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A $H^{13}CN/HN^{13}C$ linelist, model atmospheres and synthetic spectra for carbon stars

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ABSTRACT

A linelist of vibration–rotation transitions for ^{13}C substituted HCN is presented. The linelist is constructed using known experimental levels where available, calculated levels and ab initio line intensities originally calculated for the major isotopologue. Synthetic spectra are generated and compared with observations for cool carbon star WZ Cas. It is suggested that high resolution HCN spectra recorded near 14 μm should be particularly sensitive to the $^{13}C–^{12}C$ ratio.

Key words: molecular data – stars: AGB and post-AGB – stars: atmospheres – stars: carbon – infrared: stars.

1 INTRODUCTION

Carbon giant stars are thought to arise from the third dredge up of asymptotic giant branch (AGB) stars, which pollutes the envelope and atmosphere with nuclear processed material from the interior. This increases the abundance of carbon and the $^{13}C/^{12}C$ ratio to well above the terrestrial level (0.011). In fact the $^{13}C/^{12}C$ ratio in carbon giants has been measured to be as high as one-third (Abia & Isern 1997). There are a number linelists or opacity functions available for $H^{12}CN$ (Jørgensen et al. 1985; Jørgensen 1990; Aoki, Tsuji & Ohnaka 1998; Harris, Polyansky & Tennyson 2002b; Harris et al. 2006). However, when considering the contribution to the opacity by molecular species such as HCN it may not be sufficient to account only for $H^{12}CN$, but also for the isotopologue $H^{13}CN$.

The calculation of a complete triatomic linelist is computationally expensive, requiring several tens of thousands of CPU hours (Tennyson et al. 2007). However, within the Born–Oppenheimer approximation the electronic structure of isotopologues is identical. Thus both the potential energy and electric dipole moment functions are identical for all isotopologues. This implies that the vibration–rotation frequencies and transition intensities are likely to be very similar.

For a hetronuclear molecule, such as HCN, the main differences between the spectra of isotopologues are caused by the change in reduced mass. In the harmonic approximation the vibrational contribution to the line frequency is proportional to $\rho^{-\frac{1}{2}}$, where $\rho = m_1 m_2/(m_1 + m_2)$ is the reduced mass. So the frequency of the CN stretch vibrational mode of $H^{12}CN$ and $H^{13}CN$ will differ by the order of 1 per cent and the bend and H-C stretch mode by less. In terms of both the observation of $H^{13}CN$ and the line blanketing of a model atmosphere this shift in line frequency is more important than the small differences in line intensity between comparable lines of $H^{12}CN$ and $H^{13}CN$.

It is the aim of this work to compute a set of energy levels and line frequencies for $H^{13}CN$ and $HN^{13}C$. These energy levels will be used in conjunction with the Einstein A coefficients for $H^{12}CN$ and $HN^{12}C$ computed by Harris et al. (2002b), to generate a $H^{13}CN/HN^{13}C$ linelist. The line frequencies in this $H^{13}CN/HN^{13}C$ linelist have been corrected using available laboratory data in order to increase its accuracy. The new linelist has been used to compute synthetic spectra for C-stars, with different $^{13}C/^{12}C$ ratios using star WZ Cas as a prototype.

2 CONSTRUCTION OF A $H^{13}CN$ AND $HN^{13}C$ LINELIST

2.1 Ab initio energy levels

Using the existing HCN/HNC potential energy surface of van Mourik et al. (2001) a set of ab initio rotation–vibration energy levels for $H^{13}CN$ and $HN^{13}C$ were calculated for angular momenta of $J = 0, 1, 2, 3, 5, 10, 20, 30, 40, 60$ and for both even (*e*) and odd (*f*) parity. The states were computed up to an energy of at least $10\,000 + B[J(J + 1)]$ cm^{-1} above the $H^{13}CN$ ground state, where $B \sim 1.5$ cm^{-1} is the HCN rotational constant.

The DVR3D suite of codes (Tennyson et al. 2004) was used for all these calculations. DVR3D uses an exact kinetic energy

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operator and discrete variable representation for the nuclear motion wavefunctions. We have used the initial basis set functions and parameters used by Harris et al. (2002b) for the computation of an extensive $H^{12}CN/HN^{12}C$ linelist. The basis functions are Legendre polynomials for the angular grid points and Morse oscillator-like functions for the radial grids. Jacobi coordinates were used, with 50 grid points for the angular coordinate, 35 grid points for the first (R) radial coordinate, 21 for the second (r) radial coordinate. Where r is the distance from C to N nuclei and R the distance from the H nucleus to the centre of mass of the C–N diatom. The parameters for the Morse oscillator like basis functions in the r coordinate are $r_e = 2.3a_0, D_e(r) = 29.0E_h$ and $\omega_e(r) = 0.0105E_h$ and $R_e = 3.2\,a_0, D_e(R) = 5.0E_h$ and $\omega_e(R) = 0.004E_h$ for the R coordinate. Where r_e is the equilibrium distance, D_e is the dissociation energy and ω_e is the harmonic frequency.

2.2 Vibrational assignments and rotational constants

Only the exact quantum numbers for a hetronuclear triatomic, angular momentum (J) and parity are known for each state computed by DVR3D. To determine the rotational constants for each vibrational state it is first necessary to assign approximate vibrational quantum numbers to each rotation–vibration state. The approximate vibrational quantum numbers are C–H stretch (v_1), bend (v_2), C-N stretch (v_3), vibrational angular momentum (l) and isomer ($H^{13}CN$ or $HN^{13}C$). Where l take values in steps of 2 from 0 or 1, if v_2 is even or odd respectively, up to the lower of v_2 or J. So for a state with $v_2 = 5$ and $J \geq 5$ then l can take values of 1, 3, 5, but if $J =$ 3 or 4 then l can only take values of 1 or 3.

The quantum number assignments were made using a method similar to that described in Harris et al. (2006). Initially quantum numbers were assigned to the $H^{13}CN$ $J = 0$ purely vibrational states up to 10 000 cm^{-1} above the zero point energy. The first states to be assigned were the lowest lying states of each of the three $H^{13}CN$ fundamental modes. The vibrational expansion equation (1) was then least-squares fit to the assigned states, which provided values for the fundamental frequencies ω_i.

$$E(v,l) + E_0 = \sum_{i=1}^{3} \omega_i(v_i + d_i/2) + \sum_{i=1}^{3}\sum_{j=1}^{3} x_{ij}(v_i + d_i/2)(v_j + d_j/2) + x_l l^2. \quad (1)$$

The fundamental frequencies allow estimates for the energy of more highly excited states to be made, which aid further assignments. Next, equation (1) was least-squares fit to the newly assigned states so that the higher order vibrational constants x_{ij} could also be determined. This process was repeated until all $J = 0$ $H^{13}CN$ states up to 10 000 cm^{-1} were assigned. The $J = 0$ $HN^{13}C$ states were fit separately from the $H^{13}CN$ states, but the assignments made simultaneously. The $J = 1e$ and f states were assigned by comparison with the $J = 0$ states and by fitting equation (1) to verify the assignments.

In order to aid the assignments of states with $J > 1$ we have least-squares fit the assigned levels for each vibrational state and each parity with:

$$E(v,J) = E(v) + B_v[J(J+1) + l^2] - D_v[J(J+1) + l^2]^2 + \cdots, \quad (2)$$

where $E(v)$ is the vibrational energy of the band, B_v is the rotational constant and D_v is the centrifugal distortion constant. This allows energies for the states with the next highest J to be estimated and assigned. For further verification these assigned states were then fitted with the vibrational expansion. This process was carried out on an increasing J by J basis until all the computed energy levels up to $J = 60$ had been assigned. Once the assignments were completed, a final fit of the rotational expansion was performed for each vibrational state and parity. A total of 390 vibrational states of $H^{13}CN/HN^{13}C$ have been studied all with a vibrational energy [$E(v)$] less than 10 000 cm^{-1}. Using this final set of rotational constants a set of calculated rotation–vibration energy levels for $H^{13}CN$ and $HN^{13}C$ was computed for all values of J up to 60.

At stellar temperatures transitions between levels with lower state energy over 10 000 cm^{-1} do contribute significantly to the opacity. These lines tend to be weak and numerous so that they form an almost continuous opacity source. In order to account for these high temperature weak lines we have supplemented the $H^{13}CN/HN^{13}C$ energy level list with high energy $H^{12}CN/HN^{12}C$ energy levels.

2.3 Energy levels determined from laboratory data

Line frequencies determined in the laboratory are significantly more accurate than than purely ab initio data. Therefore, where possible we have incorporated laboratory determined energy levels into our linelist. $H^{13}CN$ has been well studied in the laboratory (Lehmann, Scherer & Klemperer 1982; Smith et al. 1989; Maki et al. 1995, 2000; Devi et al. 2003, 2004), but $HN^{13}C$ has been studied to a far lesser extent (Maki & Mellau 2001). $HN^{13}C$ laboratory determined energy levels have therefore not been incorporated in to the linelist.

Maki et al. (2000) have provided an electronic database of $H^{13}CN$ line frequencies, from this we have compiled a list of $H^{13}CN$ laboratory determined energy levels, in the same way as Harris et al. (2006). Many line frequencies of the studied bands remain unmeasured, there are therefore missing energy levels for many of the vibrational states. These missing energy levels were interpolated by means of the rotational expansion to give a complete list of energy levels in J for each band up to the maximum J measured by Maki et al. (2000). As the rotational expansion is divergent, it cannot be reliably used to extrapolate the laboratory determined energy levels beyond the maximum J measured by Maki et al. (2000). To extend the laboratory determined energy level list to $J = 60$, the maximum extent of the Harris et al. (2002b) linelist, we have used a correction to the *ab inito* energy levels described in 2.2. This constant is given by: $C = E_{\rm lab}(J_{\rm max}) - E_{ai}(J_{\rm max})$, where $E_{\rm lab}(J_{\rm max})$ is the energy of the state in the laboratory energy level list with the highest angular momentum ($J_{\rm max}$), and $E_{ai}(J_{\rm max})$, is the energy of the ab initio energy level with $J = J_{\rm max}$. This lab/empirical energy level list contains 4425 energy levels, which have been incorporated into the calculated list of $H^{13}CN/HN^{13}C$ energy levels described in Section 2.2. The format of the energy level data file is similar to that used by Harris et al. (2006), a extract from the file is given in Table 1.

In Table 1 the column labelled index is the index number given to the corresponding $H^{12}CN$ energy level by Harris et al. (2002b), J and P are the exact quantum numbers of angular momentum and parity, n is the number of the energy level in the J-P symmetry block, E_{ai} is the value of the calculated energy level, iso labels the state as either $H^{13}CN$ (iso=0) or $HN^{13}C$ (iso=1), v_1, v_2, l and v_3 are the approximate quantum numbers, $E_{\rm lab}$ is the lab/empirical energy, label1 is a single character label which is either ‘e’ for a laboratory determined energy level, ‘c’ for an interpolated energy level or ‘t’ for a corrected ab initio energy level, finally label2 is a single character label which identifies the calculated energy as

Table 1. A sample from the lab/empirical energy level list, which is available in full, in electronic form, from either the CDS archive (http://cdsweb.u-strasbg.fr/cgi-bin/qcat?/MNRAS/) or from our website (http://www.tampa.phys.ucl.ac.uk/ftp/astrodata).

Index	J	P	n	E_{ai} (cm^{-1})	iso	v_1	v_2	l	v_3	E_{lab} (cm^{-1})	error (cm^{-1})	label1	label2
1778	3	1	28	4867.640942	0	0	4	2	1	4862.194989	3.08E-02	c	I
1779	3	1	29	5219.561016	1	0	0	0	0				I
1780	3	1	30	5351.139192	0	1	3	1	0	5350.627028	6.08E-04	e	I
1781	3	1	31	5361.140796	0	1	0	0	1	5360.707912	3.00E-04	e	I
1782	3	1	32	5384.899692	0	1	3	3	0	5380.086981	7.55E-04	e	I
1783	3	1	33	5516.043520	0	0	8	0	0				I

either I for an interpolation made using the fitted $H^{13}CN/HN^{13}C$ rotational constants or C an ab initio $H^{12}CN/HN^{12}C$ energy from the Harris et al. (2002b) energy level list. The final energy level list is organized into symmetry blocks according to the J, P quantum numbers.

The error on the energy level takes three forms, for a lab determined energy level this is the compound error of the line frequency measurements used to derive the energy level. For an energy level computed by interpolation of laboratory data this is the standard deviation on the fit of equation (2). For a corrected ab initio energy level the error is the difference between the energy predicted by the fit of equation (2), to lab determined energy levels, and the corrected calculated $H^{13}CN$ or ab initio $H^{12}CN$ energy.

2.4 Partition function

It is essential to know the temperature dependent rotation vibration partition function to compute line intensities at thermodynamic equilibrium. The rotation–vibration partition function of $H^{13}CN/HN^{13}C$ was calculated by direct summation over all the energy levels in the energy level list, using:

$$Q_{rv}(T) = \sum_i (2J_i + 1) \exp\left(\frac{-E_i}{kT}\right), \tag{3}$$

where J is the angular momentum quantum number of the state i, E_i the energy of the state, k is the Boltzmann constant and T is temperature. For temperatures between 500 and 10 000 K the partition function was least-squares fit with the function:

$$\log[Q_r v(T)] = \sum_{i=0}^{n} a_i [\log_{10}(T)]^i \tag{4}$$

with $n = 4$. The standard deviation from $\log_{10}[Q(T)]$ is 0.0075 and the coefficients are $a_0 = -57.453223, a_1 = 86.387042, a_2 = -46.668113, a_3 = 11.018178$ and $a_4 = -0.93943933$. The summation used laboratory determined energy levels where available and in preference to the calculated $H^{13}CN$ energy levels. The calculation was augmented with $H^{12}CN$ energy levels for vibrational energies greater than 10 000 cm^{-1}. At 296 K the partition function was calculated to be 152.93. This can be compared with a value of 148.72 calculated at 296 K for $H^{12}CN$ using a similar procedure (Barber, Harris & Tennyson 2002).

2.5 Einstein A coefficients and laboratory determined band dipoles

The intensities of a few bands of $H^{13}CN$ and $HN^{13}C$ have been measured (Smith et al. 1989; Maki et al. 1995; Devi et al. 2003, 2004), these are the stretching fundamentals, the first CN stretch v_3 hot band, the $2v_1, 2v_1 + v_3$ and $2v_2$ overtone bands. The laboratory determined band dipoles of $H^{13}CN$ and $H^{12}CN$, together with ab initio band dipoles for $H^{12}CN$ calculated by Harris, Polyansky & Tennyson (2002a) and Harris et al. (2002b) are listed in Table 2. The band dipoles for $H^{13}CN$ match those of $H^{12}CN$ to within 15 per cent, except for the v_3 fundamental and its hot band. This verifies that the $H^{12}CN$ Einstein A coefficients are a reasonable approximation to those of $H^{13}CN$. The v_3 bands for both $H^{12}CN$ and $H^{13}CN$ is unusually weak and has an intensity structure which shows an unusual double peak in the R branch. These occur at slightly different J'' for each isotopologue. To more accurately account for the unusual intensity structure of the v_3 fundamental in the $H^{13}CN$ linelist, we have used the band dipoles and Herman-Wallace constants given by Maki et al. (1995) to compute Einstein A coefficients for lines of the CN stretch fundamental and hot bands. Throughout this work these lab determined Einstein A coefficients are substituted for the ab initio Einstein A coefficients of Harris et al. (2002b). Einstein A coefficients for individual rotation vibration lines are calculated from the band dipole and Herman-Wallace constants with the following formula.

$$A_i f = C \nu^3 \frac{F_{HL} F_{HW}}{(2J' + 1)} \mu^2, \tag{5}$$

Table 2. Available laboratory determined band dipoles (Debye) for $H^{13}CN$, the corresponding theoretical and laboratory data for $H^{12}CN$ are shown for comparison.

(v_1', v_2', l', v_3')	$(v_1'', v_2'', l'', v_3'')$	$H^{13}CN$	$H^{12}CN$	$H^{12}CN$ theory
(0,2,0,0)	(0,0,0,0)	0.047(4)	0.0496(2)	0.0479(11)
(0,0,0,1)	(0,0,0,0)	0.000309(2)	0.001362(4)	
(0,1,1,1)	(0,1,1,0)	0.00263(3)	0.001794(3)	
(1,0,0,0)	(0,0,0,0)	0.085(5)	0.0831(17)	0.0853(16)
(2,0,0,0)	(0,0,0,0)	0.00731	0.00881(12)	0.0086(4)
(2,0,0,1)	(0,0,0,0)	0.00065	0.00068(1)	0.000677(4)

Note. Fitting errors in the last quoted digit are given in parentheses, where available.

where F_{HL} and F_{HW} are the Hönl–London and Herman-Wallace factors as described by Maki et al. (1995), μ is the band dipole, ν is line frequency, and $C = 64\pi^4/(3c^3h)$. To return an Einstein A coefficient in s^{-1} with dipole in Debye and frequency in cm^{-1}, then C should be set to 3.136186×10^{-7}.

3 THE NEW LINELIST

Using the Harris et al. (2002b) Einstein A coefficients, the Maki et al. (1995) laboratory intensity measurements, the lab/empirical, computed and ab initio H^{12}CN/HN^{12}C energy levels, we have generated a new H^{13}CN/HN^{13}C linelist. In this linelist the weak transitions between high energy states with vibrational energy greater than 10 000 cm^{-1} are are accounted for by using only the Harris et al. (2002b) ab initio data. For the majority of transitions between states of lower energy the calculated H^{13}CN/HN^{13}C energy levels are used to give line frequency and the ab initio Einstein A coefficients of Harris et al. (2002b) to calculate the intensity. However, where available, the lab/empirical H^{13}CN/HN^{13}C energy levels (see Section 2.3) are used to calculate line frequency in preference to the calculated energy levels. For the special cases of the v_3 fundamental and first hot band we have used the band dipoles and Herman-Wallace constants of Maki et al. (1995) to compute Einstein A coefficients and intensity for individual lines.

We have truncated the H^{13}CN/HN^{13}C linelist at a minimum intensity of 3×10^{-28} cm molecule^{-1} at 3000 K. This results in a linelist of 34.1 million lines which accounts for more than 99.9 per cent of the opacity of the full linelist at 3000 K. The format of the linelist is identical to that of Harris et al. (2006) and a sample of the linelist is given in Table 3, here ν is frequency, E'' is lower state energy, A_{if} is the Einstein A coefficient, J'' and J' are lower state and upper state angular momentum quantum numbers, p is parity where 1 is even and 0 odd, n is the number of the level in the J-parity block, index is the unique label of the energy level, iso labels a H^{13}CN state if 0 or a HN^{13}C state if 1, v_1, v_2, l, v_3 are the approximate quantum numbers. Where the approximate quantum numbers have not been assigned a value of -2 is given. The full version of the linelist is available from either the CDS archive http://cdsweb.u-strasbg.fr/cgi-bin/qcat?/MNRAS/ or from our website http://www.tampa.phys.ucl.ac.uk/ftp/astrodata. Note these site provide the data in the form of Table 3 or alternatively as a file whose three columns are the wavelength in Å, g_nf_{nm}, $n > m$ for absorption and the lower state energy, E'', eV.

The untruncated linelist can be obtained by downloading the original set of Harris et al. (2002b) Einstein A coefficients, the new assigned energy level list and running the supplied FORTRAN utility program dpsort-H13CN-v2.1.f90. The Einstein A coefficient file from Harris et al. (2002b) is sorted using ab initio H^{12}CN/HN^{12}C frequencies, so that the generated H^{13}CN/HN^{13}C linelist will no longer be in full frequency order.

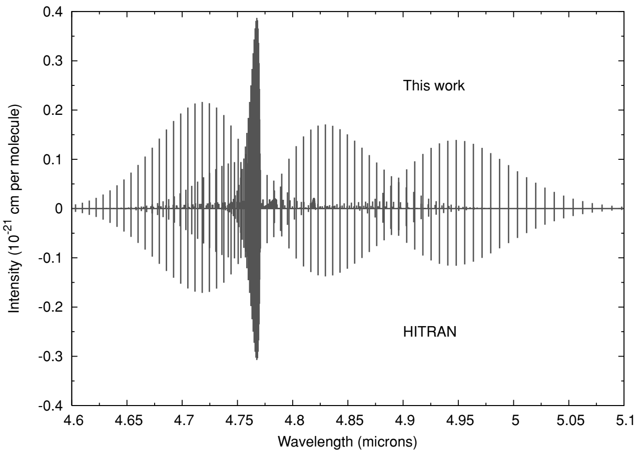

Figure 1. The integrated intensity and frequency of lines of the H^{13}CN v_3 (CN stretch) fundamental and the $3v_2$ (bend) overtone at 296 K. The lines from the linelist of this work are shown with positive intensity and lines from the HITRAN database (Rothman et al. 2005) are shown with negatively intensity.

Fig. 1 shows the intensity and frequency of the H^{13}CN lines from the HITRAN04 database (Rothman et al. 2005) against those from our new H^{13}CN linelist, for the v_3 (CN stretch) fundamentals and $3v_2$ (bend) overtone. There is very good agreement between line frequencies and good agreement between line intensities. For the $3v_2$ overtone our intensities are around 20 per cent stronger than those from HITRAN, the agreement between intensities is better for the v_3 fundamental.

Figs 2–4 show the opacity of H^{13}CN, determined in this work, compared to that of H^{12}CN computed by Harris et al. (2006) at a temperature of 3000 K. The opacity has been calculated by convolving the individual lines with Gaussians of half-width at half-maximum of ν/4000, where ν is the wavenumber of the line, this gives a resolution comparable to that achieved with the SWS spectrometer on the ISO satellite. The bands shown in these figures all show strong Q-branches, which makes the identification of some bands possible at high temperature and low resolution. The identification of absorption by H^{13}CN from the v_1–v_2 bands is likely to be made difficult by the strong background of H^{12}CN. However, the v_2 and $v_2 + v_3$ bands look to be more promising candidate for identification in a C-star. This is because the opacity of H^{13}CN at the peak of the Q-branches of these bands is up to 70 per cent stronger than the H^{12}CN opacity, making them more easily identifiable against a strong background of H^{12}CN absorption.

Table 3. A sample from the H^{13}CN/HN^{13}C linelist, the strongest 34.1 million of which are available in electronic form, from either the CDS archive http://cdsweb.u-strasbg.fr/cgi-bin/qcat?/MNRAS/ or from our website http://www.tampa.phys.ucl.ac.uk.

ν (cm^{-1})	E'' (cm^{-1})	J''	p''	n''	J'	p'	n'	A (s^{-1})	i''	i'	iso’’	v_1''	v_2''	ℓ''	v_3''	iso’	$v\prime_1$	v_2'	ℓ'	v_3'	lbl
0.508814	10 443.914579	39	1	141	39	0	109	2.379E-04	127 951	129 329	0	0	9	1	1	0	0	12	2	0	ai
0.511822	7484.879768	42	0	23	42	1	33	8.824E-09	136 763	135 483	0	0	4	4	1	0	0	4	4	1	lb
0.512459	8544.892933	12	0	116	12	1	153	2.261E-08	31 656	29 543	0	0	9	5	1	0	0	6	6	2	ai
0.512850	4906.391346	8	1	29	8	0	20	5.828E-09	14639	16 500	0	0	1	1	2	0	0	1	1	2	lb
0.513045	5741.587834	32	0	16	32	1	24	7.630E-09	108 856	107 154	0	0	6	4	0	0	0	6	4	0	lb

Note. Quantum numbers are: J rotational level, p parity, n state number in J, p block, (v_1, v_2^{ℓ}, $v3$) vibrational labels. Upper state denoted by $'$ and lower state by$''$. ind gives the unique index number of each state; iso gives the isomer (0 = H^{13}CN, 1 = HN^{13}C); lbl is ai for ab initio calculated frequency and lb for laboratory determined frequency.

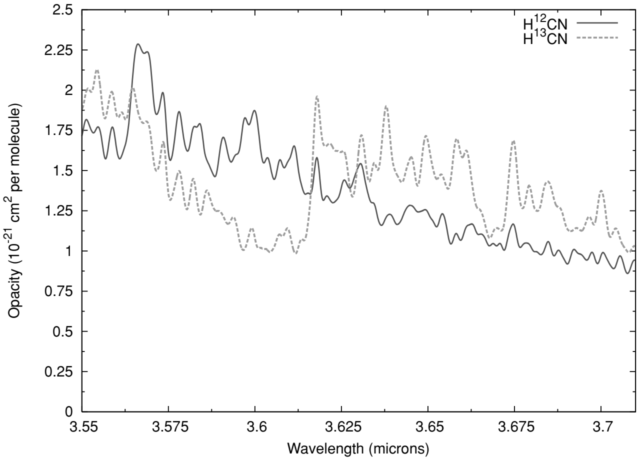

Figure 2. The absorption cross-section per molecule for the H^{12}CN and H^{13}CN $v_2 + v_3$ (bend and CN stretch) combination bands at 3000 K.

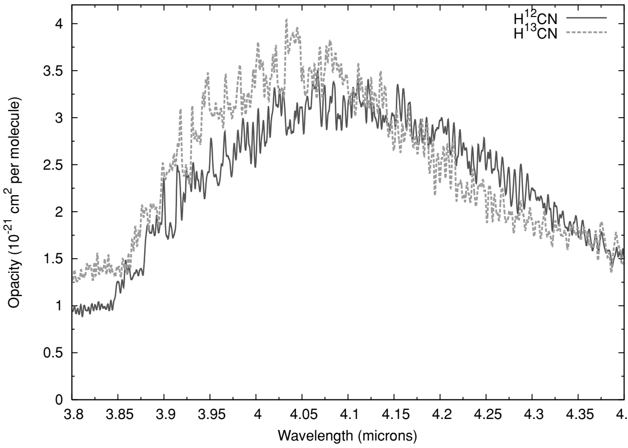

Figure 3. The absorption cross-section per molecule for the H^{12}CN and H^{13}CN $v_1 - v_2$ (bend and HC stretch) combination bands at 3000 K.

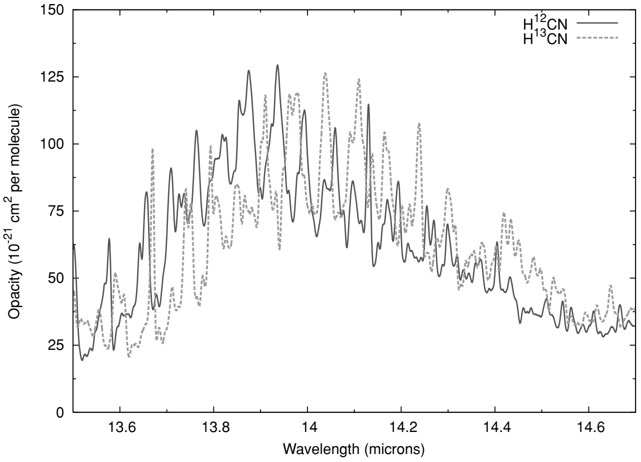

Figure 4. The absorption cross-section per molecule for the H^{12}CN and H^{13}CN v_2 (bend) fundamental and hot bands at 3000 K.

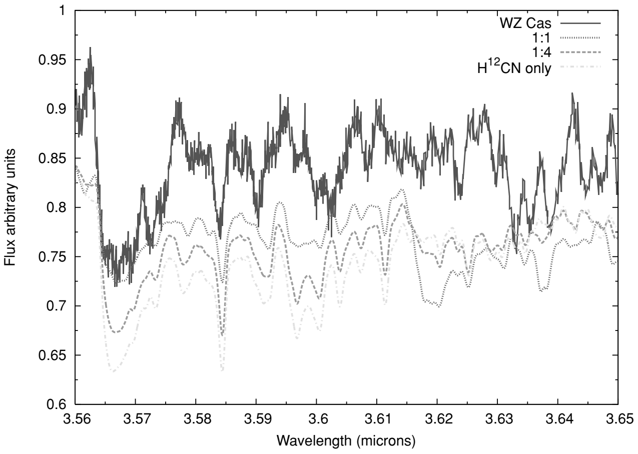

Figure 5. Synthetic and observed spectra for WZ Cas, the synthetic spectra have been displaced form the observed spectrum by 0.06 flux units. The synthetic spectra are shown for H^{13}CN to H^{12}CN ratios of 0, 1/4 and 1.

4 SYNTHETIC AND OBSERVED SPECTRA FOR WZ CAS

Synthetic spectra for the carbon star WZ Cas were calculated with the WITA6 program (Pavlenko 2000). In addition to the same approximations, opacities and input parameters as in our earlier calculations (Harris et al. 2006), we have also included our new H^{13}CN/HN^{13}C opacity. These synthetic spectra are calculated using the best fit model atmosphere for WZ Cas from Harris et al. (2006), which has $T_{\rm eff} = 2800$ K, $\log\,(\rm N_C/N_O) = -0.003$, $\log(g) = 0.0$. Synthetic spectra computed with H^{13}CN/H^{12}CN ratios of 0, 1/4 and 1 compared to the ISO/SWS observed spectrum of WZ Cas (Aoki et al. 1998) are shown in Fig. 5. The effect of H^{13}CN absorption can be seen in the synthetic spectra with H^{13}CN/H^{12}CN ratios of 1/4 and 1, however below a ratio of 1/4 it becomes difficult to identify H^{13}CN absorption on the strong background of H^{12}CN lines. Although, the strength of the some of the H^{13}CN features in the theoretical spectrum indicates a useful ^{12}C/^{13}C ratio maybe, measured around 3.62 and 3.64 μm, there remain other unidentified opacities in this region, for example, the strong observed bandhead at 3.63 μm.

Another interesting spectral region to study HCN features we find around 14 μm (see Harris et al. (2006) for more details). The predominant features in this region are the Q branches of the ($\Delta v_2 = 1$) bands. Computed spectra for the 2800/0.0 model atmosphere given by Harris et al. (2006) are shown in Fig. 6. To simplify presentation of our results only a short spectral range is shown here. As we see from the comparison of computed spectra with and without a contribution from HN^{13}C they differ significantly, at least at 14.05, 14.11, 14.23 μm, where the strong features created by H^{13}CN bands are located. This region can be considered as very promising for the future investigations of the carbon isotopic ratios in atmospheres of carbon stars.

We have searched the ISO archive for suitable high resolution data. The available data in the 14 μm regime for potentially suitable targets IRAS 15194-5115, RY Dra, T LYR, WZ CasA, Y Cvn covers a relatively large parameter space of stellar properties with high ^{12}C/^{13}C ratio although none of the available spectra offer a combination of resolution, signal-to-noise ratio and other features which we understood well enough to allow us to convincingly identify H^{13}CN or HN^{13}C features. Such analysis will have to await both

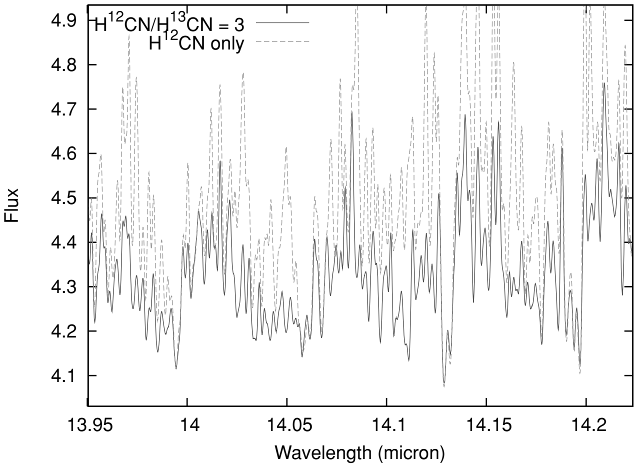

Figure 6. Synthetic spectra computed of WZ Cas computed for the pure H^{12}CN linelist (dashed line) and H^{12}CN + H^{13}CN lists. In the last case ^{12}C/$^{13}C = 3$ was adopted. The spectra are convolved to correspond to a resolution of 10 000.

better spectra and a better characterization of the other absorbing species in the same wavelength region.

5 CONCLUSION

We present a new set of ab initio rotation–vibration energy levels for H^{13}CN and HN^{13}C which were calculated for angular momenta of $J = 0, 1, 2, 3, 5, 10, 20, 30, 40, 60$ and for both even (e) and odd (f) parity. The states were computed up to an energy of at least $10\,000 + B[J(J+1)]$ cm^{-1} above the H^{13}CN ground state, where $B \sim 1.5$ cm^{-1} is the HCN rotational constant. The quantum number assignments were made using a method similar to that described in Harris et al. (2006).

The new linelist has been incorporated into our computations of C-rich synthetic spectra. The detailed analysis of the infrared spectra of C-giant star with high ^{13}C/^{12}C ratios ought to take account of H^{13}CN and HN^{13}C species. Moreover in many cases HCN spectra probably provides the best chance of determining the ^{13}C/^{12}C ratios in atmospheres of the coolest stars as the CO bands at 2.3 μm are usually saturated and other molecular bands are severely blended. Our upgraded opacity sources can be used for the determination of carbon isotopic ratios in atmospheres of carbon stars. The most promising regions are those around 3.6 and 14 μm where the the $v_2 + v_3$ (bend and CN stretch) combination bands and v_2 (bend) fundamental and hot bands of H^{12}CN and H^{13}CN molecules are located, respectively. However, to do this requires the use of spectral data of higher quality than is presently available.

Finally, the use of H^{12}CN and H^{13}CN lines for numerical analysis of infrared spectra of evolved stars is restricted by the incompleteness of presently available opacity sets, see Tennyson et al. (2007). Special attention needs be paid to the computation of other lines for polyatomic molecules such as C_3, NH_3, CH_4 and C_2H_2, and their isotopologues.

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