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Communications to the Editor

Infrared Spectrum of the H_3N-HCl Complex in Solid Neon

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Hydrogen bonding, the most wide-spread of intermolecular interactions, is responsible for the unique properties of water and molecular organization in living systems. The “hydrogen bond” arises when an H−X molecule interacts with an electron-rich center (B, a base) to give a B- -H−X species. Typically, the H−X bond is slightly elongated and its vibrational frequency decreased, and these changes relate to the strength of the “hydrogen bonding” interaction.

The ammonia−hydrogen chloride complex (H_3N-HCl) has received considerable attention as a model for the study of hydrogen bonding both by theory and by experiment. Early quantum chemical calculations[1] led to mass and nitrogen matrix infrared spectroscopic investigations.[2,3] Later calculations found the complex to be weakly bound, but the matrix infrared spectra suggested a stronger interaction.[3−5] More theoretical work[6] and rotational spectroscopic investigation using a supersonic jet[7,8] conclude that the complex exhibits a strong molecular hydrogen bond with no substantial proton transfer. Very recent calculations[9,10] have included anharmonicity and matrix effects to account for the low H−Cl stretching frequency observed in nitrogen and argon matrix infrared experiments.[3,5]

Since there are valid questions about environmental perturbations or matrix effects on the H_3N-HCl complex trapped in solid argon and nitrogen, it is desirable to obtain the spectrum in the more inert neon matrix in order to more closely approach gas-phase conditions. For the related H_3N-HF complex, the neon matrix H−F mode (3106 cm^{-1}) falls intermediate between the gas-phase (3215 cm^{-1}) and argon matrix (3041 cm^{-1}) values.[11−13] We report here the infrared spectrum of the H_3N-HCl complex isolated in solid neon, which demonstrates that the complex exhibits a strong molecular hydrogen bond and shows the considerable difference in frequencies of the hydrogen stretching modes for the complex isolated in neon and argon matrices.

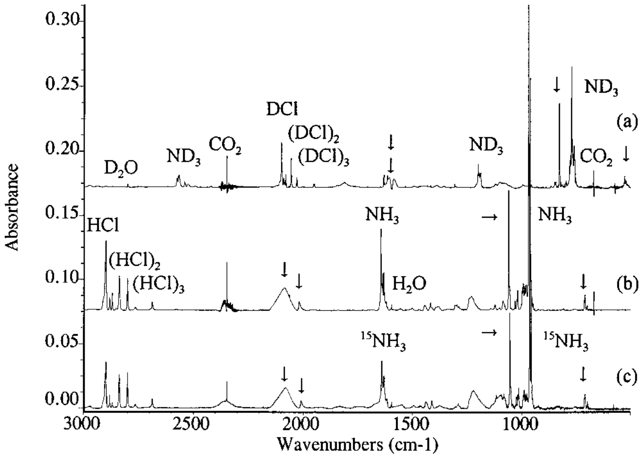

Figure 1. Infrared spectra in the 3000−500 cm^{-1} region for ammonia and hydrogen chloride vapors trapped in solid neon at 4−5 K. (a) ND_4Cl, (b) NH_4Cl, and (c) $^{15}NH_4Cl$.

Ammonia and hydrogen chloride vapors from thermal decomposition of solid NH_4Cl were co-deposited with excess neon at 3 mmol/h onto a 4−5 K substrate for two or three 30 min periods, and infrared spectra were recorded on a Nicolet 750 instrument. The solid NH_4Cl was heated[14] externally to 70−80 °C in a sample tube behind a Teflon bore right-angle valve (Ace Glass, 3 mm) with an 11 cm sidearm through a vacuum fitting to a point 2 cm from the cold surface. The NH_3 concentration in the neon matrix is estimated to be about 0.1% from published spectra.[15] Deuterated samples were prepared by exchanging NH_4Cl with D_2O in the sample tube and evaporating residual D_2O at 40−50 °C.

Representative infrared spectra are shown in Figure 1. Absorptions of NH_3, $(NH_3)_2$, HCl, $(HCl)_2$ and $(HCl)_3$ are in agreement with previous reports:[15−17] note that the monomer HCl and NH_3 species dominate in each region (recall that hydrogen-bonding intensifies dimer and trimer absorptions). The most intense new features are a characteristic, broad absorption at 2084 cm^{-1}, accompanied by weak, sharp band at 2017.4 cm^{-1}, a sharp band at 1060.2 cm^{-1}, and an additional weak band at 708.9 cm^{-1}. In the spectrum of the D_3N-DCl complex, the counterpart of the 2084 cm^{-1} absorption appears as a broad band centered at 1600 cm^{-1} with characteristic Fermi resonance window[18] at 1595 cm^{-1}. The counterparts of the 1060.2, 708.9 cm^{-1} bands appear, respectively, at 824.5 and 526.1 cm^{-1}. The above band sets exhibit constant relative intensities during deposition in different experiments and decrease in concert on annealing to 8 and 10 K while bands at 1086, 1230, 1418, 1446 and 3108 cm^{-1} increase. The latter three bands are appropriate for ionic ammonium chloride[19] and the former two for the higher $H_3N-(HCl)_2$ complex. Annealing also decreases the HCl and NH_3 absorptions in favor of their dimers and trimers. In addition we co-deposited $^{15}NH_4Cl$ vapor with excess neon: the new bands appeared at 2079, 2008.4,

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1054.8, and 708.9 cm^{-1} and decreased on final annealing while bands at 1081, 1223, 1412, 1440, and 3104 cm^{-1} increased.

Experiments were done with argon added to the neon matrix gas using between 1 and 90% argon to evolve the guest spectra as a function of matrix environment. With 1% Ar the major absorptions are 2076 and 1060.2 cm^{-1}; with 5% Ar they shift to 2045 and 1060.7 cm^{-1}, and broad bands appear at 1420 and 1300 cm^{-1}. The broad absorption is very sensitive to matrix annealing; it shifts from 2076 to 2061 cm^{-1} and from 2045 to 1975 cm^{-1} when 1 or 5% Ar matrices, respectively, are annealed to 10 K. With 10% Ar the broad, high-frequency absorption is shifted to 1920 cm^{-1}, two broad bands at lower frequencies are shifted to 1385 and 1295 cm^{-1}, and two bands are observed at 1061 and 1069 cm^{-1}. With 25% Ar, the major absorptions are 1910, 1372, 1293, and 1070 cm^{-1}. With 80 and 90% Ar, we find 1371, 1290, 1070, and 734 cm^{-1} bands, which agree with bands observed earlier in solid argon.[5,20] The latter bands were also recorded using a 100% Ar matrix: after deposition at 4−5 K, only the 2887.7, 2871.0 cm^{-1} HCl monomer, 974.7 cm^{-1} NH_3 monomer, and sharp 1070.0 cm^{-1} absorptions were observed, but annealing to 30 K produced the same bands with half the absorbance as the 90% Ar sample along with weak HCl and NH_3 dimer and trimer absorptions.[16,21]

The set of new neon matrix bands and the above argon matrix bands *observed under analogous dilute conditions where HCl and NH_3 monomer absorptions dominate the spectrum* argue convincingly that these bands are due to the $H_3N{-}HCl$ monomer complex. The neon experiments with 1−90% argon added clearly relate pure neon and argon matrix spectra through evolution of the matrix environment and show that they are due to the same 1:1 complex. The bands marked by arrows (↓) in Figure 1 are assigned to the 1:1 complex.

All of the new neon matrix bands show the large deuterium shifts expected for hydrogen motions. The ^{15}N shifts separate those motions due to the ammonia subunit from those due to HCl in the complex. The 708.9 cm^{-1} band shows no $^{15}NH_3$ shift, and the H/D ratio (1.348) is appropriate for an H−Cl librational mode in a complex; the analogous mode for $CH_3CN{-}HCl$ at 414 cm^{-1} exhibited a 1.380 ratio.[22] The sharp 1060.2 cm^{-1} band shifted 5.4 cm^{-1} to 1054.8 cm^{-1} with $^{15}NH_3$, which is slightly more than the shift for the corresponding NH_3 band (4.1 cm^{-1}) in these experiments; the 1060.2 cm^{-1} band exhibits a 1.286 H/D ratio and is assigned to the symmetric NH_3 bending mode in the $H_3N{-}HCl$ complex; ammonia itself exhibits a 1.262 ratio. This band was observed at 1093 cm^{-1} for $H_3N{-}HF$ in solid argon and at 1090 cm^{-1} in solid neon.[11,13] The weak band at 2017.4 cm^{-1} is assigned to the first overtone of the 1060.2 cm^{-1} fundamental; both its position and ^{15}N shift confirm this assignment. The observed ^{15}N shift of the 2017.4 cm^{-1} band (9.0 cm^{-1}) is less than 2×5.4 cm^{-1} owing to Fermi resonance interaction with the 2084 cm^{-1} fundamental. The characteristic strong, broad 2084 cm^{-1} band is assigned to the H−Cl stretching fundamental in the $H_3N{-}HCl$ complex. The Fermi resonance interaction between the HCl stretch and overtone of the NH_3 symmetric bending mode is matched by similar interaction between the two corresponding modes in the $D_3N{-}DCl$ complex. The location of the overtone of the ND_3 symmetric bend near the center of the broad absorption leads in this case to the appearance of a Fermi resonance window.[18] The spectroscopic evidence for Fermi resonance interaction between the 2084 cm^{-1} fundamental and 2017.4 cm^{-1} overtone in the spectra of $H_3N{-}HCl$ (and between the two corresponding modes in the $ND_3{-}DCl$ complex) strongly indicates that the broad absorption at 2084 cm^{-1} (1600 cm^{-1}) belongs to the same complex as the sharp absorption at 1060.2 cm^{-1} (824.5 cm^{-1}). Part of the 5 cm^{-1} ^{15}N shift observed for the 2084 cm^{-1} band may be due to interaction between the H−Cl stretching mode and the symmetric hydrogen bond stretching mode H_3N- -HCl. The interaction between these two modes is a well-known phenomenon in strong hydrogen-bonded systems.[23]

Table 1. Frequencies (cm^{-1}) Assigned to Ammonia−HF and Ammonia−HCl Complexes in Solid Argon and Neon

complex	H−X str	sym NH_3 bend	H−X lib
$H_3N{-}HF$ in Ar[a]	3041	1093	916
$H_3N{-}HF$ in Ne[b]	3106	1090	912
$H_3N{-}HCl$ in Ar[c]	1371	1070	734
$H_3N{-}HCl$ in Ne	2084	1060	709

[a] Reference 13. [b] Reference 11. [c] Reference 5.

The 2084 cm^{-1} fundamental for the $H_3N{-}HCl$ complex is substantially lower than HCl in solid neon (2871 cm^{-1}) but considerably higher than the previously assigned hydrogen stretching fundamental for the $H_3N{-}HCl$ complex in solid argon (1371 cm^{-1}).[5] Likewise the H−Cl librational mode and symmetric NH_3 bending mode are higher in solid argon than in solid neon (Table 1). These comparisons all point to a substantial argon matrix effect, which increases the hydrogen bonding interaction. Theoretical calculations to model the argon matrix interaction using only three argon atoms[9] do not account for the magnitude of the matrix shift observed.[5] However, the present Ne/Ar experiments suggest that the influential solvation shell is considerably larger.

It is likely that there is more H−Cl bond elongation in the $H_3N{-}HCl$ complex in solid neon than in the gas-phase complex[8] but not nearly as much as in solid argon.[5] Comparison of the frequencies in Table 1 shows that the argon host strengthens the hydrogen bonding interaction and increases proton sharing relative to the neon host and that this matrix effect is more pronounced for the $H_3N{-}HCl$ complex than for the $H_3N{-}HF$ complex owing to the lower ionic dissociation energy of HCl. On the basis of the neon matrix observation of $H_3N{-}HCl$ at 2084 cm^{-1}, we expect the gas phase complex to absorb strongly near 2200 cm^{-1}, which still indicates a strong hydrogen bond.

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