

Matrix Infrared Spectra of the NH_3 -HCN and NH_3 -(HCN)₂ Complexes in Solid Argon

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The NH_3 -HCN complex has been observed and characterized in an argon matrix. It is a strongly bonded complex with C_{3v} geometry. New absorptions attributable to perturbed vibrations in each submolecule have been observed, especially a new red-shifted absorption $\nu_2^s(\text{CH})$ for the perturbed C-H stretching fundamental with blue-shifted absorptions assigned to $\nu_1^s(\text{CN})$, $\nu_2^s(\text{HCN})$, and $\nu_2^s(\text{NH}_3)$. A low-frequency absorption assigned to the librational motion of HCN in the complex was also observed and agrees well with calculated results. Comparison with the gas-phase spectrum shows that the matrix interaction stabilizes the complex. Spectra for the higher order 1:2 NH_3 -(HCN)₂ complexes are presented, assigned, and compared to NH_3 -HCN and (HCN)₂.

Introduction

Hydrogen bonding is an important factor in determining the overall structure of many compounds including water and proteins. Matrix isolation Fourier transform spectroscopy is particularly useful in determining infrared spectra and deducing relative hydrogen bond strengths and structures of such complexes. Weakly bound complexes of ammonia, and its hydrogen-bonding capacity, have become a subject of importance. The ammonia dimer and several other ammonia complexes have been studied by the Klemperer group using molecular beam electric resonance (MBERS),^{1,2} and the NH_3 -HF complex and ammonia dimer have been characterized by matrix infrared spectroscopy.^{3,4}

In 1969, Jones, Seel, and Sheppard studied the vapor over NH_4CN by low-resolution infrared spectroscopy and observed three fundamentals for the NH_3 -HCN complex.⁵ New absorptions were identified as the ν_2 umbrella motion of NH_3 and both bond stretching modes of HCN in the complex. A very recent high-resolution spectrum in the C-H stretching region confirmed that the complex is a symmetric top.⁶ The NH_3 -HCN complex has also been studied by microwave spectroscopy, and the hydrogen bond length was determined to be 2.156 Å.⁷ MBERS has been used in tandem with an infrared laser for a series of NH_3 complexes; however, no infrared resonances for the NH_3 -HCN complex were detected within the CO_2 laser ranges.² The purpose of this study was to investigate the IR spectrum of the NH_3 -HCN complex in solid argon and to provide fundamentals that can be used as a guide for future high-resolution gas-phase studies.

Experimental Section

The vacuum and cryogenic techniques have been described previously.^{3,8} Spectra in the 4000-400- cm^{-1} range were recorded on a Nicolet 7199 FTIR spectrometer at 1- cm^{-1} resolution; frequencies are accurate to $\pm 0.5 \text{ cm}^{-1}$. Additional spectra in the 400-200- cm^{-1} range were recorded on a Nicolet 5DXB FTIR spectrometer at 2- cm^{-1} resolution. Each matrix was scanned 500-2000 times with signal averaging, and the resulting interferogram was converted to a phase-corrected single-beam spectrum using Nicolet software. The single-beam spectrum was ratioed to a similar spectrum of the 12 K CsI window to produce the final spectrum.

TABLE I: Fundamental Frequencies (in cm^{-1}) for NH_3 , ND_3 , HCN, and DCN in Solid Argon

mode	NH_3	ND_3
$\nu_2(\text{umbrella})$	974.3	759.8
mode	HCN	DCN
$\nu_1(\text{CN})$	2093.4	1924.6
$\nu_2(\text{bend})$	721.4	576.5
$2\nu_2$	1426.7	1141.5
$\nu_3(\text{CH})$	3305.1	2626.8

TABLE II: Product Absorptions (in cm^{-1}) for NH_3/HCN and ND_3/HCN Codeposition Experiments in Solid Argon

mode	HCN	
	NH_3	ND_3
$\nu_2^s(\text{NH}_3)$	1054.7	817.8
ν_1^s	2077.2	2076.9
ν_2^s	877.5	881.3
$2\nu_2^s$	1697.1	1702.9
ν_3^s	3021.6	3015.1
ν_1	279	
$\nu_2^{\text{sc}}(\text{NH}_3)$	1070.3	
ν_{1a}^s	2083.1	
ν_{2a}^s	913.3	
ν_{3a}^s	2940.9	
ν_{2b}^s	3168.0	
ν_{2b}^s	818.1	

TABLE III: Product Absorptions (in cm^{-1}) for NH_3/DCN and ND_3/DCN Codeposition Experiments in Solid Argon

mode	DCN	
	NH_3	ND_3
$\nu_2^s(\text{NH}_3)$	1054.9	817.8
ν_1^s	1841.9	1841.9
ν_2^s	680.7	682.7
$2\nu_2^s$	1332.6	1332.6
ν_3^s	2497.3	2493.6
ν_1	212	

HCN was prepared by the addition of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (50:50) to solid NaCN. The HCN gas was carried through the system with argon gas, dried through two U-tubes filled with CaCl_2 , and then finally condensed in a cold trap using liquid N_2 . DCN samples were prepared by the addition of D_2O into the stainless steel manifold, which was allowed to exchange with HCN. The H/D exchange ratio varied between 0.7 and 2 as evidenced by the relative intensities of $\nu_3(\text{CD})/\nu_3(\text{CH})$ absorptions. NH_3 (Matheson) and ND_3 (MSD Isotopes: 99% D) were used without further purification.

Most of the Ar/HCN and Ar/ NH_3 samples were diluted to M/R values of 200-400/1. To prevent exchange contamination, ND_3 was injected directly into the cold cell via a Series 203 variable leak valve (Granville-Phillips). The samples were sprayed

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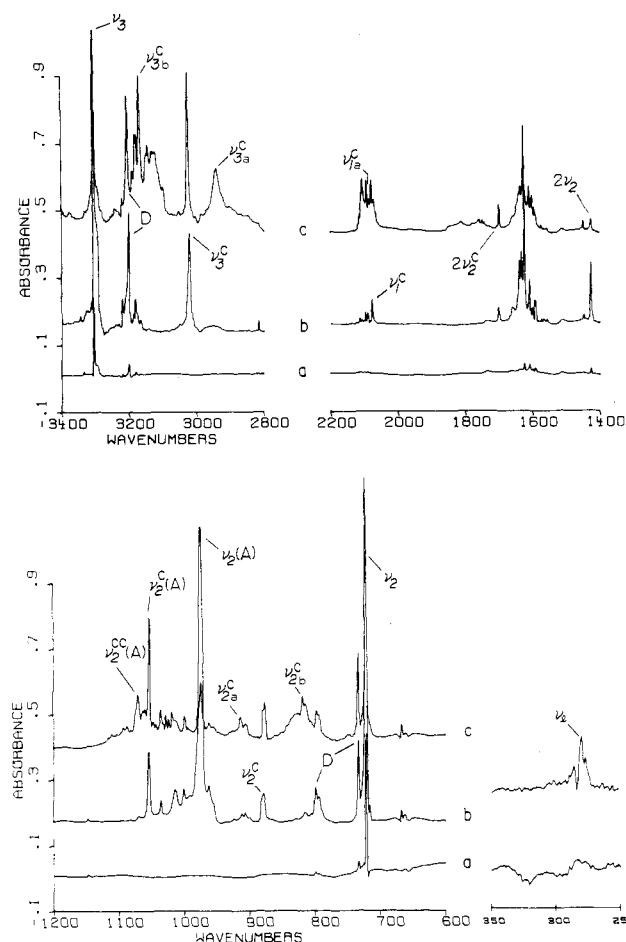


Figure 1. (a) FTIR spectrum of 6 mmol of $\text{Ar}/\text{HCN} = 300/1$. (b) FTIR spectrum of 40 mmol of $\text{Ar}/\text{NH}_3/\text{HCN} = 600/1/1$. (c) FTIR spectrum after annealing to 24 K for 5 min and then recooling to 12 K. Regions between 2200–1400 and 350–250 cm^{-1} were multiplied by a factor of 2 in the absorbance scale. Absorptions labeled D are due to HCN dimer. Absorptions labeled $\nu_2(\text{A})$, $\nu_2^{\text{c}}(\text{A})$, and $\nu_2^{\text{a}}(\text{A})$ are due to the ν_2 modes of NH_3 in free NH_3 , in the $\text{NH}_3\cdots\text{HCN}$ complex, and in the $\text{NH}_3\cdots(\text{HCN})_2$ complex, respectively. Absorptions labeled ν_3 , ν_3^{c} , ν_3^{a} , and ν_3^{b} are likewise due to HCN, HCN in 1, and HCN in 2, respectively; similar ν_1 and ν_2 labels follow accordingly.

simultaneously onto a cold CsI window at the rate of 2–4 mmol/h for approximately 6–12 h before the final spectra were recorded. The matrix was then annealed at 20–22 K for 5 min and cooled back to 12 K, and additional spectra were recorded.

Results

The results of isotopic NH_3 and HCN codeposition experiments will be presented.

$\text{NH}_3 + \text{HCN}$. Figure 1 shows the infrared spectrum of a typical experiment in which Ar/NH_3 and Ar/HCN (both M/R = 300/1) were codeposited for 6 h at 12 K. Absorptions due to reagent monomers^{4,8,9} are given in Table I; these bands are labeled $\nu_2(\text{A})$, ν_2 , $2\nu_2$, and ν_3 in Table I and the figures. Bands of HCN dimer (labeled D) and aggregates appeared at 3201, 3180, 2108, 1448, 795, and 730 cm^{-1} . The matrix also contained trace CO_2 and H_2O impurities. New bands that were not observed in the spectra of individual NH_3 or HCN samples appeared at 3021.6, 2077.2, 1697.1, 1054.7, and 877.5 cm^{-1} and are given in Table II. The matrix was annealed to 24 K and re-cooled; new absorptions were observed at 3168.0, 2940.9, 2083.1, 1070.3, 913.3, and 818.1 cm^{-1} in addition to HCN and NH_3 aggregates. These new bands were also produced in experiments using more concentrated HCN samples. A separate experiment to investigate product absorptions

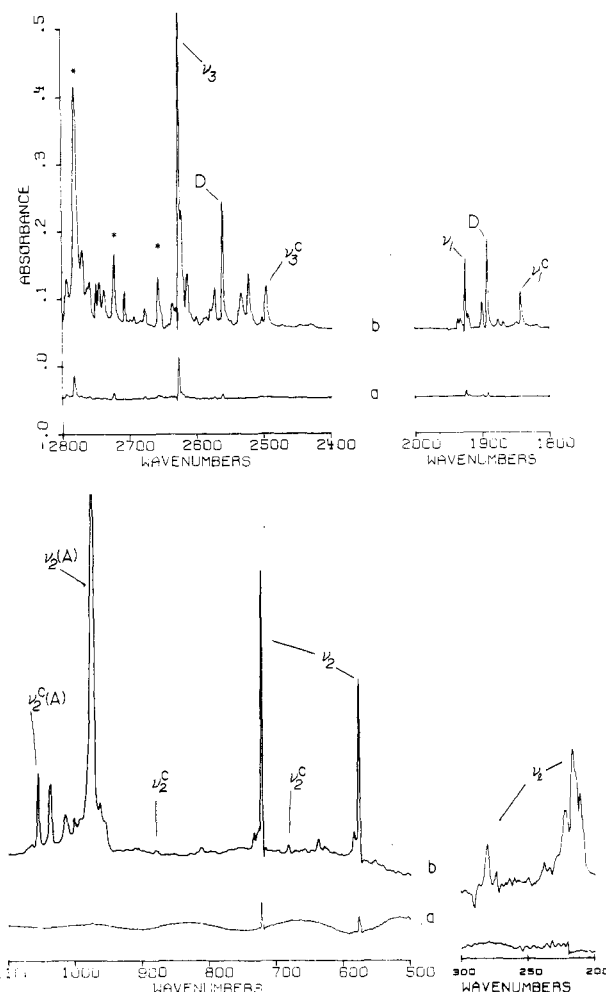


Figure 2. (a) FTIR spectrum of 10 mmol of $\text{Ar}/\text{DCN} = 300/1$. (b) FTIR spectrum of 60 mmol of $\text{Ar}/\text{NH}_3/\text{DCN} = 600/1/1$. Regions between 2200–1800 and 300–200 cm^{-1} were multiplied by a factor of 2 in the absorbance scale. Absorptions labeled D are assigned to DCN dimer. Absorptions labeled with an asterisk are impurities due to H_2O and D_2O . The ν_1 and ν_2 regions show bands for HCN and DCN complexes.

in the low-frequency region revealed a new band located at 279 cm^{-1} , which tracked in growth rate with the first set of product bands.

$\text{NH}_3 + \text{DCN}$. Figure 2 illustrates the infrared spectrum of a codeposition experiment with NH_3 and HCN/DCN in solid argon. It revealed impurity bands due to D_2O , H_2O , and H_2O and HCN that remained from the DCN exchange. Sharp absorptions probably due to DCN monomer appeared at 2626.8, 1924.6, and 576.5 cm^{-1} . New absorptions produced with the addition of NH_3 were located at 2497.3, 1841.9, 1332.3, 1054.6, and 680.7 cm^{-1} and are listed in Table III. As in the ammonia–HCN case, low-frequency studies were conducted and revealed the presence of a new absorption at 212 cm^{-1} .

$\text{ND}_3 + \text{HCN}$ and DCN . Experiments were performed with similar Ar/HCN samples, and neat ND_3 was injected directly onto the CsI window to reduce the exchange formation of NH_2D and NHD_2 . The matrix showed absorptions in similar regions as $\text{NH}_3 + \text{HCN}$ experiments except for obvious isotopic shifts involving ammonia. New product absorptions appeared at 3015.1, 2076.9, 1702.9, 881.3, and 817.8 cm^{-1} . Similar experiments were performed with HCN/DCN mixtures. New absorptions, closely related to those in the $\text{NH}_3 + \text{DCN}$ experiment, were observed at 2493.6, 1332.0, 817.8, and 680.8 cm^{-1} .

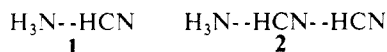
Discussion

The NH_3 and HCN cocondensation reaction products will be identified and their infrared absorption spectra assigned. Structure and bonding of the product complexes will be characterized and

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compared to other similar species. The matrix and gas-phase spectra are contrasted and molecule-complex shifts are compared with the results of ab initio calculations.

Identification. The 3021.6-, 2077.2-, 1697.1-, 1054.7-, and 877.5-cm⁻¹ bands grow in monotonically with both NH₃ and HCN concentration. The 2940.9-, 2083.1-, 1070.3-, 913.3-, and 818.1-cm⁻¹ bands were only present with high concentrations of HCN in the matrix or after annealing to 24 K and recooling. Since the growth rates of these two sets of bands are different, they can be confidently assigned to two different species. The first set belongs to the 1:1 NH₃-HCN complex (**1**), and the second set probably belongs to a NH₃-(HCN)₂ complex (**2**). There was no evidence for an NH₃-(DCN)₂ complex owing to the lower concentration of DCN.



Spectral Assignments. The microwave spectrum of NH₃-HCN is characteristic of a symmetric top. Given a C_{3v} structure, this complex has 15 IR-active modes that transform as 5A + 5E. The description of a 1:1 complex can be rationalized in terms of the unperturbed submolecule vibrations. Certainly in a hydrogen-bonded complex, the perturbed CH stretch, ν_3^c , will be intense and red shifted from the fundamental. The red shift of ν_3^c will be primarily influenced by the basicity of the electron-pair donor and the amount of coupling involved in these motions. The CN stretch, ν_1 , will be perturbed as well since it is also coupled to the CH stretch. In DCN, ν_3 and ν_1 are more strongly coupled since their stretching frequencies are closer together. This leads to an intensification of ν_1 as is found in gas-phase (HCN)₂ and (DCN)₂ dimers.¹⁰ Furthermore, the bending mode, ν_2 , of HCN will be blue shifted. In free HCN this mode is very intense, and the overtone is also observed. Similar intensity features are expected to remain in the complex as well.

Perturbations of the ν_2 umbrella motion of NH₃ are characteristic of these complexes. In solid argon ν_2 for isolated NH₃ appears at 974 cm⁻¹. The amount of blue shift on this absorption is related to the strength of the hydrogen-bonding interaction. In the H₂O and HF complexes with NH₃, ν_2^c has been found at 1035 and 1093 cm⁻¹, respectively.^{3,11}

In addition to the above-mentioned vibrations, five new low-frequency modes are also expected for the complex. They arise from the loss of rotational and translational degrees of freedom of HCN. The rotational motions are transformed into a degenerate set of librational modes (ν_l), while the translational motions become an A + E set of vibrations. The A mode consists mainly of the hydrogen bond stretching motion (ν_s), the weak N-H hydrogen bond stretch. The E mode (ν_β), which transforms as (x,y), is a "shearing" motion of the HCN molecule in the x or y direction; this motion has been observed at 140 ± 5 cm⁻¹ in combination with the C-H stretching fundamental,⁶ which is in agreement with SCF calculations.¹² The librational modes are very sensitive to the overall geometry of the complex, and any deviation from C_{3v} symmetry will split the degeneracy and give two distinct absorptions.

NH₃-HCN (1**).** The perturbed CH stretch, ν_3^c , is found at 3021.6 cm⁻¹. This band is assigned because of its close proximity to the monomer CH stretching fundamental at 3305.1 cm⁻¹ and also on the basis of its deuterium shift. The DCN analogue appears at 2497.3 cm⁻¹ for the NH₃ complex. The isotopic ratios are (3305.1/2626.8) = 1.258 for the molecular fundamentals and (3021.6/2497.3) = 1.210 for the submolecules in the complexes. These values are slightly different because of more CD and CN mode mixing in the complex than in free DCN. In free DCN the energy difference between ν_3 (CD) and ν_1 (CN) is 702 cm⁻¹. In **1**, the separation between ν_3^c and ν_1^c decreases to 655 cm⁻¹. Since the separation is smaller in the complex, the normal modes, ν_1^c

and ν_3^c , will interact with each other to a greater extent. Substitution of ND₃ for NH₃ in a similar series of experiments gave product absorptions that were slightly more perturbed from the molecular fundamentals. The HCN and DCN complexes with ND₃ absorbed at 3015.1 and 2493.6 cm⁻¹, respectively, with additional red shifts of 6.5 and 3.7 cm⁻¹ from the corresponding NH₃ complexes. The ND₃ submolecule sustains a slightly stronger interaction with HCN than NH₃ does. The isotopic ratio (3015.1/2493.6 = 1.209) is extremely close to the NH₃ complex ratio. The original gas-phase data for the NH₃-HCN and ND₃-DCN complexes show perturbed ν (CH) and ν (CD) stretching combination bands at 3150 and 2560 cm⁻¹, respectively.⁵ The origin of the C-H band has recently been measured at 3110 cm⁻¹.⁶ Interaction with the argon matrix lowers the frequency of the band origin by 89 cm⁻¹.

The sharp absorption at 877.5 cm⁻¹ is assigned to the perturbed bending motion, ν_2^c , of the cyanide hydrogen in the complex. The overtone, 2 ν_2^c , at 1697.1 cm⁻¹ has a similar band shape and is less intense as expected. The ν_2^c mode of **1** showed an unusually large blue shift, 156 cm⁻¹, from the submolecule value. Other HCN complexes such as HF-HCN⁸ and (HCN)₂¹⁰ exhibit ν_2^c modes 38 and 76 cm⁻¹ higher than the bending fundamental. Similar behavior in the NH₃-DCN complex is found as well. The ν_2 fundamental for DCN appears at 576.5 cm⁻¹ and its overtone appears near 1141.5 cm⁻¹. Complex bands near 680.7 and 1332.6 cm⁻¹ are assigned to ν_2^c and 2 ν_2^c , respectively. The H/D isotopic ratios of ν_2 and ν_2^c for the molecular fundamentals and the complexes are 1.250 and 1.289, respectively. The 2 ν_2 / ν_2 ratios for HCN and **1** are 1.982 and 1.934. This decrease in the ratio for the complex as compared to isolated HCN implies that anharmonicity in the bending mode increases upon complexation with NH₃. There is no splitting of the ν_2^c bands, which implies that the degeneracy for the perturbed bending motion persists in **1**, and C_{3v} geometry is maintained in the complex. An additional blue shift of 3.8 cm⁻¹ was found for ν_2^c (HCN) and of 2.0 cm⁻¹ for ν_2^c (DCN) in the ND₃ complexes, again owing to the stronger interaction with ND₃.

In the CN stretching region, an intense new product absorption appeared at 2077.2 cm⁻¹, just below ν_1 for HCN at 2093.4 cm⁻¹, which can be confidently assigned to ν_1^c in the complex. In isolated DCN this mode was found at 1924.6 cm⁻¹. Since a vibrational analysis for (DCN)₂ describes the ν_1 mode as 66% CN + 34% CD stretching character,¹⁰ an additional red shift is expected for the ν_1^c fundamental owing to the C-D stretching character. The product absorption at 1841.9 cm⁻¹ is assigned to ν_1^c for the DCN complex on the basis of the increased red shift (83 vs 16 cm⁻¹) and the intensity enhancement. The matrix results are also at lower frequencies from the gas-phase data. The ν_1^c mode of **1** is observed at 2086 cm⁻¹ in the gas-phase experiments, which is 9 cm⁻¹ higher than the ν_1^c mode in an argon matrix. The gas-phase ND₃-DCN complex exhibits ν_1^c at 1890 cm⁻¹, which is 48 cm⁻¹ higher than the matrix value.

Regarding the ν_2 region of NH₃, bands that are assigned to ammonia dimer, trimer, and water complex are present.⁴ A new absorption was found in this region at 1054.7 cm⁻¹, which grows in steadily with additional NH₃ and also upon annealing. Since this is the only new absorption in this region, it is most likely due to ν_2^c of **1**. In ND₃, the corresponding product absorption appeared at 817.8 cm⁻¹. The matrix bands are in accord with broad bands in the gas-phase spectra of NH₃/HCN and ND₃/DCN at approximately 1040 and 805 cm⁻¹, respectively, that were assigned to the ammonia ν_2 motions in the complexes.⁵ This band is sharp and also exhibits an isotopic ratio of 1.288 as compared to the 1.282 isotopic ratio for the ν_2 fundamentals of NH₃ and ND₃. No additional shifting of these bands was observed in DCN experiments. The matrix results for **1** exhibit a ν_2^c (NH₃) at a slightly higher frequency than the gas-phase mode.⁵ The slight 14-cm⁻¹ blue shift is indicative of additional perturbation by the matrix on this mode. The ND₃-DCN complex shows a similar blue shift in argon. The gas-phase value for ν_2^c (ND₃) is 805 cm⁻¹ as compared to the 817.8-cm⁻¹ argon matrix result. In the NH₃-HF complex, ν_2^c was found 126 cm⁻¹ higher than the fundamental.

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TABLE IV: Comparison of NH₃-HCN Complex Vibrational Spectra in the Gas Phase and in Solid Argon, and ab Initio SCF Calculated Shifts for the Complex

	NH ₃	HCN			ND ₃	DCN		
		ν_2	ν_2	ν_1		ν_2	ν_2	ν_1
complex (gas) ^{a,b}	1040	3110		2086	805	2560		1890
submolecule (gas) ^c	950	3312	712	2089	749	2629	569	1906
observed shift (gas)	+90	-202		-3	+56	-69		-16
complex (Ar)	1055	3022	877	2077	818	2494	681	1842
submolecular (Ar) ^d	967	3306	721	2093	760	2627	576	1925
observed shift (Ar)	+88	-284	+156	-16	+59	-133	+105	-83
calculated shift ^e	+93	-189	+153	-29	+70	-82	+95	-78

^a Reference 5. ^b Reference 6 for 3110-cm⁻¹ origin. ^c Herzberg, G. *Infrared and Raman Spectra*; Van Nostrand: Princeton, NJ, 1945. ^d NH₃ and ND₃ values are average Q-branch bands; see ref 4 and Abouaf-Marguin, L.; Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1977**, *67*, 34. ^e Reference 12.

TABLE V: Results of FG-Matrix Calculations for HCN and DCN and Their Respective NH₃ Complexes^{a,b}

assign	ν_{obsd}	ν_{calcd}	<i>F</i>	<i>f</i>	% (CH)	% (CN)	% (CH,CN)
$\nu(\text{CH})$	3305.0	3310.8	5.72	-0.157	93.5	5.8	0.7
$\nu^s(\text{CH})$	3021.5	3025.6	4.72	-0.187	89.2	9.6	1.2
$\nu(\text{CN})$	2093.5	2102.6	18.32	-0.157	6.5	94.3	-0.8
$\nu^s(\text{CN})$	2077.2	2087.5	18.40	-0.187	10.8	90.4	-1.2
$\nu(\text{CD})$	2626.5	2619.1	5.72	-0.157	63.0	35.5	1.5
$\nu^s(\text{CD})$	2497.3	2486.6	4.72	-0.187	46.1	52.0	1.9
$\nu(\text{CN})$	1925.0	1914.8	18.32	-0.157	37.0	64.5	-1.5
$\nu^s(\text{CN})$	1841.9	1829.8	18.40	-0.187	53.9	48.1	-2.0

^a Average error for HCN and DCN = 8.1 cm⁻¹ for all frequencies. ^b Average error for complexes = 9.7 cm⁻¹ for all frequencies.

which is the only NH₃ complex observed to date that has a greater blue shift in ν_2 than **1**. ν_2^s of the ammonia submolecule was blue shifted by 68 and 47 cm⁻¹, respectively, in the H₂O and C₂H₂ complexes.^{11,13}

In the NH₃/HCN experiments, one product absorption was detected near 279 cm⁻¹ and shows a deuterium cyanide counterpart at 212 cm⁻¹. This frequency is too high and too intense for either the ν_s or the ν_B modes; these motions are especially weak and fall within the 100–200-cm⁻¹ region.¹² Librational motions of base/HF complexes have been observed in the 900–300-cm⁻¹ region; these values reflect the rigidity of the orientation the acid has with the base and correlate to the free rotation of the acid.¹⁴ Since no other absorptions are likely to occur here, these bands are assigned to the librational modes of HCN and DCN in **1**. Ab initio calculations have predicted the HCN librational mode, ν_1 , at 303 cm⁻¹ in a TZ + 2P basis¹² and at 364 cm⁻¹ using a STO 4-31G basis set.¹⁵ These values are in excellent agreement with the matrix observation.

The matrix observations for the NH₃-HCN complex are in good agreement with gas-phase spectra and shifts predicted from SCF calculations. Table IV compares the relevant data. The argon matrix blue shifts the $\nu_2^s(\text{NH}_3)$ mode in the complex by 15 cm⁻¹, an amount comparable to the matrix shift on ammonia itself such that the molecule-complex shifts are essentially the same in the gas-phase, solid argon, and SCF calculations.⁴ The largest matrix effect is on the $\nu_2^s(\text{CH})$ stretching mode, which sustains the greatest perturbation by the hydrogen-bonding interaction, involves the largest dipole derivative, and forms a basis for stronger interaction with the argon matrix. Finally, the observed relative infrared intensities for the complex are also in very good agreement with the calculated values.¹²

Many of the statements regarding the vibrational coupling between the CH(D) and CN stretching vibrations of the free and complexed acid can be substantiated through FG-matrix calculations via the Schachtschneider program. The results are presented in Table V. Using a 2 × 2 determinant, we calculated the frequencies, force constants, and potential energy distribution of the CH(D) and CN stretches for the free and complexed molecules. For HCN and DCN, three force constants were fit to four frequencies.

The calculated harmonic frequencies of the CH and CN stretches of HCN and NH₃-HCN are slightly larger than the observed results. In contrast, the opposite behavior was observed for DCN and NH₃-DCN. This artifact of the calculation arises from different anharmonicities for HCN and DCN. Since the CH stretch lies higher in the potential well than the CD stretch of DCN does, the anharmonic effects on the CH stretch in HCN are greater than in the CD stretch of DCN. The use of observed fundamentals underestimates the true anharmonic correction for HCN and overestimates that of DCN.

The force constant for the CH stretch, F_{11} , in the complex is reduced by 1.0 mdyn/Å from the free HCN value. This is expected and results from the hydrogen-bonding interactions between the lone pair of electrons of the NH₃ and the CH group. Furthermore, the force constant for the CN stretch, F_{22} , is slightly increased even though the calculated frequency in the complex is red shifted from the uncomplexed CN stretching frequency. The interaction force constant, f_{12} , is lowered by 0.03 mydn/Å from the free HCN value. The additional lowering of f_{12} allows F_{22} to be increased while the CN stretching frequency is simultaneously lowered.

The potential energy distribution (PED) of the normal modes indicate that amount of vibrational coupling between the CH and CN stretches. For example, the free CH stretch in HCN is described as 93.5% (CH) character + 5.8% (CN) stretching character. In agreement with previous normal-mode calculations, the CD stretching mode is described as 63% (CD) + 36% (CN) stretching character.

In the complexes, one observes only slight differences in the HCN system, but much larger effects are manifested in the DCN system. Surprisingly, the 2497.3-cm⁻¹ band assigned to the CD stretch in NH₃-DCN is described as 46% (CD) + 52% (CN) stretching character. Perhaps if anharmonic corrections were employed, the mixing would indicate more CD stretching character. However, it is interesting to note that much more mixing is evident in the DCN complexes than in the HCN complexes (vide infra) with ammonia, and a greater overall mixing is produced as well, since the complexed CD and CN stretching frequencies become closer to each other in the complex.

NH₃-(HCN)₂ (**2**). In this description of the 1:2 complex, we designate the HCN subunit bonded to the ammonia nitrogen as HCN_a and the terminal hydrogen-bonded HCN subunit as HCN_b. In a similar manner, for HCN dimer, the HCN with the complexed nitrile is designated HCN_a and the hydrogen-bonded HCN is HCN_b.

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Annealing of the matrix revealed a sharp absorption at 3168.0 cm^{-1} and a broad band at 2940.6 cm^{-1} . In $(\text{HCN})_2$, ν_{3a} and ν_{3b} appear at 3304 and 3210 cm^{-1} , respectively. A stronger interaction is expected in 1:2 base/acid complexes, so a greater red shift than 284 cm^{-1} would be expected for ν_{3a} of $(\text{HCN})_2$ in **2** because it corresponds to a HCN subunit that is involved in two distinct hydrogen bonds. Also, it seems unlikely that an NH_3 molecule could promote a 250- cm^{-1} red shift on ν_{3b} of $(\text{HCN})_2$ through the $(\text{HCN})_2$ subunit. Therefore the 2940.6- and 3168- cm^{-1} bands are assigned to the ν_{3a}^c and ν_{3b}^c modes of **2**.

The 913.3- and 818.1- cm^{-1} absorptions are assigned to ν_{2a}^c and ν_{2b}^c in **2**, respectively. In **2**, ν_{2a}^c is expected to be slightly blue shifted from ν_2^c of **1** because HCN_a is hydrogen bonded on both ends, and the 913.3- cm^{-1} absorption is a good candidate for this assignment. The other perturbed bend of **2**, ν_{2b}^c , should be blue shifted from ν_{2b} of the dimer as well. The 818.1- cm^{-1} absorption, which is about 20 cm^{-1} higher than ν_{2b} of $(\text{HCN})_2$, is assigned to ν_{2b}^c of **2**. This slight amount of blue shift indicates a small increase in electron density at the CN group of HCN_a when it is complexed to NH_3 (as in **1**).

In the ν_2 region of NH_3 , the 974- cm^{-1} monomer band intensity decreased by a factor of 6 on annealing. Correspondingly, dimer, trimer, and aggregate absorptions⁴ also increased and doubled the concentration of **1** in the matrix. A new product band at 1070.3 cm^{-1} is assigned to ν_2^c of NH_3 in **2**. This absorption is 15.6 cm^{-1} higher than ν_2^c of NH_3 in **1**. By virtue of this fact, **2** must also have a stronger hydrogen-bonding interaction than **1**.

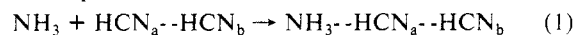
Another new absorption appeared at 2083.9 cm^{-1} , which was not observed in other IR spectra of HCN in solid argon. Since this is also in the ν_1 CN stretching region, it is most likely due to a perturbed CN stretching mode of **2**. The gas-phase spectra of $(\text{HCN})_2$ showed ν_{1a} blue shifted more than ν_{1b} . Consistent with this idea, ν_1^c of **1** at 2077.2 cm^{-1} should blue shift with the addition of a second HCN subunit. Information from the ν_2^c mode of NH_3 lends more credence to the possibility of slightly increased electron density in CN_a . Therefore, we assign the 2083.9- cm^{-1} band to the perturbed CN stretching frequency of CN_a of **2**, ν_{1a}^c .

Bonding. The bonding in **1** and **2** can be characterized by the displacements of the HCN fundamentals and the perturbation of the ν_2 mode of NH_3 in the complex itself. Further understanding of their bonding is also possible by comparing them to $(\text{HCN})_2$ and NH_3 -HF molecular complexes.

The displacement of the CH stretching fundamental to a lower frequency is indicative of the formation of a hydrogen-bonded species. The accompanying electrostatic interaction results in a decrease in the CH fundamental stretching frequency. A red shift of 6 cm^{-1} on ν_3 was observed when NH_3 was changed to ND_3 . The same trend also appears in the ammonia complexes of HF and C_2H_2 where the ND_3 complexes show additional red shifts on $\nu_s(\text{HF})$ and $\nu(\text{CH})$ of 24 and 2 cm^{-1} , respectively.^{3,13} Therefore, the greatest NH_3 - ND_3 effect was observed for the shortest hydrogen bond (NH_3 -HF, $r(\text{HB}) = 1.74 \text{ \AA}$)¹⁶ and the smallest effect for the longest hydrogen bond (NH_3 - HC_2H , $r(\text{HB}) = 2.33 \text{ \AA}$).¹⁷ This implies that an interaction between acid and base may be involved that depends on distance and is slightly different for ND_3 than NH_3 . Since the relative strength of the interactions are not drastically affected, ND_3 must cause this additional perturbation through a vibrational mechanism. The small red shift implies that ND_3 interacts more strongly with HCN than NH_3 does. The hydrogens, due to their small mass, oscillate with a greater amplitude during the NH_3 umbrella motion. This causes electrostatic repulsions with the CH hydrogen of the acid. A greater mass like deuterium does not have as large an amplitude for the same motion. Hence, the lone pair of the nitrogen can approach the acid proton closer and red shift the CH fundamental further, before the accompanying repulsions become as large. The matrix infrared spectrum predicts a slightly shorter hydrogen bond length in D_3N -HCN. A similar conclusion has been reached

for the NH_3 and ND_3 complexes with water.¹¹

The formation of a 1:2 $\text{NH}_3/(\text{HCN})_2$ complex in the matrix can occur via two different mechanisms. Under annealing conditions, more dimer is produced at the expense of the monomer; therefore, it is possible to rationalize the vibrational spectrum of **2** in terms of perturbations on either set of reactants.



The amount of electronic redistribution and vibrational coupling in **1** and **2** are well represented by investigating displacements from the CN stretching fundamental. In the 1:1 complex, the intensity of ν_1^c is approximately 10 times that of ν_1 of the monomer and it appears at 2077.2 cm^{-1} , about 13 cm^{-1} lower than the monomer fundamental. In NH_3 -DCN, ν_1^c appears at 1846 cm^{-1} , approximately 80 cm^{-1} lower than the fundamental. This happens because deuterium decreases the energy gap between the CD and CN oscillator frequencies and more interaction between them is possible. The CN_a bond in **1** seems to be slightly weakened, by virtue of the red shift, by interaction with NH_3 and possible transfer of electron density from the ammonia lone pair upon complexation. Therefore, the basicity of CN_a in **1** should be slightly greater than CN of the monomer. In **2** the extra electron density, donated from NH_3 , should red shift the ν_{1a}^c from the ν_{1a} value of $(\text{HCN})_2$. This also makes CN_a in $(\text{HCN})_2$ more similar to CN_a in **1**. The 2103- cm^{-1} band position is consistent with these conclusions because it lies between ν_{1a} of $(\text{HCN})_2$ and ν_{1a}^c of **1**.

The perturbed CH stretching fundamentals can also be used to qualitatively measure trends in the basicity of CN_a in these complexes. NH_3 is a strong base and red shifts ν_3 of HCN from 3305 to 3021 cm^{-1} . In $(\text{HCN})_2$, the HCN_a submolecule is a weaker base since it red shifts ν_{3b} only to 3201 cm^{-1} . The addition of HCN_b to **1** involves HCN_a in another hydrogen-bonding interaction. The additional electron density in the CN_a region makes it more basic than in $(\text{HCN})_2$. This is evident by the additional red shift on ν_{3b}^c as it is lowered to 3168 cm^{-1} in **2** from 3201 cm^{-1} in **1**. Since HCN_a of **2** is involved in a stronger interaction with HCN_b , this allows the NH_3 submolecule to create a stronger interaction with HCN_a than the interaction in the 1:1 complex. The perturbed CH stretching fundamental, ν_{3a}^c , is lowered from 3021 to 2941 cm^{-1} . Therefore, the addition of NH_3 to HCN or $(\text{HCN})_2$ increases the basicity at CN_a with respect to each uncomplexed submolecule.

The perturbed bending motions and librations in the complexes imply much about their geometry and the amount of directionality in the newly formed interaction in complexes **1** and **2**. The perturbed bends give relative indications of the rigidity of the interaction. Hydrogen-bonded complexes like HF-HCN¹⁰ and $(\text{HCN})_2$ ¹¹ exhibit absorptions that are blue shifted from the bending fundamental. The perturbed bends of **1**, $(\text{HCN})_2$, and HF-HCN are found 157, 77, and 38 cm^{-1} higher than the isolated molecule values. In the 1:2 complex the ν_{2a}^c and ν_{2b}^c absorptions are found at 913.3 and 818.1 cm^{-1} . They are blue shifted by 36 and 20 cm^{-1} from ν_2^c of **1** and ν_{2a} of $(\text{HCN})_2$, respectively. These blue shifts imply that a stronger interaction exists between HCN_a with NH_3 and the two HCN subunits in **2** than is found in **1**. The amount of the blue shift also gives relative indications of the resistance to bending. By this account, **2** shows the greatest rigidity and then **1**, followed by $(\text{HCN})_2$ and HF-HCN.

The absorptions assigned to the perturbed bends in **2**, ν_{2a}^c and ν_{2b}^c , show no signs of being split, and therefore no removal of the degeneracy which is inherent in these motions occurs. Since this happens for both **1** and **2**, we conclude that the local structures are C_{3v} at the amine site. In the gas phase, **1** is found to have a highly directional hydrogen bond with small average angular displacement between the HCN and NH_3 subunits. The librational motions are closely related to the bending motions as well. They too are highly sensitive to geometry, and their angular amplitudes are dependent upon the degree of association formed with the base. In many base/HF complexes, $\nu_{\text{lib}}(\text{HF})$ splits into two different absorptions, which is caused by a reduction of symmetry in the complex.¹³

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The umbrella-like ν_2 absorptions of NH_3 in **1** and **2** are also diagnostic of the hydrogen-bonding interaction. In the complex of interest, **1**, ν_2^s appears at 1054 cm^{-1} ; this is blue shifted from the 974-cm^{-1} isolated ammonia band. The ν_2^s mode of NH_3 in **2** is 15.6 cm^{-1} more blue shifted from ν_2^s of NH_3 in **1** owing to a still stronger hydrogen-bonding interaction in **2**. This is consistent with the additional 61-cm^{-1} blue shift in $\text{NH}_3\text{--}(\text{HF})_2$ from the ν_2^s motion of NH_3 in $\text{NH}_3\text{--HF}$.

The cooperative bonding effect in the ternary complex **2** is more extensive than in the binary complex **1** as is shown by the observed frequency shifts. This effect is also substantiated by ab initio calculations¹⁸ on **2** which also show that the shifts in **1** are enhanced in **2**. Excellent agreement is found for the matrix and calculated shifts for **2**, except for the perturbed C–H stretching fundamentals, which are red shifted by interaction with the matrix.

Conclusions

In this investigation the $\text{NH}_3\text{--HCN}$ (**1**) and $\text{NH}_3\text{--HCN--HCN}$ (**2**) complexes were formed in an argon matrix and studied by FTIR. These C_{3v} complexes (**1** and **2**) exhibit strong linear hydrogen bonds to the lone pair of NH_3 . These conclusions are supported by the large red shift found on the C–H stretching

fundamental and the large blue shifts on the HCN bending mode and the ν_2 umbrella mode of NH_3 , and the lack of splitting on the HCN bending mode. The molecule–complex shifts are in good agreement with the values from the gas-phase observations and ab initio calculations, except for the C–H stretching fundamental, which sustains a larger shift owing to interaction with the matrix.

Low-frequency librational modes have been observed for HCN and DCN in the respective NH_3 complexes and are in good agreement with theoretical calculations. The mixing of internal coordinate stretching modes in the normal coordinates for HCN and DCN changes slightly in the complex as compared to the isolated molecules. Species **2** has an increased hydrogen-bonding interaction, as evidenced by the additional red shift of ν_{3a} and the added blue shift of the ν_2^s mode of NH_3 in **2**. Electronic interaction through the CN groups is evidenced by the intensity enhancements upon complexation. Matrix infrared spectra make possible the observation of a complete spectrum with absorptions of each submolecule in the 1:2 complex. The frequency shifts in **2** compared to **1** are also in good agreement with values predicted from ab initio calculations.

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Registry No. NH_3 , 7664-41-7; HCN, 74-90-8; D_2 , 7782-39-0; Ar, 7440-37-1.

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Infrared Spectra of the Weak H_2 , O_2 , and N_2 Complexes with HCl in Solid Neon

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Weak 1:1 hydrogen-bonded complexes of molecular hydrogen, oxygen, and nitrogen with HCl have been prepared in solid neon at 4–5 K. Their infrared spectra have been characterized and H–Cl stretching fundamentals with chlorine isotopic splittings have been identified. The $\text{H}_2\text{--HCl}$ complex has a $\nu_s(\text{HCl})$ absorption at 2879.4 cm^{-1} and $\text{N}_2\text{--HCl}$, which is a stronger complex, has a ν_s mode at 2871.4 cm^{-1} . The $\text{O}_2\text{--HCl}$ complex has the smallest red shift (1.8 cm^{-1}) from the Q branch of HCl with $\nu_s(\text{HCl})$ at 2881.9 cm^{-1} . The H_2 and N_2 complexes are believed to be structurally similar to the corresponding HF complexes; however the $\text{O}_2\text{--HCl}$ complex may be anti-hydrogen-bonded owing to the very small perturbation of the HCl stretching fundamental. The 1:2 base/HCl complexes were also prepared under conditions with higher HCl concentrations. Furthermore, a 2:1 O_2/HCl complex was characterized and identified under reaction conditions with high O_2 concentrations or annealing of the $\text{Ne}/\text{O}_2/\text{HCl}$ matrices.

Introduction

Hydrogen bonding and van der Waals interactions are much weaker than typical chemical bonds; however, they play important roles in the structures of liquids and molecular complexes. Interest in van der Waals molecules has widened with supersonic jet and diode laser technology. The high-resolution infrared spectrum of the $\text{H}_2\text{--HF}$ complex in the gas phase has been observed.^{1,2} The shape of the potential energy surface for the hydrogen-bonded H atom in the stretching coordinate has been deduced by ab initio and electrostatic potential calculations.³ Matrix infrared spectroscopy has already characterized a number of stronger hydrogen-bonded complexes with HF in solid argon.⁴ However, perturbations by the argon matrix may be comparable to the interaction between the molecules themselves for very weak complexes like $\text{H}_2\text{--HF}$. Accordingly, the matrix material must be

less polarizable and more inert than argon; hence neon is preferred for weaker complexes. The neon matrix spectrum⁵ of $\text{H}_2\text{--HF}$ revealed $\nu(\text{H}_2)$ red-shifted by 6 cm^{-1} and $\nu(\text{HF})$ red-shifted by 15 cm^{-1} from submolecule values, whereas in the gas-phase complex, $\nu(\text{HF})$ was red-shifted by 11 cm^{-1} , and $\nu(\text{H}_2)$ was not observed. Theoretical calculations predicted small red shifts in both bond-stretching fundamentals.³

It is the purpose of this study to investigate the infrared spectrum of HCl in solid neon, to characterize the H_2 , O_2 , and N_2 complexes with HCl, and to provide a guide for future gas-phase spectroscopy on these very weak complexes.

Experimental Section

The vacuum, FTIR, and refrigeration system have all been described previously.⁵ The Heliplex (Air Products) three-stage closed-cycle refrigeration system attained temperatures of 4–5 K. HCl (Matheson) and DCl (MSD Isotopes) samples were purified by pumping at 77 K in separate passivated stainless-steel vacuum systems. H_2 and O_2 (Matheson) samples were used

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