IMPROVING THE QUALITY OF HCN/HNC AND $H^{13}CN$ DATA.

G. J. Harris[1], J. Tennyson[1], B. Kaminskiy[2], Ya. V. Pavlenko[2], and H. R. A. Jones[3].

[1]Department of Physics and Astronomy, University College London, Gower street, London. WC1E 6BT. UK.
[2]Main Astronomical Observatory, National Academy of Sciences, Zabolotnoho 27, Kyiv-127 03680, Ukraine.
[3]Astrophysics Research Institute, Liverpool John Moores University, Twelve Quays House, Egerton Wharf, Birkenhead. CH41 1LD, UK.

ABSTRACT

The HCN/HNC linelist of Harris et al. (2002) ApJ, 578, 657, is the most accurate and extensive *ab initio* linelist in existence. It has been used to identify HNC in a carbon star for the first time (Harris et al. 2003, MNRAS, 344, 1107). However, it suffers from the inherent accuracy problems of *ab initio* data. The band centres of some overtone bands deviate by up to 10 cm^{-1} from experimental values. To improve the quality of many of our line frequencies we have substituted the available experimentally determined HCN energy levels for their *ab initio* counterparts, thus improving the accuracy of many of the strongest HCN/HNC line frequencies. We are currently repeating this process for $H^{13}CN$ in order to create a $H^{13}CN$ linelist.

Key words: Molecular data – Stars: synthetic spectra – Carbon stars.

1. INTRODUCTION

In cool carbon rich atmospheres, such as those of AGB carbon stars HCN is known to be a very important source of opacity Eriksson et al. 1984. It is near-impossible to measure the intensities and frequencies of all the lines of astrophysical importance in the laboratory, making theoretical studies vital. The HCN linelist of Harris et al. 2002 is calculated to a higher level of theory and is more extensive than all other theoretical linelists. The linelist of Harris et al. 2002 also contains HNC which has been shown (Harris et al. 2003) to have a significant effect on the atmospheric structure and spectra of C-stars.

However our linelist suffers from the usual inherent accuracy problems of *ab initio* data, the line positions of hot bands often deviate by up to 10 cm^{-1} from experimental data. Furthermore as the atmospheres of C-giants are enriched with ^{13}C, the ideal HCN linelist would account for the isotopomer $H^{13}CN$. Here we discuss our progress and preliminary results in improving the accuracy of our HCN/HNC linelist and our attempt to account for $H^{13}CN$ by using experimental data.

2. THE *ab initio* HCN/HNC LINELIST

The calculation of the original *ab initio* linelist[1] of Harris et al. 2002 took 18 months on a 24-processor SGi Origin2000, and was performed using the discrete variable representation (DVR) in conjunction with the CCSD(T)/cc-CVQZ HCN/HNC global potential energy surface of van Mourik et al. 2001. The linelist contains nearly 400 million lines and over 150 000 rotation-vibration energy levels. The maximum energy cut-off is at 18000 cm^{-1} above the HCN zero point energy and the linelist extends to a maximum rotational quantum number J of 60. The HCN/HNC partition function calculated with this data set at 3000 K is 93% of the rotationally converged partition function of Barber et al. 2002, indicating that the linelist accounts for approximately 93% of all HCN/HNC opacity.

Figure 1 shows a plot of an ISO-SWS spectrum Aoki et al. 1998 of WZ Cas in the 3.55 to 3.65 micron region, also shown is the synthetic spectrum of Harris et al. 2003 calculated with the Harris et al. 2002 HCN linelist. The centres of the HCN Q branches have been marked on the spectra. There are clear differences between the synthetic and observed spectra brought about by inaccurate line frequencies in the Harris et al. 2002 linelist. It is the goal of this project to improve the accuracy of the *ab initio* line frequencies using laboratory data, and so allow us to create more accurate synthetic spectra.

3. EXPERIMENTAL HCN/HNC AND $H^{13}CN$ DATA

HCN and HNC have attracted much attention from experimental molecular spectroscopists. As a consequence there exists a significant amount of data for the strongest low temperature bands. These studies (Smith et al. 1989; Maki et al. 2000; Lecoutre et al. 2000) have yielded excellent data for HCN and $H^{13}CN$ up to a maximum of 6 quanta in the bending and H-C stretch modes and 4 quanta in the C-N stretch mode. For HNC, the data (Northrup et al. 1997; Maki & Mellau 2001) is much less extensive, up to 2 quanta of bend, 4 quanta of H-N stretch and 2 quanta on C-N stretch. All this laboratory data is presented in varying formats, from line frequencies to polynomial expansions in angular momentum for each vibrational band.

---

[1] The linelist of Harris et al. 2002 is publicly available from http://www.tampa.phys.ucl.ac.uk

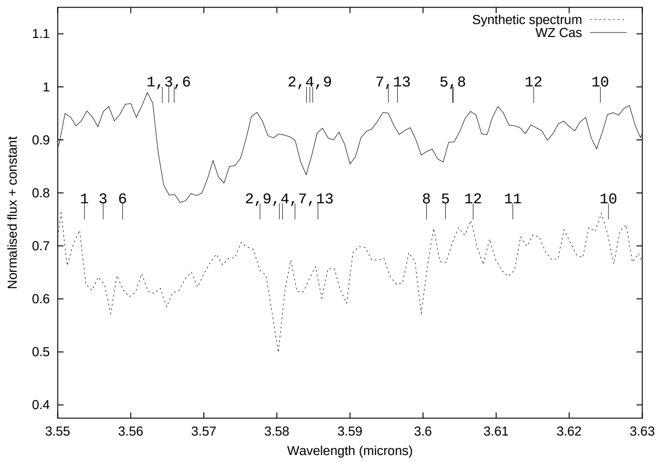

Figure 1. Synthetic and observed spectra of WZ Cas. The upper marks and labels refer the experimentally determined band centres and the lower digits and marks to the ab initio *band centres, see table 1.*

Using line frequencies from Maki et al. 2000; Maki & Mellau 2001; Northrup et al. 1997 we have compiled a list of 5200 HCN/HNC and 4400 H^{13}CN lab/empirical energy levels up to a maximum of 6 Quanta in bend, 3 quanta of H-C stretch and 3 quanta of C-N stretch and to a maximum angular momentum (J) of 60.

We have combined this lab/emprical data with our existing *ab initio* list of energy levels, replacing *ab initio* energy levels with their experimental counterparts. This has resulted in greatly improved line frequencies for the strongest bands in our linelist. Work is continuing to include high lying energy levels.

4. THE NEW LINELISTS

Line frequencies for the improved HCN/HNC linelist, are calculated using lab/empirical energy levels where available. If both the upper and lower levels of a transition is within our lab/empirical energy level list, we are able to determin a lab/empirical frequency for that transition. However, if neither, or only one of the upper and lower levels is within our lab/empirical energy level list we use the old Harris et al. 2002 *ab initio* line frequencies. The band intensities of the linelist of Harris et al. 2002 agree to within error with experimental line intensities, so for consistency we use only the Harris et al. 2002 line intensities. This results in a linelist which has accurate line frequencies for the low lying bands, but also accounts for the many high lying bands.

As with the improved HCN/HNC linelist, our H^{13}CN linelist uses accurate lab/empirical line frequencies for the low lying bands, whilst our old *ab initio* HCN/HNC line frequencies are used for the bulk of the high lying, low intensity bands. This gives accurate frequencies for the strong bands, but relies upon the *ab intio* HCN line frequencies to represent opacity from the weaker lines.

Figures 2 shows the opacity of our old *ab initio* linelist and the improved linelist in the 3.6 μm region. The differences which the lab/empirical line frequencies make to the opacity is significant. If figure 2 is compared with the spectrum of WZ Cas in figure 1, then it is clear that the improved HCN/HNC linelist will give much better agreement with the observed spectrum of WZ Cas. Figure 3 shows the opacity of the improved HCN/HNC linelist and the H^{13}CN linelist at 3.6 μm. There are clear differences in the opacity of H^{13}CN and HCN in this region, this is reflected in table 1. If H^{13}CN is present in sufficient quantities then it should be visible at 3.6 μm region.

Table 1. Laboratory and ab initio band centres for $\Delta v_2 = 1$, $\Delta v_3 = 1$ bands of HCN and H^{13}CN. The index corresponds to the numbers on figure 1.

index	(v_1', v_2', l', v_3')	$(v_1'', v_2'', l'', v_3'')$	HCN Theory λ_c μm	HCN Lab λ_c μm	H^{13}CN Lab λ_c μm
1	(0,1,1,1)	(0,0,0,0)	3.5537	3.5643	3.6144
2	(0,2,0,1)	(0,1,1,0)	3.5777	3.5841	3.6385
3	(0,2,2,1)	(0,1,1,0)	3.5562	3.5652	3.6339
4	(0,3,1,1)	(0,2,0,0)	3.5808	3.5845	3.6355
5	(0,3,1,1)	(0,2,2,0)	3.6031	3.6040	3.6630
6	(0,3,3,1)	(0,2,2,0)	3.5589	3.5659	3.6093
7	(0,1,1,2)	(0,0,0,1)	3.5825	3.5953	3.6462
8	(0,4,0,1)	(0,3,1,0)	3.6005	3.6041	3.6596
9	(0,4,2,1)	(0,3,1,0)	3.5803	3.5849	3.6324
10	(0,4,2,1)	(0,3,3,0)	3.6254	3.6243	3.6879
11	(0,4,4,1)	(0,3,3,0)	3.6123	–	3.6065
12	(0,2,0,2)	(0,1,1,1)	3.6069	3.6151	–
13	(0,2,2,2)	(0,1,1,1)	3.5856	3.5965	–

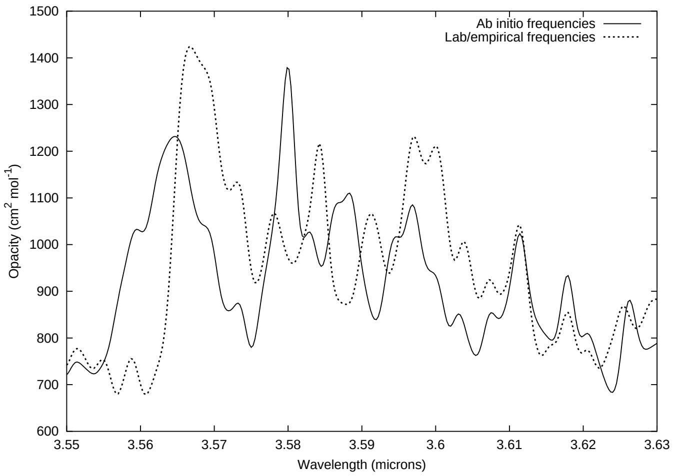

Figure 2. The opacity of our 2 HCN/HNC linelists. calculated using a Gaussian line profile of half width 0.75 cm^{-1}.

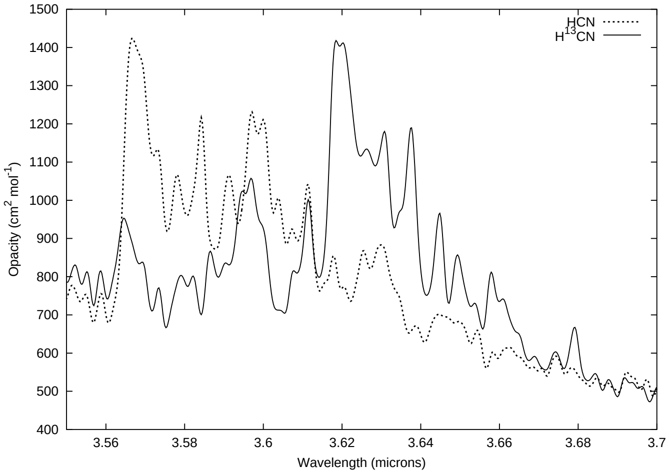

Figure 3. The opacity of our $H^{13}CN$ and improved HCN/HNC linelists. calculated using a Gaussian line profile of half width 0.75 cm^{-1}

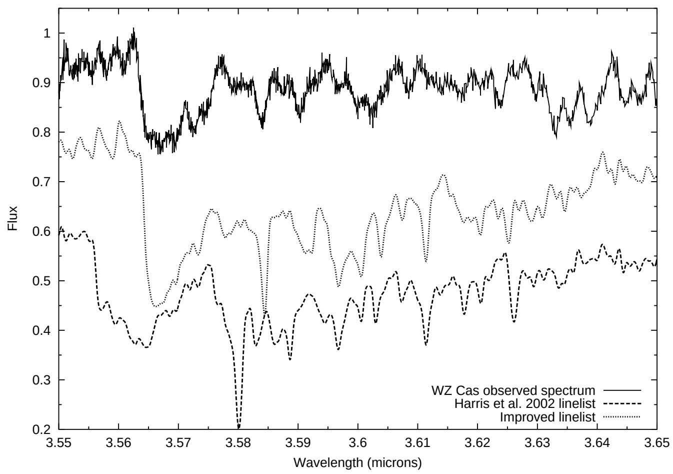

Figure 4. Observed spectrum of WZ Cas, with synthetic spectra calculated at an effective temperature of 2800 K, log g = 0 and log(C/O) = 0.02. One of the synthetic spectra is calculated with the linelist of Harris et al. 2002, the other with the improved Lab/empirical linelist.

5. Preliminary Synthetic spectra

New synthetic spectra for carbon stars are currently being calculated using the improved HCN/HNC and $H^{13}CN$ linelists. These spectra use the model atmospheres calculated by Harris et al. 2003 and the WITA6 spectrum synthesis code (Pavlenko 2000). Figure 4 shows the spectrum of WZ Cas, taken by Aoki et al. 1998 with the ISO-SWS, in the 3.6 micron together with 2 synthetic spectra. Thes synthetic spectra are calculated at $T_{eff} = 2800$ K, with $\log g = 0$ and $\log(C/O) = 0.02$, one is calculated with the *ab initio* linelist of Harris et al. 2002 and the other is calculated with the improved HCN/HNC and $H^{13}CN$ linelists. In order to stagger the spectra constants of 0.4 and 0.2 have been subtracted from the flux of the synthetic spectra calculated with the old and new linelists, respectively. We stress that these synthetic spectra are not fits to the observed spectrum of WZ Cas, but are shown here to illustrate the better quality of the synthetic spectra calculated using the improved HCN/HNC and $H^{13}CN$ linelists. Hence the depth of the absorption is a relatively poor fit to observation.

As with the opacity, the improvement in the synthetic spectra is most evident at 3.565 μm, which corresponds to the position of the lowest lying band with $\Delta v_2 = -1$ and $\Delta v_3 = 1$. The absorption here is considerably better modelled with the improved linelists than it was with the old ab initio list. We expect these improvements to be evident in other spectral regions in which HCN is an important opacity source.

6. Conclusion

As part of our ongoing project on HCN in stellar atmospheres we have compiled a list of laboratory/empirical energy levels for HCN, HNC and $H^{13}CN$. These energy levels have been used to improve the accuracy of the line frequencies in our HCN/HNC linelist and also to calculate an approximate $H^{13}CN$ linelist. We are in the process of adding laboratory data for the high lying stretching bands to our energy level lists. Once this is complete we will make our linelist publicly available.

These linelists are being used to calculate new synthetic spectra for cool carbon stars, which show far better agreement with observation.

Acknowledgements

GJH would like to thank the UK particle physics and astronomy research council (PPARC) for post-doctoral funding.

References

Aoki, W., Tsuji, T., and Ohnaka, K., 1998, A&A, 340, 222

Barber, R. J., Harris, G. J., Tennyson, J., 2002, J. Chem. Phys. 117, 11239

Eriksson, K, Gustafsson, B., Jørgensen. U. G., Nordlund, Å., 1984, A&A, 132, 37

Harris, G. J., Polyansky, O. L., Tennyson, J., 2002, ApJ 578, 657

Harris, G. J., Pavlenko, Ya., V., Jones, H. R. A., Tennyson, J., 2003, MNRAS 344, 1107

Lecoutre, M., Rohart, F., Huet, T. R, Maki, A. G., 2000, J. Mol. Spectroscopy 203, 158

Maki, A. G., Mellau, G. CH., Klee, S., Winnewisser, M., Quapp, W., 2000, J. Mol. Spectroscopy 202, 67

Maki, A. G., Mellau, G. CH., 2001, J. Mol. Spectroscopy 206, 47

Northrup, F. J., Bethardy, G. A., Macdonald, R. G., 1997, J. Mol. Spectroscopy 186, 349

Pavlenko, Ya. V., 2000, Astron. Rep., 44, 219.

Smith, A. M., Coy, S. L., Klemperer, W., Lehmann, K. K., 1989, J. Mol. Spectroscopy 134, 124

Van Mourik, T., Harris, G. J., Polyansky, O. L., Tennyson, J., Császár, A. G., Knowles, P. J., 2001, J. Chem. Phys. 115, 3706