Improving the Accuracy of HCN/HNC Opacity Data and Accounting for Isotopomers.

Gregory J. Harris[1], Jonathan Tennyson[1], Hugh R.A. Jones[2], and
Yakiv. V. Pavlenko[3]

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

Abstract. The HCN/HNC linelist of Harris et al. ApJ, **578**, 657, (2002), is the most accurate and extensive *ab initio* linelist in existence. 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 are in the process of substituting 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 propose to generate an approximate H^{13}CN linelist using experimentally determined energy levels of H^{13}CN with our HCN line intensities. Our preliminary results are presented here.

1 Introduction

In cool carbon rich atmospheres, such as those of AGB carbon stars HCN is known to be an important source of opacity [1]. Triatomic molecules such as HCN have rich and varied infrared spectra containing billions of rotational-vibrational lines. It is near-impossible to measure the intensities and frequencies of all the lines, of astrophysical importance, in the laboratory. Therefore *ab initio* spectroscopic studies of the spectra of these molecules is of great importance.

For HCN, the most accurate and complete linelist in existence is that of Harris and co-workers [2]. This linelist also contains the often neglected isomer of HCN, HNC, which has been shown [3] to have a significant effect on the atmospheric structure and spectra of C-stars. The linelist of Harris and co-workers 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 laboratory data. Such large deviations in band and line frequencies make comparison of synthetic and observed spectra difficult at medium to high resolution. Furthermore as the atmospheres of C-giants are usually enriched with ^{13}C, thus the ideal HCN linelist would account for the isotopomer H^{13}CN. In this poster we discuss the our linelist and our progress toward improving the accuracy of the linelist and accounting for H^{13}CN by using experimental data.

2   The HCN/HNC Linelist.

The calculation of the HCN/HNC linelist of Harris and co-workers [2] took 18 months on a 24-processor SGi Origin2000. It 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 and co-workers [4]. The linelist contains nearly 400 million lines and over 150 000 rotation-vibration energy levels. The maximum energy cut-off is at 18 000 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 and co-workers [5], indicating that the linelist accounts for approximately 93% of all HCN/HNC opacity.

Our calculation considers the HCN/HNC as one system so uses only the 3 rigorous quantum numbers, these are the angular momentum quantum number (J), the parity and n the number of the energy level in the J-parity block.

3   Improving the Accuracy of the Linelist and Accounting for Isotopomers

Figure 1 shows a synthetic stellar spectrum calculated with the HCN/HNC linelist of Harris and co-workers and also the observed spectrum of WZ Cas, between 3.55 and 3.63 μm.

This corresponds to the region in which the Q branch of the HCN band Δv_2=1, Δv_3=1 is important. We have labelled the band centres of the Q branches of the fundamental and the hot bands using both experimental and *ab initio* data. The band centres are listed in table 1. Clearly the *ab initio* band centres deviate from the experimental band centres by an amount that less than the resolving power of the ISO/SWS. This is reflected in the differences between the experimental and *ab initio* band centres seen in table 1. To improve the accuracy of the line positions we intend to substitute experimentally determined HCN energy levels for our *ab initio* energy levels. Many rotation-vibration lines have been measured in the laboratory by Maki and co-workers [6]. In particular energy levels up to (0,5,5,1) have been determined for both HCN and H^{13}CN. In order to substitute in experimental energy levels we must assign approximate quantum numbers v_1, v_2, l, v_3, to our energy levels. We have assigned 18 000 of our lowest lying energy levels by, firstly manually assigning the J=0 and 1 levels up to 10 000 cm^{-1}. We fitted these states with the ridged rotor expansion combined with a polynomial expansion in the vibrational quantum numbers. This allowed us to estimate the positions of the energy levels with higher rotational excitation and hence by comparison, make energy level assignments.

Figure 2 shows a plot of the absorbance of the low lying Δv_2=1, Δv_3=1 bands, which we have been able to calculate using our energy level assignments. This enables us to determine which bands are responsible for absorption in our synthetic spectra. We are currently in the process of collating the experimental
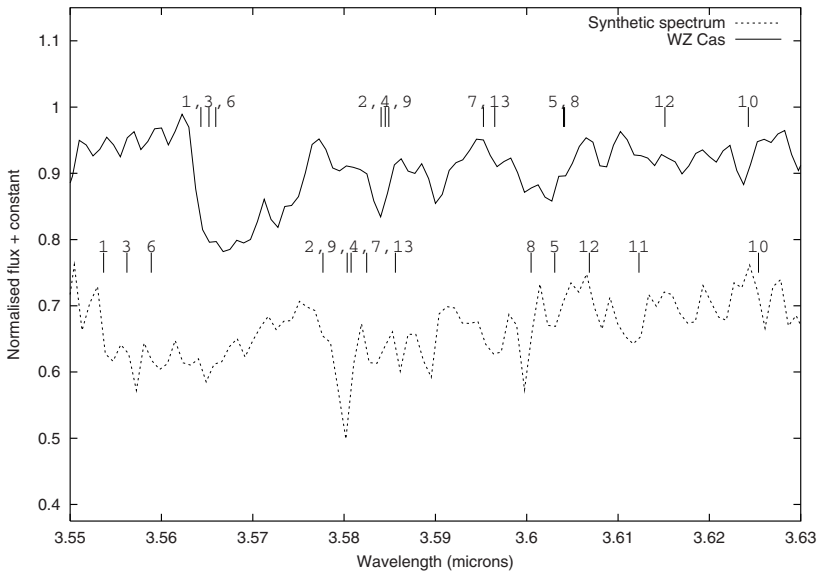
Fig. 1. Synthetic and observed spectra of WZ Cas between 3.55 and 3.63 μm. The marks and integers are the centres and indexes (see table 1) of the bands, the upper set are from experimental data and the lower set from *ab initio* data.

Table 1. Laboratory and *ab initio* band centres for $\Delta v_2 = 1$, $\Delta v_3 = 1$ bands of HCN and $H^{13}CN$. Values in square brackets indicate bands which have not been directly measured, but can be calculated from other measured transitions.

Index	(v'_1,v'_2,l',v'_3)	(v''_1,v''_2,l'',v''_3)	λ_c (μm)		
			HCN (theory)	HCN (Exp)	$H^{13}CN$ (Exp)
1	(0,1,1,1)	(0,0,0,0)	3.5537	3.5643	3.6162
2	(0,2,0,1)	(0,1,1,0)	3.5777	3.5841	3.6366
3	(0,2,2,1)	(0,1,1,0)	3.5562	3.5652	3.6175
4	(0,3,1,1)	(0,2,0,0)	3.5808	3.5845	3.6374
5	(0,3,1,1)	(0,2,2,0)	3.6031	3.6040	[3.6093]
6	(0,3,3,1)	(0,2,2,0)	3.5589	3.5659	3.6187
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]	[3.6880]
11	(0,4,4,1)	(0,3,3,0)	3.6123	[3.5535]	[3.6065]
12	(0,2,0,2)	(0,1,1,1)	3.6069	[3.6151]	-
13	(0,2,2,2)	(0,1,1,1)	-	[3.5965]	-

data of Maki and co-workers, prior to its insertion in our linelist. Also in table 1 we list the band centres of the Q branches of the $\Delta v_2=1$, $\Delta v_3=1$ bands for both HCN and $H^{13}CN$. There are clearly significant differences between the band centres of the HCN and $H^{13}CN$ bands. As $H^{13}CN$ has a near-identical electronic structure to HCN its dipole is close to that of HCN, and so its line intensities are
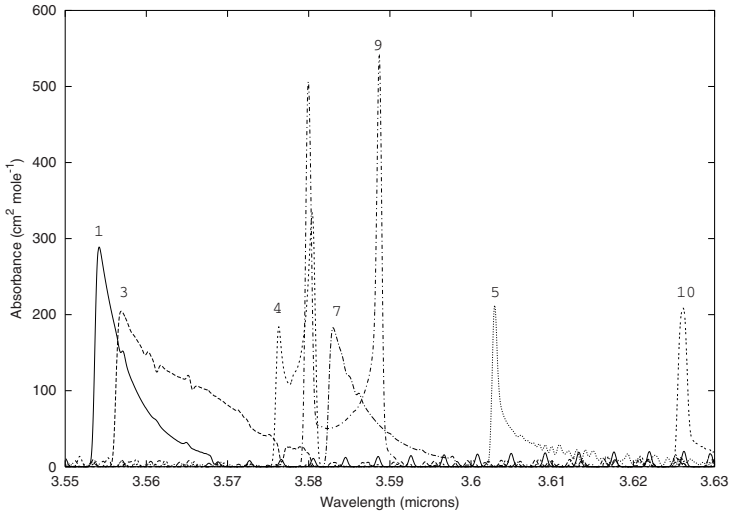
Fig. 2. The opacity function of the strongest $\Delta v_2 = 1$, $\Delta v_3 = 1$ HCN bands. Calculated at T=2800 K and using Gaussian line profiles with a half width of 0.2 cm^{-1}. The integers give the index, see table 1, of each band.

close to those of HCN. With this in mind we intend to substitute experimental H^{13}CN data into our HCN linelist and so make an approximate H^{13}CN linelist, to account for H^{13}CN absorption.

4 Conclusion.

In an effort to improve the accuracy of our linelist we have assigned 18 000 of the lowest lying energy levels in our linelist. Using these assignments we intend to substitute experimental HCN and H^{13}CN data into our linelist. This will allow us to achieve better agreement with observed stellar spectra and also to account for H^{13}CN absorption.

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