HCN and HCl in argon have also shown that the heterodimer is linear with the HCl hydrogen bound to the nitrile group.[18] The –185-cm^{-1} red shift of the ν_s mode from the ν_{HCl} stretch of HCl in argon is less than the –328 cm^{-1} shift of the ν_s mode of II from ν_{HF}, but this is to be expected due to the weaker hydrogen bond formed by HCl. In the C$_2$H$_2$--HCl complex, the HCl is bonded at a right angle to the C≡C with a shift of –124 cm^{-1} of ν_s from ν_{HCl}, vs. a –207 cm^{-1} shift of the HF ν_s mode from ν_{HF}. The smaller ν_s shifts for HF and HCl in the C$_2$H$_2$ complexes show that the directionality of the σ lone pair of HCN increases the hydrogen bonding interaction in the HCN system, while the diffuse π orbitals of C$_2$H$_2$ cannot effectively perturb the acid submolecule as much.

The bands at 2632 and 422 cm^{-1} show respective H/D ratios of 1.376 and 1.343 with DCl substitution, and their shifts from ν_s and ν_l indicate a 2:1 complex of the type HCN--H$_a$–Cl--H$_b$–Cl, analogous to III, where the H$_b$–Cl submolecule acts as a further

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perturbation upon the H_a–Cl bond.

Reactions in the Matrix. HCN undergoes two association reactions with HF in the matrix due to the two ways HCN can bond to HF. Even though complex I has not been observed in the gas phase, the relative intensities for ν_s in complex II and the HF reagent absorption compared to ν_3^c in complex I and ν_3 of the HCN reagent suggest that complex I is the primary product formed upon codeposition of HF and HCN at 12 K. This occurs even though I is a weaker complex than $(HCN)_2$, based on the shift in ν_3, and the calculated hydrogen bond energy in complex I is nearly half that of complex II.[11] This implies that the formation of I must take place on the cold surface as the matrix is being formed, where the complex is frozen and trapped before rearrangement can take place. When the matrix is warmed above 20 K and recooled, most of product I disappears while the concentration of II in the matrix more than doubles. In general, an increase in the concentration of complexes similar to II is expected after diffusion is allowed in the matrix due to migration of unreacted HF to sites where unreacted base molecules are located, and this mechanism is probably responsible for some of the increase in the amount of II. This mechanism does not explain the decrease of I in the matrix or the extraordinarily large increase of II; however, the higher temperature (22 K) may allow a simple rearrangement of the HF submolecule to form the more stable complex II that is hindered at the lower temperature (12 K) and more rigid trapping sites in the matrix. The bent geometry of the complex means that the HF hydrogen could be attracted to the nitrogen while in a librational state with a large amplitude. The amplitude for the librations should be large because of the weak F–H bond and the low mass of the hydrogen. The Boltzmann factor, assuming a $\nu_{1 \leftarrow 0}$ librational transition energy of 100 cm^{-1}, is on the order of 6×10^{-6} at 12 K, as opposed to a factor of about 1×10^{-3} at 22 K. The factor of 170 increase in the population of the $v = 1$ state that occurs on warming would increase the probability of the rearrangement so that over a period of time the amount of I would decrease. In the case of I formed with DF, where the initial yield was low and the amount increased upon warming, the amplitude of the libration is lower because of the increased mass, but the Boltzmann factor is near 2×10^{-4} at 12 K vs. 8×10^{-3} at 22 K because of the deuterium frequency shift. The higher Boltzmann factor suggests that even at 12 K there is enough population of the $v = 1$ state to account for a decrease in total yield over a long period of time, whereas the smaller difference in the factors between 12 and 22 K, along with the decreased amplitude of the libration motion, could result in an increase in the yield from the diffusion of DF to unreacted HCN. This mechanism would explain the concentration changes observed upon annealing, and also why very little of the HCl analogue of I was observed since the HCl experiments were all performed at 20 K.

Species III is formed when another HF attaches to complex II. In II the HF bond has been weakened by partial charge transfer, giving the fluorine atom more fluoride ion character. This near fluoride ion will have a high proton affinity and should be the site where the second HF molecule will attack. In the case where another HF molecule reacts with I, enough energy should be released by the reaction to allow rearrangement to III to take place.

Conclusions

The reaction between HF and HCN in the matrix has revealed interesting chemistry due to the dual acid–base nature of the hydrogen cyanide molecule. The matrix isolation technique has been particularly useful in that it allowed the observation of the less stable HF--HCN (I) complex, which has not been observed in the gas phase due to the ease of rearrangement to the more stable HCN--HF (II) structure. The HF--HCN complex was found to be nonlinear, as evidenced by splitting of the ν_2^c mode at 761 and 758 cm^{-1}, and to have a weaker association than $(HCN)_2$ as indicated by the smaller shift of ν_3^c (3271 cm^{-1}) for I as opposed to $(HCN)_2$. A mechanism for the rearrangement of I to II has been postulated to explain the changes that occur after annealing the matrix. The HCN--HF complex is linear, with the HF hydrogen bound to the nitrogen lone pair, as indicated by a single sharp HF librational mode. This contrasts with the "T-shaped" C_2H_2--HF complex involving HF hydrogen bonded to the C≡C π-orbital system. As in the case of several other HF complexes, complex II is attacked by a second HF at the fluorine, when unreacted HF is diffused through the matrix, resulting in a 2:1 HF complex with further perturbations in the vibrational modes.

Dynamics of Fatty Acids in Phospholipid Vesicles Using Spin Relaxation of Proton-Coupled Carbon-13 Spectra[1]

M. M. Fuson[†] and J. H. Prestegard*

Contribution from the Chemistry Department, Yale University, New Haven, Connecticut 06511. Received April 26, 1982

Abstract: Spin relaxation of a ^{13}C-enriched methylene at the 2 position of myristic acid dissolved in small unilamellar vesicles has been examined under proton-coupled conditions. The data obtained are analyzed using a formalism that considers both autocorrelation and cross-correlation dipolar spectral densities leading to an improved definition of motional properties of a fatty acid chain in a membrane environment. Several motional models are tested for consistency with the data. Among suitable models, one that includes axial diffusion, rotational bond isomerization, and rapid wobbling of the director axis proves most appealing. This model assigns a short correlation time to bond isomerization, 4×10^{-11} s, and a rather long correlation time to axial diffusion, 2×10^{-7} s. A small C–H order parameter of -0.1 is predicted. This can be compared to order parameters obtained on multilayer membranes. The results are discussed in terms of implications for the effect of vesicle curvature and presence of membrane protein on acyl chain motion.

Introduction

It is widely recognized that biological membranes are dynamic structures which must allow both the movement of membrane proteins and the passage of metabolically important solutes. The dependencies of these membrane processes on both membrane lipid

†Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

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