High resolution spectrum of the v=1 Π state of ArHCN

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The molecular complex ArHCN shows extreme non-rigidity in the rotational spectrum of the ground vibrational state.[1-3] This state appears to be that of a linear molecule with very large zero point amplitude in the v_5 van der Waals bend. The most dramatic evidence for this interpretation is seen in the centrifugal distortion constants, $D(\text{ArHCN}) = 172.3$ kHz and $D(\text{ArDCN}) = 101.8$ kHz.[1] These constants are an order of magnitude larger than those of the prototypical species ArHCl, and their ratio is also an order of magnitude larger than the $D(\text{ArHCl})/D(\text{ArDCl})$ ratio.[4] This indicates that the quasiadiabatic separation usually effected between the bending and stretching coordinates is not possible because of a large angular–radial coupling. Regarding the HCN as a rigid rod, the dynamics of ArHCN are usually treated using the standard Jacobi coordinate system of centers of mass separation R and internal orientation θ. The minimum energy of the linear configuration ($\theta = 0°$) has a larger center of mass separation than the "tee" shaped configuration ($\theta = 90°$), which the strong angular–radial coupling argues is nearly isoenergetic. The nonrigidity is a consequence of motion along a path between these two structures.

Several experimental and theoretical studies of this system have focused on the properties of the excited vibrational states of ArHCN.[2,5,6,8] In addition, semiempirical treatments have been designed to fit the bizarre consequences of the nonrigidity of the ground state.[7] These lead to predictions of the properties of the excited bending states. In this letter, we present observations of the first excited Π bending state by millimeter spectroscopy.

The experimental apparatus is very similar to the spectrometer of Fraser et al.[9] It has three separate diffusion-pumped chambers. In the first chamber, a molecular beam is generated by adiabatic expansion and collimated with a 1.0 mm diam skimmer. Transitions are induced in a second chamber of 15 cm length. Microwave radiation from 2–300 GHz is focused into this chamber by means of a Teflon lens. The third chamber is occupied by a 100 cm long hexapole focuser with 6.35 mm diam rods and 11.4 mm diam central aperture. Nominal focusing voltages of 2–35 kV are applied. An x-y positioned 1.6 mm diam beamstop blocks the on-axis component of the molecular beam from entering the third chamber, preventing the nonfocused car-

rier gas from reaching the detector. The detector is a liquid helium-cooled bolometer (Infrared Laboratories), mounted on a vacuum-sealed x-y positioner.

In the present experiment, the beam of ArHCN is generated by a room temperature expansion of 2–3 atm. of $\frac{1}{2}$% HCN in argon through a circular nozzle of approximately 40μ diam. Radiation near 6 cm^{-1} is generated by doubling the output of a 3 cm^{-1} klystron, phase locked to a harmonic of a frequency synthesizer.[10] The frequency is modulated by applying a 200 Hz square wave to the phase-lock loop reference oscillator.

Resonances $P(2)-P(6)$, $Q(1)-Q(5)$, and $R(0)-R(2)$ are observed. A typical spectrum is shown in Fig. 1. Nearly all of the resonances were observed as enhancement of the bolometer signal, indicating that both halves of the *l*-doublet contain components with positive Stark coefficients. The molecular carrier and lower state rotational quantum numbers are ascertained by double resonance, using the precisely determined rotational transition frequencies of the ground vibrational state. The term values of the observed levels and their effective quadrupole coupling constants are given in Table I. For the Q branch lines, these are determined from the following energy expression:

$$E_\Pi/h = v_0 + B'[J(J+1) - l^2] - D'[J(J+1) - l^2]^2 + H'[J(J+1) - l^2]^3.$$

The values determined are $v_0 = 181\,984.410(11)$ MHz, $B' = 2031.3646(38)$ MHz, and $D' = 153.6(3)$ kHz.[11] ($H' = -0.1$ kHz is found in the fit but is highly correlated with D'.) These rotational constants may be compared to the ground state values $B = 1609.832(6)$ MHz and $D = 172.3(6)$ kHz.[1] The term values obtained from the P and R branch lines are fitted to the same expression with an added *l*-doubling term to account for Coriolis interaction with the nearby Σ_1 level,

$$\delta(J) = q_l J(J+1)/[1 + \Delta b J(J+1)] - q_D J^2(J+1)^2 + q_H J^3(J+1)^3,$$

where Δb is $(B_\Pi - B_\Sigma)/(E_\Pi - E_\Sigma)$. Holding B' fixed, the results are $q_l = 68.660(4)$ MHz, $\Delta b = 0.014\,84(6)$, $q_D = -101(3)$ kHz, and $q_H = -0.64(4)$ kHz, where q_D is highly correlated with Δb and with q_H.
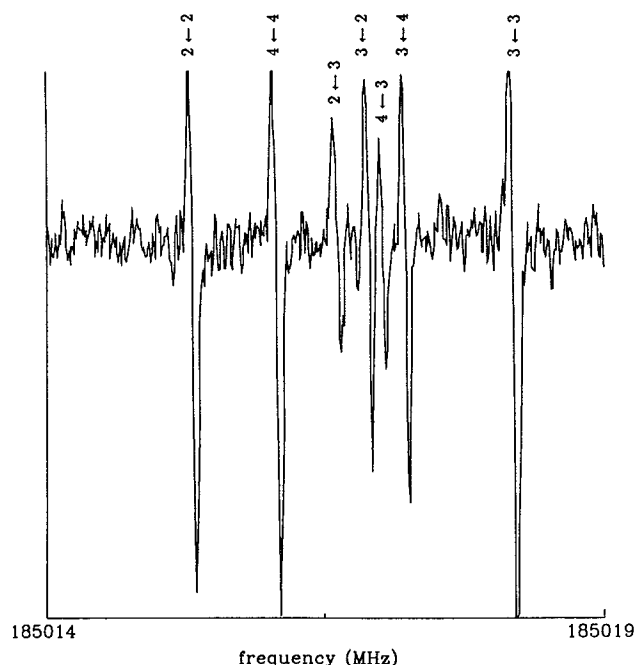
FIG. 1. The $Q(3)$ transition of ArHCN. The signal results from enhanced focusing of the upper state population, and appears with a first derivative line shape due to frequency modulation at a modulation depth of roughly 60 kHz. The apparent asymmetry in the lines is an artifact due to the lock-in offset and sensitivity. The spectrum shown is the average of three 250 s sweeps, using a 0.3 s time constant and 500 points. The F quantum numbers for each of the hyperfine components of the transition are given as $F' \leftarrow F''$.

We note that both q_l and Δb are positive, showing that the perturbing Σ_1 level lies below (we estimate by about $\frac{2}{3}$ cm^{-1}) and has a smaller rotational constant than the observed Π state. Since work is in progress to observe this state directly, we do not discuss in greater detail the frag-

TABLE I. Term values[a] and effective quadrupole coupling constants of the observed levels of Π $(j=1)$ state of ArHCN.

J	Parity	E(MHz)	$-\dfrac{eQq_J(2J+3)}{J}$(MHz)
1	+	184 015.621(16)	2.454(53)
1	−	184 149.404(16)P	− 3.284(50)
		184 149.393R^{b}	− 3.370^{b}
2	−	192 137.3800(54)	3.280(29)
2	+	192 519.1673(22)P	− 2.372(11)
		192 519.167(22)R	− 2.416(95)
3	+	204 310.6931(21)	3.510(11)
3	−	205 023.5914(22)P	− 2.082(11)
		205 023.5926(29)R	− 2.065(14)
4	−	220 524.1621(33)	3.578(17)
	+	221 618.5495(84)P	− 1.876(40)
5	+	240 762.1891(42)	3.600(23)
5	−	242 261.514(25)P	− 1.796(42)

[a]The lower state rotational energies are conveniently given by Bumgarner and Blake (Ref. 3), and by Fraser and Pine (Ref. 5). We believe that no errors are incurred by giving the Π state term values rather than the observed spectral transition frequencies [with the exception of the level $J=5$ −, where the lower energy uncertainty is slightly greater than that of the $P(6)$ transition frequency].

[b]The three lines observed for $R(0)$ do not allow a meaningful statistical uncertainty to be obtained.

mentary data available from the l doubling. The Stark coefficients of the Π state are being measured as well.

The quadrupole hyperfine structure of the transitions is well resolved, as seen in Fig. 1. Using the $K=1$ asymmetric top formalism,[12] the quadrupole coupling constants are fit in the Q branch levels with $eqQ_{aa}=0.836(28)$ MHz, $\eta = -6.88(25)$, and in the P and R branch levels with $eqQ_{aa}=1.035(28)$ MHz, $\eta = -5.48(14)$. These values give $\langle P_2(\cos\theta)\rangle = -0.177(6)$, "$\theta$" $= 62.3$ or $117.7 \pm .1°$ (Q branch levels), and $\langle P_2(\cos\theta)\rangle = -0.220(6)$, "$\theta$" $= 64.4$ or $115.6 \pm 0.1°$ (P and R branch levels). As noted above, the P and R branch levels are perturbed by Coriolis interaction with the very nearby Σ_1 level, which is probably the origin of the slight difference in average alignment angle. The vibrationally averaged structure is 27° from $\theta = 90°$, which is clearly compatible with zero point oscillation about a roughly "tee" shaped configuration. The results are in very good agreement with the predictions of Yaron[7] [B_{Π}(geometric) $= 2079$ MHz, $E_{\Pi}=5.3$ cm^{-1}] and those of Clary[6] [B_{Π}(geometric) ≈ 2025 MHz, $E_{\Pi}=6.6$ cm^{-1}, $\langle P_2(\cos\theta)\rangle = -0.137$]. The dramatic increase in B over the ground state value indicates the predicted contraction of the van der Waals bond upon excitation of the Π bend. Therefore, the very soft potential with large angular–radial coupling for ArHCN is fully established by these observations.

We briefly comment on the difference between the present results and those of the important experiment of Fraser and Pine,[5] where the Π state was observed in combination with the 3311.5 cm^{-1} v_1 C–H valence vibration. These authors point out that the v_1 is redshifted by 2.7 cm^{-1} from the v_1 of free HCN. For the ArHCN v_1 fundamental, the relevant molecular geometry is approximately linear (i.e., θ small) and the van der Waals bond is principally an Ar–H bond, as it is in the ground state. On the other hand, in the combination state $v_1 + v_5$, the Ar lies off the C–H bond axis (i.e., $\theta \approx 90°$) and is presumably interacting with the C–N π^* electron system. One may therefore expect that the C–H stretching mode of the HCN subunit will be more strongly perturbed by interaction with the argon in the v_1 state than it is in the $v_1 + v_5$ state.[13] If excitation of the C–H stretch does not greatly alter the intermolecular potential in the configuration space sampled by $v_5 = 1$, one would anticipate the B values for the v_5 and $v_1 + v_5$ states to be the same. This may be observed with a small reassignment of the spectrum measured by Fraser and Pine. The five lines originally assigned to the R branch are now assigned to the Q branch, with the same ground state J assignments (which were established by double resonance). This gives the band origin of the $v_1 + v_5$ mode as 3316.845 23(15) cm^{-1}, the rotational constant $B=2018.58(47)$ MHz, and the distortion constant $D=201(10)$ kHz. This reassignment now places the 3316.5 cm^{-1} lines, previously assigned to the Q branch, near the predicted P branch bandhead of 3316.54 cm^{-1} [the $P(4)$ line], assuming the l-doubling constants to be the same in the $v_1 + v_5$ as in the v_5. The difference between the $v_1 + v_5$ and v_5 band origins is 3310.8 cm^{-1}, which corresponds to a redshift of only 0.7 cm^{-1} from the free HCN

when the complex is "tee" shaped. The similarity of the B and D values for the Π bend with and without the C–H stretch, under this reassignment, supports this interpretation.

This work establishes that use of the Fraser type spectrometer for millimeter spectroscopy produces very high resolution spectra with linewidths far below Doppler. The ArHCN system indeed has a very flat intermolecular potential with large coupling of the angular and radial coordinates along the minimum energy contour. Its properties are in very good agreement with previous theoretical and semiempirical models. The frequency of the bending mode ν_5 is 30% larger in combination with the valence C–H stretching vibration than in the fundamental, although the rotational constants are virtually identical.

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