The intensities of HCN overtone transitions from 12 600–18 400 cm$^{-1}$ a)

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The absolute intensities of 12 visible overtone bands of HCN have been determined using intracavity photoacoustic detection and a long pathlength absorption cell. The relative intensities of nine of these weak overtone bands (from 14 600–18 400 cm$^{-1}$) were obtained by using intracavity photoacoustic detection. The absolute intensity of the (0,0,5) band, obtained previously using a multipass cell with an optical pathlength×pressure of about 34 km Torr, was used to calibrate the photoacoustic response, and thus to obtain the absolute intensities for eight more HCN overtone bands. The absolute intensities of three HCN overtone bands between 12 600–13 800 cm$^{-1}$ were measured using a multipass cell. Optical pathlengths×pressure from 10 to 15 km Torr were used for these three bands. The band origins in cm$^{-1}$, the band labels (CN, bend, CH), and the intensities in cm/mole are: 12 636, (0,0,4), 154(3); 12 658, (3,0,2), 9.7(3); 13 702, (2,0,3), 3.1(2); 14 654, (4,0,2), 8.0(4); 14 670, (1,0,4), 7.2(4); 15 552, (0,0,5), 17.5(4); 15 711, (3,0,3), 0.05(1); 16 164, (0,1,5), 0.047(8); 16 640, (5,0,2), 0.40(4); 16 674, (2,0,4), 1.7(1); 17 550, (1,0,5), 13.9(4); 18 377, (0,0,6), 2.4(2). This work represents the most complete study to date of the overtone intensities of a polyatomic molecule. We have shown that the typical method of intracavity laser power correction is likely to introduce serious errors in relative intensity measurement. We also have found evidence, namely the anomalously large intensity of the (1,0,5)–(0,0,0) transition, for the breakdown of the typically invoked bond-dipole model for overtone and combination band intensities. As well as discussing the astronomical interest in predicting overtone intensities of HCN, we present a thorough comparison of the measured absolute overtone intensities with ab initio results.

INTRODUCTION

Reliable measurements of overtone intensities exist for very few molecules, especially the polyatomics. The large body of intensity data presented here for HCN represents the most complete measurements of overtone intensities for a polyatomic. In addition, these can be directly compared to the recent ab initio results of Botschwina.1

Combining this intensity data to the vast collection of highly accurate frequency data2–5 on vibration–rotation bands of HCN from the infrared to the visible, makes the determination of a semiempirical dipole moment function for HCN much more feasible. An attempt has previously been made to deduce a dipole moment function for HCN from the measured intensities of some of the infrared transitions and the observed vibrational dependence of the dipole moment function.6 Several attempts have also been made to calculate this function by ab initio methods.1,7 Because the harmonically forbidden overtone bands are so weak, gaining what intensity they have from mechanical and electrical anharmonicity, predicting their intensities offers a substantial challenge to the theorist.

Using CEPA-1 (ED), Botschwina has recently calculated the intensities and dipole moments for the stretching states of HCN with up to 20 000 cm$^{-1}$ of vibrational energy.1 The agreement with our absolute intensities and his ab initio predictions is quite impressive. In addition to only modeling the two stretches (ignoring the bend), Botschwina has used empirical data, such as the fundamental vibrational frequencies and bend–stretch anharmonicity constants to obtain an improved potential. Since nearly all of the bright states in the visible region involve only the stretching quanta, his calculation is clearly the best choice to compare to our results.

Jørgensen et al. have carried out a much more ambitious, purely ab initio, calculation, which includes the bending quanta. Their motivation for this is astrophysical, as it has been proven7,8 that the weak “veil”-like structure that the many combination, overtone, and hot bands of HCN produce at the high temperature of a stellar atmosphere, is one of the most important—if not the most important—absorber governing the structure of the upper layers in cool carbon-rich stars. Comparing the observed and calculated intensities in this case will provide knowledge concerning the feasibility of calculating, to a sufficient accuracy, the absorption coefficient of the spectrum forming regions of stars near the end stages of their life (where three- and four-atomic molecules seem to govern the structure of the upper layers of the stars). It is these considerations that were the motives for initiating the measurements presented here.

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b) National Science Foundation Predoctoral Fellow.

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Local mode theory has been successful in predicting the energy levels and at least qualitatively, the intensities, of the overtones of simple molecules like HCN with a CH oscillator. The general picture of the intensities of the observed levels is that the CH oscillator carries almost all of the oscillator strength gained from anharmonicity. Combination bands draw their intensity by intensity borrowing from the nearby pure CH stretching states. Even when there is strong mixing due to anharmonic resonance, this model has proven useful. However, we present here the first reported evidence that this local mode model fails to predict the qualitative ordering of the intensities; \((1,0,5) \approx (0,0,5) > (0,0,6) > (1,0,5)\).

By using two experimental techniques: conventional absorption spectroscopy using a multipass cell and the much more sensitive intracavity photoacoustic spectroscopy, we are able to report the intensities of nearly all of the expected bands of HCN in the visible region. The absolute intensity of the three reddest bands were determined using the multipass cell. One more absolute intensity measurement using the multipass cell was performed on the strongest of the remaining visible bands, the (0,0,5). This measurement served as a calibrant of the photoacoustic cell response. Intracavity photoacoustic spectroscopy, because of its much greater sensitivity, was used to measure the relative intensity of the (0,0,5) and the rest of the bands. Since it was necessary to accurately correct for the intracavity power to obtain accurate relative intensities, care was used in finding a viable method. We discovered that the standard method of intracavity laser power correction (i.e., reflection off of a Brewster window or other optics in the cavity) is likely to introduce substantial errors. Because the large intensity of the (1,0,5) band (almost as intense as the (0,0,5) band) was unexpected, we did not realize the feasibility of measuring its absolute intensity using the multipass cell until after the experiments were completed and the data analyzed.

With this large body of intensity data presented here, HCN may prove to be a useful intensity calibrant for obtaining intensity data for other molecules using solely photoacoustic spectroscopy.

EXPERIMENTAL DETAILS

White cell experiments (12 600–18 800 cm⁻¹)

For labeling the HCN transitions, we follow the convention of Herzberg. That is, \(v_1\) is the CN stretch, \(v_2\) is the bend, and \(v_3\) is the CH stretch. The transmission spectra of the (0,0,4), (3,0,2), and (2,0,3) bands were obtained using a multipass cell as described by White and a Coherent Autoscop model 699/299 ring dye laser pumped by a Kr⁺ laser. The dye laser was mechanically chopped at about 500 Hz. The laser light before (laser power) and after the White cell (transmitted laser light) were detected with photodiodes (EG&G SGD 040L), whose signals were sent to two separate lock-in amplifiers. The transmitted laser light was ratioted by the laser power using an analog divider and then read by a 12 bit A/D attached to the Apple IIe used to scan the laser and store the data. Zero transmission was determined by blocking the laser input to the White cell. The HCN pressure in the White cell was 50.7 Torr, as measured with a MKS baratron capacitance manometer (Type 222B, 1000 Torr sensor head). The HCN (Fumico, Inc.) had a claimed purity of 99% and was used as obtained.

The White cell, constructed from a glass pipe and three mirrors cut from half of a round telescope mirror, had a base length of 3.048(5) m. One hundred passes [or an optical pathlength, \(l = 304.8(5)\) m] of the laser light were used for the (2,0,3) band, and both 72 and 80 passes [\(l = 219.5(4)\) and 243.8(4) m] were used to measure the (3,0,2) and (0,0,4) band intensities.

Photoacoustic experiments (14 600–18 400 cm⁻¹)

Overview of photoacoustic scans

The absorption spectra of nine weak overtone bands of HCN, the (4,0,2), (1,0,4), (0,0,5), (3,0,3), (0,1,5), (0,5,2), (2,0,4), (1,0,5), and (0,0,6), were recorded using intracavity photoacoustic detection in the extended cavity of a standing wave cw dye laser pumped by a visible Ar⁺ laser. The details of the laser scanning, three channel data storage, and the photoacoustic technique have been discussed previously. Briefly, three tuning elements control the laser frequency and provide a narrow (< 400 MHz) linewidth. The pump laser is mechanically chopped at the resonant frequency of the longitudinally resonant photoacoustic cell.

The photoacoustic spectra were taken with about 30 Torr of HCN and 170 Torr of neon in the cell. Our reasons for choosing this particular mixture over pure HCN were twofold. Firstly, we had observed a fivefold increase in the trifluoromethane photoacoustic signal when using a 20/200 Torr mixture of CF₃H/Ne rather than 20 Torr of pure CF₃H. Secondly, we have previously observed pressure narrowing of ammonia overtone resonances for a mixture of about 15/170 Torr of NH₃/Ne.

The (0,0,5) band was chosen to calibrate the photoacoustic response, since it is the strongest band in the 14 600–18 400 cm⁻¹ region and we had previously measured the absolute intensity of this band using a multipass cell. This calibration is only applicable for a given gas mixture, microphone and photoacoustic cell, so several photoacoustic scans of the (0,0,5) band were performed as needed. (See, e.g., Table I.)

Calibration for obtaining relative intensities

The nature of the photoacoustic signal. The intracavity photoacoustic technique provides the sensitivity needed to observe these very weak overtone transitions, (the weakest band measured, the (0,1,5) perpendicular band, is about 10⁴ times weaker than the CH stretching fundamental, which has an intensity of about 60 km/mol), but must be carefully calibrated to be quantitative. The strength of a photoacoustic signal depends on many parameters. Most of these parameters; such as the vibration-to-translation, rotation relaxation rate of the excited vibration–rotation state, the specific heat of the sample, the heat conductivity of the cell walls, and the microphone sensitivity, are generally unknown. However, the vibration-to-vibration relaxation rates
are much faster than the vibration-to-translation relaxation rate and the modulation frequency, so that vibrational equilibrium is reached for each of the overtone bands before the photoacoustic signal is produced. Thus, for a given cell, microphone, and gas mixture, the photoacoustic signal only varies with the strength of the transition and the intracavity laser power.

**Intracavity laser power determination.** The intracavity photoacoustic signal must be divided by the instantaneous intracavity laser power in order to obtain relative band intensity information. To monitor the intracavity laser power during a scan, one option is to measure the reflected light from a brewster window in the cavity, such as on the photoacoustic cell itself. The power in this reflection is very small; under ideal conditions, it is zero. The light that is reflected arises from nonidealities, such as; dust and films on the window, deviation of the window orientation from exactly brewster angle, and deviation of the laser polarization from exactly linear. With this knowledge, we were apprehensive to use this method before testing it.

Thus, we performed a simple test: the photoacoustic cell was placed outside the cavity of the laser, a thermopile (Coherent model 210) measured the power of the laser light transmitted through the cell, and a photodiode power meter (Spectra-Physics model 404) measured the laser power reflected in two well-separated spots from one of the 3 mm thick brewster windows on the cell. The laser was scanned at low resolution (about 1 cm⁻¹ linewidth). If the brewster reflection power measurement method was viable, the ratio between the two detector signals would be constant with wavelength. On the contrary, however, interference fringes with a free spectral range of 9.7 cm⁻¹ were observed (Fig. 1). It should be emphasized that the two spots from the brewster window could not possibly interfere since they were separated by at least 3 spot diameters. Furthermore, the free spectral range of interference fringes from a 3 mm thick quartz brewster window is 2 cm⁻¹, or about five times less than what was observed. The peaks and valleys of the observed fringes varied by 33% from the mean ratio. It is unlikely that those using this method of intracavity power correction could produce any reliable quantitative result.

As an alternative power correction method, we chose to monitor the extracavity laser power during a high resolution scan. This was done with a photodiode power meter (Spectra-Physics model 404) whose wavelength response \( S(\lambda) \) was calibrated using a thermopile (Coherent model 210). Then, we determined the transmission curves \( T(\lambda) \) of the each appropriate output coupler over the wavelength range of the band of interest by obtaining an additional set of output couplers that would allow the laser to lase in the appropriate wavelength regions and a very sensitive power meter (Coherent 212) for measuring the light transmitted through the output couplers. Given both \( S(\lambda) \) and \( T(\lambda) \), the true intracavity power can be deduced from the measured extracavity power.¹⁴

**Applying the calibration factors.** Before applying any of the calibration factors, the "band intensities" (B₁), in units of A/D number • cm⁻¹, were calculated from the fits to the photoacoustic data according to Eq. (1) of Ref. 12. The true relative band intensities were then calculated by solving for (signal/intracavity power) in an expression involving the "band intensity" and several calibration factors.¹⁵

**DATA PROCESSING**

**White cell data: (0,0,4), (3,0,2), and (2,0,3) bands**

The logarithm of the measured transmission intensities, corrected for the zero transmission offset, was taken to obtain the absorption intensities. A nonlinear least-squares fitting routine using a finite difference Levenberg–Marquardt algorithm¹⁶ was used to fit the absorption intensities to a four-parameter (height, half-width at half-maximum, center frequency, and base line) Lorentzian model. Most of the (3,0,2) lines fell in the wings of the approximately 15 times more intense (0,0,4) lines. In such case, various fitting methods were tried to extract the best fits of the (3,0,2) resonances. One method used was to fit the two lines with seven parameters to the sum of two Lorentzians having a common base line. Another method tried was to first fit the larger (0,0,4) transition to a four-parameter Lorentzian, excluding in the fit the tail containing the weak (3,0,2) transition. Then the fitted intensity of the (0,0,4) resonance was sub-

![FIG. 1. Interference fringes observed when monitoring (extracavity) (brewster window reflected power/transmitted power). See the text for further details.](image1)

![FIG. 2. The logarithm of the transmission intensity (absorption intensity) of the \( R(17) \) line of the (0,0,4)→(0,0,0) band of HCN and the Lorentzian fit to the absorption data. \( P = 50.7 \) Torr, \( T = 290 \) K, \( I = 219.5 \) m. The observed-minus-calculated residuals are shown at the bottom and offset for visibility.](image2)
TABLE I. Experimental intensities and error analysis.

<table>
<thead>
<tr>
<th>B and</th>
<th>Absolutenumber of lines used to determine the final intensity</th>
<th>( \sigma_{n-1} ) sample s.d.</th>
<th>( \frac{%\sigma_x}{x} = \frac{%\sigma_{n-1}}{\sqrt{n}x} ) percent s.d. of the mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>White cell data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,5)</td>
<td>17.5</td>
<td>14</td>
<td>0.80</td>
</tr>
<tr>
<td>(0,0,4)</td>
<td>154</td>
<td>16</td>
<td>6.5</td>
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<tr>
<td>(3,0,2)</td>
<td>9.7</td>
<td>4</td>
<td>0.32</td>
</tr>
<tr>
<td>(2,0,3)</td>
<td>3.1</td>
<td>3</td>
<td>0.16</td>
</tr>
<tr>
<td>Photoacoustic data</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First calibration scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,5)</td>
<td>17.5</td>
<td>10</td>
<td>0.20</td>
</tr>
<tr>
<td>(1,0,4)</td>
<td>7.2</td>
<td>10</td>
<td>0.64</td>
</tr>
<tr>
<td>(4,0,2)</td>
<td>8.0</td>
<td>10</td>
<td>0.59</td>
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<tr>
<td>Second calibration scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,5)</td>
<td>17.5</td>
<td>10</td>
<td>0.42</td>
</tr>
<tr>
<td>(0,0,4)</td>
<td>2.4</td>
<td>6</td>
<td>0.18</td>
</tr>
<tr>
<td>(2,0,4)</td>
<td>1.7</td>
<td>14</td>
<td>0.12</td>
</tr>
<tr>
<td>(5,0,2)</td>
<td>0.40</td>
<td>2</td>
<td>0.03</td>
</tr>
<tr>
<td>(3,0,3)</td>
<td>0.05</td>
<td>3</td>
<td>0.009</td>
</tr>
<tr>
<td>(0,1,5)</td>
<td>0.047</td>
<td>10</td>
<td>0.012</td>
</tr>
<tr>
<td>Third calibration scan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0,0,5)</td>
<td>17.5</td>
<td>11</td>
<td>0.51</td>
</tr>
<tr>
<td>(1,0,5)</td>
<td>13.9</td>
<td>13</td>
<td>0.32</td>
</tr>
</tbody>
</table>

tracted from the observed intensity, leaving the (3,0,2) resonance, which was subsequently fitted to its own four-parameter Lorentzian. Thirdly, plain four-parameter Lorentzians were tried for the more isolated (3,0,2) resonances, still excluding in the fit the tail nearest the (0,0,4) transition. Best fits were chosen to calculate the band intensity based on the overall sigmas of the fits and the resultant uncertainty in the height × half-width, since this quantity is proportional to the integrated line intensity. In general, the second method, involving first subtracting off the fitted (0,0,4) transition intensity, performed the best. Data points occurred every 35 MHz, so for a typical line, about 400 points were used in the fit if it extended four half-widths to either side of the center frequency. Figure 2 shows a typical fit to the (0,0,4) White cell data. The rotational assignment of these three bands was taken from Douglas and Sharma.2

The integrated band intensity in cm/mol was calculated from each integrated line intensity according to Eq. (1) of Ref. 12. In the first section of Table I, the absolute intensities determined from the White cell data and statistical information, such as the number of lines used to find the mean or final intensity and the sample standard deviation, are given.

Photoacoustic data: The rest of the bands

The photoacoustic data was fit in the same manner as the White cell absorption data. We compared fits which differed in the number of data points included in the fit (fits extending 6–15 half-widths from the center frequency were performed) and found that for isolated lines, the band intensities derived from the different fits differed by at most 2%–3% and that this variance was lower than the variance due to a different set of measurements. A typical accepted fit, exhibiting one of our best signal-to-noise photoacoustic spectra, is shown in Fig. 3. Figure 4, finally, shows the accepted fit to three lines of the weakest band measured photoacoustically and, hence, illustrates the quality of our poorest signal-to-noise ratio.

For most of these bands, the rotational assignments

![Absorption spectrum](attachment://absorption_spectrum.png)

FIG. 3. Absorption spectrum, recorded photoacoustically, of the R(10) line of the (0,0,5)–(0,0,0) band: 30 Torr HCN; 170 Torr neon. The observed-minus-calculated (Lorentzian fit) residuals are shown at the bottom. The structure in the residuals reflect the fact that the true line shape is neither Lorentzian nor Voigt because of the effect of motional narrowing on the Doppler profile (Ref. 17). A Voigt fit would produce residuals of the opposite phase to those shown here.
were taken from Lehmann, Scherer, and Klemperer. The assignments for the (4,0,2) and (1,0,4) anharmonic resonant pair were taken from Ref. 2 and the assignments for the (0,1,5)−(0,0,0) Q-branch lines were derived using the molecular constants for the Π−Π hot band (0,1,0)−(0,1,5) and the constants for the (0,0,0)−(0,1,0) band. The absolute integrated band intensities for the bands scanned photoacoustically were determined from the true relative band intensity for the appropriate (0,0,5) calibration scan, the true relative band intensity for the band of interest, and the absolute intensity of the (0,0,5) band determined in a White cell experiment described in Ref. 12.

The section labeled “photoacoustic data” in Table I lists the absolute intensities and statistical information for the bands scanned photoacoustically. The bands are grouped according to which (0,0,5) calibration scan they belong to. This organization is useful for determining the final reported error in the intensities, since the error in the particular (0,0,5) calibration scan contributes to the final error for the band of interest. In addition, the error for the (0,0,5) White cell result also contributes to the final error. The final error (that reported in Table II as ± two standard deviations of the mean) for the intensities determined photoacoustically was calculated by adding in quadrature the percent standard deviation of the mean (last column of Table I) for the (0,0,5) White cell result, the appropriate (0,0,5) photoacoustic calibration scan result, and that for the band of interest.

RESULTS AND DISCUSSION

The local mode model for overtone and combination band intensities is based upon the familiar bond dipole approximation, namely

$$\mu(r_1, r_2) = \mu_1(r_1) + \mu_2(r_2).$$

The physical basis for this approximation is that if the bonding does not change in one bond as the other is stretched, then the cross terms will be small. Since the force constants of C−H and C−N are not very different than the corresponding force constants in HCN, one would expect this to be a good approximation for HCN. Under this bond dipole approximation, in the basis of local mode states, only pure local mode states, (n,0) and (0,m), have nonzero transition moments. Because at the same energy in the visible, the pure C–N overtone will be higher in overtone quanta and since the C–N stretch is of much smaller amplitude and is thus expected to be much more harmonic, it is traditional to neglect its transition moment, and to assign all of the observed as coming from the sequence of states (0,n). Empirical evidence suggests that each successive overtone is about a factor of 10 weaker for most first and second row hydrides. The intensity of bands assigned to combination states (n,m) are predicted to arise from mode mixing with nearby pure overtone states. Thus the combination bands are expected to be always weaker than the nearby pure overtone states and only similar in intensity if there is a strong anharmonic resonance between the states.

An unexpected experimental result, which violates the bond dipole approximation prediction that (0,5) > (0,6) > (1,5), is that the (1,0,5) band is almost as intense as the (0,0,5) band, and is much stronger than the (0,0,6) band, the pure CH state to which it is closest in energy. Because this intensity anomaly was so unexpected, we repeated the measurement of this band, using another photoacoustic cell and a different output coupler optimized for that region. After the (0,0,5) calibration scan was repeated and the new calibration factors accounted for, a similar intensity was found. Note that the (1,0,4) band is also stronger than expected, when one adds the intensity of the (1,0,4) and (4,0,2) states since they share the true (1,0,4) intensity by anharmonic resonance. But the effect is not nearly as striking as the (1,0,5) intensity. In the fit of Douglass and Sharma to the vibrational spectrum of HCN, they found that the discrepancy between the observed and calculated band origins for the (1,0,5) was 5−10 times larger than for the other overtone bands in this region.

Both of these observations probably reflect a strong resonance between the C−N and C−H modes at this energy. Such a resonance was found in classical trajectories run on an HCN potential at this energy. But such a resonance by itself would not result in the (1,0,5) state being stronger than the (0,0,6) state. This anomaly is the only strong deviation from the local mode intensity model that we are aware of, and thus is a significant observation.

By recalling the difference between the normal and local modes in HCN, we formulated a possible solution to the (1,0,5) intensity anomaly. The $v_5$ normal mode includes some CN motion which is oppositely phased to the CN motion in $v_1$. Thus to create the true CH local mode we need to mix in some $v_1$ character to $v_5$. It may then be that the amount of CH character in $5v_5$ just happens to be $1v_1$, so that the (1,0,5) is a true local mode state. Then, its large intensity would be expected according to the local mode intensity model. Quantitatively (see the Appendix), we found that this harmonic model was not adequate to describe our observation that $I_{1,0,5} > I_{0,0,6}$, because the degree of CN motion in $v_5$ is simply too small. For this model to predict that $I_{1,0,5} > I_{0,0,6}$, the CN character in $v_5$ would


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have to be about four times larger.

Other than the vibrational coupling mechanism presented in the Appendix, we can conceive of no possible explanations, within the context of the bond dipole approximation, for the (1,0,5) intensity anomaly. Thus, we must conclude that the bond dipole approximation fails for HCN. This conjecture is supported by observing the relative magnitude of diagonal (in bond or internal coordinates) and off-diagonal terms in Botschwina's dipole moment function. He expands the dipole moment function in a Taylor series in the internal stretching coordinates \( A \), \( \Delta A \), \( \Delta r \). After scaling Botschwina's Taylor expansion coefficients by the rms internal coordinate displacements (0.034 Å for CN and 0.0731 Å for CH), we note that the (2,1) term of \( \mu(\Delta A, \Delta r) \) is over half as large as the diagonal (0,2) term and the (1,2) term is somewhat larger than this diagonal term.

As a consequence of the astrophysical intentions of the CASSCF calculation, it is not trivial to compare these theoretical results band-by-band with the measured intensities, but a preliminary calculation indicates that the sum of calculated intensities, within the interval measured by us, agrees to within a factor of 3 with the experimental sum. As the measurements performed in the present investigation concern the most uncertain part of the CASSCF calculation, this relatively good agreement is a very promising result for the future possibility of calculating opacities of polyatomic molecules in all types of stars. A more detailed comparison with the CASSCF results, including a detailed investigation of the effect of dipole moment grid size and the restriction in choice of basis set, is postponed to a forthcoming paper.

Following our measurements of HCN overtone intensities, Botschwina extended his CEPA-I potential and CEPA-I (ED) dipole moment function to make reliable predictions for HCN bands with origins of up to 20,000 cm\(^{-1}\). By modeling only the two stretches, he is not limited by vibrational basis set size or by the density of points in the dipole moment grid. Table II compares band-by-band our experimental results with his recent calculations. The CEPA-I potential used to calculate the values shown in this table makes use of experimental values for \( \nu_1 \) and \( \nu_3 \) and anharmonicity constants \( X_{12} \) and \( X_{23} \). No empirical information is used to obtain this dipole moment function however. A more detailed description of his calculation will be given by himself.

Botschwina's new intensity for the (0,0,5) is in closer agreement with experiment than that reported in Ref. 12. The agreement for the (0,0,6) band is also quite good. Three pairs of bands in this table are anharmonic resonant pairs: these are the (0,0,4) + (3,0,2), the (4,0,2) + (1,0,4), and the (2,0,4) + (5,0,2). For these bands, it is only meaningful to compare the summed intensity, since their calculated relative intensity is so sensitive to the energy gap between the resonant states. The ratio (theory/expt.) of the summed intensity for these three pairs is 1.7, 1.9, and 0.76, respectively. The (4,0,2) and (1,0,4) states undergo quite strong anharmonic interaction. According to Botschwina's calculations, the lower energy state should more accurately be labeled (1,0,4).

The only notable deviations between theory and experiment concern the intensity of the (0,0,4), the strongest band studied here, and the (1,0,5), which we found unusually strong. Although Botschwina predicts the (1,0,5) to be more intense than the (0,0,6), he finds it to be more similar in intensity to the (0,0,6) than to the (0,0,5), in contrast to our results. On the average, the agreement is within a factor of 2, which must be considered remarkable for such weak transitions. So far, this type of agreement has rarely been achieved for the diatomics, where no delicate coupling mechanisms are involved.

When calculating the band intensities using individual rotational line intensities, we have assumed that any rotational corrections to the band intensity are negligible. We checked for an \( n \) dependence of the type discussed by Herman and Wallis:

\[
S(m) = S^0[1 + \beta m]
\]

and found that for the (0,0,4) band, \( |\beta| < 0.003 \). If this limit applies for the other bands as well, then corrections to the band intensities of the order of 3% apply for the Boltzmann peaks (\( J = 8 \)).

Using the White cell data, taken at an HCN pressure of 50.7 Torr, the self-broadening coefficients for the (0,0,4) band were determined. These are nearly the same as those determined for the corresponding rotational line in the (0,0,5) band (12); the falloff of the rotational relaxation rate with increasing \( J \) is less for the (0,0,4) band. As discussed in our previous paper, the collisional broadening of HCN is dominated by rotationally resonant collisions in which \( J \) changes by 1.\(^{12}\) Therefore, as \( J \) increases, the smaller \( \Delta B \) for the (0,0,4) transition as compared to the (0,0,5) transition, leads to a slower increase in the energy mismatch and correspondingly a slower decrease in the rotational relaxation rate.

These results represent the most complete set of accurate overtone intensities for one molecule. We have recently scanned the overtone region of HCN in the near-infrared

---

**TABLE II. Intensities (cm/mol) for HCN overtone bands between 12 600–18 400 cm\(^{-1}\).**

<table>
<thead>
<tr>
<th>Band origin (cm(^{-1}))</th>
<th>Intensity (cm/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory Botschwina</td>
</tr>
<tr>
<td></td>
<td>Ref. 5</td>
</tr>
<tr>
<td>(0,0,4)</td>
<td>12 635.86(^{16})</td>
</tr>
<tr>
<td>(0,0,5)</td>
<td>15 551.94(^{18})</td>
</tr>
<tr>
<td>(1,0,5)</td>
<td>17 550.39(^{12})</td>
</tr>
<tr>
<td>(3,0,2)</td>
<td>12 657.90(^{19})</td>
</tr>
<tr>
<td>(4,0,2)</td>
<td>14 653.65(^{20})</td>
</tr>
<tr>
<td>(1,0,4)</td>
<td>14 670.38(^{21})</td>
</tr>
<tr>
<td>(2,0,3)</td>
<td>13 702.30(^{22})</td>
</tr>
<tr>
<td>(0,0,6)</td>
<td>15 377.00(^{23})</td>
</tr>
<tr>
<td>(2,0,4)</td>
<td>16 674.21(^{24})</td>
</tr>
<tr>
<td>(5,0,2)</td>
<td>16 640.31(^{25})</td>
</tr>
<tr>
<td>(3,0,3)</td>
<td>15 710.53(^{26})</td>
</tr>
<tr>
<td>(0,1,5)</td>
<td>16 164.07(^{27})</td>
</tr>
</tbody>
</table>

\(^{16}\) The error reported below is two standard deviations of the mean.

\(^{18}\) After Refs. 18 and 19.

\(^{22}\) Reference 2.
using the Kitt Peak Fourier transform spectrometer. Because of the superior qualities of this instrument, we expect to be able to determine rotational corrections to the band intensity. These Herman–Wallis-type parameters will give additional information that will be used in testing both ab initio and experimentally parametrized dipole moment functions.

As well as the intensity work, the dipole moments of the (0,0,5), (1,0,5), (1,0,4), and (4,0,2) states have been measured at Harvard using a photoacoustic/Stark method. Using the intensity and dipole moment data, as well as any Herman–Wallis factors we have determined, we hope to deduce an experimentally parametrized dipole moment function for HCN.

Note added in proof: Recently, Botschchina has recalculated the intensities of our observed transitions, including only the diagonal terms in his electric dipole moment function (the bond dipole approximation) and including only the CH diagonal terms. The change in the predicted intensities is surprisingly small. For example, the intensity of the (1,0,5) transition changes from 4.5 to 4.3 to 4.1 cm mol⁻¹ and the (0,0,6) transition changes from 2.9 to 2.6 to 2.4 cm mol⁻¹. Thus, contrary to our discussion in the text, the fact that the (1,0,5) transition is more intense than the (0,0,6) does not necessitate the breakdown of the bond dipole approximation. At least the amount of extra intensity Botschchina predicts for the (1,0,5) transition must have a source other than the breakdown of the bond dipole approximation. We hope that further variational calculations will resolve this issue.

ACKNOWLEDGMENTS

We are grateful to Dr. Michael Otteson for his assistance with the Coherent 699/29 ring dye laser. We also thank Dr. Ed Eyler of the physics department at Yale for his help in converting the data recorded with this system to a useful form for data processing. K.K.L acknowledges support from the Camille and Henry Dreyfus Foundation and the National Science Foundation through the Presidential Young Investigator Award.

APPENDIX: THE DISTRIBUTION OF LOCAL MODE INTENSITIES AMONG NORMAL MODE STATES

A sharing of the |n⟩ₖₙ local mode intensity over the normal mode states |m,0,n−m⟩ occurs in the harmonic limit due to the fact that the ν₃ normal mode is not a pure C–H stretch, but rather has some C–N character. In what follows, we will predict the extent of intensity mixing by this mechanism.

The internal coordinate Δr(CH) can be expressed in terms of the normal mode displacements Q₁ and Q₃ via the L matrix

Δr(CH) = L₁₁Q₁ + L₁₃Q₃.  (A1)

Furthermore, we can write the Q_i's in Eq. (A1) in terms of the raising and lowering operators for the normal modes:

Q_i = \sqrt{\frac{\hbar}{4\pi \omega_i}} (a_i^+ + a_i),  (A2)

where the \omega_i are the harmonic frequencies for the normal modes:

Δr(CH) (Å) = 0.014 275(a_1^2 + a_1) + 0.071 698(a_3^2 + a_3).  (A3)

Then, since Δr(CH) is proportional to the sum of the raising and lowering operators for the internal coordinate (CH stretch), the expression for the raising operator for the CH stretch is formed by dropping the terms in Eq. (A3) involving the lowering operators. Normalizing the coefficients of the a_i’s for the normal coordinates so that the sum of their squares is one, we have

a_1^2 = \frac{1}{\sqrt{2}} (a_1^+ + \sqrt{2}a_1),  (A4)

where for HCN, g = 0.961 87.

The normalized nth eigenstate is generated from the normalized ground state through

|n⟩ₖₙ = \frac{1}{\sqrt{n!}} (a_1^+)^n |0⟩,  (A5)

which together with Eq. (A4), implies that

|n⟩ₖₙ = \sum_{m=0}^{n} \sqrt{(n,m)(1-g)^m(g)^{n-m}} |m,0,n−m⟩,  (A6)

where (n,m) is the binomial coefficient for integers m,n and 0<m<n. This expansion predicts that the intensity of the normal mode state |m,0,n−m⟩ is proportional to |⟨n|₁ₙ |m,0,n−m⟩|², which is

I(m,0,n−m) = (n,m)(1-g)^m(g)^{n-m}Iₙₖₙ,  (A7)

where Iₙₖₙ is the intensity of the |n⟩ₖₙ local mode state. As g decreases from one, a shifting of intensity to the combination bands is expected. This can be understood physically by realizing that in the normal mode ν₀, the C–N stretch is excited to some extent. At some degree of excitation of the ν₀ mode, the CN motion will become large enough in this highly excited state so that by adding one quanta of ν₁, in which the CN motion has a phase opposite that for ν₂, we can nearly freeze all CN motion and thus approach the true CH local mode state. Upon substituting in Eq. (A7) the g appropriate for HCN, we find that this mechanism does not quantitatively describe the large intensity of the (1,0,5) state. From Eq. (A7), we predict that

I(1,0,5) = 0.18836,  (A8)

I(0,0,6) = 0.79196 = 0.238.

Therefore, while predicting a significant intensity for the (1,0,5) state, this normal mode projection cannot account even qualitatively for our observation of

I(1,0,5) = 5.8.  (A9)

1P. Botschchina, Chem. Phys. 81, 73 (1983); Habilitationsschrift (University of Kaiserslautern, Germany, 1984); NATO Advanced Research Workshop, Maratea, Italy, 1986.
where \(1 + (1 - T)\) gives the power of the forward and backward waves in the laser cavity and \(T\) gives the extracavity power.

Utilizing five calibration factors (defined below) and the band intensity (BI) calculated from the fits to the photoacoustic data, the true relative band intensity (TBI) is given by

\[
\text{TBI} = \left[ \frac{\text{BI} \times \text{LIA scale}}{\text{PM scale}} \right] \times \frac{T(\lambda)}{2 - T(\lambda)} \times \frac{1}{S(\lambda)}
\]

where LIA scale = the scale of the lock-in amplifier used to demodulate the photoacoustic signal.

PM scale = the scale of the photodiode power meter used to measure the extracavity power.

\(G\) = Gain of the analog divider which ratioed the photoacoustic signal by the extracavity laser power, and \(T(\lambda)\) and \(S(\lambda)\) are defined in Ref. 14.

IMSL library, Routine ZXSSQ. Vol. 4, ed. 9.0 (IMSL, Houston, 1982).


