

## **An ab initio HCN and HNC Rotational Vibrational Linelist for Astronomy.**

G. J. Harris, O. Polyansky<sup>1</sup> and J. Tennyson

*Department of Physics and Astronomy, University College London,  
Gower Street, London, WC1E 6BT, United Kingdom.*

### **Abstract.**

We present a new ab initio HCN/HNC linelist. The linelist forms the most accurate and extensive HCN/HNC data set presently in existence. The data contain rotation vibration line frequencies and line strengths, for all transitions that are not rigorously dipole forbidden, between states with energy less than 18 000 cm<sup>-1</sup> and with  $J \leq 60$ .

### **1. Introduction**

HCN and HNC molecules are of great interest in astronomy. They have been observed in many galactic and extragalactic objects, ranging from circumstellar masers through interstellar clouds to planetary atmospheres. However from our point of view the most interesting role of HCN in astrophysics is in carbon star atmospheres. Early calculations by Jørgensen and co-workers (Erikson et al. (1984), Jørgensen et al (1985)) suggested that the proper detailed treatment of the vibration-rotation spectrum of HCN can have a profound effect on the structure of model C-star atmospheres.

The existing HCN opacity data that are currently used for model C-star atmospheres all have their limitations and all neglect the HNC isomer. For example the data based upon laboratory measurements, such as Jørgensen (1990) and Aoki et al. (1998), are limited by the amount of laboratory data available. Whereas existing ab initio linelists, such as Jørgensen (1985), are inaccurate by todays standards. In an attempt to remedy this problem we have calculated an extensive HCN/HNC linelist, which contains just under 400 million lines and 168 000 energy levels.

### **2. Calculation.**

The accuracy of a vibration rotation calculation depends upon the accuracy of the underling electronic structure calculations, namely the potential energy surface (PES) and the dipole moment surface (DMS). Consequently we have used the best available ab initio surfaces, these are detailed in van Mourik et

---

<sup>1</sup>Permanent address: Institute of Applied Physics, Russian Academy of Science, Uljanov Street 46, Nizhnii Novgorod, Russia 603024.

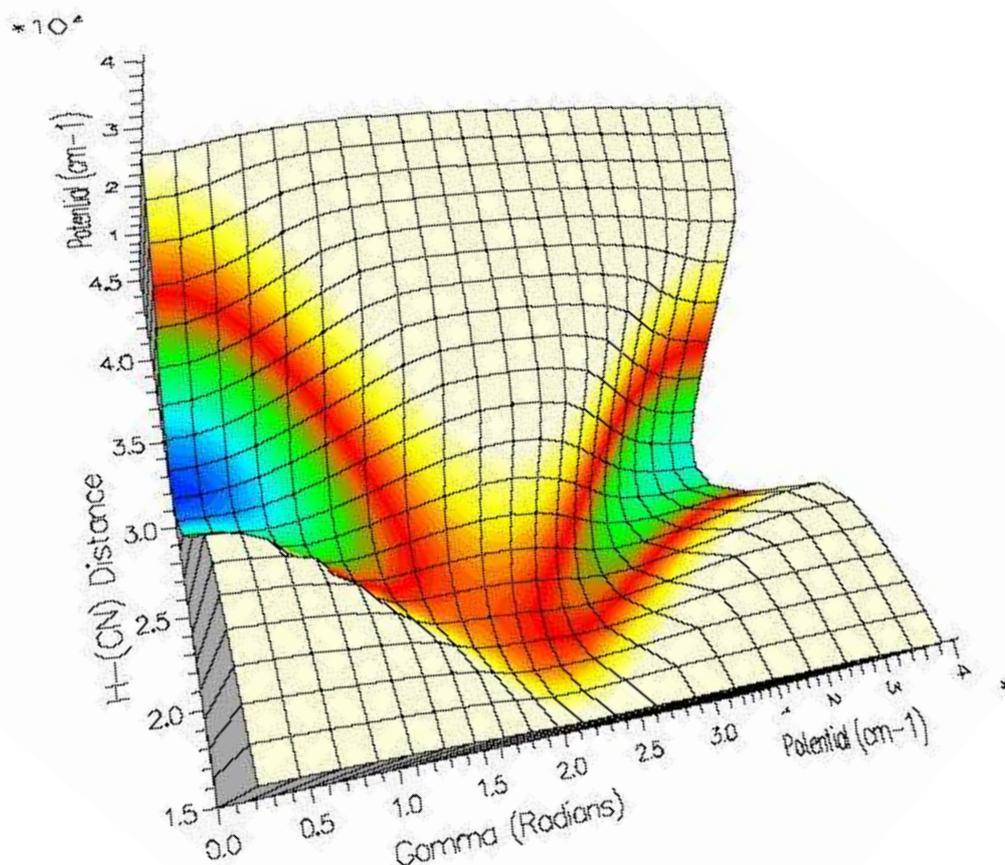


Figure 1. The van Mourik et al. (2001) potential energy surface, the C-N distance is fixed at the near equilibrium value of  $2.179 a_0$ . The two minima correspond to linear HCN and Linear HNC. Energy is in  $\text{cm}^{-1}$ , and  $a_0$  are used for length.

al (2001). Figure 1 shows a plot of the van Mourik (2001), VQZANO+ PES. This PES uses scattering co-ordinates which are defined for HCN as  $r$  the C to N internuclear distance,  $R$  the H to CN centre of mass distance and  $\gamma$  the angle between the  $r$  and  $R$  co-ordinates. The vibration rotation calculations were performed with the DVR3D suite of programs detailed in J. Tennyson et al. (1994,2002). The linelist was calculated on a line by line basis, which allows an accurate representation of the intensity structures of the vibration rotation bands to be obtained. A full discussion of the calculation is given in Harris et al. (2002a,b).

The high temperatures within a stellar atmosphere excite HCN/HNC molecules into highly rotationally excited states. This requires us to calculate the linelist up to a high value of the rotational quantum number  $J$ . To satisfy this requirement we have calculated the linelist to  $J \leq 60$ . and an energy of  $18\,000 \text{ cm}^{-1}$ . The calculation started in December 2000 and took 16 months.

The linelist shows good agreement with laboratory data, see van Mourik et al. (2001) and Harris et al. (2002). The energies and transition dipoles of the fundamental bands are shown in table 1. The band fundamentals are reproduced to within  $4 \text{ cm}^{-1}$  of laboratory data, except the HNC H-N stretch fundamental which is reproduced to  $12 \text{ cm}^{-1}$ . The band transition dipoles are, in general, reproduced to within combined experimental and theoretical error and agree more closely with experiment than do the results of Jørgensen et al. (1985).

Table 1. Comparison of some ab initio and experimental HCN and HNC band centres and band transition dipoles. The experimental data quoted here is compiled from Maki et al. (1995a,1995b,2000), Maki and Mellau (2001) and Nezu et al. (1999).

Isomer	Band	$\nu_0^a$		$\mu^b$		CASSCF/CCI <sup>c</sup>
		Exp.	This work	Exp.	This work	
HCN	(0,1 <sup>1</sup> ,0)	711.98	715.93	0.189(1)	0.200(1)	0.27
HCN	(1,0,0)	3311.48	3307.75	0.0831(17)	0.0853(16)	0.095
HNC	(0,1 <sup>1</sup> ,0)	462.72	465.19	-	0.463(3)	
HNC	(0,0,1)	2023.86	2024.94	0.108(16)	0.104(2)	
HNC	(1,0,0)	3652.66	3665.12	0.156(23)	0.151(2)	

<sup>a</sup>The band centre in  $\text{cm}^{-1}$ , the experimental data is accurate to better than 2 decimal places.

<sup>b</sup>The band transition dipole in Debye. The standard deviation of band dipole fits using Hönl London factors are quoted in parentheses in the magnitude of the last digit, where appropriate.

<sup>c</sup>The ab initio CASSCF and CCI calculations of Jørgensen et al. (1985). Here the integrated band absorption intensities quoted by Jørgensen et al. (1985) have been converted to band transition dipoles.

The rotational vibrational partition function at  $T=3000 \text{ K}$ , calculated with our new linelist, is 35653. This is 93% of the rotationally converged value of 38405 (Barber et al (2002)), this indicates that our linelist accounts for around 93% of the opacity of HCN/HNC at  $T=3000\text{K}$ .

## 2.1. The Linelist and Illustrative Spectra.

There are just under 400 million lines and 168 000 energy levels in the linelist. This vast amount of data requires that the linelist be stored in a compact format. To reduce the storage space the full linelist file is split into an energy level file and a transition strength file. The quantum numbers and energies of each level are stored in the energy level file and the transition strengths are stored, in ascending frequency, in the transition strength file. This reduces the overall storage space by a factor of three. The transition strength data is split into 40 gzipped text files which requires a total of 4.26 Gb. The linelist can be retrieved via anonymous ftp from:

ftp.tampa.phs.ucl.ac.uk:/pub/astrodata/HCN.

To demonstrate the usefulness of the linelist we have generated some simple absorption spectra using the Lambert-Beer law. The resulting ab initio spectrum from 2.6 to 8 microns is shown in figure 2. Figure 3 shows the C-star spectra

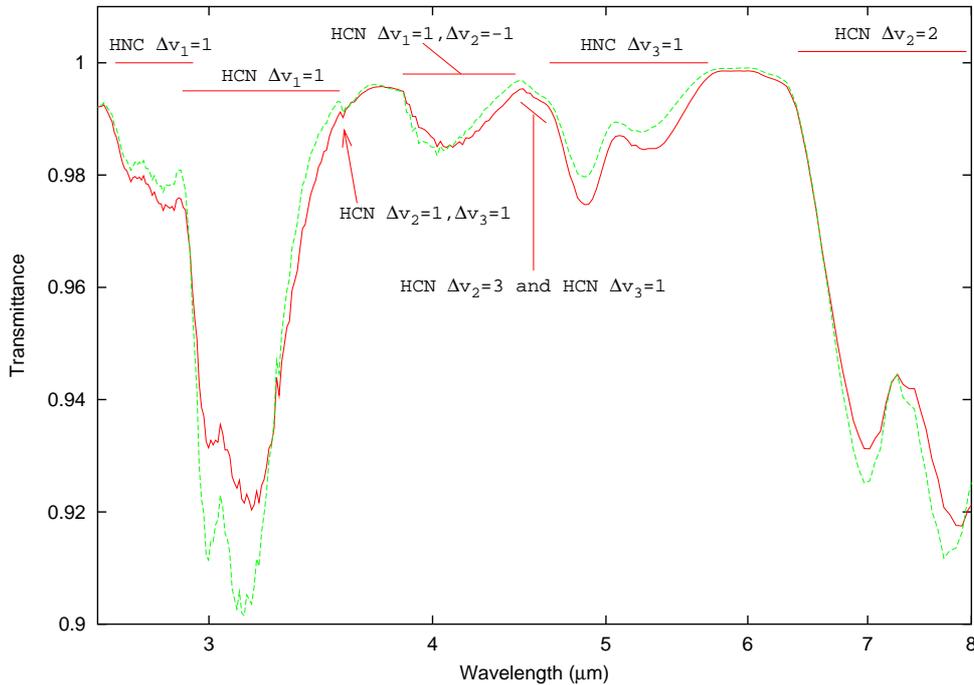


Figure 2. Theoretical HCN/HNC spectra at  $T=3000$  K (red) and  $T=2500$  K (green). A path length of 2 cm is used at a gas pressure of 1 atm.

taken by Aoki et al. (1998) for comparison with figure 2. Figure 4 shows the ab initio spectra at a higher resolution, over the range 2.75 to 4.2  $\mu\text{m}$ . For comparison the observed spectra of WZ Cas taken by Aoki et al. (1998) is also plotted in figure 4. The main features of the ab initio spectra, including the 3.2, 3.6, 4.2 and 7-8  $\mu\text{m}$  features, are in good qualitative agreement with the stellar spectra. A more detailed discussion is given in Harris et al (2002b).

HNC features are notably present in the ab initio spectra. This indicates that if HCN and HNC are in thermodynamic equilibrium HNC will be a significant contributor to opacity in C-stars.

### 3. Conclusion.

A new ab initio HCN/HNC linelist is presented, which is the most extensive and most accurate ab initio HCN/HNC linelist in existence. The main HCN features in spectra calculated with the ab initio HCN/HNC linelist are in good qualitative agreement with observed C-star spectra. The ab initio spectra suggest that if HCN and HNC are in thermodynamic equilibrium, then HNC has a significant effect on the opacity of the stellar atmosphere. A new high temperature HCN and HNC partition function based on this data is awaiting publication. The linelist has been made publicly available.

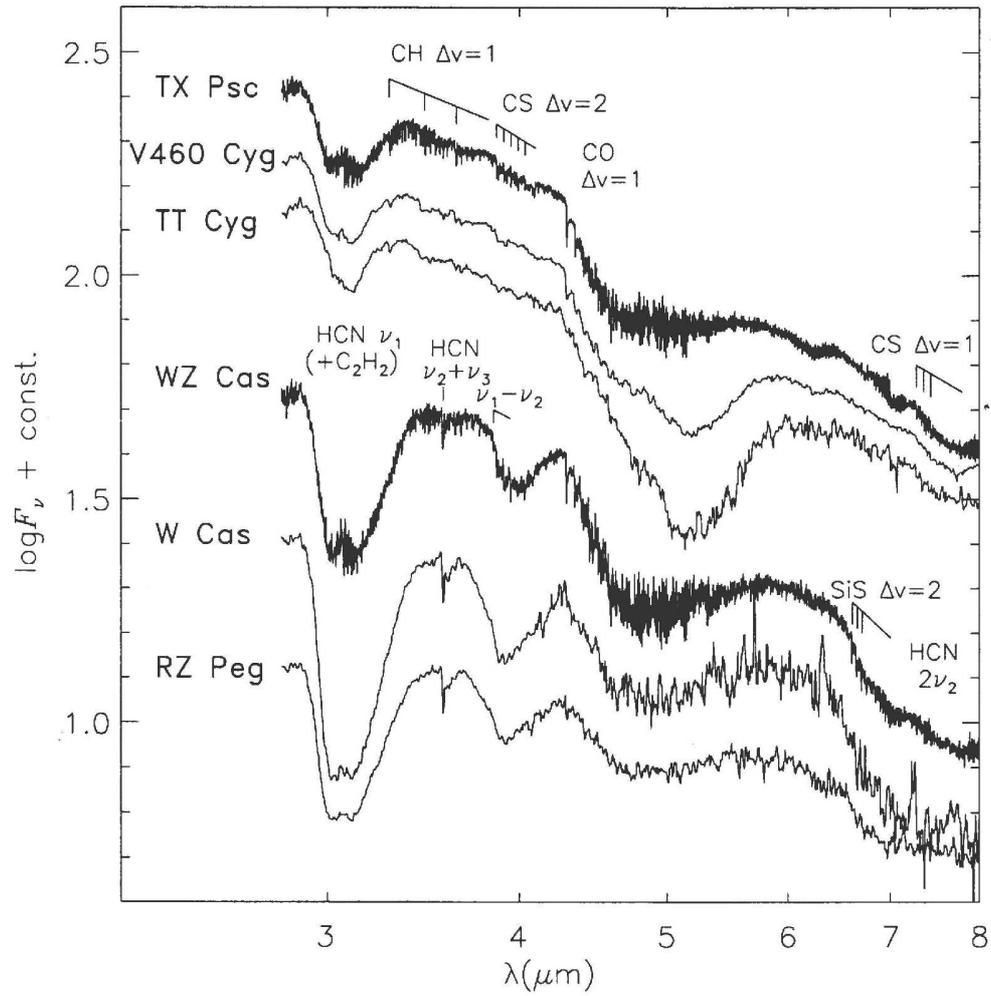


Figure 3. The C-star spectra observed with the ISO SWS by Aoki et al. (1998).

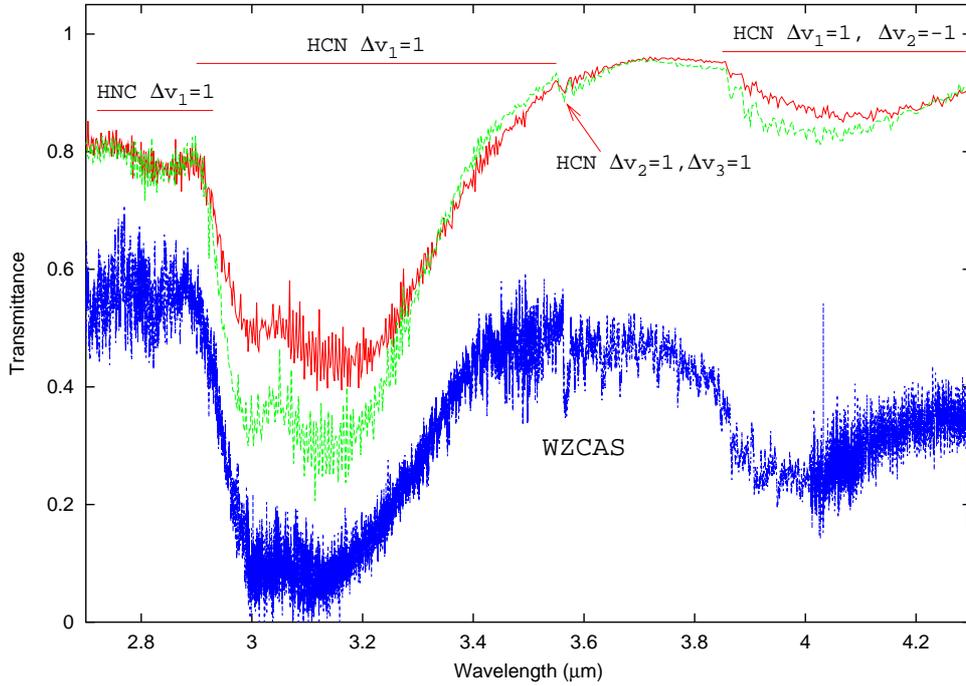


Figure 4. Theoretical HCN/HNC spectra at  $T=3000$  K (red) and  $T=2500$  K (green) with a path length of 20 cm and at a gas pressure of 1 atm. For comparison the spectrum of the C-star WZ Cas taken by Aoki et al (1998) is also plotted.

**Acknowledgments.** We thank Callum Wright for help with high performance computing issues. We thank Dr. H. A. Jones for extracting the spectra ISO public archive and Dr. Y. Pavlenko for helpful discussions. The calculations were carried out on the miracle 24 processor computer at the HiPerSPACE computing centre at UCL, which is part funded by the UK particle physics and astronomy research council (PPARC). PPARC are also thanked for Ph.D. studentship funding.

**References**

- Aoki, W., Tsuji., and Ohnaka, K. 1998, *Astron. Astrophys.*, 340, 222.
- Barber, R. J., Harris, G. J., and Tennyson, J., 2002, *J. Chem. Phys.*, (submitted).
- Eriksson, K., Gustafsson, B., Jørgensen, and Å. Nordlund., 1984, *Astron. Astrophys.* 132, 37.
- Harris, G. J., Polyansky, O. L., and Tennyson, J., 2002a, *Spectrochimica Acta part A.* 58, 673
- Harris, G. J., Polyansky, O. L., and Tennyson, J., 2002b, *Ap. J.* (In press).
- Jørgensen, U. G., Almlöf, J., Gustafsson, B., Larsson, M., and Siegbahn, P., 1985, *J. Chem. Phys.*, 83, 3034.
- Jørgensen, U. G., 1990, *Astron. Astrophys.*, 232, 420
- Maki, A. G., Quapp, W., and Klee, S., *J. Mol. Spectrosc.*, 1995a, 171, 420.
- Maki, A. G., Quapp, W., Klee, S., Mellau, G. Ch., and Albert, S., *J. Mol. Spectrosc.*, 1995b, 174, 365.
- Maki, A. G., Mellau, G. Ch., Klee, S., Winnewisser, M., and Quapp, W., *J. Mol. Spectrosc.*, 2000, 202, 67.
- Maki, A. G., and Mellau, G. Ch., *J. Mol. Spectrosc.*, 2001, 206, 47.
- Nezu, M., Amano, T., and Kawaguchi, K., *J. Mol. Spectrosc.*, 1999, 198, 186.
- Tennyson, J., Henderson, J. R., and Fulton, G., 1995, *Computer Physics Communications*, 86, 175.
- Tennyson, J., Kostin, M. A., Harris, G. J., Polyansky, O. L., and Zobov, N. F., 2002, *Computer Physics Communications*, TO BE SUBMITTED.
- Van Mourik, T., Harris, G. J., Polyansky, O. L., Tennyson, J., Császár, A. G., and Knowles, P. J., 2001, *J. Chem. Phys.*, 115, 3706.