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B. A. Wofford

M. W. Jackson

Shannon Lieb
Butler University, slieb@butler.edu

J. W. Bevan

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B. A. Wofford, M. W. Jackson, S. G. Lieb, and J. W. Bevan

The spectroscopy and molecular dynamics of the high frequency ν_6^1 intermolecular vibrations in HCN---HF and DCN---DF

B. A. Wofford, M. W. Jackson, S. G. Lieb, and J. W. Bevan

Chemistry Department, Texas A&M University, College Station, Texas 77843

Gas phase rovibrational analysis of the high frequency intermolecular hydrogen bonded bending overtone $2\nu_6^0$ [$\nu_0 = 1132.4783(2)$ cm^{-1}] in HCN---HF and its corresponding perdeuterated fundamental ν_6^1 [$\nu_0 = 409.1660(2)$ cm^{-1}] are reported. Evaluated rovibrational parameters provide the basis for quantitative modeling of the molecular dynamics associated with this vibration. A quantum mechanical calculation permits determination of the quadratic and quartic force constants $K_{66} = 537(17)$ and $K_{6666} = 4.98(12)$ cm^{-1} which in turn are used to estimate the pertinent cubic band stretching interaction constants $K_{466} = -149.3(50)$ cm^{-1} and account for the unexpected behavior in the rotational constant B_6^1. Second order expansion of the vibrational term energies, give $X_{46} = -21.61(2)$, $X_{67} = -7.694(1)$, $X_{66} = -14.84(90)$, $g_{66} = -31.04(90)$ cm^{-1}, neglecting corrections for Fermi resonance. The common isotopic species equilibrium rotational constant B_e is evaluated to be 3681.1(11) MHz.

INTRODUCTION

Static gas phase Stark microwave spectroscopy of the common and isotopically substituted species of HCN---HF has permitted determination of its geometry, approximate force constants, dissociation energies, and electric dipole moment.[1] A subsequent pulsed-nozzle Fourier transform microwave study[2] provided accurate values of the ^{14}N and D nuclear quadrupole coupling constants in addition to providing more precise ground state rotational and distortion constants. This latter study also yielded important information about the lengthening of the H–F bond upon complex formation. However, the low concentration of ν_6^1 states in equilibrium gas phase mixtures ($\leqslant 7.5\%$ of its ground state) prevented observation of their corresponding microwave spectra.

Infrared spectra of the intermolecular bending ν_6^1 bands of HCN---HF and DCN---DF were first observed in the gas phase by Thomas[3] at a resolution of 3 cm^{-1}. Due to the low instrumental resolution available in this experiment, Thomas was unable to resolve the rotational structure of this perpendicular band. These studies, however, have provided a foundation for subsequent high resolution infrared investigations directed toward a quantitative characterization of molecular dynamics in this hydrogen bonded species. Recently all the HCN--HF band origin fundamental frequencies have been accurately determined. In addition, several hot bands of the hydrogen-bonded complex have been observed in the gas phase using Fourier transform and color center laser spectroscopic techniques.[4,5] Previously, we have also observed overtones of the H–F stretching vibration $2\nu_1$, the H–C stretching mode $2\nu_2$, and the intramolecular bending vibration $2\nu_5^0$ in HCN---HF.[6-8] In particular, it was possible to rovibrationally analyze both the $2\nu_2$ and $2\nu_5^0$ bands and some of their accompanying hot bands originating from the low frequency ν_7^1 Π state. In fact, the data available from rovibrational analyses in both the common and perdeuterated species of HCN---HF has permitted the calculation of an approximate anharmonicity corrected stretching harmonic force field.[9] Thus, these infrared investigations have provided more accurate values for the harmonic force constants governing the bending and stretching of the hydrogen bond. Furthermore, these studies[10] have recently been extended to permit an accurate determination of the hydrogen bond dissociation energies D_0 and D_e, and subsequently evaluation of the thermal functions of hydrogen bond formation $\Delta H_{298.2}^0$, $\Delta U_{298.2}^0$, $\Delta G_{298.2}^0$, and $\Delta S_{298.2}^0$. More recently, the rovibrational line profiles of ν_1 and ν_2 bands in HCN--HF have been reinvestigated using molecular beam optothermal spectroscopy.[5(c)]

The previous rovibrational analysis of the ν_6^1 fundamental in HCN---HF resulted in the observation of a pronounced $R(J)$ bandhead associated with a large decrease in excited state rotational constant B_6^1 relative to the ground state B_0 [$(B\nu_6^1 - B_0) = -64.31(27)$ MHz]. Such information is indicative of unusual molecular dynamics in this high frequency intermolecular hydrogen-bond vibration and warrants further investigation. Corresponding spectroscopic analyses of the fundamental ν_6^1 band in the perdeuterated species DCN---DF together with the overtone $2\nu_6^0$ and its hot bands $2\nu_6^0 + \nu_7^1 - \nu_7^1$, $2\nu_6^0 + \nu_4 - \nu_4$ in HCN---HF, offer the opportunity of greater insights into the quantitative characterization of the molecular dynamics associated with this vibration. Furthermore, this ν_6^1 intermolecular hydrogen-bonded vibration, together with the low frequency intermolecular stretching vibration ν_4 are associated with the dissociative coordinates of this weakly bound system. Consequently, quantitative characterization of its molecular dynamics could indicate a dramatic influence on possible channels of energy transfer and product distribution associated with vibrational predissociation in this complex. Such information thus has direct significance for theoretical modeling of vibrational predissociation, in HCN---HF specifically, and is of more general relevance to corresponding effects in similar linear complexes such as N$_2$---HF and OC---HF.

In this paper, we report the spectroscopic analysis of the overtone in the high frequency intermolecular bending vibration $2v_6^0$ and its hot bands $2v_6^0 + v_7^1 - v_7^1$, $2v_6^0 + v_4 - v_4$ in HCN---HF. We also report the observation and rovibrational analysis of the intermolecular bending vibration v_6^1 in DCN---DF.

The unexpected B_6 value of v_6^1 HCN---HF is confirmed by rovibrational analysis of $2v_6^0$ HCN---HF and v_6^1 DCN---DF bands in the complex. The overtone spectrum of HCN---HF supplies the minimum rovibrational data needed to evaluate the quadratic (K_{66}) and quartic (K_{6666}) vibrational constants, as well as a one-dimensional, first order rotational constant expansion.[11] It will be demonstrated that comparison of the one-dimensional effective rotational constant values[12] of B_6^* [defined in Eq. (6)], α_6^* and λ_6^* with the experimentally determined counterparts are quite favorable. This indicates a degree of confidence in the K_{66} and K_{6666} values which are generated. Similar comments apply to the anharmonic wave functions used in the vibrationally dependent, rotational constant expansion. Use of perturbation expansions which relate the estimated cubic stretching–bending force constant K_{466}, harmonic vibrational frequencies and K_{6666} result in the evaluation of the anharmonicity constant X_{66} found in the multidimensional anharmonic oscillator term energy expansion. The evaluation of K_{466} provides the basis for physical interpretation of the $B_{mv_6}^{\,n}$ vibrational dependence. Determination of $B_{2v_6^0}$ also provides the minimum information necessary to calculate the common isotopic species equilibrium rotational constant B_e for this hydrogen-bonded species.[13]

EXPERIMENTAL

The spectra were recorded using a Bomen DA3-002 Fourier transform infrared spectrophotometer. Due to the fact that the equilibrium constant for HCN---HF complex formation is small[10] ($\simeq 9 \times 10^9$ ground state molecules/cc, e.g., under the experimental conditions included in column 1, Table I), we employed a temperature-controlled corrosion resistant multireflection White cell. This permits optimization of complex formation and enhancement of instrumental sensitivity by increasing the effective absorption path length. The transfer optics interfacing the interferometer and the White cell have been described previously.[4] The entire optics train was evacuated to eliminate extraneous absorptions due to water vapor and carbon dioxide present in the atmosphere. Experimental conditions for each run are given in Table I. These resulted in signal-to-noise ratios

TABLE I. Experimental conditions for FTIR spectroscopy.

Band	$2v_6^0$ (HCN---HF)	v_6^1 (DCN---DF)
Detector	HgCdTe	Cu:Ge
Beam splitter	KBr	Mylar
Windows	CaF_2	Polyethylene
Pressure	7.07 Torr	4.70 Torr
Temperature	241 K	238 K
Path length	100 m	64 m
Resolution	$0.01\ cm^{-1}$	$0.01\ cm^{-1}$
Scan time	48 h	40 h

($>$20:1) for the most intense observed transitions.

The deuterium fluoride in the study of isotopic species DCN---DF was purchased from MSD Isotopes; and the common isotopic species hydrogen fluoride from Matheson, Inc. The hydrogen and deuterium cyanide gases were generated by the reaction of KCN with H_3PO_4 and D_3PO_4, respectively.[14] The gases were loaded and mixed to the desired temperature by the circulation of liquid nitrogen cooled isopentane through the external jacket of the White cell.

RESULTS

Infrared and microwave data demonstrate that the complexes HCN---HF and DCN---DF reflect the influence of a linear equilibrium state structure. Each P, Q, and R branch of the fundamental $\Pi \leftarrow \Sigma v_6^1$ band of DCN---DF is resolved. This is the first fundamental bending vibration which has been resolved for this deuterated complex. As mentioned previously, the latter was first investigated by Thomas,[3] but the relatively low instrumental resolution precluded observation of its rotational fine structure. The R branch in the v_6^1 scan of this deuterocomplex is shown in Fig. 1. An unusual feature of this spectrum is the formation of an R bandhead due to a rather large and negative change in the vibrationally dependent B_6 rotational constant. This feature is consistent with the results reported for the v_6^1 spectra of HCN---HF, indicating that the latter was not an artifact of Fermi resonance. The hot band $v_6^1 + v_7^1 - v_7^1$ of DCN---DF is shifted to lower frequency, with a pronounced R bandhead occurring within the P branch of the v_6^1 fundamental. This complicating feature somewhat obscured the fundamental band origin making initial assignment difficult. To overcome the problem of the overlapping bands, the R-branch and lower Q-branch transitions were assigned to provide an initial assessment of the band origin. P-branch transitions were then assigned and ground state combination frequency differences used to confirm both the R- and P-branch assignments. The ground state constants were previously determined from analysis of microwave[2] together with IR data of the v_1, v_2, and v_3 bands.[15] Each datum was weighted by the
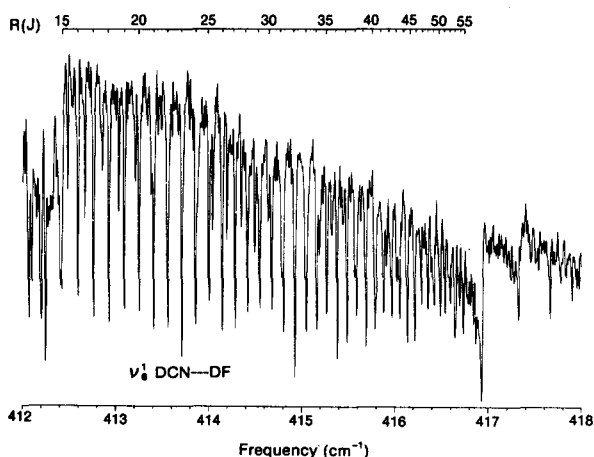

FIG. 1. Partially resolved $R(J)$ bandhead in v_6^1 DCN---DF.

TABLE II. Rovibrational constants associated with ν_6 in HCN--HF and DCN--DF.[a]

Rovibrational parameter	ν_6^1 (HCN–HF)	ν_6^1 (DCN–DF)	$2\nu_6^0$ (HCN–HF)	$2\nu_6^0 + \nu_7^1 - \nu_7^1$ (HCN–HF)
ν_0	550.0285(1)[b]	409.1660(2)	1132.4738(2)	1117.0862(8)
B''	0.119 787 9(7)	0.111 807(1)	0.119 787 9(7)	0.120 828(3)
D_J''	$2.377(5) \times 10^{-7}$	$1.946(4) \times 10^{-7}$	$2.377(5) \times 10^{-7}$	$2.76(2) \times 10^{-7}$
q_7''	$\cdots$	$\cdots$	$\cdots$	$4.22(3) \times 10^{-4}$
B'	0.117 651 2(7)	0.110 434(1)	0.112 680(1)	0.113 847(3)
D_J'	$2.801(5) \times 10^{-7}$	$2.172(4) \times 10^{-7}$	$2.54(1) \times 10^{-7}$	$2.52(2) \times 10^{-7}$
q_7'	$\cdots$	$\cdots$	$\cdots$	$4.02(3) \times 10^{-4}$
q_6	$5.70(1) \times 10^{-5}$	$6.14(2) \times 10^{-7}$	$\cdots$	$\cdots$
σ[c]	0.000 47	0.000 76	0.000 47	0.0012

[a] All parameters in cm^{-1}.
[b] Uncertainties cited are one standard deviation as specified by fit.
[c] σ = standard deviation.

inverse square of the estimated uncertainty. Lower state combination difference frequencies were used to evaluate the lower state constants B_0, D_J^0 given in Table II. The transitions are fitted to the following expression for linear molecules:

$$\nu = \nu_0 + B_6[J'(J' + 1) - l'^2]$$
$$\pm (\tfrac{1}{2}q_6)[J'(J' + 1)] - D_6^J[J'(J' + 1) - l'^2]^2$$
$$- B_0 J''(J'' + 1) - D_0^J[J''(J'' + 1)]^2. \qquad (1)$$

The single prime refers to the upper state and double prime to the lower state. B_0 and D_0^J are the ground state rotational and distortion constants, respectively, and B_6, D_6^J, and q_6 are the corresponding excited vibrational state rotation, distortion and l-type doubling constants. The fundamental frequency is designated as ν_0. The P- and R-branch transition use the negative sign associated with the q_6 portion of the equation, whereas, the Q branch uses the positive sign in Eq. (1). The multiple linear least squares regression of the above 6 parameter equation utilized 94 data points to yield an overall standard deviation of 0.0008 cm^{-1}. The results of the analysis are presented in Table II. The ground state constants predicted from this data are within one standard deviation of those more accurately determined constants of combined microwave and aforementioned IR data.

The bending vibrations of a linear molecule usually result on average in an overall decrease in atomic displacement from the center of mass relative to the ground vibrational state. A resulting decrease in the moment of inertia was thus expected and a consequent increase in $B\nu_6^1$ relative to B_0. However, in both DCN---DF and HCN---HF the reverse behavior is observed. This raises the question of whether or not this vibration is accompanied by a simultaneous increased displacement of the component centers of mass. To obtain a quantitative assessment of this behavior, rotational constants of the overtone $2\nu_6^0$ and its hot bands would be useful. Fortunately, it was possible to rovibrationally resolve and assign the overtone spectrum $(2\nu_6^0)$ of HCN---HF and assign it (Fig. 2). Along with the $2\nu_6^0$ overtone bands, several hot bands were observed including $2\nu_6^0 + \nu_7^1 - \nu_7^1$ and $2\nu_6^0 + \nu_4 - \nu_4$. Both $2\nu_6^0$ (Σ–Σ) and $2\nu_6^0 + \nu_7^1 - \nu_7^1$ (Π–Π) are rovibrationally resolved and the results of their multiple linear regression fit are shown in Table II. The hot band

$(2\nu_6^0 + \nu_4 - \nu_4)$ is not resolved but can be unequivocally identified by its characteristic ν_7^1 hot band series. An estimate of the band origin is possible by fitting excited state rovibrational parameters to its characteristic R band profile. The band origin was estimated to be 1091.17(2) cm^{-1}. If one uses the second order expansion of the vibrational term energies[16]

$$G(\nu_1, \nu_2, ..., \nu_7)$$
$$= \sum_i \omega_i (\nu_1 + d_i/2)$$
$$+ \sum_i \sum_{i>j} x_{ij}(\nu_1 + d_i/2)(\nu_j + d_j/2) + \sum_{i>j} g_{ij} l_i l_j, \qquad (2)$$

where ω_i is the harmonic frequency, d_i is the degeneracy factor, x_{ij} is the anharmonic cross term corrections, x_{ii} is the anharmonicity constants, and g_{ij} is the l-dependent term of the bending vibrational modes. Evaluation of the anharmonic cross terms x_{46} and x_{67} is thus possible. The latter constants are related to the observed band origins through the following expressions:

$$2x_{46} = (2\nu_6^0 + \nu_4 - \nu_4) - (2\nu_6^0), \qquad (3)$$
$$2x_{67} = (2\nu_6^0 + \nu_7^1 - \nu_7^1) - (2\nu_6^0). \qquad (4)$$
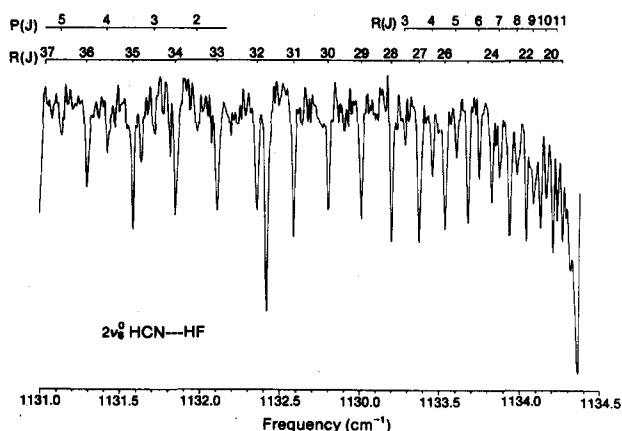
FIG. 2. Assigned rovibrational transitions in the $2\nu_6^0$ intermolecular overtone band in HCN---HF.

From the data given one finds that $x_{46} = -21.61(2)$ cm^{-1} and $x_{67} = -7.694(1)$ cm^{-1}. These values compare with those recently predicted on the basis of *ab initio* molecular orbital calculations,[17] $x_{46} = -15.12$ cm^{-1} and $x_{67} = -13.38$ cm^{-1}.

The unexpected Bv_6^l value behavior is demonstrated in Table III for HCN---HF and DCN---DF. As one progresses to higher vibrational states in the bending mode v_6, the rotational constants decrease. Our investigation of this anomalous characteristic is based on a quantum mechanical model described by Duckett *et al.*[18] The model Hamiltonian for large amplitude linear molecule bending vibrations is broken into a vibrational Hamiltonian of the form

$$\mathbf{H}_{\omega_b/hc} = \tfrac{1}{2}\nu_6 \mathbf{p}^2 + K_{66}\mathbf{q}^2 + K_{6666}\mathbf{q}^4, \tag{5}$$

where ν_6 is the fundamental frequency of the oscillator, K_{66} and K_{6666} are the quadratic and quartic constants of the potential (with units of cm^{-1}), and $\mathbf{p}$ and $\mathbf{q}$ are the dimensionless momentum and position operators of the vibrational Hamiltonian. The potential function is the radial portion of the linear bending mode and therefore does not have an odd power of the displacement coordinate. The values of K_{66} and K_{6666} are determined through a least squares fitting of the calculated to the observed vibrational frequencies. The results are $K_{66} = 537(17)$ cm^{-1} and $K_{6666} = 4.98(12)$ cm^{-1} which indicates a nearly harmonic potential surface. The small magnitude of the quartic term will be important in evaluating some approximations used later. More significantly, the expansion of the quartic oscillator wave function in terms of a harmonic oscillator basis is obtained. The effect of the anharmonicity on the vibrational dependence of the rotational constants is now defined in the following effective rotational Hamiltonian[18]:

$$\mathbf{H}_{rot/hc} = B_b^* \mathbf{J}^2 + (-\alpha_6^* \mathbf{q}^2 + \lambda_6^* \mathbf{q}_\phi^2)\mathbf{J}^2. \tag{6}$$

The constants to be determined are (i) B_b^* which is analogous to the equilibrium rotational constant but does not properly represent the "true" equilibrium rotational constant since this is only a one-dimensional representation of the entire rovibrational potential surface, (ii) α_6^* which is the vibration–rotation interaction constant, and (iii) λ_6^* which is the l-dependent term. The operators are $\mathbf{J}^2$—the total angular momentum operator, $\mathbf{q}^2$—the dimensionless position operator, and $\mathbf{q}_\phi^2$—the angular portion of the two-dimensional operator. The total wave function is a direct product of the quartic oscillator basis set and the usual spherical harmonic basis set. Evaluating the effective rotational operator with this basis set yields

$$B_{v,l} = B_b^* - \alpha_6^* \langle v \rangle. \tag{7}$$

If the vibration is harmonic, the expectation value of q^2 is simply $(v + 1)$ and the resulting expression is a one-dimensional expression found as a limit to the usual rovibrational expansion of the rotational constant, $B_{v,l}$. The anharmonic dependence of the rovibration interaction is thereby absorbed in the $\langle q^2 \rangle_{v,l}$ term.

The $B_{v,l}$ values for HCN---HF v_6 vibrational mode (Table III) were analyzed according to the formalism shown in Eq. (7). The results are shown in Table IV and are compared with the corresponding experimentally determined values. The usual vibrationally dependent rotational constant expansion is written as[13]

$$B_{v,l} = B_b - \sum_i \alpha_i (\nu_i + d_i/2) + \sum_j \gamma_j l_j^2, \tag{8}$$

where ν_i is the vibrational quantum state of the ith vibrational mode, d_i is the degeneracy of the ith mode, and l_i is the l quantum number associated with the angular dependence of a bending mode of a linear molecule. The worst approximation to the experimentally determined parameters is found in B_b^*. This is to be expected since the intercept of a hyperplane as described in Eq. (8) would not be well represented by the one-dimensional approximation shown in Eq. (7). The other two calculated constants differ by less than 0.4% from their experimental counterparts.

Analysis of the vibrational potential surface is furthered by analyzing and approximating expression (9) which relates the rovibrational interaction constant to the cubic force constants K_{stt} (the subscript "s" denotes the nondegenerate vibrational modes of a linear molecule and "t" denotes the degenerate modes). According to Alieu and Papousek[11] these constants are related by the expression

$$-\alpha_t = q_t + 2B_b^2(c/h) \frac{1}{2}\sum_s K_{stt} a_s/\omega_s^{3/2}, \tag{9}$$

where q_t is the l-doubling constant, a_s is the structure factor, ω_s is the harmonic frequency, and c,h are the speed of light and Planck's constant, respectively. The experimental values of α_6 and q_6 are $-0.003\,549$ cm^{-1} and 5.79×10^{-5} cm^{-1}. The structure factors[11] have the following values based on a normal coordinate analysis of the stretching modes of vibration and the equilibrium displacements of the atoms in the complex $a_1 = 2.167 \times 10^{-20}$ g$^{1/2}$ cm, $a_2 = 1.288 \times 10^{-20}$ g$^{1/2}$ cm, $a_3 = 8.46 \times 10^{-20}$ g$^{1/2}$ cm, and $a_4 = 2.900 \times 10^{-19}$ g$^{1/2}$ cm. The harmonic frequencies for the stretching modes are $\omega_1 = 3941.78$ cm^{-1}, $\omega_2 = 3439.62$ cm^{-1}, $\omega_3 = 2153.36$ cm^{-1}, and $\omega_4 = 185.81$ cm^{-1}. Because ω_4 is so small relative to the other frequencies, the coefficient

TABLE III. Observed vibrational frequencies and associated rotational constants (cm^{-1}) used in dynamic calculations.

| Band | HCN---HF | | DCN---DF | |
	ν^a	$B_{v,l}$	ν	$B_{v,l}$
$0\,\nu_6$	0	0.119 789(1)	0	0.118 07(1)
$1\,\nu_6^1$	550.0285(1)	0.117 651(1)	409.1660(2)	0.110 434(1)
$2\,\nu_6^0$	1132.4738(1)	0.112 680(2)		

^{a} Units cm^{-1}.

TABLE IV. Comparison of the expansion terms of the vibrationally dependent rotational constants.

Calculated (cm^{-1})	Experimental (cm^{-1})
$B_b^* = 0.123\,33(5)$	$B_b = 0.125\,63(1)$
$\alpha_6^* = 0.003\,536(1)$	$\alpha_6 = -0.003\,549(1)$
$\lambda_6^* = 0.001\,398(1)$	$\lambda_6 = 0.001\,404(1)$

of the cubic force constant (K_{466}) is at least two orders of magnitude larger than the other cubic force constants. This leads to a simplification of Eq. (9) based on the assumption that the cubic force constants K_{s66} ($s \neq 4$) are not significantly larger than K_{466}. Ignoring the other cubic force constants in the equation yield a value of $K_{466} = -149.3(50)$ cm^{-1}. This evaluation gives the physical interpretation of anomalous $B_{v,l}$ dependence of the v_6 vibrational mode and an estimation of the anharmonic force constant x_{66}.

The rather large negative value of the cubic force constant K_{466} leads to the conclusion that there is a significant interaction between the high frequency hydrogen-bond bending mode v_6^1 and the low frequency hydrogen-bond stretching mode v_4. This implies that the large amplitude bending motion is coupled to a significant displacement of the centers of mass of the monomer units comprising the hydrogen-bond complex. The end result is analogous to the same $B_{v,l}$ dependence found in stretching modes of vibration.

The final result obtained from this analysis is an estimate of x_{66} which we have not been able to determine directly using Eq. (2) because the $2v_6^2$ band was not observed directly. Once again an expansion of a potential surface constant can be approximated by analyzing the coefficients of the terms in a sum and ignoring the smallest terms in favor of one dominating contribution. The expression of the anharmonic force constant x_{66} in terms of the quartic force constant K_{6666}, cubic force constants K_{s66}, and the harmonic frequencies ω_s and ω_t is

$$x_{66} = -1/16 K_{6666} - \frac{1}{16} \sum_s K_{s66}^2 \frac{(8\omega_6^2 - 3\omega_s^2)}{\omega_s(4\omega_6^2 - \omega_s^2)} . \quad (10)$$

Noting that K_{6666} amounts to 4.98 cm^{-1} and the coefficient $(8\omega_6^2 - 3\omega_4^2)/\omega_4(4\omega_6^2 - \omega_4^2)$ is considerably larger than the other coefficients leading to the approximation

$$x_{66} \simeq -1/16 K_{466}^2 (8\omega_6^2 - 3\omega_4^2)/\omega_4(4\omega_6^2 - \omega_4^2). \quad (11)$$

This results in the evaluation of x_{66} as $-14.84(90)$ cm^{-1}. The calculation is based on $\omega_4 = 185.8$ cm^{-1}, a value not corrected for Fermi resonance. Such a correction cannot be accurately made at present due to insufficient experimental data. However, preliminary calculations give a lower limit of ω_4 (>171.5 cm^{-1}). This value gives $X_{66} \geq -16.1$ cm^{-1} and $g_{66} \geq -32.3$ cm^{-1} when substituted in Eq. (11) but less than the previously calculated values. Such values do not significantly change the previously determined values and the best values we can currently propose are $x_{66} = -15.5(7)$ and $g_{77} = -31.7(7)$ cm^{-1}, respectively, if the maximum Fermi resonance correction is taken into account. The anharmonic oscillator term energy expansion is determined from Eq. (2), where g_{ij} is the *l*-dependent term for the bending modes of vibration and the other symbols are as previously defined. All observed transitions are a difference between term energies as shown in Eq. (2). If one subtracts twice the fundamental frequency from the overtone frequency ($2v_6^0$), the resultant algebra involving the term energies shown in Eq. (2) yields $2(x_{66} - g_{66})$. According to the frequencies given in Table III, $x_{66} - g_{66}$ equals 16.2084(2) cm^{-1}. Using the

estimated x_{66} value of $-14.84(90)$ cm^{-1} leaves a g_{66} value of $-31.04(90)$ cm^{-1}.

Again the values of x_{66} and g_{66} can be compared with corresponding predictions based on *ab initio* molecular orbital calculations, i.e., $x_{66} = 51.3$ and $g_{66} = +22.3$ cm^{-1}, respectively.[17] It is pertinent to note that the value of $(x_{66} - g_{66})$ determined directly from spectroscopic analysis is $+16.2084(2)$. This value compares with the corresponding predicted theoretical value of $(x_{66} - g_{66}) = -73.6$ cm^{-1}. In this case both the magnitude and sign of the theoretical and experimental values are at variance.

The evaluation of the excited state rotational constant $B_{2v_6^0}$ now permits an estimation of the common isotopic equilibrium rotational constants B_e for HCN---HF using Eq. (8) and the available rotational constants given in Table V.

Within this approximation B_e for the common isotopic species of $^1H^{12}C^{14}N$---$^1H^{19}F$ is evaluated to be 3681.1(11) MHz compared to the value of 3591.187(18) MHz determined for the ground state rotational constant B_0. This indicates a significant difference between these two constants. It would be interesting to improve the precision of B_e and extend the analysis of a sufficient number of other isotopic species thus providing the data for an effective r_e structure for this hydrogen bonded complex. (^{19}F coordinates cannot be isotopically substituted and would have to be evaluated by moment conditions.)

CONCLUSIONS

A rovibrational analysis of the v_6^1 fundamental in the perdeuterated isotopic species DCN---DF and the $2v_6^0$ overtone in HCN---HF have been completed, providing quantitative information relevant to the molecular dynamics in this vibration. These results are consistent with a highly anisotropic intermolecular potential which strongly favors a linear configuration. Any departure from linearity will weaken the intermolecular interaction resulting in the observed variation in rotational constants. The strong anharmonic coupling between the v_4 and v_6^1 vibrations is one of the most significant in the HCN---HF complex as it involves two dissociative modes of this weakly bound complex. Such coupling could significantly affect possible channels of energy redistribution associated with vibrational predissociation from certain states of the complex. It would also be of interest to determine whether such behavior is a general charac-

TABLE V. Rotational constants for evaluation of the equilibrium rotational constant B_e of $^1H^{12}C^{14}N$---$^1H^{19}F$.[a]

B_0	3591.187(18)	B_5^1	3588.998(33)
B_1	3660.326(30)	$B_{2v_5^0}$	3587.86(12)
B_2	3586.09(19)	B_6^1	3526.88(27)
B_3	3576.01(57)	$B_{2v_6^0}$	3378.061(30)
B_4^c	3517.11(12)[b]	B_7^{1c}	3622.48(9)
		$B_{2v_6^0 c}$	3653.6(2)

[a] Constants in units MHz.
[b] Corrected for Fermi resonance.
[c] Reference 1.

teristic of this type of hydrogen-bonded complex, in particular of N_2--HF, OC--HF.

The evaluation of the anharmonicity constant x_{66} and g_{66} for HCN---HF are critically important for characterization of the bending force field of the complex. Although we have observed both ν_6^1 and $2\nu_6^0$ bands in the complex, the selection rule $\Delta l = 0, \pm 1$ results in the $2\nu_6^2$ overtone being weakly allowed so that we were not able to observe it. Thus it was not possible to directly evaluate g_{66} and x_{66}. However, estimations based on a first order approximate relationship between K_{466} and x_{66} enable evaluation of x_{66} and g_{66} as $-14.84(90)$ and $-31.04(90)$ cm^{-1}, respectively. It is interesting to compare these values with those predicted on the basis of recent *ab initio* molecular orbital calculations ($x_{66} = -51.3$ cm^{-1} and $g_{66} = 22.3$ cm^{-1}). The g_{66} values thus do not have either the same sign or absolute magnitude when compared with that evaluated in this experimental work. The majority of the anharmonicity constants experimentally evaluated in our previous work, however, compare remarkably well with corresponding predictions from these latter calculations.[4,5] There is an impetus to extend current experimental investigations to a wider range of overtones and combination bands. Such investigations would provide us with the precise data needed to quantitatively investigate the limitations of the second order approximation used to evaluate these anharmonicity constants and cross terms.

Finally, the observation and rovibrational analysis of the $2\nu_6^0$ band of $^1H^{12}C^{14}N$---$^1H^{19}F$ has enabled an evaluation of the equilibrium rotational constant B_e for this isotopic species. To our knowledge this is the first experimental evaluation of an equilibrium rotational constant for a hydrogen bonded complex. The primary uncertainty in evaluation of this constant is associated with the determination of the B_{ν_3} constant of this complex. Attempts are currently underway to reinvestigate the rovibrational analysis of the ν_3 fundamental. As expected the value of B_e [3681.1(11) MHz] is significantly larger than the corresponding value determined in the ground state B_0 [3591.187(18) MHz].

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