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Observation and Rovibrational Analysis of the Intermolecular NH_3 Libration Band ν_9^1 of H_3N-HCN

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The high-resolution far-infrared absorption spectrum of the gaseous molecular complex H_3N-HCN is recorded by means of static gas-phase Fourier transform far-infrared spectroscopy at 247 K, using a synchrotron radiation source. The spectrum contains distinct rotational structures which are assigned to the intermolecular NH_3 libration band ν_9^1 (ν_B) of the pyramidal H_3N-HCN complex. A rovibrational analysis based on a standard semirigid symmetric top molecule model yields the band origin of 260.03(10) cm^{-1}, together with values for the upper state rotational constant B' and the upper state quartic centrifugal distortion constants D'_J and D'_{JK}. The values for the upper state spectroscopic constants indicate that the hydrogen bond in the H_3N-HCN complex is destabilized by 5% and elongates by 0.010 Å upon excitation of a quantum of libration of the hydrogen bond acceptor molecule.

1. Introduction

High-resolution spectroscopic studies of weakly bound molecular complexes provide important information about the intermolecular interactions involved in the transition from isolated gaseous molecules to the formation of condensed phases. The first high-resolution rotationally resolved infrared studies of simple gaseous molecular complexes using static gas-phase FTIR spectroscopy and conventional radiation sources were published in the mid-1980s. In particular, a wide range of vibrations of the linear prototype HCN−HF heterodimer was observed and assigned by Bevan et al. [see ref 1 and references therein]. Subsequently, the investigation of such species were extended by slit supersonic jet techniques and laser radiation sources leading to improved experimental sensitivity and complementary rovibrational assignments owing to the much lower rotational temperatures of supersonic jets. However, only a limited number of studies have dealt with the important intermolecular part of the vibrational spectrum for such molecular complexes. The reason appears to be that there exist few suitable spectroscopic radiation sources in the far-infrared spectral region where the floppy intermolecular vibrations of molecular complexes are normally observed. In the present study we use the highly brilliant source of synchrotron radiation offered from the electron storage ring MAX-I at MAX-lab in Lund for the study of the intermolecular NH_3 libration band of the weakly bound H_3N-HCN dimer by means of high-resolution static gas Fourier transform far-infrared spectroscopy

The ionic solid NH_4CN consisting of NH_4^+ and CN^- subunits, which dissociates in the gas phase into a pair of covalent bound acid (HCN) and base (NH_3) molecules, is a prototype system and spectroscopic information is available for the ionic solid,[2,3] the hydrogen-bonded gaseous heterodimer H_3N-HCN,[4−9] and the covalent subunits HCN[10−12] and NH_3.[13] An accurate characterization of the intermolecular potential energy surface for the H_3N-HCN dimer is required in order to achieve a detailed picture of the energetics and structural changes associated with this phase transition. The direct observation and rovibrational analysis of intermolecular vibration bands of the H_3N-HCN dimer is important for the elucidation of the intermolecular potential energy surface away from the equilibrium configuration.

The first observation of the dimer between NH_3 and HCN in the gas phase was reported by Jones et al.[4] The low-resolution IR absorption spectrum of a mixture of NH_3 and HCN showed a parallel band, which was assigned to the C≡N stretching vibration for the hydrogen-bonded H_3N-HCN complex. A contour analysis of the band showed that the molecular complex is a symmetric top. The first MW spectrum of the H_3N-HCN complex was measured by Fraser et al.[6] using molecular beam electric-resonance spectroscopy. This study confirmed the C_{3v} symmetry with the HCN subunit as the hydrogen bond donor and yielded values for the spectroscopic ground-state constants. The hydrogen bond length was estimated to 2.156(10) Å and the harmonic value of the hydrogen bond stretching vibration (ν_σ) to 141(3) cm^{-1} from the values of the ground-state constants. The high-resolution infrared absorption spectrum of the ν_4 band (the NH_3 umbrella vibration) of H_3N-HCN was obtained later by Fraser et al.[7] by means of a microwave-sideband CO_2 laser and optothermal electric-resonance (EROS) detection. The observed band origin of 1041.7 cm^{-1} for this mode is blue shifted 91.8 cm^{-1} relative to the band origin of the hypothetical inversion-free umbrella vibration of the NH_3 monomer indicating a significant destabilization of the hydrogen bond in the molecular complex upon vibrational excitation of the ν_4 mode. Smith et al.[8] and Hilpert et al.[9] have both reported the high-resolution infrared absorption spectrum of the ν_2 (ν_S) band (the C−H stretching vibration) of H_3N-HCN by means of Fourier transform static gas-phase and molecular-beam EROS spectroscopies, respectively. The band origin of the ν_2 band is red shifted by 200.8 cm^{-1} relative to the band origin for the C−H stretching vibration of the HCN monomer indicating a

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significant strengthening of the hydrogen bond upon vibrational excitation of the ν_2 mode.

Bohn and Andrews[5] observed a vibration band at 279 cm^{-1} in the far-infrared absorption spectrum of $H_3N{-}HCN$ in a solid argon matrix, which was assigned to the intermolecular HCN libration band. The results from high-level quantum chemical calculations have later established that the observed band should be assigned to the intermolecular NH_3 libration mode. In the present study we report the direct observation and rovibrational analysis of the intermolecular NH_3 libration band ν_9^1 (ν_B) of the $H_3N{-}HCN$ dimer.

2. Experimental Section

The present experiments were carried out at the infrared beam-line at MAX-Lab at Lund University with use of a temperature controlled 200-L static gas absorption cell interfaced with a Bruker IFS 120 HR Fourier transform spectrometer (FTS) described in refs 14−16. The absorption cell has a White type multipass mirror system. The base length of the absorption cell is 2.85 m and the optics provides a total optical path length of ca. 91.2 m. The absorption cell is equipped with two sets of 3.2 mm thick CsI windows. The cell temperature is measured in the middle and at both ends of the inner cell with standard Pt100 resistance thermometers. A computer emulated PID temperature controller regulates the current supplied to the three different resistive heaters welded to the outside of the inner cell and maintained the cell temperature of 247 ± 0.25 K during these experiments. This temperature is close to the condensation point of HCN at the pressure used for the experiments.

HCN is prepared by dropwise addition of diluted H_2SO_4 onto KCN in vacuo and condensation of the gas evolved. The hydrogen cyanide samples are dried by vacuum distillation through a column containing the P_2O_5 drying agent. Impurities of CO_2 and $(CN)_2$ are then removed from the samples by fractional distillation. The partial pressures of HCN and NH_3 in the absorption cell are 2 and 5 Torr, respectively

The radiation source is synchrotron radiation from the electron storage ring MAX-I at MAX-lab. MAX-I is a 550 MeV electron storage ring with a 250 mA maximum ring current and a mean lifetime of 4 h. The transfer optics are described elsewhere.[17] The CsI exit window from the electron storage ring is mounted at Brewster's angle to the horizontally polarized radiation. The plane of polarization is then converted to vertical, since far-infrared beam splitters are more effective with this polarization. The electron storage ring is a high-brightness source of broadband infrared radiation, covering the full far-infrared spectral region. Synchrotron radiation is very close to a point source and is very suitable for high-resolution infrared absorption spectroscopy. The radiation output from the electron storage ring relative to the radiation output from a conventional globar source is characterized in refs 17 and 18. The interferometer is equipped with a 6 μm multilayer beam splitter that operates well over the entire spectral range of 50−600 cm^{-1}. The detector is a liquid He cooled Si-bolometer operating at 1.7 K (Infrared Laboratories, Inc.). The detector element is small, and allows us to use high scanning speeds making the bolometer less sensitive to motions of the electron beam. A cold band-pass optical filter (0−370 cm^{-1}) is mounted in the bolometer to reduce the photonic noise level in the final spectra. The FTS instrument resolution (RES) is defined as RES = 0.9/(MOPD), where MOPD is the maximum optical path difference in the interferometer. Sample interferograms are recorded with a resolution of 0.005 cm^{-1} (MOPD = 180 cm). The sample interferograms are transformed by using Mertz phase correction and boxcar apodization. A total scan collection time of ca. 12 h is achieved. Background interferograms of the evacuated absorption cell are recorded with a resolution of 0.08 cm^{-1}. These are transformed and interpolated onto a wavenumber grid matching that of the sample spectra by using a zero-filling factor of 16. This background resolution is appropriate for the cancellation of the dominating interference fringes. The resulting signal-to-noise ratio in the final absorbance spectra is about 30:1 for the most intense observed dimer transitions.

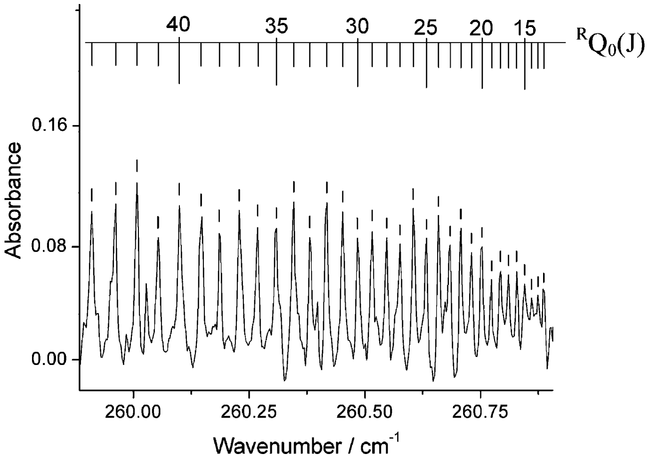

Figure 1. The *J*-assignment of the assumed $^RQ_0$-branch in the ν_9^1 band of $H_3N{-}HCN$.

The absolute wavenumber scale of the spectra is that determined from a calibration of the internal FTS He−Ne laser. The accuracy of this calibration is checked by comparing line positions from H_2O in the spectra with literature values reported by Johns.[19] The water lines appear in our spectra due to residual water vapor in the evacuated interferometer tank. The accuracy of these water line positions is estimated to be 0.0002 cm^{-1}. Lists of line positions from the absorbance spectra are generated with the Microcal Origin 7.0 software package (Microcal Software, Inc.). The precision of the line positions reported in the present study is estimated to be equal to the spectral resolution, that is, 0.0050 cm^{-1}. The observed FWHM line width of ca. 0.01 cm^{-1} is dominated mainly by instrumental broadening and pressure broadening by the NH_3 and HCN subunits.

3. Results and Analysis

The high-resolution far-infrared absorption spectrum of the NH_3/HCN mixture is very congested by the pure rotational transitions of NH_3 and the spectrum is fully saturated for 3−4 cm^{-1} wide spectral regions in ca. 20 cm^{-1} intervals. Several distinct rotational structures are, however, observed in the spectrum which do not appear in the spectra for the pure monomeric species obtained with identical sample pressure, sample temperature, and optical path length. The rotational structure consists of at least two isolated Q-branches with origins at 240.2 and 261.0 cm^{-1}, the latter having more intensity than the first. The Q-branches both degrade widely at lower wavenumbers, and their subband origins are rather easy to locate. We have not been able to observe accompanying P- and R-branch transitions for reasons discussed above. This means that we were not able to perform an unambiguous *J*-assignment of the Q-branch lines by means of ground-state combination differences based on the ground-state constants from ref 8. However, from the shape of the Q-branches and the observed subband origins we are able to propose reasonable *J*-assignments. In Figure 1 the proposed *J*-assignment of the $^RQ_0$-branch is shown. The appearances of the Q-branches are very similar and suggest that these belong to the same perpendicular band of a symmetric top molecule. The Q-branches are therefore assigned to the intermolecular NH_3 libration band ν_9^1(E) (ν_B) of $H_3N{-}HCN$.

The relative intensities strongly suggest that the 240.2 and 261.0 cm^{-1} structures constitute the expected strong $^PQ_3$- and $^RQ_0$-branches of the band, respectively, since subbands with $K = 3n$ have three times more intensity than other subbands owing to the different nucleir spin statistical weights. We have unsuccessfully searched the spectrum for the corresponding $^RQ_3$-branch around 281 cm^{-1}. This Q-branch may be obscured by strong NH_3 absorption lines. A total number of 77 observed rovibrational transitions for the two Q-branches are fitted to a standard semirigid symmetric top frequency expression[20] with a standard deviation of 0.00108 cm^{-1}. In this fit the spectroscopic ground-state constants B'', D''_J, and D''_{JK} are fixed to the values given by Fraser et al.[7] The values for the rotational constant A and the quartic centrifugal distortion constant D_K cannot be determined from the present analysis. The assigned rovibrational transitions for the $^RQ_0$- and $^PQ_3$-branches are listed in Tables 1 and 2.

The determined values for the upper state spectroscopic constants are listed in Table 3. The value obtained for the upper state constant D'_{JK} seems rather large. Both upper state constants D'_{JK} and B' are effective constants since these may include contributions from the l-type doubling constant q_9. This is because the upper states $v_9 = 1$, $l_9 = \pm1$, $K = \pm1$ of the $^RQ_0$-transitions are influenced by l-type doubling. Since we only observe two Q-branches, $^RQ_0$ and $^PQ_3$, we have no possibility to separate the l-type contribution from D'_{JK} and B' which may be seen from the conventional symmetric top frequency expressions for these Q-branches:

$$^{R}Q_0(J) = \nu_9^0 + (A - B - 2A\varsigma_9) + (\Delta B + q_9/2 - D'_{JK})J(J+1) - \Delta D_J J^2(J+1)^2 \quad (1)$$

$$^{P}Q_3(J) = \nu_9^0 + (A - B - 2A\varsigma_9) - 6(A - B - A\varsigma_9) + (\Delta B - 4D'_{JK} + 9D''_{JK})J(J+1) - \Delta D_J J^2(J+1)^2 \quad (2)$$

In eqs 1 and 2 contributions from ΔA, ΔB, and D_K are neglected in the subband terms. Since we are forced to use a model neglecting l-type doubling to obtain the values of the upper state constants, the observed value of $-4.643(6) \times 10^{-4}$ cm^{-1} for ΔB includes contribution from this effect. In the following we assume that this is of minor importance. The values of the Coriolis coupling constant ζ_9 and the NH_3 libration band origin ν_9^0 are estimated from the $^PQ_3$ and $^RQ_0$ subband origins at 240.1670(7) and 260.9674(4) cm^{-1}, respectively. A value of 0.415(5) for ζ_9 and a band origin of 260.03(10) cm^{-1} for the ν_9^1 mode are estimated by using the values of the ground-state constants A'' and B'' reported in ref 8.

The far-infrared absorption spectrum of the $NH_3/H^{13}CN$ mixture contains one distinct Q-branch at 259.5 cm^{-1}, which is assigned to $^RQ_0$ for the ν_9^1 band of $H_3N{-}H^{13}CN$. The observed $^RQ_0$-transitions are not sufficient for a semirigid symmetric top model fit. The observations are, however, fitted to a conventional diatomic molecule model to make a tentative J-assignment leading to an estimated subband origin of 259.52 cm^{-1}. The band origin of the ν_9^1 mode of $H_3N{-}H^{13}CN$ is red shifted by 1.44(14) cm^{-1} relative to $H_3N{-}H^{12}CN$ assuming the values of A, B, and ζ_9 are identical for the two isotopomers.

TABLE 1: The Assigned Line Positions for the $^RQ_0$-Branch for the ν_9^1 Band of $H_3N{-}HCN$

transition	obsd line position/cm^{-1}	obsd − calcd/ cm^{-1}
$^RQ_0$(62)	258.7822	−0.0004
$^RQ_0$(61)	258.8596	0.0014
$^RQ_0$(59)	259.0031	−0.0015
$^RQ_0$(58)	259.0749	−0.0006
$^RQ_0$(57)	259.1466	0.0019
$^RQ_0$(55)	259.2786	0.0000
$^RQ_0$(54)	259.3446	0.0013
$^RQ_0$(53)	259.4049	−0.0017
$^RQ_0$(52)	259.4680	−0.0002
$^RQ_0$(50)	259.5857	−0.0017
$^RQ_0$(49)	259.6460	0.0012
$^RQ_0$(48)	259.7005	−0.0003
$^RQ_0$(46)	259.8095	0.0009
$^RQ_0$(44)	259.9100	−0.0010
$^RQ_0$(43)	259.9616	0.0014
$^RQ_0$(42)	260.0075	−0.0005
$^RQ_0$(41)	260.0535	−0.0012
$^RQ_0$(40)	260.0994	−0.0006
$^RQ_0$(38)	260.1855	−0.0012
$^RQ_0$(37)	260.2285	0.0004
$^RQ_0$(36)	260.2687	0.0003
$^RQ_0$(35)	260.3089	0.0015
$^RQ_0$(34)	260.3462	0.0010
$^RQ_0$(33)	260.3806	−0.0012
$^RQ_0$(32)	260.4179	0.0007
$^RQ_0$(31)	260.4524	0.0010
$^RQ_0$(30)	260.4839	−0.0005
$^RQ_0$(29)	260.5155	−0.0008
$^RQ_0$(28)	260.5471	0.0000
$^RQ_0$(27)	260.5758	−0.0009
$^RQ_0$(26)	260.6044	−0.0006
$^RQ_0$(25)	260.6331	0.0008
$^RQ_0$(24)	260.6590	0.0004
$^RQ_0$(23)	260.6848	0.0011
$^RQ_0$(22)	260.7078	0.0001
$^RQ_0$(21)	260.7307	0.0002
$^RQ_0$(20)	260.7537	0.0013
$^RQ_0$(19)	260.7738	0.0007
$^RQ_0$(18)	260.7939	0.0012
$^RQ_0$(17)	260.8111	−0.0002
$^RQ_0$(16)	260.8283	−0.0005
$^RQ_0$(15)	260.8455	0.0003
$^RQ_0$(14)	260.8599	−0.0008
$^RQ_0$(13)	260.8742	−0.0008
$^RQ_0$(10)	260.9115	−0.0003
$^RQ_0$(9)	260.9201	−0.0019
$^RQ_0$(8)	260.9316	−0.0005

4. Discussion

The observed negative value of $\Delta B = -4.643(6) \times 10^{-4}$ cm^{-1} together with the simultaneous positive value of $\Delta D_J = 1.344(13) \times 10^{-8}$ cm^{-1} indicate that the hydrogen bond in the $H_3N{-}HCN$ dimer is destabilized upon excitation of the intermolecular NH_3 libration mode. This observation agrees well with the electrostatic viewpoint that the dominant contribution to the hydrogen bond is the interaction between the electric dipole moments of NH_3 and HCN. The dipole−dipole interaction is strongest in the pyramidal equilibrium configuration when the electric dipole moments are aligned parallel to each other. The observed destabilization of the hydrogen bond can be explained by the angular dependence of the dipole−dipole interaction. The electric dipole moment of NH_3 is tilted away from the intermolecular symmetry axis in the molecular complex as the NH_3 subunit carries out the librational motion and the dipole−dipole interaction becomes more unfavorable owing to the enhanced nonlinearity of the hydrogen bond. In the harmonic oscillator approximation based on the NH_3 libration band origin

TABLE 2: The Assigned Line Positions for the $^{P}Q_3$-Branch for the ν_9^1 Band of $H_3N{-}HCN$

transition	obsd line position/cm^{-1}	obsd − calcd/ cm^{-1}
$^{P}Q_3(47)$	238.9494	0.0002
$^{P}Q_3(46)$	239.0039	0.0013
$^{P}Q_3(45)$	239.0555	0.0009
$^{P}Q_3(43)$	239.1531	−0.0017
$^{P}Q_3(42)$	239.2019	−0.0010
$^{P}Q_3(41)$	239.2507	0.0010
$^{P}Q_3(39)$	239.3396	0.0003
$^{P}Q_3(37)$	239.4229	−0.0010
$^{P}Q_3(36)$	239.4630	−0.0013
$^{P}Q_3(35)$	239.5032	−0.0003
$^{P}Q_3(34)$	239.5405	−0.0009
$^{P}Q_3(33)$	239.5778	−0.0003
$^{P}Q_3(32)$	239.6151	0.0014
$^{P}Q_3(31)$	239.6496	0.0015
$^{P}Q_3(29)$	239.7127	−0.0006
$^{P}Q_3(28)$	239.7443	0.0002
$^{P}Q_3(27)$	239.7730	−0.0009
$^{P}Q_3(26)$	239.8017	−0.0007
$^{P}Q_3(25)$	239.8304	0.0006
$^{P}Q_3(23)$	239.8820	0.0007
$^{P}Q_3(22)$	239.9050	−0.0004
$^{P}Q_3(21)$	239.9279	−0.0004
$^{P}Q_3(20)$	239.9509	0.0006
$^{P}Q_3(18)$	239.9911	0.0003
$^{P}Q_3(17)$	240.0112	0.0017
$^{P}Q_3(16)$	240.0284	0.0014
$^{P}Q_3(15)$	240.0427	−0.0008
$^{P}Q_3(14)$	240.0571	−0.0019

TABLE 3: Spectroscopic Constants for the Intermolecular NH_3 Libration Band ν_9^1 of the $H_3N{-}HCN$ Heterodimer

ν_0/cm^{-1}	260.03(10)[a]
B''/cm^{-1}	0.10062809[b]
B'/cm^{-1}	0.1001638(6)[a]
$10^7D_J''$/cm^{-1}	1.8446[b]
$10^7D_J'$/cm^{-1}	1.9814(13)[a]
$10^5D_{JK}''$/cm^{-1}	1.3896[b]
$10^5D_{JK}'$/cm^{-1}	4.250(13)[c]
N[d]	77
σ^e/cm^{-1}	0.00108

[a] Uncertainties quoted are one standard error. [b] Reference 8. [c] Influenced by l-type doubling (see text). [d] Number of observations in fit. [e] Standard deviation of fit.

and the rotational constant for NH_3 the bending amplitude θ_{NH_3} increases from 15.8° in the ground state to 22.4° upon excitation of the NH_3 libration mode.

The effect of destabilization can be quantified approximately in terms of the harmonic force constant k_σ for the stretching vibration of the intermolecular hydrogen bond ν_σ since the harmonic force constant for this mode is directly correlated to the dissociation energy of the molecular complex. Millen[21] has developed an expression for the harmonic force constant for the intermolecular stretching vibration of the hydrogen bond in symmetric top dimers based on a modified pseudodiatomic approximation. The harmonic force constant is related to the rotational constant B_D and the quartic centrifugal distortion constant D_J for the symmetric top dimer according to eq 3 assuming that the dominating contribution to the centrifugal distortion of the center of mass distance comes from the hydrogen bond stretching vibration:

$$k_\sigma = \frac{16\pi^2\mu_D B_D}{D_J}\left(1 - \frac{B_D}{B_{NH_3}} - \frac{B_D}{B_{HCN}}\right) \qquad (3)$$

B_D, B_{NH_3}, and B_{HCN} are the values of the rotational constant of the symmetric top dimer and the subunits NH_3 and HCN, respectively, and μ_D is the reduced mass of $H_3N{-}HCN$. The values of the harmonic force constant for the stretching vibration of the hydrogen bond in the vibrational ground state and the excited NH_3 libration state ($\upsilon_9 = 1$) are listed in Table 4 together with values for the corresponding harmonic stretching frequencies ω_σ for the hydrogen bond stretching vibration. The value of the force constant decreases by 5% upon intermolecular vibrational excitation of the ν_9^1 mode and thereby indicates that the destabilization of the hydrogen bond is about 5% within the harmonic oscillator approximation. The intermolecular stretching vibration of the hydrogen bond in $H_3N{-}HCN$ is highly anharmonic and the estimated values of the force constants are therefore approximate numbers.

TABLE 4: The Center of Mass Distance r, the Harmonic Frequency ω_σ, and Harmonic Force Constant k_σ for the Hydrogen Bond Stretching Vibration in the Ground State and the Excited NH_3 Libration State

r''/Å	3.844
r'/Å	3.853
ω''_σ/cm^{-1}	143
ω'_σ/cm^{-1}	136
k''_σ/mdynÅ^{-1}	0.125
k'_σ/mdynÅ^{-1}	0.115

The elongation of the hydrogen bond can be estimated according to the expression for the intermolecular center of mass distance r in eq 4:

$$r = \sqrt{\frac{h/8\pi^2 cB_D - I_{NH_3} - I_{HCN}}{\mu_D}} \qquad (4)$$

where B_D is the rotational constant of the dimer, I_{NH_3} and I_{HCN} are the moments of inertia of the NH_3 and HCN subunits, respectively, and μ_D is the reduced mass. The values of the center of mass distance for the ground and excited NH_3 libration state are listed in Table 4. The hydrogen bond thus appears to elongate by 0.010 Å upon intermolecular vibrational excitation of the ν_9^1 mode.

The destabilization of the hydrogen bond in the symmetric top complex $H_3N{-}HCN$ upon intermolecular vibrational excitation of the high-wavenumber intermolecular bending vibration ν_B seems to be less pronounced than that observed for the linear complexes OC−HCl,[14] HCN−HCl,[16] and HCN−HF[22] where the destabilization of the hydrogen bond proves to be at least 20% and even 30% for OC−HCl. The librational motion of the acceptor subunit NH_3 affects the strength of the hydrogen bond in the $H_3N{-}HCN$ dimer less than the librational motion of the donor subunits HCl and HF affects the strengths of the hydrogen bond in the OC−HCl, HCN−HCl, and HCN−HF dimers. The reason seems to be that the NH_3 librational motion mostly involves displacements of the H atoms whereas the displacement of the N atom is rather small. The lone pair on the N atom therefore changes direction in the course of the libration but the interaction between the acceptor atom N and the H atom in the donor molecule does not change much. The librational motion of the donor subunit HCl or HF, however, involves a rather large displacement of the H atom in the donor molecule and the interaction between the acceptor atom (the C atom in OC−HCl and the N atom in HCN−HCl and HCN−HF) and the displaced H atom weakens significantly.

5. Conclusions

The high-resolution far-infrared absorption spectrum for the intermolecular NH_3 libration band ν_9^1 (ν_B) of the pyramidal molecular complex H_3N-HCN is recorded by means of static gas-phase Fourier transform far-infrared spectroscopy at 247 K and a synchrotron radiation source. A rovibrational analysis based on a standard semirigid symmetric top molecule model yields the band origin of 260.03(10) cm^{-1}, together with values for the upper state rotational constant B' and the upper state quartic centrifugal distortion constants D'_J and D'_{JK}. The values for the upper state spectroscopic constants indicate that the hydrogen bond in the H_3N-HCN complex is destabilized by 5% and is elongated by 0.010 Å upon excitation of a quantum of libration of the hydrogen bond acceptor molecule.

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