# *Ab initio* rotation-vibration spectra of HCN and HNC.

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**Abstract**

We have calculated an *ab initio* HCN/HNC linelist for all transitions up to $J = 25$ and 18000 cm$^{-1}$ above the zero point energy. This linelist contains more than 200 million lines each with frequencies and transition dipoles. The linelist has been calculated using our semiglobal HCN/HNC VQZANO+ potential energy surface and dipole moment surface, which were reported in van Mourik *et al.*, J. Chem. Phys., 115 (2001), 3706. With this linelist we synthesise absorption spectra of HCN and HNC at 298K and we present the band centre and band transition dipoles for the bands which are major features in these spectra. Several of the HCN bands and many of the HNC bands have not been previously studied. Our line intensities reproduce via fully *ab initio* methods the unusual intensity structure of the HCN CN stretch fundamental ($00^01$) for the first time and also the forbidden ($02^20$) HCN bending overtone. We also compare the $J = 1 \rightarrow 0$ pure rotational transition dipole in the HCN/HNC ground and vibrationally excited states with experimental and existing *ab initio* results.

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# 1  Introduction.

The infrared spectrum of the HCN/HNC system has been the subject of numerous theoretical and experimental studies and continues to be of great interest to both molecular spectroscopy and astronomy. Within molecular spectroscopy the HCN/HNC system is a prototypical isomerising molecule with stable (HCN) and a metastable (HNC) isomers both with linear geometries. The H nucleus in the bending mode of the molecule undergoes large amplitude motion, so much so that high excitation can result in the H nucleus becoming delocalised and can provide an isomerisation pathway. However despite many theoretical studies of the isomerising motion of the molecule [1–3] these so called delocalised states have yet to be observed experimentally. The relatively simplicity of the HCN/HNC system can provide a benchmark for theoretical analysis which can be extended to more complex molecules. HCN and HNC, are also important molecules throughout astronomy, for example HCN has been observed in comets [4,5], planetary atmospheres [6], molecular clouds [7,8], carbon star atmospheres [9,10] and circumstellar masers [11]. In fact, prior to its detection in the interstellar medium in 1971 by the radio astronomers Snyder and Buhl [12,13], HNC had only been observed in the laboratory by means of matrix isolation spectroscopy. Of particular interest to us is the role of HCN in C-star atmospheres, calculations by Jørgensen and co-workers [14,15] suggest that the proper detailed treatment of the vibration-rotation spectrum of HCN can have profound effect on the structure of the C-star model atmospheres. It is this problem that motivated our ongoing project to calculate an extensive rovibrational linelist upto high levels of rotational excitation to aid the modelling of theses stars.

Much experimental work has been done to measure the intensities and frequencies of both HCN and HNC bands, however beyond the fundamental bands *ab initio* intensity calculations have been performed only on the stretching bands of HCN and HNC by Botschwina and co-workers and Jakubetz and Lan [2]. Jakubetz and Lan [2] and Bowman *et al.* [3] have treated HCN and HNC simultaneously by using semi-global dipole and potential surfaces, to simulate isomerisation and to calculate vibrationally average dipole moments respectively.

In this work we present *ab initio* room temperature (298K) synthetic spectra for HCN and HNC along with band centres and transition dipoles for the prominent features in the room temperature spectra. We also quote line intensities for the HCN CN stretch fundamental band, which has unusual intensity structure, and also for the forbidden $(02^20)$ bend overtone. These spectra form part of our ongoing work and were calculated from line frequencies and transition dipoles which were computed simultaneously for HCN and HNC using our VQZANO+ potential energy surface (PES) and dipole moment surface (DMS)

reported in our earlier work [16]. We also present pure rotational $J = 1 \rightarrow 0$ transition dipoles in the ground and excited states of HCN/HNC.

Ultimately the accuracy of any nuclear motion calculation is dependent upon the accuracy of the preceding electronic structure calculations and the potential and dipole surfaces. It is therefore desirable that we use the best potential and dipole surface that are available to us, in section 2 we review the merits of existing HCN/HNC PES and DMS. In section 3 we describe our computational method, in section 4 we present our spectra and finally we conclude in section 5.

## 2   The Potential Energy and Dipole Surfaces.

Our ongoing project of the calculation of an *ab initio* HCN/HNC linelist for application in astronomy imposes limits on the type of potential surface that we will be using. At the C-star temperatures in which HCN has a major role in opacity ($T_{eff} < 3000$ K) [14], a significant amount of HCN/HNC will be in the HNC form. It is also important to note that the transition dipoles of HNC bands are more than twice as strong as the corresponding HCN band transition dipoles, so although HNC will be much less abundant than HCN each HNC molecule will have a larger effect on opacity than each HCN molecule. This makes it desirable to be able to study the behaviour of both HCN and HNC, which requires a global HCN/HNC potential surface that maintains accuracy to high energies.

Wu *et al.* [17] have fitted a global HCN/HNC potential energy surface (PES) to experimental data to create a PES which can reproduce known experimental vibrational energy levels to within 1 cm$^{-1}$. However although spectroscopically fitted surfaces reproduce known experimental data to high accuracy, they tend to extrapolate high lying energy levels outside the fitted region far more poorly than do *ab initio* surfaces. We intend to perform calculations on HCN/HNC upto 18000 cm$^{-1}$ above the zero point energy (ZPE). At the high end of this range only a few HCN/HNC energy levels have been measured so a fitted PES is likely to perform poorly, for this reason we have chosen to use an *ab initio* PES.

There are currently two *ab initio* semi-global HCN/HNC PES available these are the ANO/CCSD(T) PES of Bowman *et al.* [1] and VQZANO+ PES covered in an earlier paper [16]. Our *ab initio* VQZANO+ PES simultaneously fits 1527 ANO/CCSD(T) points calculated by Bowman *et al.* [1] with 242 cc-pCVQZ/CCSD(T) points, the surface is morphed with 17 aug-cc-pCVQZ/CCSD(T) calculated in the HNC region of the PES. Finally to improve the representation of the HNC part of the surface. The VQZANO+

surface is also adjusted to coincide with three cc-pCV5Z/CCSD(T) points calculated at the critical points of the HCN/HNC system. The VQZANO+ PES includes relativistic and adiabatic corrections, which are often neglected when constructing an *ab initio* PES.

Vibrational energy level calculations with the VQZANO+ PES give stretching band origins that more closely match experiment than do the stretching band origins calculated with the Bowman *et al.* PES [1] and the bending band origins are of a comparable level of accuracy, see below. The positions of the HCN and HNC minima of the VQZANO+ PES are considerably closer to experimental equilibrium bond lengths, determined by isotopic substitution [18,19], than those of the Bowman *et al.* PES. This is likely to result in the VQZANO+ PES giving a better representation of the molecules rotational motion than the Bowman *et al.* PES. Overall the VQZANO+ PES is in general superior to the PES of Bowman *et al.*, as a result we use the VQZANO+ PES for the calculations presented here.

There are three semi-global dipole moment surfaces (DMS) available these are the TZP/AQCC DMS of Jakubetz and Lan [2], the aug-cc-pCVTZ/CCSD(T) DMS of Bowman *et al.* [3] and cc-pCVQZ/CCSD(T) DMS of van Mourik *et al.* [16]. The DMS of Jakubetz and Lan was calculated with the smallest basis of these three DMS, the intensities calculated with it compare with experiment far less favourably than do our calculations with the van Mourik *et al.* DMS, see below. The DMS of Bowman *et al.* [3], uses fewer points and a smaller basis than the van Mourik *et al.* DMS [16]. The van Mourik *et al.* surface as a result is the best available DMS and the one which will be employed here.

## 3   The Calculation.

Frequencies and dipole transition strengths have so far been calculated for all the HCN/HNC rotational vibrational transitions between states with energy less than 18000 cm$^{-1}$ and J$\leq$25. This data set contains more than 200 million lines and 80 000 rotational vibrational energy levels. Our vibrational, rotational, and dipole transition calculations were performed with the DVR3D program suite [20], which uses an exact kinetic energy (EKE) operator and a discrete variable representation (DVR) for the vibrational motions. Jacobi coordinates were used with Legendre polynomials to give the angular grid points and Morse oscillator-like functions for the radial grids. 35 grid points were used for the $R$ coordinate, 21 for the $r$ coordinate and 50 for the angular coordinate. This basis was optimised to obtain a balance between the level of convergence and the required computer resources. Although this basis is slightly smaller than the one used in our previous work [16], it is sufficient to converge all calculations reported here. The parameters for the morse os-

cilator like basis in the r coordinate are $r_e = 2.3\ a_0$, $D_e(r) = 29.0\ E_h$ and $\omega_e(r) = 0.0105\ E_h$. The parameters for the morse oscilator like basis in the R coordinate are $R_e = 3.2\ a_0$, $D_e(R) = 5.0\ E_h$ and $\omega_e(R) = 0.004\ E_h$. Where $r_e$ is the equalibrium distance, $D_e$ is the disociation energy and $\omega_e$ is the harmonic frequency, see ref [20].

The huge number of lines that we have calculated required a large amount of processing power which make it necessary to parallelise the processor intensive routines of the DVR3D codes. The openMP fortran API multiprocessing directives [21] with the MIPSpro 7 Fortran 90 compiler [22] on the 'Miracle' 24 processor SGI Origin 2000 computer, were used to perform the parallelisation. The most processor intensive module of the DVR3D suite is DIPOLE3, which calculates dipole transition strengths between states which are not rigorously dipole forbidden. One loop of this module calls a rank 1 matrix update subroutine and consumes 95% of the runtime. By parallelising this loop we were able to reduce the run time by a factor of five when running on eight processors.

We have used our linelist to calculate room temperature (298 K) absorption spectra of both HCN/HNC and HNC as a separate molecule. The spectral calculations were limited to bands which have lines with absolute intensity above 4 cm$^{-1}$mol$^{-1}$. Figures 1 and 2 show a spectral map of the HCN/HNC spectrum over the range 0 to 18000 cm$^{-1}$, the intensity of HNC bands at room temperature is less than the cut off intensity, so there are no HNC bands shown in this spectrum. Figure 3 show the spectrum in the region of the $(40^00)$ stretching overtone.

To ease comparison with experiment and earlier *ab initio* work, the line transition dipole data was reduced to band transition dipoles for all the HCN bands shown in the spectrum and for other selected bands, see tables 1 and 2. For a given band this was done by dividing each line transition dipole by the square root of the appropriate Hönl–London and vibrational intensity factors to give the band dipole for that line. The mean band dipole and the standard deviation were calculated using the band dipole calculated from each line. Our standard deviation thus measures the reliability of using band dipoles and Hönl–London factors, it does not account for the systematic errors in our calculation.

The Hönl–London factors used in experimental works by two different groups, Maki *et al.* [23] and Smith *et al.* [24] differ by a constant in some cases. Van Mourik *et al.* [16] re-derived the Hönl–London factors from the matrix elements given by Gordy and Cook [25] and they agree with the Hönl–London factors of Maki *et al.*. In all cases we have used the Hönl–London and vibrational factors of Maki *et al.* and in the cases where we have used the data of Smith *et al.* we have converted from their Hönl–London factors to those of Maki *et al.*.

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For a band with unusual or perturbed structure it is more meaningful to compare line intensities directly than it is to compare fitted band dipoles and Herman-Wallis constants. For this reason two bands for which band transition dipoles are inappropriate are not included in the band dipole table. These bands are the HCN C-N fundamental $(00^01)$ (see table 3) which has unusual R branch structure, see Maki $et$ $al.$ [26], and the forbidden HCN bend overtone $(02^20)$ (see table 4). For these bands we compare our calculated absolute lines intensities with experimental absolute line intensities. Line intensity can be calculated from line transition dipole by using:

$$I_L = \frac{2\pi^2 L\nu}{3hc\epsilon_0 Q_{vr}} \left(\frac{273.15}{T}\right) \exp\left(\frac{-E''}{kT}\right) \left[1 - \exp\left(\frac{-hc\nu}{kT}\right)\right] \mu_L^2 \tag{1}$$

Here, for clarity we use SI units where possible, $I_L$ is line intensity (m$^{-2}$ atm$^{-1}$), $L$ is Loschmidt's number ($2.686763 \times 10^{25}$ molecules m$^{-3}$ at 1 atm and 273.15 K), $\nu$ is the wavenumber in m$^{-1}$ of the line, $h$ is Planck's constant, $c$ is the speed of light, $\epsilon_0$ is the permittivity of free space, $k$ is Boltzmanns constant, $E''$ is the energy of the lower ro-vibrational energy level, T is the temperature, $Q_{vr}$ is the ro-vibrational partition function and $\mu_L$ is the line transition dipole in coulomb meters (1 Debye $= 3.33564 \times 10^{-30}$ C m). For the particular combination of units of dipole moment in Debye, intensity in cm$^{-2}$ atm$^{-1}$ and wavenumber in $cm^{-1}$, equation 1 becomes:

$$I_L = \frac{11.183309 \times \nu}{Q_{vr}} \left(\frac{273.15}{T}\right) \exp\left(\frac{-E''}{kT}\right) \left[1 - \exp\left(\frac{-hc\nu}{kT}\right)\right] \mu_L^2 \tag{2}$$

In this work a value of $Q_{vr}(298\ K) = 149.944$ given by Maki $et$ $al.$ [33] was used.

The experimental data of Smith $et$ $al.$ [24,27,28] and the earlier theoretical work of Botschwina and co-workers [29–31], was originally reported as integrated band intensities (cm mol$^{-1}$). For constsistancy we have converted these band intensities to band transition dipoles. Band intensity is related to band transition dipole by the formula:

$$I_B \approx \frac{2\pi^2 N_A \nu_0}{3hc\epsilon_0} \left[1 - \exp\left(\frac{-hc\nu_0}{kT}\right)\right] \mu^2 \tag{3}$$

Again for clarity we use SI units, where $I_B$ is band intensity in m mol$^{-1}$, $N_A$ is Avogadro's number, $\nu_0$ is the wavenumber in m$^{-1}$ of the band center and $\mu$ is the transition dipole in coulomb meters. This formula is based upon equation 1 and takes into account the manipulation that Smith $et$ $al.$ [24] performed on their data to give integrated band intensities. The approximation here is a result of using the wavenumber of the band centers rather than that of the

individual lines. At worst this approximation is accurate to a few percent, better than the approximation made when using Hönl–London factors and less than the experimental statistical error. The factor in square brackets on the RHS of eq. 3 is the population difference between the two states. It gives rise to induced emission and is very close to 1 for the range of results reported in this work. With rearrangement and using the particular combination of units of dipole moment in Debye, intensity in cm mol$^{-1}$ and wave number in cm$^{-1}$, the above formula becomes:

$$\mu \approx \sqrt{\frac{I_B}{2.5066379 \times 10^5 \times \nu_0}} \tag{4}$$

This equation is of the same form as used by Botschwina $et$ $al.$ [29], to convert between band transition dipole and band intensity.

The aim of our calculations is to produce a complete linelist of the HCN/HNC system including transitions to and from HCN, HNC and the delocalised states. Consequently localised HCN and HNC transitions are mixed together with the delocalised states. To produce a room temperature HNC only spectrum it is necessary to separate the localised HNC transitions from the other transitions. Bowman $et$ $al.$ [3] have suggested using the sign of the permanent dipole moment of a vibrational level to identify it as a HCN or HNC state. It is difficult to obtain absolute information from our calculated transition dipoles, so in this work HNC and HCN states are separated by comparing the transition dipole of a rovibrational state to the ground HCN state and to the ground HNC state. Localised HNC states will have a far greater transition dipole to the HNC ground state than to the HCN ground state. This allowed us to identify localised HNC energy levels and transitions between them. Using this method only a handful of HCN states were mis-identified as HNC states, these tended to be HCN states with extremely low transition dipoles to the ground state, for example the HCN bending overtone $(08^80) \leftarrow (00^00)$ which is a forbidden transition. Transitions involving these few miss-identified states were removed by hand. It may also be possible to identify delocalised states using this method. The wave functions of delocalised states have significant magnitude in both HCN and HNC potential wells and so should have similar transition dipole to the low lying localised states. However as a result of the problems discussed above this is a qualitative method and is not wholly reliable.

We are in the process of calculating a fully $ab$ $initio$ partition function, but at present despite our literature searches we have not found a partition function for HNC. This effects only calculation of absolute intensities for HNC and will not effect our spectra in which we give relative intensities or our band transition dipoles.

Figure 5 shows a spectral map of HNC in absorption for 0 to 8000 cm$^{-1}$, figure 6 is the absorption spectrum in the region of the Q and R branch of the bending fundamental. Band transition dipoles for the prominent HNC bands are compared with existing experimental and theoretical values in tables 5 and 6.

Finally from the $J = 0 \rightarrow 1$ pure rotational transitions in the HCN and HNC ground and some HCN excited states, we give vibrationally averaged permanent dipoles and compare them with experiment and the *ab initio* vibrationally averaged dipole moments calculated by Bowman *et al.* [3], see table 7.

The vibrationally averaged dipole moment of a given state is approximately equal to the J$= 0 \rightarrow 1$ pure rotational transitions from the following argument. The rotational transition dipole moment for a given vibrational level $n$ is given by: $\langle nJ'|\underline{\mu}|nJ''\rangle$. The vibrationally averaged dipole moment is the case where $J' = J'' = 0$ and can be approximately equated to the rotational transition dipole multiplied by the correct Hönl–London factor:

$$\langle n0|\underline{\mu}|n0\rangle \approx \langle nJ'|\underline{\mu}|nJ''\rangle H_J \tag{5}$$

Furthermore $H_J = 1$ for the case where $J' = 1$ and $J'' = 0$. Therefore the $J = 1 \rightarrow 0$ pure rotational transition dipole is equal to the vibrationally averaged dipole moment within the approximations made when using Hönl–London factors.

## 4   Results and Discussion.

*4.1   HCN Spectrum.*

Overall for transitions involving the lower energy levels ($< 10000$ cm$^{-1}$) the transition dipoles of our bands (see tables 1, 2) agree in most cases to within combined errors with experimental work and and the *ab initio* work of Botschwina *et al.* [29]. However for transitions involving the higher energy levels ($> 10000$ cm$^{-1}$) there are more significant deviations from experiment with five band dipoles differing from experiment by a factor of two. These transitions are $(20^03)$, $(31^10)$, $(41^10)$, $(20^04)$ and $(40^02)$. There appears to be something anomalous about the $(31^10)$ measurement which is not reproduced by our calculations which predict that $(n1^10)$ should have $\mu \sim 10^{-(n+1)}$ D and agree well with experiment and theory for $n =1,2,4,5$. The stretching combination bands $(20^03)$, $(20^04)$ and $(40^02)$ each lie within 40 cm$^{-1}$ of a strong stretching combination band, these bands forming a pair of bands which interact, the band pairs being: $(40^00)$ and $(20^03)$, $(20^04)$ and $(40^01)$, $(20^05)$ and $(40^02)$.

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The difference between the band centres of each band pair in our calculations tends to differ from experiment by about $10 \text{ cm}^{-1}$, this will serve to increase or decrease the interaction between the bands in each pair depending on whether the bands are closer together or further apart. The individual band intensities of these pairs of bands have not been reproduced accurately via fully *ab initio* techniques. Indeed Botschwina *et al.* [29] who used a smaller 130 cGTO basis HCN stretching PES and 110 cGTO basis DMS, sidestepped the problem by calculating combined band intensities for each pair. To accurately reproduce experiment for these interacting bands, very accurate wave functions are needed, as was shown by Botschwina [30] who reproduced experiment more accurately by using an empirical correction to his wavefunctions.

Overall our calculations agree to a similar level of accuracy as the calculations of Botschwina *et al.* [29] and agree more closely to experiment in the case of the $(30^03)$ overtone from which the dipole from Botschwina deviates by a factor of two. It must be stressed that the calculations of Botschwina *et al.* involve only 2 dimensional HCN stretching coordinates and use 2 dimensional potential and dipole functions only and give no information on bending excitations. Our band transition dipoles are significantly better than the AQCC calculations of Jakubetz and Lan [2] supporting our choice of dipole surface.

There are two bands in our spectrum which have not yet been experimentally identified and may well be experimentally detectable, these are $(11^12) \leftarrow (00^00)$ and $(23^11) \leftarrow (00^00)$. There is an element of intensity borrowing present in some bands, one particular example is the $(40^00) \leftarrow (00^00)$ band, see fig 3. This band shows a significant dip in intensity as a result of intensity borrowing by the $(23^12) \leftarrow (00^00)$ band in the region of the R(15) and P(17) line. Intensity borrowing is not accounted for by Hönl–London factors, so our band intensities were calculated using lines from outside the regions in which intensity stealing was taking place. The errors on our band transition dipoles are a statistical measure of how well suited to fitting the intensity structure of a band Hönl–London factors are. For some bands, such as the $(04^{2e}0) \leftarrow (01^10)$ bend hot band, errors are as much as 20%. Hönl–London factor will not accurately reproduce the intensity structure of these bands.

Table 3 compares the experimental results of Maki *et al.* [26] for the $(00^01)$ band with our *ab initio* line intensities. The P branch *ab initio* line intensities are approximately 30% stronger that the experimental intensities. The *ab initio* R branch peak, reach minimum and peak again at $J'' = 2, 8$ and 18 respectively each of which are just above the experimental values at $J'' = 1,7$ and 16 respectively. The intensities of the R branch lines beyond the minimum $(J'' > 11)$ agree well with experiment. None the less for the band our calculations are in reasonable agreement with experiment and amount to the first fully *ab initio* reproduction of the intensity structure of this band. The spectrum in the region of the $(00^01)$ fundamental is plotted in figure 4. The P

branch of the $(00^01)$ fundamental band and the P, Q and R branches of the $(03^10)$ overtone band are the major features in the spectrum. The unusually low intensity of the R branch of the $(00^01)$ fundamental is clear in this figure.

Botschwina *et al.* [31] using wavefunctions determined from the spectroscopically fitted HCN potential surface of Carter *et al.* [32] and their own *ab initio* 110 cGTO/CCSD(T) dipole surface have calculated the band dipole for the $(00^01)$ fundamental to within experimental error. The calculations of Botschwina *et al.* described the unusual structure of this band for the first time and they determined a value of $A_1 = -0.188$ for the first order Herman-Wallis constant which agrees reasonably well with the experimentally determined value $A_1 = -0.1254$ of Maki *et al.* [26]. Their value of $A_1$, however, under predicts the position of the minimum in the R branch putting it at about $J'' = 4$ compared to the experimental value of $J'' = 7$ and our *ab initio* value at $J'' = 8$. This highlights the high level of sensitivity of the R branch structure to the wave functions and dipole surfaces used in the calculation.

The $(02^20)$ bend overtone is forbidden by the normal dipole selection rules for a linear triatomic which are, for parallel transitions:

$$\Delta J = 0, \pm 1, \ \Delta l = 0 \tag{6}$$

with $\Delta J = 0$ not allowed if $l = 0$. For perpendicular transitions:

$$\Delta J = 0, \pm 1, \ \Delta l = \pm 1 \tag{7}$$

Some bending states with different orbital angular momentum ($l$) can become coupled by coriolis interactions, resulting in $l$ being poorly defined. In this event the selection rules on $l$ are not rigidly obeyed. The $(02^20)$ overtone intensities we have calculated are given in table 4, they compare well with the experimental intensities of Maki *et al.* [33]. The P and R branch, except for the $J'' = 5$ line, agree to within 25% of experiment and the Q branch also agrees well, to within 30% of experiment. The calculated band centre at 1432.24 cm$^{-1}$ agrees to within 8cm$^{-1}$ with the experimental value from Maki *et al.* [34] of 1424.76 cm$^{-1}$.

The band centres are compared with experiment and the stretching vibrational band origins of Bowman *et al.* [1], in table 2. Our calculated HCN band centres agree reasonably well with experiment, for transitions with frequency of less than 10000 cm$^{-1}$ the mean deviation from experiment is 5 cm$^{-1}$, for transitions with frequency greater than 10000 cm$^{-1}$ the mean deviation from experiment is 11 cm$^{-1}$. In general our stretching band centres are closer to experiment than those of Bowman *et al.* [1]. A fuller discussion of band origins calculated with the VQZANO+ surface is given in [16].

Figure 5 is a spectral map of room temperature (298K) HNC in absorption, and figure 6 plots our spectrum against the experimental spectrum of Burkholder *et al.* [35] in the region of the Q and R branch of the HNC bending fundamental. The dominant features of both the experimental and *ab initio* spectra in fig 6 are the Q and R branch of the bending fundamental, but also visible are the Q branches of the bending hot bands. The Q branch of the $(02^00) \leftarrow (01^10)$ band in the experimental spectrum can just be made out within the Q branch of the bending fundamental and the Q branch of the $(02^20) \leftarrow (01^10)$ is clearly visible. The Q branches of the $(02^00) \leftarrow (01^10)$ and $(02^20) \leftarrow (01^10)$ in the *ab initio* spectrum at 476.794 cm$^{-1}$ and 481.117 cm$^{-1}$ respectively are displaced from the experimental Q branches at 463.787 cm$^{-1}$ and 473.471 cm$^{-1}$ due to inaccuracy of the VQZANO+ potential surface. All the band transition dipoles and the band centres of the major features in the spectrum (fig. 5 ) are tabulated in tables 5 and 6.

Experimental data for band dipoles are only available for the HNC fundamentals [36,37], our *ab initio* calculations agree very well with both experimental and theoretical work for the stretching fundamentals. However for the bend fundamental our calculation is in agreement with the only other theoretical value [38], but disagrees with experiment. The bending transition dipole was not directly measured by Nezu *et al.* [36], but determined from the transition dipoles of the stretching fundamentals using the Herman-Wallis effect. As both theoretical values agree it is likely that the value of Nezu *et al.* is in error, in fact Nezu *et al.* [37] express doubts about the accuracy of their determination of the transition dipole of the bending fundamental. Beyond the fundamental bands theoretical intensity work has been done only on the stretching overtones [2,29], our stretching overtones are in agreement with both theoretical works.

Our calculated band centres and the *ab initio* energy levels of Bowman *et al.* [1] for the CN stretching bands are of comparable accuracy, for the HN stretching bands our calculations are closer to experiment, see table 5. Maki and Mellau [39] estimated the band centre of the $(03^10)$ overtone from anharmonic vibration constants of HNC up to the quartic terms which were fitted to their experimental data with a standard deviation of 16 cm$^{-1}$. The large standard deviation of their fit implies that estimates of band centres from these constants will not be very accurate and as a result the large deviation from theory seen in table 6 is to be expected. The stretching only HNC band centre calculations of Botschwina *et al.* [29] are in good agreement with experiment. This is despite using a 133 cGTO basis which is smaller than the cc-pCVQZ basis (198 cGTO) used for part of the VQZANO+ PES [16]. However the HNC potential of Botschwina *et al.* [29] considered stretching

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only coordinates. Experiment and the *ab initio* calculations of this work for the band centers of the HNC N-H stretch fundamental and overtone deviate by 12.5 and 18.0 cm$^{-1}$ respectively. It is likely that this deviation is caused by the cc-pCVQZ/aug-cc-pCVQZ basis not being large enough to accurately describe the electronic structure of the molecule at HNC geometries in the R coordinate.

*4.3  Dipole Moments.*

The $J = 1 \rightarrow 0$ pure rotational transition dipole calculated in this work is compared to experimental data and the *ab initio* vibrationally averaged dipole moments calculated by Bowman *et al.* [3] in table 7. The HCN ground state and excited states for our dipole moment agree marginally less favorably with experiment than those of Bowman *et al.*. However for the HNC ground state we agree significantly better with observation than Bowman *et al.* [3], which deviates from experiment by $-0.078$ D and gives a value for the HNC ground state dipole that is lower than that of the HCN ground state dipole. Botschwina *et al.* [31] used the empirical PES of Carter *et al.* [32] and a 110 GTO *ab initio* dipole moment surface for their calculations. Their results agree more closely with experiment than do the two fully *ab initio* calculations. Implying that the errors in the fully *ab initio* calculations are primarily due to the ab initio wavefunctions not being accurate enough.

Stanton [40] provided Bowman *et al.* [3] with benchmark calculations, at the cc-pCVQZ/CCSD(T) level, of the dipole moment at the three critical points of the system. The dipole moment given by the cc-pCVQZ/CCSD(T) DMS of van Mourik *et al.* at the geometries of the critical points calculated at the cc-pCV5Z/CCSD(T) level by van Mourik *et al.* [16] are given in table 8. The dipole moments from the DMS of van Mourik *et al.* are in good agreement with the calculations of Stanton [40] and the dipole moment from the DMS of Bowman *et al.* [1].

## 5   Conclusion

We have computed room temperature spectra, band centres and band transition dipoles of HCN and HNC using purely *ab initio* techniques. Features in our spectra, including the region of the HCN CN stretching fundamental and the HNC bending fundamental, match well the features of HCN and HNC spectra in published figures. We have plotted and assigned bands to a HCN spectral map in the range 0–18000 cm$^{-1}$ and to a HNC spectral map in the range 0–8000 cm$^{-1}$.

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In general our band centres agree more closely with experiment than do the *ab initio* energy levels of Bowman *et al.* [1] calculated with their global *ab initio* PES. Our band transition dipoles for both HCN and HNC agree more closely with experiment than do those of the *ab initio* global DMS Jakubetz and Lan [2] and are of comparable accuracy to the stretching only CCSD(T) calculations of Botschwina *et al.* [29]. We have also reproduced the unusual structure of the HCN CN stretch fundamental via fully *ab initio* techniques for the first time and have calculated the intensities of the forbidden Q branch of the HCN ($02^20$) overtone, which compare well with experiment.

Finally our HCN $J = 1 \rightarrow 0$ transition dipoles compare well with experiment and also with the vibrationally averaged dipole moments of Bowman *et al.*.

Reported here are band transition dipoles for several HCN and many HNC bands for which no experimental or computationally determined band transition dipoles have previously been reported.

An important reason for using *ab initio* techniques for calculating rotation-vibration is that these predictions are useful for spectral analysis. In particular the use of variational nuclear motion calculations and ab initio has provided means of assigning otherwise unanalysable spectra [41]. A key feature of this *ab initio* procedure, often not shown by methods which involve fitting to spectra, is that once rotational progressions can be reliably extrapolated [42]. This means that once allowance is made for the overall band error, predictions can be very reliable. The present calculations, see Fig 6 for example, reproduce the rotational structure of the spectra accurately and will form a good starting point for further spectral analysis.

This calculation is presently being extended to the high temperatures required for astrophysical studies.

**Acknowledgements**

# References

[1] J. M. Bowman, B. Gazdy, J. A. Bentley, T. J. Lee, and C. E. Dateo, J. Chem. Phys. 99 (1993) 308.

[2] W. Jakubetz and B. Leong Lan, Chem. Phys. 217 (1997) 375.

[3] J. M. Bowman, S. Irle, K. Morokuma and A. Wodtke, J. Chem. Phys. 114 (2001) 7923.

[4] W. F. Huebner, L. E. Snyder and D. Buhl. Icarus 23 (1974) 580.

[5] W. M. Irvine *et al.*. Nature, 383 (1996) 418.

[6] T. Hidayat, A. Marten, B. Beźard, D. Gautier, T. Owen, H. E. Matthews and G. Paubert. Icarus 126 (1997) 170.

[7] J. Hatchell, T. J. Millar and S. D. Rodgers. Astron. Astrophys. 332 (1998) 695.

[8] T. Hirota, S. Yamamoto, H. Mikami and M. Ohishi. Ap. J. 503 (1998) 717.

[9] W. Aoki, T. Tsuji and K. Ohnaka. Astron. Astrophys. 340 (1998) 222.

[10] J. H. Bieging, S. Shaked and P. D. Gensheimer. Ap. J. 543 (2000) 897.

[11] J.H. Bieging. Ap. J. 549 (2001) L125.

[12] L. E. Snyder and D. Buhl. BAAS 3 (1971) 388.

[13] L. E. Snyder and D. Buhl. Ann. N.Y. Acad. Sci. 194 (1972) 17.

[14] K. Eriksson, B. Gustafsson, U. G. Jørgensen and Å. Nordlund, Astron. Astrophys. 132 (1984) 37.

[15] U. G. Jørgensen, J. Almlöf, B. Gustafsson, M. Larsson, and P. Siegbahn, J. Chem. Phys. 83 (1985) 3034.

[16] T. van Mourik, G. J. Harris, O. L. Polyansky, J. Tennyson, A. G. Csaśzar̀ and P. J. Knowles, J. Chem. Phys. 115 (2001) 3706.

[17] Q. Wu, J. Z. H. Zhang and J. M. Bowman, J. Chem. Phys. 107 (1997) 3602.

[18] G. Winnewisser, A. G. Maki and D. R. Johnson, J. Mol. Spectry. 39 (1971) 149.

[19] R. A. Creswell and A. G. Robiette, Mol. Phys. 36 (1978) 867.

[20] J. Tennyson, J. R. Henderson and N. G. Fulton, Computer phys. Comms. 86 (1995) 175.

[21] openMP consortium, http://www.openmp.org

[22] Silicon Graphics Inc. http://www.sgi.com/developers/nibs/1998/mipspro_apr98.html

[23] A. Maki, W. Quapp and S. Klee, J. Mol. Spectry. 171 (1995) 420.

[24] A. M. Smith, U. G. Jørgensen and K. K. Lehmann, J. Chem. Phys. 87 (1987) 5649.

[25] W. Gordy and R.L. Cook, Microwave Molecular Spectra, 3$^{rd}$ edition (Wiley, New York, 1984).

[26] A. Maki, W. Quapp, S. Klee, G. Ch. Mellau and S. Albert, J. Mol. Spectry. 174 (1995) 465.

[27] A. M. Smith, W. Klemperer and K. K. Lehmann, J. Chem. Phys. 90 (1989) 4633.

[28] D. Romanini and K. K. Lehmann, J. Chem. Phys. 99 (1993) 6287.

[29] P. Botschwina, B. Schulz, M. Horn and M. Matuscheweski, Chem. Phys. 190 (1995) 345.

[30] P. Botschwina, J. Chem. Soc., Faraday Trans. 2, 84 (1988) 1263.

[31] P. Botschwina, M. Horn, M. Matuscheweski, E. Schick and P. Sebald, J. Mol. Struct. (Theochem) 400 (1997) 119.

[32] S. Carter, I. M. Mills and N. C. Handy, J. Chem. Phys. 97 (1992) 1606.

[33] A. Maki, W. Quapp, S. Klee, G. Ch. Mellau and S. Albert, J. Mol. Spectry. 185 (1997) 365.

[34] A. Maki, W. Quapp, S. Klee, G. Ch. Mellau and S. Albert, J. Mol. Spectry. 180 (1996) 323.

[35] J. B. Burkolder, A. Sinha, P. D. Hammer and C. J. Howard, J. Mol. Spectry. 126 (1987) 72.

[36] M. Nezu, T. Amano and K. Kawaguchi, J. Mol. Spectry. 192 (1998) 47.

[37] M. Nezu, T. Amano and K. Kawaguchi, J. Mol. Spectry. 198 (1999) 186.

[38] T. J. Lee and A. P. Rendell, Chem. Phys. Lett. 177 (1991) 491.

[39] A. Maki and G. Ch. Mellau, J. Mol. Spectry. 206 (2001) 47.

[40] J. F. Stanton quoted by ref. [3], see also K. L. Bak et al. J. Chem. Phys. 114 (2001) 6548.

[41] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, Science, 277 (1997) 346.

[42] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath and L. Wallace, Astrophys. J., 89 (1997) L205.

[43] A. Maki, G. Ch. Mellau, S. Klee, M. Winnewisser, and W. Quapp, J. Mol. Spectry. 202 (2000) 67.

[44] M. Lecoutre, F. Rohart, T. R. Huet and A. G. Maki, J. Mol. Spectry. 203 (2000) 158.

[45] D. Jonas, X. Yang and A. Wodtke, J. Chem. Phys. 97 (1992) 2284.

[46] F. J. Northrup, G. A. Bethardy and R. G. Macdonald, J. Mol. Spectry. 186 (1997) 349.

[47] R. L. DeLeon and J. S. Muenter, J. Chem. Phys. 80 (1984) 3892.

[48] G. L. Blackman, R. D. Brown, P. D. Godfrey, H. I. Gunn. Nature 261 (1976) 395.

Fig. 1. *Ab initio* spectral atlas for HCN in absorption, between 0 and 8000 cm$^{-1}$ at 298 K. transitions are labelled $v_1' v_2' l' v_3'$ for transitions from the ground state and $v_1' v_2' l' v_3' - v_1'' v_2'' l'' v_3''$ for transitions from an excited state.

Fig. 2. *Ab initio* spectral atlas for HCN in absorption, between 8000 and 18000 cm$^{-1}$ at 298 K. transitions are labelled $v_1' v_2' l' v_3'$ for transitions from the ground state and $v_1' v_2' l' v_3' - v_1'' v_2'' l'' v_3''$ for transitions from an excited state.

Fig. 3. Absorption spectrum in the region of the HCN ($40^0 0$) overtone at 298K. The HCN ($40^0 0$) overtone shows a significant dip in intensity as a result of intensity borrowing in the region of the $J'' = 17$ P branch line and the $J'' = 15$ R branch line.

Fig. 4. The *ab initio* HCN absorption spectrum in the region of the HCN ($00^0 1$) fundamental at 298 K. Some lines for the P and R branches of the ($00^0 1$) fundimental and the ($03^1 0$) bend overtone are labeled.

Fig. 5. *Ab initio* spectral atlas for HNC in absorption, between 0 and 8000 cm$^{-1}$ at 298 K. transitions are labelled $v_1' v_2' l' v_3'$ for transitions from the ground state and $v_1' v_2' l' v_3' - v_1'' v_2'' l'' v_3''$ for transitions from an excited state.

Fig. 6. A comparison of *ab initio* and experimental [35] absorption spectra in the region of the Q and R branch of the HNC ($01^1 0$) fundamental at 298 K.

Table 1: A comparison of experimental and theoretical band centres and transition dipoles for the most prominent HCN bands at 298 K that have excitation in the bending mode, in cm$^{-1}$ and Debye and standard deviation in the last digit given in brackets.

| $v_1' v_2' l' v_3'$ | $v_1'' v_2'' l'' v_3''$ | Experiment[a] | | This Work[b] | |
|---|---|---|---|---|---|
| | | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ |
| 0 4 2 0 | 0 3 1 0 | 674.414 | | 668.30 | 0.184(3) |
| 0 3 1e 0 | 0 2 2 0 | 686.921 | 0.188(1) | 682.13 | 0.175(13) |
| 0 3 1f 0 | 0 2 2 0 | 686.921 | 0.189(1) | 682.22 | 0.202(11) |
| 0 4 0 0 | 0 3 1 0 | 689.509 | 0.185(3) | 687.10 | 0.196(26) |
| 0 2 0 0 | 0 1 1 0 | 699.434 | 0.183(5) | 699.03 | 0.199(17) |
| 0 3 1 0 | 0 2 0 0 | 702.037 | 0.190(2) | 699.50 | 0.197(8) |
| 0 4 2e 0 | 0 3 1 0 | 704.725 | 0.196(5) | 702.91 | 0.187(31) |
| 0 4 2f 0 | 0 3 1 0 | 704.725 | 0.188(7) | 703.00 | 0.196(4) |
| 0 1 1 0 | 0 0 0 0 | 711.980 | 0.189(1) | 715.93 | 0.200(1) |
| 0 2 2e 0 | 0 1 1 0 | 714.550 | 0.189(4) | 716.30 | 0.196(17) |
| 0 2 2f 0 | 0 1 1 0 | 714.550 | 0.188(4) | 716.35 | 0.200(2) |
| 0 3 3e 0 | 0 2 2 0 | 717.231 | 0.196(1) | 716.87 | 0.198(5) |
| 0 3 3f 0 | 0 2 2 0 | 717.231 | 0.197(1) | 716.87 | 0.198(6) |
| 0 4 4e 0 | 0 3 3 0 | 720.021 | | 718.22 | 0.198(5) |
| 0 4 4f 0 | 0 3 3 0 | 720.021 | 0.201(5) | 718.22 | 0.198(5) |
| 0 4 2e 0 | 0 2 2 0 | 1391.65 | 0.0486(2) | 1385.12 | 0.0470(14) |
| 0 4 2f 0 | 0 2 2 0 | 1391.65 | 0.0488(2) | 1385.12 | 0.0475(12) |
| 0 4 0 0 | 0 2 0 0 | 1391.56 | 0.0489(2) | 1386.55 | 0.0470(10) |
| 0 3 1e 0 | 0 1 1 0 | 1401.47 | 0.0471(2) | 1398.43 | 0.0496(35) |
| 0 3 1f 0 | 0 1 1 0 | 1401.47 | 0.0475(4) | 1398.57 | 0.0463(32) |
| 0 2 0 0 | 0 0 0 0 | 1411.41 | 0.0496(2) | 1414.92 | 0.0479(11) |
| 1 0 0 0 | 0 2 0 0 | 1900.06 | | 1892.83 | 0.00498(7) |

| $v_1'v_2'l'v_3'$ | $v_1''v_2''l''v_3''$ | Experiment[a] | | This Work[b] | |
|---|---|---|---|---|---|
| | | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ |
| 0 4 0 0 | 0 1 1 0 | 2090.98 | 0.00320(1) | 2085.62 | 0.00369(50) |
| 0 4 2e 0 | 0 1 1 0 | 2106.20 | 0.00330(2) | 2101.43 | 0.00342(65) |
| 0 4 2f 0 | 0 1 1 0 | 2106.20 | 0.00327(1) | 2101.48 | 0.00357(14) |
| 0 3 1 0 | 0 0 0 0 | 2113.45 | 0.003263(1) | 2114.46 | 0.00359(15) |
| 1 2 0 0 | 0 3 1 0 | 2570.86 | 0.0228(1) | 2571.81 | 0.0236(14) |
| 1 1 1e 0 | 0 2 2 0 | 2577.63 | 0.0232(1) | 2571.98 | 0.0229(17) |
| 1 1 1f 0 | 0 2 2 0 | 2577.63 | 0.0232(1) | 2572.03 | 0.0245(15) |
| 1 1 1 0 | 0 2 0 0 | 2592.75 | 0.0226(1) | 2589.31 | 0.0239(24) |
| 1 0 0 0 | 0 1 1 0 | 2599.50 | 0.0226(1) | 2591.75 | 0.0238(10) |
| 0 1 1 1 | 0 0 0 0 | 2807.06 | 0.00824(5) | 2813.98 | 0.00906(36) |
| 0 2 0 1 | 0 0 0 0 | 3502.12 | | 3510.99 | 0.00313(6) |
| 1 1 1 0 | 0 0 0 0 | 4005.63 | 0.00986(11) | 4004.27 | 0.00986(94) |
| 1 3 1e 0 | 0 1 1 0 | 4654.89 | 0.000784(3) | 4650.21 | 0.000785(110) |
| 1 3 1f 0 | 0 1 1 0 | 4654.89 | 0.000786(4) | 4650.34 | 0.000781(80) |
| 1 2 0 0 | 0 0 0 0 | 4684.31 | 0.000795(5) | 4686.28 | 0.000735(93) |
| 0 1 1 2 | 0 0 0 0 | 4879.73 | | 4891.88 | 0.000310(51) |
| 0 2 0 2 | 0 0 0 0 | 5571.89 | | 5586.50 | 0.000272(3) |
| 2 0 0 0 | 0 1 1 0 | 5806.15 | 0.00137(1)[c] | 5797.45 | 0.00172(8) |
| 1 1 1 1 | 0 0 0 0 | 6084.80 | 0.00052(4)[c] | 6088.56 | 0.000545(19) |
| 2 2 0 0 | 0 2 0 0 | 6441.54 | 0.00892(14) | 6440.92 | 0.00789(1) |
| 2 1 1e 0 | 0 1 1 0 | 6480.78 | 0.00889(4) | 6474.62 | 0.00835(22) |
| 2 1 1f 0 | 0 1 1 0 | 6480.78 | 0.00901(4) | 6474.71 | 0.00826(6) |
| 1 2 0 1 | 0 0 0 0 | 6761.33 | | 6768.51 | 0.000479(7) |
| 2 1 1 0 | 0 0 0 0 | 7194.22 | | 7190.60 | 0.00146(12) |
| 1 3 1 1 | 0 0 0 0 | 7440.48 | | 7445.62 | 0.000107(8) |
| 2 2 0 0 | 0 0 0 0 | 7853.51 | | 7855.83 | 0.000150(20) |

| $v_1'v_2'l'v_3'$ | $v_1''v_2''l''v_3''$ | Experiment[a] | | This Work[b] | |
|---|---|---|---|---|---|
| | | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ |
| 1 1 1 2 | 0 0 0 0 | | | 8182.18 | $4.14(6) \times 10^{-5}$ |
| 2 1 1 1 | 0 1 1 0 | 8544.07 | $0.00071(5)^c$ | 8543.75 | 0.000625(4) |
| 1 2 0 2 | 0 0 0 0 | 8816.00 | | 8830.27 | $6.35(10) \times 10^{-5}$ |
| 2 1 1 1 | 0 0 0 0 | 9257.53 | $8.2(6) \times 10^{-5\ c}$ | 9259.64 | $9.48(19) \times 10^{-5}$ |
| 3 1 1 0 | 0 1 1 0 | 9568.35 | $0.0010(4)^{\ c}$ | 9560.81 | 0.001082(9) |
| 2 2 0 1 | 0 0 0 0 | 9914.40 | $5.5(2) \times 10^{-5\ c}$ | 9922.92 | $4.31(2) \times 10^{-5}$ |
| 3 1 1 0 | 0 0 0 0 | 10281.8 | $3.2(2) \times 10^{-5\ c}$ | 10276.7 | 0.000210(19) |
| 2 3 1 1 | 0 0 0 0 | | | 10580.5 | $1.43(15) \times 10^{-5}$ |
| 3 2 0 0 | 0 0 0 0 | | | 10925.2 | $3.78(28) \times 10^{-5}$ |
| 4 1 1 0 | 0 1 1 0 | 12557.3 | $0.00023(3)^c$ | 12548.1 | 0.000218(5) |
| 2 3 1 2 | 0 0 0 0 | | | 12624.3 | $1.55(1) \times 10^{-6}$ |
| 4 1 1 0 | 0 0 0 0 | 13270.8 | $1.4(4) \times 10^{-5\ c}$ | 13264.1 | $3.47(42) \times 10^{-5}$ |
| 5 1 1 0 | 0 1 1 0 | 15452.1 | $6.6(5) \times 10^{-5\ c}$ | 15441.0 | $5.32(6) \times 10^{-5}$ |
| 5 1 1 0 | 0 0 0 0 | 16165.6 | $3.4(3) \times 10^{-6\ c}$ | 16156.9 | $6.67(115) \times 10^{-6\ d}$ |

[a] Experimental data, band centres taken from refs [34,43,27,44,45], transition dipoles from Maki *et al.* [23] and from Smith *et al.* [24,27] where marked.

[b] The *ab initio* calculations of this work, using the VQZANO+ PES and the cc-pCVQZ/CCSD(T) DMS of van Mourik *et al.* [16].

[c] Experimental measurements of Smith *et al.* [24,27].

[d] This band is involved in intensity stealing.

Table 2: A comparison of experimental and theoretical stretching band centres and transition dipoles for some of the most prominent HCN stretching bands at 298 K, in cm$^{-1}$ and Debye ($\times 10^{-3}$), with standard deviation in the last digit given in brackets.

| | | Experiment[a] | | This Work[b] | | Earlier *ab initio* Work | | |
|---|---|---|---|---|---|---|---|---|
| $v_1' v_2' l' v_3'$ | $v_1'' v_2'' l'' v_3''$ | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ | ANO[c] $\nu_0$ | $\mu_{GTO}$ [d] | $\mu_{AQCC}$ [e] |
| 1 0 0 0 | 0 0 0 0 | 3311.48 | 83.1(17) | 3307.75 | 85.3(16) | 3334.1 | 83.4 | 0.0703 |
| 0 0 0 2 | 0 0 0 0 | 4173.07 | | 4181.45 | 0.466(52)[h] | 4161.5 | 0.130 | 0.773 |
| 1 0 0 1 | 0 0 0 0 | 5393.70 | | 5394.43 | 4.37(2) | 5399.4 | 4.63 | 2.41 |
| 0 0 0 3 | 0 0 0 0 | 6228.60 | 0.12(2)[f] | 6242.42 | 0.198(12) | 6211.4 | 0.117 | 0.247 |
| 2 0 0 1 | 0 0 0 1 | 6488.74 | 8.7(3) | 6484.16 | 8.49(3) | | | |
| 2 0 0 0 | 0 0 0 0 | 6519.61 | 8.81(12) | 6513.50 | 8.60(4) | 6553.2 | 8.78 | 5.22 |
| 1 0 0 2 | 0 0 0 0 | 7455.42 | 0.11(1)[f] | 7461.58 | 0.0959(91) | 7445.7 | 0.0974 | 0.245 |
| 2 0 0 1 | 0 0 0 0 | 8585.58 | 0.68(1)[f] | 8584.59 | 0.677(4) | 8595.9 | 0.785 | 0.468 |
| 1 0 0 3 | 0 0 0 0 | 9496.44 | 0.066(3)[f] | 9508.91 | 0.0648(8) | 9474.5 | 0.0771 | 0.0796 |
| 3 0 0 0 | 0 0 0 0 | 9627.09 | 1.03(2)[f] | 9619.20 | 1.138(6) | 9668.3 | 1.12 | 1.11 |
| 2 0 0 2 | 0 0 0 0 | 10631.4 | 0.050(2)[f] | 10636.8 | 0.0320(4) | 10623.7 | 0.0614 | 0.0229 |
| 1 0 0 4 | 0 0 0 0 | 11516.6 | | 11536.1 | 0.0114(7) | 11487.4 | | |

Table 2: continued.

| $v_1'v_2'l'v_3'$ | $v_1''v_2''l''v_3''$ | Experiment[a] | | This Work[b] | | Earlier *ab initio* Work | | |
|---|---|---|---|---|---|---|---|---|
| | | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ | ANO[c] $\nu_0$ | $\mu_{GTO}$ [d] | $\mu_{AQCC}$ [e] |
| 3 0 0 1 | 0 0 0 0 | 11674.5 | 0.185(4)[f] | 11672.2 | 0.179(5) | 11686.9 | 0.202 | 0.283 |
| 4 0 0 0 | 0 0 0 0 | 12635.9 | 0.222(7)[f] | 12626.2 | 0.225(2)[h] | 12686.1 | | |
| 2 0 0 3 | 0 0 0 0 | 12658.0 | 0.053(4)[f] | 12669.9 | 0.0239(5) | 12638.6 | | |
| 3 0 0 2 | 0 0 0 0 | 13702.2 | 0.029(2)[f] | 13708.5 | 0.0216(1) | 13695.5 | 0333 | 0.0499 |
| 2 0 0 4 | 0 0 0 0 | 14653.7 | 0.048(2)[f] | 14685.0 | 0.0187(6) | 14642.8 | | |
| 4 0 0 1 | 0 0 0 0 | 14670.5 | 0.051(2)[f] | 14656.9 | 0.0513(3) | 14683.9 | | |
| 5 0 0 0 | 0 0 0 0 | 15551.9 | 0.067(8)[f] | 15539.3 | 0.0550(5) | 15604.1 | 0.0671 | 0.165 |
| 3 0 0 3 | 0 0 0 0 | 15710.5 | 0.0036(4)[f] | 15721.7 | 0.00487(3)[h] | 15700.3 | 0.00730 | 0.00196 |
| 2 0 0 5 | 0 0 0 0 | 16640.3 | 0.0098(6)[f] | 16660.7 | 0.00793(17) | 16634.5 | | |
| 4 0 0 2 | 0 0 0 0 | 16674.2 | 0.0202(8)[f] | 16685.0 | 0.00786(20) | 16683.6 | | |
| 5 0 0 1 | 0 0 0 0 | 17550.4 | 0.0282[g] | 17551.0 | 0.0154(58)[h] | 17574.4 | 0.0286 | 0.0755 |

[a] Experimental data, band centres taken from refs [34,43,27,44,45], transition dipoles from Maki *et al.* [23] and others where where marked.

[b] The *ab initio* calculations of this work, using the VQZANO+ PES and the cc-pCVQZ/CCSD(T) DMS of van Mourik *et al.* [16].

[c] The *ab initio* ANO/CCSD(T) vibrational energy level calculations of Bowman *et al.* [1].

[d] The *ab initio* 110 cGTO stretch only HCN DMS and calculations of Botschwina *et al.* [29], Botschwina *et al.* also calculated a combined intensities for three pairs of strong stretching bands: $(40^00)$ and $(20^03)$, $(20^04)$ and $(40^01)$, $(20^05)$ and $(40^02)$, see text.

[e] The *ab initio* TZP AQCC semi-global DMS and calculations of Jakubetz and Lan [2], using the Bowman *et al.* [1] potential surface.

[f] Measurements of Smith *et al.* [24,27].

[g] Measurement from Romanini and Lehmann [28].

[h] These bands are involved in intensity stealing.

Table 3
A comparison of experimental and theoretical line intensities $(\mathrm{cm}^{-2}\mathrm{atm}^{-1} \times 10^{-3})$ for the HCN $(00^{0}1)$ fundamental band.

| P Branch | | $J''$ | R Branch | |
|---|---|---|---|---|
| Expt[a] | This work | | Expt[a] | This work |
| | | 0 | 0.193 | 0.323 |
| 0.337 | 0.487 | 1 | 0.300 | 0.497 |
| 0.839 | 1.14 | 2 | 0.295 | 0.541 |
| 1.36 | 1.92 | 3 | 0.236 | 0.497 |
| 2.03 | 2.81 | 4 | 0.171 | 0.385 |
| 2.87 | 3.75 | 5 | 0.0725 | 0.256 |
| | 4.71 | 6 | 0.0161 | 0.133 |
| 4.23 | 5.61 | 7 | | 0.0445 |
| 4.97 | 6.44 | 8 | 0.0297 | 0.00249 |
| 5.55 | 7.08 | 9 | 0.124 | 0.0124 |
| 5.86 | 7.53 | 10 | 0.222 | 0.0705 |
| 6.11 | 7.80 | 11 | 0.358 | 0.167 |
| 6.09 | 7.85 | 12 | 0.506 | 0.288 |
| 6.00 | 7.70 | 13 | 0.670 | 0.420 |
| 5.84 | 7.37 | 14 | 0.796 | 0.544 |
| 5.46 | 6.91 | 15 | 0.910 | 0.651 |
| 5.08 | 6.31 | 16 | 1.00 | 0.730 |
| 4.66 | 5.67 | 17 | | 0.778 |
| 4.06 | 4.97 | 18 | 0.988 | 0.792 |
| 3.51 | 4.26 | 19 | 0.967 | 0.778 |
| 2.97 | 3.60 | 20 | 0.895 | 0.736 |

[a] Experimental measurements of Maki *et al.* [26].

Table 4
A comparison of experimental and theoretical line intensities $(\mathrm{cm}^{-2}\mathrm{atm}^{-1} \times 10^{-3}$, standard deviation given in the last digit) for the HCN $(02^20)$ forbidden overtone band.

| $J''$ | P Branch | | R Branch | | Q Branch | |
|---|---|---|---|---|---|---|
| | Expt.[a] | This work | Expt.[a] | This work | Expt.[a] | This work |
| 2 | | | | 0.000251 | | 0.00606 |
| 3 | | 0.00606 | | 0.00601 | | 0.0203 |
| 4 | | 0.0104 | | 0.0330 | | 0.0442 |
| 5 | 0.022(8) | 0.150 | 0.149(5) | 0.106 | 0.061(3) | 0.0785 |
| 6 | 0.481(8) | 0.343 | | 0.253 | | 0.121 |
| 7 | 0.834(9) | 0.663 | 0.80(2) | 0.507 | 0.201(7) | 0.171 |
| 8 | 1.357(21) | 1.14 | 1.392(18) | 0.890 | 0.252(6) | 0.225 |
| 9 | 2.246(28) | 1.77 | | 1.41 | 0.291(5) | 0.276 |
| 10 | 3.264(24) | 2.56 | 2.899(37) | 2.08 | 0.354(6) | 0.326 |
| 11 | 4.445(25) | 3.48 | 4.073(26) | 2.82 | 0.406(6) | 0.365 |
| 12 | 5.673(36) | 4.48 | 5.352(25) | 3.68 | 0.469(5) | 0.397 |
| 13 | 7.097(36) | 5.47 | 6.337(28) | 4.52 | 0.455(6) | 0.415 |
| 14 | 8.251(36) | 6.41 | 7.447(37) | 5.29 | 0.470(5) | 0.422 |
| 15 | 9.141(46) | 7.20 | 8.378(49) | 5.96 | 0.439(7) | 0.417 |
| 16 | 10.200(48) | 7.82 | 8.895(47) | 6.46 | | 0.400 |
| 17 | 10.579(47) | 8.19 | 9.357(52) | 6.76 | 0.405(5) | 0.375 |
| 18 | 10.645(79) | 8.30 | 9.478(40) | 6.83 | 0.390(5) | 0.343 |
| 19 | 10.492(50) | 8.17 | | 6.70 | 0.346(5) | 0.305 |
| 20 | | 7.80 | 8.577(41) | 6.32 | | 0.266 |

[a] The experimental measurements of Maki et al. [33].

Table 5
A comparison of experimental and theoretical band centres (cm$^{-1}$) and transition dipoles (Debye, with standard deviation given in the last digit in brackets) for HNC fundamentals and some stretching overtones which are the prominent features of the spectrum at 298 K.

| $v'_1 v'_2 l' v'_3$ | Experiment[a] | | This Work[b] | | aug-cc-pVTZ[c] | | Other Theory | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ | $\nu_0$ | $\mu$ | $\nu_0^d$ | $\mu^e$ | $\mu^f$ |
| 0 1 1 0 | 462.722 | $[1.04(27)]^h$ | 465.190 | 0.463(3) | | | | | 0.490 |
| 0 0 0 1 | 2023.86 | 0.108(16) | 2024.94 | 0.104(2) | 2023.9 | 0.106 | 2024.6 | 0.103 | 0.102 |
| 1 0 0 0 | 3652.66 | 0.156(23) | 3665.12 | 0.151(2) | 3652.7 | 0.157 | 3599.1 | 0.157 | 0.164 |
| 0 0 0 2 | 4026.40$^g$ | | 4029.20 | 0.0138(3) | 4026.4 | 0.0136 | 4024.4 | 0.0126 | |
| 1 0 0 1 | 5664.85$^g$ | | 5676.51 | 0.00943(2) | 5664.1 | 0.00999 | 5628.7 | 0.00985 | |
| 2 0 0 0 | 7171.40$^g$ | | 7189.53 | 0.0179(1) | 7172.1 | 0.0163 | 7116.7 | 0.0134 | |

[a] Experimental data, band centres from Maki and Mellau [39] and Northrup et al. [46] and band transition dipoles from Nezu et al. [36,37].
[b] The ab initio calculations of this work, using the VQZANO+ PES and the cc-pCVQZ/CCSD(T) DMS of van Mourik et al. [16].
[c] The ab initio stretch only cc-pVQZ/CCSD(T) potential and aug-cc-pVTZ/CCSD(T) dipole surface calculations of Botschwina et al. [29].
[d] The ab initio ANO/CCSD(T) vibrational energy level calculations of Bowman et al.[1], quoted here are stretching levels only, see text.
[e] The ab initio TZP AQCC calculations of Jakubetz and Lan [2], using the Bowman et al. [1] potential surface.
[f] The TZ2P/CCSD(T) calculations of Lee and Rendell [38].
[g] These transitions have not been directly measured, but have been inferred from other transitions.
[h] The transition dipole of the bending fundamental was estimated from the stretching fundamental transition dipoles using Herman-Walis effect by Nezu et al. [36], see text.

Table 6
A comparison of experimental and theoretical band centres $(cm^{-1})$ and transition dipoles (Debye, with standard deviation give to the last digit in brackets) of HNC hot bands and overtones which involve a degree of bending mode excitation and are prominent features in the spectrum at 298 K.

| $v_1'v_2'l'v_3'$ | $v_1''v_2''l''v_3''$ | Experiment[a] | This work | |
| | | $\nu_0$ | $\nu_0$ | $\mu$ |
|---|---|---|---|---|
| 0 2 0 0 | 0 1 1 0 | 463.787 | 476.794 | 0.466(154) |
| 0 2 2 0 | 0 1 1 0 | 473.471 | 481.117 | 0.424(188) |
| 0 2 0 0 | 0 0 0 0 | 926.507[b] | 941.910 | 0.0976(67) |
| 0 3 1 0 | 0 0 0 0 | [1400.51][c] | 1428.85 | 0.0673(77) |
| 0 0 0 1 | 0 1 1 0 | | 1559.69 | 0.0199(1) |
| 0 1 1 1 | 0 1 1 0 | 2015.76 | 2017.54 | 0.103(16) |
| 0 1 1 1 | 0 0 0 0 | 2478.48[b] | 2482.67 | 0.0141(1) |
| 1 0 0 0 | 0 1 1 0 | | 3199.88 | 0.0407(16) |
| 1 1 1 0 | 0 1 1 0 | 3630.19 | 3640.77 | 0.146(5) |
| 1 1 1 0 | 0 0 0 0 | 4092.91[b] | 4105.90 | 0.0227(14) |
| 1 2 0 0 | 0 0 0 0 | 4534.45[b] | 4558.15 | 0.00455(42) |

[a] Experimental band centres from Maki and Mellau [39] and Northrup *et al.* [46].
[b] These transitions have not been directly measured, but have been inferred from other transitions.
[c] This band centre was estimated by Maki and Mellau [39] from anharmonic vibration constants of HNC upto the quartic terms, see text.

Table 7

A comparison of experimental and theoretical vibrationally averaged dipole moments of $J = 0$ low lying HCN states and the HNC ground state.

| $(v_1, v_2, v_3)$ | Expt. | aug-cc-pCVTZ[a] | cc-pCVQZ[b] | 110 cGTO[c] |
|---|---|---|---|---|
| (0,0,0) | $2.985^d$ | 2.9752 | 2.9641 | 2.9800 |
| (0,2,0) | $2.899^d$ | 2.8793 | 2.8776 | 2.8935 |
| (0,0,1) | $2.981^d$ | 2.9698 | 2.9599 | 2.9753 |
| (1,0,0) | $3.017^d$ | 3.0054 | 2.9961 | 3.0116 |
| $(0,0,0)^f$ | $3.05^e$ | 2.9721 | 3.0320 | – |

[a] Dipole moment calculations of Bowman *et al.* [3] with aug-cc-pCVTZ/CCSD(T) DMS.
[b] This work, $J = 0 \rightarrow 1$ rotational transition dipole using cc-pCVQZ/CCSD(T) DMS.
[c] Dipole moment calculations of Botschwina *et al.* [31] with HCN-only 110 cGTO/CCSD(T) DMS.
[d] Deleon and Muenter [47].
[e] Blackman *et al.* [48].
[f] HNC ground state.

Table 8

A comparison of *ab initio* dipole moments (Debye) at the three critical points.

| | aug-cc-pCVTZ DMS[a] | cc-pCVQZ DMS[b] | Optimised cc-pCVQZ[c] |
|---|---|---|---|
| HCN | 2.999 | 2.993 | 2.994 |
| TS[d] | 1.171 | 1.181 | 1.178 |
| HNC | −3.087 | −3.121 | −3.094 |

[a] Dipole moments from the aug-cc-pCVTZ/CCSD(T) DMS of Bowman *et al.* [3] at the coordinates of the critical points calculated by Stanton [40] at the cc-pCVQZ/CCSD(T) level.
[b] The Dipole moments from the cc-pCVQZ/CCSD(T) DMS of van Mourik *et al.* [16] at the coordinates of the critical points calculated at the cc-pCV5Z/CCSD(T) level.
[c] Dipole moment at the critical points calculated by Stanton [40] at the cc-pCVQZ level.
[d] The transition state of [H,C,N].