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Preliminary rovibrational analysis of the $n\nu_6 + \nu_1 - n\nu_6$ vibration in HCN···HF

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A preliminary rotation-vibration analysis of the $n = 0$ and $n = 1$ subbands associated with the $n\nu_6 + \nu_1 - n\nu_6$ hydrogen-bonded vibration in HCN···HF has been completed. The following excited state rotational constants B' and band origin frequencies ν_0 have been determined for the complex.

States	ν_0/cm^{-1}	B'/cm^{-1}
$n = 0$	3716.20(2)	0.12206(5)
$n = 1$	3720.21(1)	0.12326(1)

The results are consistent with a rotation-vibration interaction constant $\alpha_1 = -68.3 \pm 1$ MHz which correlates with an excited state $r(N\cdots F)$ internuclear distance of 2.762 Å, a decrease of 0.034 Å relative to the ground state. Excited state lifetimes associated with assigned transitions are demonstrated to be $\geq 1.8 \times 10^{-10}$s while the x_{16} anharmonic constant is evaluated to be 4.01 ± 0.03 cm^{-1}.

INTRODUCTION

Spectroscopic investigations of fundamental X–H hydrogen-bonded vibrations in the near infrared[1,2] have not only played an important role in demonstrating the existence of such molecular complexes but have also provided information with which to probe numerous theories of hydrogen bonding.[3,4] In particular, the frequency shift of this vibration relative to the free HX stretching vibration, the corresponding increase in bandwidth often accompanied by submaxima and the enhancement of integrated intensity[3,4] have been pivotal in investigating dynamical theories of hydrogen bonding.[5,6] Experimental studies have, however, primarily been limited to the condensed phase or low resolution gaseous phase studies. This has thus restricted the extent of such analyses and placed severe restrictions on the investigation and assessment of relevant theoretical models including the Stepanov approximation,[7] coupling theories[8–10] and models of predissociation.[11,12]

In this paper, we report preliminary studies of the gaseous phase rotation-vibration spectrum of the $n = 0$ and $n = 1$ bands associated with the $n\nu_6 + \nu_1 - n\nu_6$ vibration in the common isotopic species of the hydrogen-bonded complex HCN··· HF using a single-frequency sequential-mode-hop color center laser spectrometer. Spectral assignment, evaluation of rovibrational parameters and transition linewidths relevant to relaxation line broadening processes will be discussed.

EXPERIMENTAL

Spectroscopic investigations were performed using a single-frequency sequential-mode-hop color center laser spectrometer (Fig. 1). A microcomputer system described previously[13] controls the synchronous tuning of grating and internal etalon in the Burleigh FCL-20 color center laser providing single-mode sequential-mode-hop scans over broad frequency ranges (≥ 100 cm^{-1}) at a

time with a resolution determined by the frequency separation between the adjacent longitudinal cavity modes (300 MHz = 0.01 cm^{-1}). For the frequency range of interest 3690–3730 cm^{-1} a KCl:Li crystal of the color center laser was pumped with 1.5 W single line 6471 Å output of a Spectra-Physics 171-01 Kr$^+$ laser. The 15–20 mW infrared output beam is directed into the evacuated diagnostic box where it is beam split. At the first beam splitter, part of the beam is passed through a high resolution spectrum analyzer (Burleigh CFT-500, 150 MHz FSR) which monitors the spectral purity of the laser output. The remainder of the beam is chopped before a second beam splitter directs part of the remaining beam through a marker cavity (Burleigh CF-25 3 GHz FSR) providing frequency markers every 0.100 cm^{-1}. A small subsidiary vacuum box containing a beam director is used to pass the last part of the beam (~4 mW) into the multireflection cell. This cell has 4 m physical length and can be adjusted to give effective absorption pathlengths up to 320 m. The vacuum box containing the beam director can also be filled with a reference gas at low pressure to provide a frequency calibration of the recorded spectrum. In the present case, water vapor was used for this purpose.[14] The beam exiting the multireflection cell is then detected by a PbS detector, the output signal of which is amplified and sent to a lock-in amplifier and recorder arrangement.

Gaseous phase mixtures of HCN and HF were prepared using corrosion resistent vacuum lines, vacuum gauges, and transfer vessels. All components were constructed from Teflon, brass, copper, calcium fluoride, and stainless steel.

The multireflection White cell was temperature controllable to -100 °C using an isopentane refrigeration system cooled by a liquid nitrogen Cryoson V temperature controller.
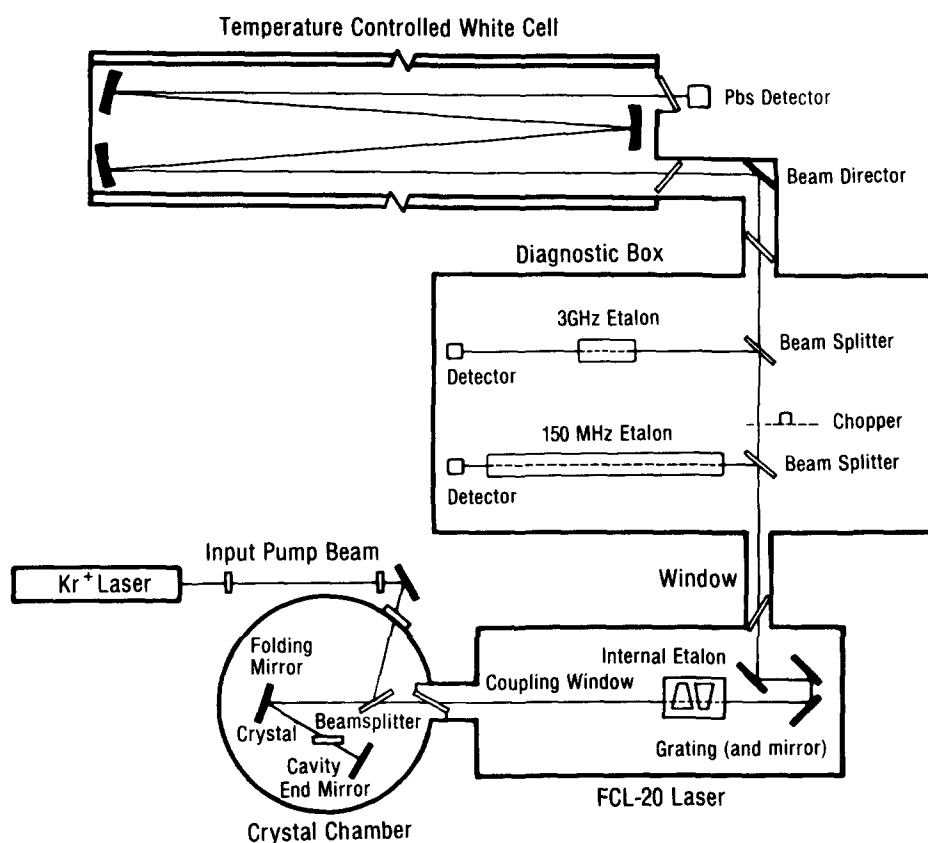
Temperature Controlled White Cell

Pbs Detector

Beam Director

Diagnostic Box

3GHz Etalon

Beam Splitter

Detector

150 MHz Etalon

Chopper

Beam Splitter

Detector

FIG. 1. Color center laser spectrometer used to record hydrogen-bonded spectrum.

Kr⁺ Laser

Input Pump Beam

Window

Folding Mirror

Internal Etalon

Coupling Window

Crystal

Beamsplitter

Cavity End Mirror

Grating (and mirror)

Crystal Chamber

FCL-20 Laser

RESULTS

Figure 2 illustrates the $n\nu_6 + \nu_1 - n\nu_6$ rotation-vibration spectrum obtained using the color center laser spectrometer in the frequency range 3707–3724 cm^{-1}. The spectrum was recorded at a total gaseous phase pressure of 0.5 Torr and a temperature of 213 K with an effective pathlength of 96 m. The P bandheads with maxima at 3710.06 and 3714.17 cm^{-1} have been assigned previously[15] at lower resolution. They are associated with rotation-vibration transitions from the ground vibrational state and first excited state of the low frequency hydrogen-bond bending vibration $\nu_6 \sim 70 \pm 24$ cm^{-1}. The heads were interpreted as arising because the ex-

3710   3715   3720   cm^{-1}

HCN----HF

n = 0   n = 1   n = 0

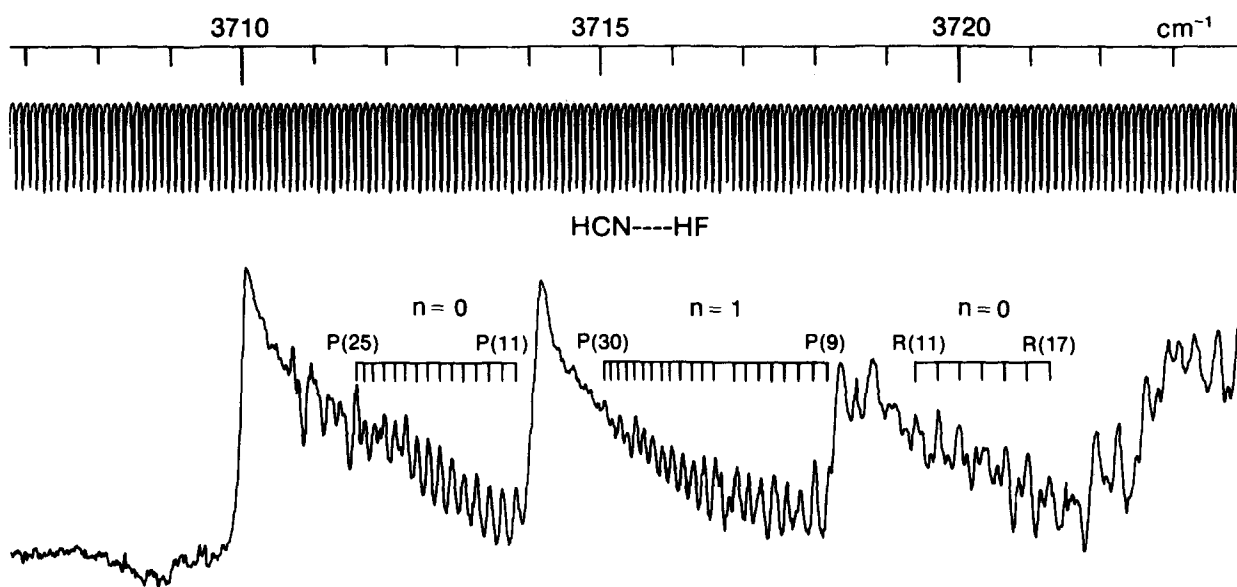P(25)   P(11)   P(30)   P(9)   R(11)   R(17)

FIG. 2. Part of the $n\nu_6 + \nu_1 - n\nu_6$ high resolution infrared spectrum in HCN···HF illustrating the partially resolved $P(J)$ and $R(J)$ branch transitions associated with $n = 0$ and $n = 1$ states. Total pressure 0.5 Torr, temperature 213 K and 96 m effective pathlength. Etalon markers are separated by 0.10 cm^{-1}, time constant 1s, scan time 15.1 min.

TABLE I. Rotational vibrational frequencies associated with $n\nu_6 + \nu_1 - n\nu_6$ vibration in HCN···HF.

| Transition | n = 0 Subband | | n = 1 Subband | |
	Obs. Freq.	Obs.−Calc.	Obs. Freq.	Obs.−Calc.
R(11)	3719.424	-0.10×10^{-1}		
R(12)	3719.744	$+0.11 \times 10^{-1}$		
R(13)	3720.032	-0.45×10^{-2}		
R(14)	3720.371	$+0.27 \times 10^{-1}$		
R(15)	3720.690	$+0.33 \times 10^{-1}$		
R(16)	3721.008	$+0.34 \times 10^{-1}$		
R(17)	3721.319	$+0.23 \times 10^{-1}$		
P(9)			3718.222	$+0.15 \times 10^{-1}$
P(10)			3718.010	$+0.63 \times 10^{-3}$
P(11)	3713.822	$+0.26 \times 10^{-2}$	3717.815	-0.68×10^{-2}
P(12)	3713.630	$+0.64 \times 10^{-4}$	3717.619	-0.60×10^{-2}
P(13)	3713.445	-0.47×10^{-4}	3717.441	-0.51×10^{-2}
P(14)	3713.260	-0.47×10^{-2}	3717.268	-0.99×10^{-2}
P(15)	3713.085	-0.39×10^{-2}	3717.090	-0.46×10^{-2}
P(16)	3712.919	$+0.13 \times 10^{-2}$	3716.923	-0.30×10^{-2}
P(17)	3712.754	$+0.29 \times 10^{-2}$		
P(18)	3712.584	-0.50×10^{-2}	3716.625	$+0.17 \times 10^{-1}$
P(19)	3712.429	-0.24×10^{-2}	3716.451	$+0.16 \times 10^{-2}$
P(20)	3712.275	-0.34×10^{-2}	3716.309	$+0.89 \times 10^{-2}$
P(21)	3712.135	$+0.50 \times 10^{-2}$	3716.160	0.44×10^{-2}
P(22)	3711.989	$+0.29 \times 10^{-2}$	3716.007	-0.90×10^{-2}
P(23)	3711.840	-0.68×10^{-2}	3715.878	-0.31×10^{-2}
P(24)	3711.714	$+0.20 \times 10^{-2}$	3715.746	-0.51×10^{-2}
P(25)	3711.582	$+0.17 \times 10^{-3}$	3715.627	$+0.11 \times 10^{-2}$
P(26)			3715.508	$+0.24 \times 10^{-2}$
P(27)			3715.393	$+0.31 \times 10^{-2}$
P(28)			3715.288	$+0.88 \times 10^{-2}$
P(29)			3715.170	-0.32×10^{-2}
P(30)			3715.065	-0.71×10^{-2}

cited vibrational state rotational constants B' are such that $B' - B'' \simeq 0.002$ cm^{-1} resulting in the convergence of $P(J)$ branch transitions to form the bandheads. Resolved rotation-vibration transitions associated with these bands are given in Table I. We were able to assign 15 $P(J)$ and 7 $R(J)$ branch transitions for $n = 0$ and 22 $P(J)$ branch transitions for $n = 1$ subbands, respectively. The observed linewidths of unblended assigned lines are $\sim 0.06-0.09$ cm^{-1} full width at half-maximum which placed severe limitations on our accuracy of transition frequency determination. We estimate the latter to be ± 0.010 cm^{-1} for unblended lines. The data were fit to the expression for a linear molecule

$$\nu_m^{P,R} = \nu_0 + B'(m + m^2) + B''(m - m^2) , \qquad (1)$$

where ν_0 is the origin frequency, B' and B'' the excited and ground vibrational state rotational constants, and $m = -J$ and $J + 1$ for $P(J)$ and $R(J)$ branch transitions, respectively. The latter transitions are partially blended and thus weighted at 0.083.

Results for two parameter fits are given in Table II using constrained B'' values previously determined from microwave spectroscopy.[16] Estimated errors are based on two standard deviations determined from the fits. Standard deviations of frequencies fitted to the assigned transitions are 0.014 cm^{-1}. We consider the quality and relatively limited number of transitions in our currently available data not to warrant incorporation of the two

additional distortion parameters D_J'' and D_J' in these constrained fits. It is pertinent to note that the observed linewidths combined with the available data results in some ambiguity over the spectral assignment despite the fact that the complex is linear. Independent of line assignment the difference $B' - B''$ of the rotational constants can be evaluated with high accuracy [0.002 278(3) cm^{-1} for $n = 0$ and $+0.002 43(1)$ for $n = 1$]. However, we ran several constrained fits varying the line assignment and chose that which gave the respective B'' constants closest to the corresponding values determined from microwave spectroscopy.[16] For the $n = 0$ subband, shifting the line assignment by one step (i.e., $m \to m + 1$) changes the B'' constant obtained by an amount $|\Delta B''|$ ~ 0.003 cm^{-1}, which corresponds to ten standard deviations. In the corresponding $n = 1$ subband, such a change correlates with one standard deviation. Consequently,

TABLE II. Molecular constants[a] for HCN···HF determined from $n\nu_6 + \nu_1 - n\nu_6$ analysis[b].

States	ν_0/cm^{-1}	B'/cm^{-1}
n = 0	3716.20(2)	0.12206(5)
n = 1	3720.21(1)	0.12326(1)
	$\alpha_1 = -68.3 \pm 1$ MHz	$x_{16} = 4.01 \pm 0.03$ cm^{-1}

[a]Estimated errors, two standard deviations in fits.
[b]Lower state constants from Ref. (16).

we are more confident about the assignment of the $n = 0$ subband than we are of the $n = 1$ subband. The reason for the poorer statistics in this latter analysis reflects our inability to assign $R(J)$ branch transitions resulting in a comparatively narrow m range. Furthermore, some of the $n = 1$ subband transitions are overlapped with lines from the $n = 0$ subband thus slightly shifting the measured peak frequencies. It is pertinent to note that a perturbation is probably responsible for the displaced $n = 1$ $P(17)$ transition.

The above assignments and derived molecular parameters (given in Table II) enable the determination of quantities important in characterization of the HCN⋯HF hydrogen bond. Application of the vibrational energy expression

$$G(v_1, v_2, v_3, \dots)$$
$$= \sum_i \nu_i[v_i + (d_i/2)] + \sum_i \sum_{k \geq i} x_{ik}\left[v_i + \left(\frac{d_i}{2}\right)\right]\left[v_k + \frac{d_k}{2}\right] \quad (2)$$

to the $n = 0$, $n = 1$ $n\nu_6 + \nu_1 - n\nu_6$ subband origin frequencies ν_0 enables evaluation of the anharmonic constant x_{16} as 4.01 ± 0.03 cm^{-1}.

The rotational-vibrational constant α_1 can be estimated using the expression

$$B_v = B_e - \alpha_i(v_i + d_i/2) \quad (3)$$

and is evaluated as -68.3 ± 1 MHz.

Relative intensity measurements on relatively unblended individual and corresponding $P(J)$ transitions in $n = 0$ and $n = 1$ subbands also provide an estimate of the low frequency double degenerate ν_6 bending vibration in the complex. The determined frequency of this vibration was 84 ± 19 cm^{-1} which compares with the previously estimated values of 70 ± 24 cm^{-1}, 90 ± 20 cm^{-1}, and 86.3 cm^{-1} determined from lower resolution infrared studies,[15] gaseous phase microwave intensity measurements,[16] and *ab initio* molecular orbital calculations.[17] These measurements provide independent confirmation of the assignment of the subbands as being associated with the $n\nu_6 + \nu_1 - n\nu_6$ vibration in the complex.

Although the variation of the ν_1, B' rotational constant with respect to the corresponding ground state value should strictly be interpreted in terms of anharmonicity it is interesting to fit its corresponding moment of inertia to excited state structural parameters of the complex. Assuming the monomer component parameters remain invariant on complex formation,[16] the r_1 $(N \cdots F)$ intermolecular distance can be estimated as $2.762(1)$ Å. This indicates a shortening of 0.034 Å relative to the corresponding ground state bond length.

Our observed linewidths are typically $0.06 - 0.09$ cm^{-1} ($1800 - 2700$ MHz) full width at half-maximum. These linewidths have been found invariant under the gaseous phase conditions used in current investigations which involved total pressure of 25 Torr at 300 K down to 0.5 Torr at 213 K. The results indicate excited state lifetimes $\geq 1.8 \times 10^{-10}$ s for the complex assuming that the relaxation line broadening full width at half-maximum is given by $1/\pi\tau$ and can be compared with previous results obtained at higher pressures.[15]

CONCLUSIONS

We have partially resolved the rovibrational spectrum of the $n = 0$ and $n = 1$ subbands associated with the $n\nu_6 + \nu_1 - n\nu_6$ vibration of the common isotopic species in HCN⋯HF at low pressure gaseous phase mixtures providing, in particular, complex parameters for the excited vibrational state. The band origins of the $n = 0$ and $n = 1$ subbands are shown to be 3716.20 ± 0.01 and 3720.21 ± 0.01 cm^{-1}. Thus, part of the information necessary to evaluate the anharmonicity corrected ν_1 fundamental frequency necessary for frequency shift correlations with bond length and bond strength,[4] force field calculations and comparison with the results of *ab initio* calculations,[17] has been determined.

If the interaction constant α_1 is used to interpret the excited state structure, it is consistent with an $r(N \cdots F)$ intermolecular distance of 2.762 Å. This is a 0.034 Å shortening of this bond length relative to the corresponding ground vibrational state value.[16] Sheppard[3] has previously explained this phenomena. In our case, it is considered as resulting from anharmonicity of the hydrogen-bonded F–H vibration causing the proton to move on average nearer to the nitrogen atom of hydrogen cyanide in the excited state consequently causing the hydrogen bond to become stronger. The corresponding α_1 constant is determined to be -68.3 MHz which compares with the α_3 value of $+61.79 \pm 0.03$ MHz determined from previous gaseous phase microwave results.[16]

Observed linewidths for the assigned transitions are typically $1800 - 2700$ MHz under our experimental conditions. The Doppler contribution to these lines is predicted to be ~ 162 MHz whereas the spectrometer bandwidth is determined by the 300 MHz frequency separation of adjacent longitudinal cavity modes. For the 0.5 Torr total pressure at which the spectrum in Fig. 2 is recorded, pressure broadening is expected to be less than 50 MHz. The remaining broadening could be contributed by overlapped unresolved transitions, but this is considered improbable for the particular complex under consideration. An alternative explanation is that the residual linewidth is primarily a consequence of the short excited state lifetime of $\sim 1.8 \times 10^{-10}$ s. This could be a consequence of fast intramolecular or predissociative relaxation. The latter effect has recently been the subject of considerable theoretical investigation.[11,12] As $\nu_1 = 3716.20$ cm^{-1} for HCN⋯HF, the absorbed photon energy is greater than the experimentally determined dissociation energies ($D_e = 2180$ cm^{-1}, $D_0 = 1581$ cm^{-1}) of the complex.[16] These excited states of the complex are thus metastable and predissociative line broadening could be an important consideration. Molecular beam and other spectroscopic experiments are currently in progress to make more definitive statements concerning this phenomenon and improve our currently available transition frequencies.

ACKNOWLEDGMENTS

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