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The Spectroscopy and Molecular Dynamics of the High Frequency $\nu_1$ 6 Intermolecular Vibrations in HCN---HF and DCN---DF

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The spectroscopy and molecular dynamics of the high frequency v1 6 intermolecular vibrations in HCN---HF and DCN---DF

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Preliminary rovibrational analysis of the nν6+v1−nν6 vibration in HCN---HF
The spectroscopy and molecular dynamics of the high frequency $v_4$ intermolecular vibrations in HCN---HF and DCN---DF

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Gas phase rovibrational analysis of the high frequency intermolecular hydrogen bonded bending overtone $2v_4^0$ ($v_0 = 1132.4783(2)$ cm$^{-1}$) in HCN---HF and its corresponding perdeuterated fundamental $v_4^0$ ($v_0 = 409.1660(2)$ 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 $K_{66}$ and $K_{6666}$, and subsequently evaluation of the thermal functions of hydrogen bond formation $\Delta H^0_{298.2}$, $\Delta U^0_{298.2}$, $\Delta G^0_{298.2}$, and $\Delta S^0_{298.2}$. More recently, the rovibrational line profiles of $v_4$ and $v_4$ bands in HCN--HF have been reinvestigated using molecular beam optothermal spectroscopy.

The previous rovibrational analysis of the $v_4$ fundamental in HCN---HF resulted in the observation of a pronounced $R(J)$ bandhead associated with a large decrease in excited state rotational constant $B_4$ relative to the ground state $B_0$ ($B_4 - B_0 = -64.31(27)$ 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 $v_4^0$ band in the perdeuterated species DCN---DF together with the overtone $2v_4^0$ and its hot bands $2v_4^0 + v_4 - v_4^0$, $2v_4^0 + v_4 - v_4$ in HCN---HF, offer the opportunity of greater insights into the quantitative characterization of the molecular dynamics associated with this vibration. Furthermore, this $v_4^0$ intermolecular hydrogen-bonded vibration, together with the low frequency intermolecular stretching vibration $v_4$ 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 of more general relevance to corresponding effects in similar linear complexes such as N$_2$--HF and OC--HF.

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. A subsequent pulsed-nozzle Fourier transform microwave study 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 $v_4^0$ states in equilibrium gas phase mixtures (<7.5% of its ground state) prevented observation of their corresponding microwave spectra.

Infrared spectra of the intermolecular bending $v_4^0$ bands of HCN---HF and DCN---DF were first observed in the gas phase by Thomas 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. Previously, we have also observed overtones of the H--F stretching vibration $2v_4$, the H--C stretching mode $2v_2$, and the intramolecular bending vibration $2v_4^0$ in HCN--HF. In particular, it was possible to rovibrationally analyze both the $2v_2$ and $2v_4^0$ bands and some of their accompanying hot bands originating from the low frequency $v_4$ II state. In fact, the data available from rovibrational analyses in both the common and perdeuterated species HCN---HF has permitted the calculation of an approximate anharmonicity corrected stretching harmonic force field. Thus, these infrared investigations have provided more accurate values for the harmonic force constants governing the bending and stretching of the hydrogen bond.
In this paper, we report the spectroscopic analysis of the overtone in the high frequency intermolecular bending vibration $2v^2_6$ and its hot bands $2v^2_6 + v^1_4 - v^1_4$, $2v^2_6 + v^4_4 - v^4_4$ in HCN---HF. We also report the observation and rovibrational analysis of the intermolecular bending vibration $v^4_6$ in DCN---DF.

The unexpected $B^e$ value of $v^4_6$ HCN---HF is confirmed by rovibrational analysis of $2v^2_6$ HCN---HF and $v^4_6$ DCN---DF bands in the complex. The overtone spectrum of HCN---HF supplies the minimum rovibrational data needed to evaluate the quadratic ($K_{466}$) and quartic ($K_{6666}$) vibrational constants, as well as a one-dimensional, first order rotational constant expansion. It will be demonstrated that comparison of the one-dimensional effective rotational constant values of $B^e_6$ [defined in Eq. (6)], $\alpha^e_6$ and $\lambda^e_6$ with the experimentally determined counterparts are quite favorable. This indicates a degree of confidence in the $K_{46}$ 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 $K_{666}$, 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 $B^e_6$, vibrational dependence. Determination of $B^e_2v^2_6$ also provides the minimum information necessary to calculate the common isotopic species equilibrium rotational constant $B^e_6$ for this hydrogen bonded species.

**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 ($\approx 9 \times 10^6$ 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. 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 (>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$_3$PO$_4$ and D$_3$PO$_4$, respectively. The gases were loaded and mixed to the desired temperature by the circulation of liquid nitrogen cooled isotopentane 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 $+ \Sigma v^4_6$ 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, but the relatively low instrumental resolution precluded observation of its rotational fine structure. The $R$ branch in the $v^4_6$ 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 $B^e_6$ rotational constant. This feature is consistent with the results reported for the $v^4_6$ spectra of HCN---HF, indicating that the latter was not an artifact of Fermi resonance. The hot band $v^4_6 + v^1_4 - v^1_4$ of DCN---DF is shifted to lower frequency, with a pronounced $R$ bandhead occurring within the $P$ branch of the $v^4_6$ 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 data together with IR data of the $v_1$, $v_2$, and $v_3$ bands. Each datum was weighted by the

<table>
<thead>
<tr>
<th>Band</th>
<th>$2v^2_6$ (HCN---HF)</th>
<th>$v^4_6$ (DCN---DF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detector</td>
<td>HgCdTe</td>
<td>CuGe</td>
</tr>
<tr>
<td>Beam splitter</td>
<td>KBr</td>
<td>Mylar</td>
</tr>
<tr>
<td>Windows</td>
<td>CaF$_2$</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>Pressure</td>
<td>7.07 Torr</td>
<td>4.70 Torr</td>
</tr>
<tr>
<td>Temperature</td>
<td>241 K</td>
<td>238 K</td>
</tr>
<tr>
<td>Path length</td>
<td>100 m</td>
<td>64 m</td>
</tr>
<tr>
<td>Resolution</td>
<td>0.01 cm$^{-1}$</td>
<td>0.01 cm$^{-1}$</td>
</tr>
<tr>
<td>Scan time</td>
<td>48 h</td>
<td>40 h</td>
</tr>
</tbody>
</table>

**FIG. 1.** Partially resolved $R(J)$ bandhead in $v^4_6$ DCN---DF.
TABLE II. Rovibrational constants associated with \( v_6 \) in HCN---HF and DCN---DF.\(^a\)

<table>
<thead>
<tr>
<th>Rovibrational parameter</th>
<th>( v_6 ) (HCN---HF)</th>
<th>( v_6 ) (DCN---DF)</th>
<th>( 2v_6 ) (HCN---HF)</th>
<th>( 2v_6 + v_4 - v_6 ) (HCN---HF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_6 )</td>
<td>550.0285(1)(^b)</td>
<td>409.1660(2)</td>
<td>1132.4738(2)</td>
<td>1117.0862(8)</td>
</tr>
<tr>
<td>( B^* )</td>
<td>0.119 787 9(7)</td>
<td>0.111 807(1)</td>
<td>0.119 787 9(7)</td>
<td>0.120 828(3)</td>
</tr>
<tr>
<td>( D_0^* )</td>
<td>2.377(5) \times 10^{-7}</td>
<td>1.946(4) \times 10^{-7}</td>
<td>2.377(5) \times 10^{-7}</td>
<td>2.76(2) \times 10^{-7}</td>
</tr>
<tr>
<td>( \phi )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( 4.22(3) \times 10^{-4} )</td>
</tr>
<tr>
<td>( B' )</td>
<td>0.117 651 2(7)</td>
<td>0.110 434(1)</td>
<td>0.112 680(1)</td>
<td>0.113 847(3)</td>
</tr>
<tr>
<td>( D_0' )</td>
<td>2.801(5) \times 10^{-7}</td>
<td>2.172(4) \times 10^{-7}</td>
<td>2.54(1) \times 10^{-7}</td>
<td>2.32(2) \times 10^{-7}</td>
</tr>
<tr>
<td>( \phi' )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
<td>( 4.02(3) \times 10^{-4} )</td>
</tr>
<tr>
<td>( q_6 )</td>
<td>5.70(1) \times 10^{-5}</td>
<td>6.14(2) \times 10^{-7}</td>
<td>( \ldots )</td>
<td>( \ldots )</td>
</tr>
<tr>
<td>( \sigma^e )</td>
<td>0.000 47</td>
<td>0.000 76</td>
<td>0.000 47</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

\(^a\) All parameters in cm\(^{-1}\).
\(^b\) Uncertainties cited are one standard deviation as specified by fit.
\(^e\) \( \sigma \) = standard deviation.

Inverse square of the estimated uncertainty. Lower state combination difference frequencies were used to evaluate the lower state constants \( B_0, D_0 \) given in Table II. The transitions are fitted to the following expression for linear molecules:

\[
\nu = \nu_0 + B_0[J'(J' + 1) - I^2] + \frac{(1/q_6)}{[J'(J' + 1)] - D_0^*[J(J + 1) - I^2]^2] - B_0 J^* (J^* + 1) - D_0^*[J^*(J^* + 1)]^2.
\]

Where \( \nu_0 \) is the frequency of the band origin, \( B_0, D_0^* \) are the ground state vibrational constants, \( J \) is the angular momentum quantum number, \( q_6 \) is the torsional barrier constant, \( q_6 \) is the corresponding excited vibrational state constant, \( J \) is the upper state vibrational quantum number, \( J^* \) is the degeneracy factor, \( x_6 \) is the anharmonic constant, \( g_6 \) is the \( J \)-dependent term of the bending vibrational modes.

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 occur 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 \( Bv_6 \) 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 change in the moment of inertia. To obtain a quantitative assessment of this behavior, rotational constants of the overtone \( 2v_6 \) and its hot bands would be useful. Fortunately, it was possible to rovibrationally resolve and assign the overtone spectrum \((2v_6)\) of HCN---HF and assign it (Fig. 2). Along with the \( 2v_6 \) overtone bands, several hot bands were observed including \( 2v_6 + v_4 - v_6 \) and \( 2v_6 + v_4 - v_4 \). Both \( 2v_6 \) (\( \Sigma - \Sigma \)) and \( 2v_6 + v_4 - v_4 \) (\( \Pi - \Pi \)) are rovibrationally resolved and the results of their multiple linear regression fit are shown in Table II. The hot band \((2v_6 + v_4 - v_6)\) is not resolved but can be unequivocally identified by its characteristic \( v_6 \) 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

\[
G(v_1,v_2,...,v_T) = \sum_i \omega_i (v_i + d_i/2) + \sum_i \sum_j x_{ij} (v_i + d_i/2) (v_j + d_j/2) + \sum_{i,j} g_{ij} l_i l_j,
\]

where \( \omega_i \) is the harmonic frequency, \( d_i \) is the degeneracy factor, \( x_{ij} \) is the anharmonic cross term corrections, \( g_{ij} \) is the anharmonicity constants, and \( g_{ij} \) is the \( J \)-dependent term of the bending vibrational modes. Evaluation of the anharmonic cross terms \( x_{66} \) and \( x_{67} \) is thus possible. The latter constants are related to the observed band origins through the following expressions:

\[
2x_{66} = (2v_6^2 + v_4 - v_4) - (2v_6),
\]

\[
2x_{67} = (2v_6^2 + v_4^2 - v_4^2) - (2v_6^2).
\]

FIG. 2. Assigned rovibrational transitions in the \( 2v_6^2 \) 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 \textit{ab initio} molecular orbital calculations,\(^{17}\) \( x_{46} = -15.12 \) cm\(^{-1}\) and \( x_{67} = -13.38 \) cm\(^{-1}\).

The unexpected \( B_{v} \) value behavior is demonstrated in Table III for HCN--HF and DCN--DF. As one progresses to higher vibrational states in the bending mode \( \nu_{46} \), the rotational constants decrease. Our investigation of this anomalous characteristic is based on a quantum mechanical model described by Duckett \textit{et al.}\(^{18}\) The model Hamiltonian for large amplitude linear molecule bending vibrations is broken into a vibrational Hamiltonian of the form

\[
H_{\nu_{46}} = \frac{1}{2} v \mathbf{a}^2 + K_{66} q^2 + K_{666} q^4,
\]

where \( v \) is the fundamental frequency of the oscillator, \( K_{66} \) and \( K_{666} \) are the quadratic and quartic constants of the potential (with units of cm\(^{-1}\)), and \( \mathbf{a} \) and \( q \) 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 \( K_{666} \) 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 \( K_{666} = 4.98(12) \) 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\(^{18}\):

\[
H_{\text{rot/hc}} = B_0 \mathbf{J}^2 + ( - \alpha_2 \mathbf{q}^2 + \lambda_2 \mathbf{q}_2^2 ) \mathbf{J}^2.
\]

The constants to be determined are (i) \( B_0 \) 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) \( \alpha_2 \) which is the vibration-rotation interaction constant, and (iii) \( \lambda_2 \) 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 \( \mathbf{q}_2^2 \)—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

\[
B_{v,l} = B_0 - \alpha_2 \mathbf{q}^2 - \lambda_2 \mathbf{q}_2^2.
\]

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

<table>
<thead>
<tr>
<th>Band</th>
<th>HCN--HF ( \nu )</th>
<th>B(_{v,l})</th>
<th>DCN--DF ( \nu )</th>
<th>B(_{v,l})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ( \nu_4 )</td>
<td>0</td>
<td>0.119 789(1)</td>
<td>0</td>
<td>0.118 071(1)</td>
</tr>
<tr>
<td>1 ( \nu_4 )</td>
<td>550.0285(1)</td>
<td>0.117 651(1)</td>
<td>409.1660(2)</td>
<td>0.110 434(1)</td>
</tr>
<tr>
<td>2 ( \nu_4 )</td>
<td>1132.4738(1)</td>
<td>0.112 680(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Units cm\(^{-1}\).*
of the cubic force constant \( K_{g66} \) 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 \( K_{g66} \) (\( i \neq 4 \)) are not significantly larger than \( K_{g66} \). Ignoring the other cubic force constants in the equation yield a value of \( \Delta K_{g66} = -149.3(50) \text{ cm}^{-1} \). This evaluation gives the physical interpretation of anomalously \( B_{1i} \) dependence of the \( \nu_6 \) vibrational mode and an estimation of the anharmonic force constant \( x_{66} \).

The rather large negative value of the cubic force constant \( K_{g66} \) leads to the conclusion that there is a significant interaction between the high frequency hydrogen-bond bending mode \( \nu_6 \) and the low frequency hydrogen-bond stretching mode \( \nu_4 \). 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 \( B_{1i} \) 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). The \( 2\nu_6^2 \) band was not observed directly. Once again an expansion of a potential surface constant can be approximated by calculating 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 \( K_{g66} \), and the harmonic frequencies \( \omega_1 \) and \( \omega_2 \) is

\[
x_{66} = -\frac{1}{16}K_{6666} - \frac{1}{16} \sum_\tau K_{g66} \left( 8\omega_1^2 - 3\omega_2^2 \right) \omega_2(4\omega_1^2 - \omega_2^2).
\]

(10)

Noting that \( K_{6666} \) amounts to 4.98 cm\(^{-1} \) the coefficient \( (8\omega_1^2 - 3\omega_2^2)\omega_2(4\omega_1^2 - \omega_2^2) \) is considerably larger than the other coefficients leading to the approximation

\[
x_{66} \approx -\frac{1}{16}K_{6666} (8\omega_1^2 - 3\omega_2^2)/\omega_2(4\omega_1^2 - \omega_2^2).
\]

(11)

This result in the evaluation of \( x_{66} \) as \( -14.84(90) \text{ cm}^{-1} \). The calculation is based on \( \omega_1 = 185.8 \text{ cm}^{-1} \), 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 \( \omega_2 \) (\( >171.5 \text{ cm}^{-1} \)). This value gives \( x_{66} \approx -16.1 \text{ cm}^{-1} \) and \( g_{66} \approx 32.3 \text{ cm}^{-1} \) 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 \( g_{77} = -31.7(7) \text{ cm}^{-1} \), 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 \( i \)-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 (\( 2\nu_6 \)), 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 \( -14.84(90) \text{ cm}^{-1} \) leaves a \( g_{66} \) value of \( -31.04(90) \text{ cm}^{-1} \).

Again the values of \( x_{66} \) and \( g_{66} \) can be compared with corresponding predictions based on \textit{ab initio} molecular orbital calculations, i.e., \( x_{66} = 51.3 \) and \( g_{66} = -22.3 \text{ cm}^{-1} \), 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 \( (x_{66} - g_{66}) = -73.6 \text{ cm}^{-1} \). 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 \( B_{2v_6} \) now permits an estimation of the common isotopic equilibrium rotational constants \( B_i \) for HCN---HF using Eq. (8) and the available rotational constants given in Table V.

Within this approximation \( B_i \) for the common isotopic species of \( ^3\text{H}^1\text{C}^1\text{N} --- \text{H}^9\text{F} \) 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 \( B_i \) and extend the analysis of a sufficient number of other isotopic species thus providing the data for an effective \( r_{\text{e}} \) structure for this hydrogen bonded complex. (\(^9\text{F} \) coordinates cannot be isotopically substituted and would have to be evaluated by moment conditions.)

**CONCLUSIONS**

A rovibrational analysis of the \( \nu_6^1 \) fundamental in the perdeuterated isotopic species DCN---DF and the \( 2\nu_6^2 \) 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 \( \nu_4 \) and \( \nu_6^1 \) 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-
teristic of this type of hydrogen-bonded complex, in particular of \( \text{N}_2--\text{HF}, \text{OC}--\text{HF} \).

The evaluation of the anharmonicity constant \( \alpha_{66} \) and \( g_{66} \) for \( \text{HCN}--\text{HF} \) are critically important for characterization of the bending force field of the complex. Although we have observed both \( \nu_6^0 \) and \( 2\nu_6^0 \) bands in the complex, the selection rule \( \Delta l = 0, \pm 1 \) results in the \( 2\nu_6^0 \) overtone being weakly allowed so that we were not able to observe it. Thus it was not possible to directly evaluate \( g_{66} \) and \( \alpha_{66} \). However, estimations based on a first order approximate relationship between \( K_{466} \) and \( \alpha_{66} \) enable evaluation of \( \alpha_{66} \) 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 \textit{ab initio} molecular orbital calculations (\( \alpha_{66} = -51.3 \text{ cm}^{-1} \) and \( g_{66} = 22.3 \text{ cm}^{-1} \)). 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 \( \text{H}^{12}\text{C}^{14}\text{N}--\text{H}^{19}\text{F} \) 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 \( B_e \) constant of this complex. Attempts are currently underway to reinvestigate the rovibrational analysis of the \( \nu_6 \) 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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6. Compare Ref. 4(d).