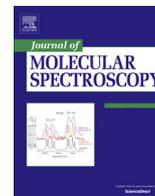




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Note

Rotational analysis of the $B^2\Sigma^+-X^2\Sigma^+$ transition of the $^{13}C^{15}N$ moleculeReginald Colin^a, Peter F. Bernath^{b,c,*}^aService de Chimie Quantique et Photophysique, Université Libre de Bruxelles (ULB), 50, av. F.D. Roosevelt, 1050 Brussels, Belgium^bDepartment of Chemistry & Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, VA 23529-0126, United States^cDepartment of Chemistry, University of York, Heslington, York YO10 5DD, UK

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ABSTRACT

The $B^2\Sigma^+-X^2\Sigma^+$ (violet system) electronic transition of the $^{13}C^{15}N$ free radical was recorded with a Fourier transform spectrometer. The 0-0, 1-1, 1-0, 0-1 and 1-2 bands were rotationally analyzed to obtain spectroscopic constants. There have been no previous measurements of any electronic transitions for the $^{13}C^{15}N$ isotopologue.

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The $A^2\Pi-X^2\Sigma^+$ (red) and $B^2\Sigma^+-X^2\Sigma^+$ (violet) systems of the main isotopologue of the CN molecule ($^{12}C^{14}N$) have been extensively studied. The most recent high resolution papers are those of Ram et al. [1,2] which include a review of previous spectroscopic studies of this free radical. There is strong interest in CN because it is found in many energetic environments with applications in astronomy and combustion science. The red and violet systems of the $^{13}C^{14}N$ isotopologue have also been studied [3–5]. The $^{12}C^{15}N$ isotopologue is particularly useful because it is present in comets and allows the $^{14}N/^{15}N$ relative abundance to be measured; a recent paper [6] has reported an analysis at high resolution of both its red and violet systems. To determine abundances, line strengths are required and an extensive new line list including line strengths has just been calculated for CN [7].

This paper concerns the analysis of the $B^2\Sigma^+-X^2\Sigma^+$ (violet) system of a fourth isotopologue: $^{13}C^{15}N$. The only previous experimental study of this molecule is that of Hubner et al. [8] who measured the fundamental bands of all four isotopologues by diode laser spectroscopy. A wavenumber list of nine P and nine R lines of the 1-0 band is given for the $^{13}C^{15}N$ isotopologue (see Appendix Table A).

The emission spectrum of CN was recorded on September 18, 1989 (#3) by J. Brault (deceased) and R. Engleman using an electrodeless microwave discharge lamp filled with CH_4 and N_2 or NH_3 . The spectrum was obtained with the McMath-Pierce

Fourier transform spectrometer (FTS) of the National Solar Observatory at Kitt Peak. The FTS had a quartz UV beamsplitter with Si photodiode detectors and a $CuSO_4$ filter to cover the 18700 to 33000 cm^{-1} region. Three scans were co-added in 20 min at a spectral resolution of 0.036 cm^{-1} .

The B–X system appears in the 23650–28500 cm^{-1} region as three sequences corresponding to $\Delta v = 0, 1$ and -1 . Each sequence contains a very large number of overlapping lines.

A portion of the $B^2\Sigma^+-X^2\Sigma^+$ spectrum of the CN molecule in the region of the origin showing the presence of four isotopologues is shown in Fig. 1. This portion shows that the isotopic mixture of the gases gave roughly the same intensities for all four isotopologues.

Using approximate constants derived from isotopic relations, the 5 following bands of the $^{13}C^{15}N$ were identified: 0-0, 1-1, 1-0, 0-1 and 1-2. The R and P lines measurements were calibrated with respect to the corresponding lines of $^{12}C^{14}N$ and are given in Table B of the Appendix. Each B–X band was first analyzed separately using the PGOPHER program [9] of C. Western which uses the effective N^2 Hamiltonian of Brown et al. [10]. As the spin-rotation constants for upper and lower states are difficult to determine independently in a $^2\Sigma^-2\Sigma$ transition, ground state γ and γ_D values were calculated for $v = 0, 1$ and 2 using the isotopic relations and the $^{13}C^{14}N$ values [4]. They are given in Table 1 and were kept fixed in the fits. A simultaneous fit of all 5 bands was performed that included 477 lines and yielded 17 constants. In the fit, the 36 IR lines taken from [8] were added. This addition changed only very slightly the values of the constants. The final constants for the X and B states are presented in Table 1 and the unweighted root mean square deviation of the line positions in the fit is 0.021 cm^{-1} .

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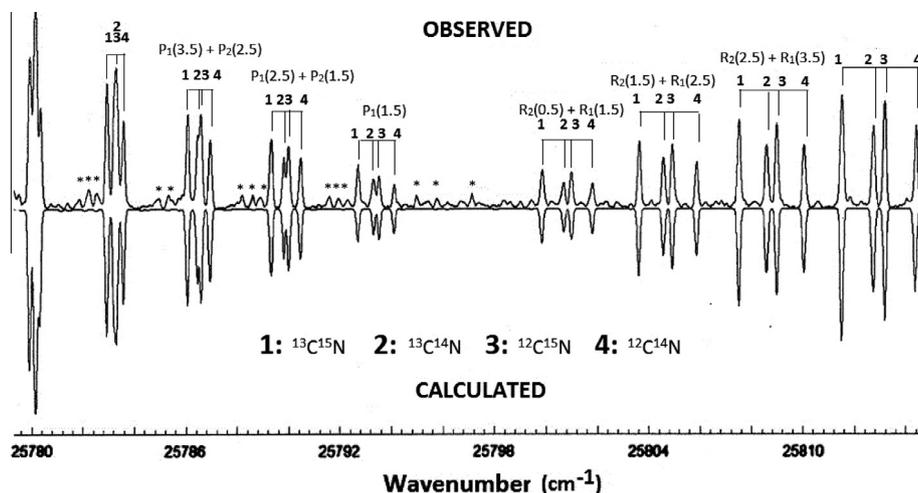


Fig. 1. A portion of the $B^2\Sigma^+-X^2\Sigma^+$ spectrum of the CN molecule in the region of the origin showing the presence of four isotopologues. The weak lines indicated by an asterisk are the result of the overlap of the 8 separate returning O-0 P branches (P_{11} and P_{22} for each of the four isotopologues) and are therefore difficult to identify precisely.

Table 1
Molecular constants of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states of the $^{13}C^{15}N$ molecule (cm^{-1}).

	v	T	B	$D \times 10^6$	$\gamma \times 10^2$	$\gamma_D \times 10^8$
$X^2\Sigma^+$	0	0	1.754685(66)	5.410(54)	0.6730 ^a	-0.67 ^a
	1	1968.2143(35)	1.739134(66)	5.441(49)	0.6653 ^a	-0.87 ^a
	2	3912.0371(64)	1.723531(89)	5.50(11)	0.6586 ^a	-1.43 ^a
$B^2\Sigma^+$	0	25796.2039(26)	1.817466(66)	5.594(52)	1.471(19)	-17.2(85)
	1	27843.0354(40)	1.799055(70)	5.882(64)	1.461(21)	-

^a Fixed in fit.

Using these constants, the portion of the spectrum shown in Fig. 1 was recalculated using the PGOPHER program and by adjusting the relative intensities of the four isotopologues. Also the term values for all the observed levels of $^{13}C^{15}N$ were calculated and can be found in Tables C and D of the Appendix (Science-Direct (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jma_hp.htm)). Although only based on three levels, the following equilibrium constants were calculated for the $X^2\Sigma^+$ state: $\omega_e = 1992.606 \text{ cm}^{-1}$, $\omega_e x_e = 12.20 \text{ cm}^{-1}$, $B_e = 1.76244 \text{ cm}^{-1}$ and $\alpha_e = 1.56 \times 10^{-4} \text{ cm}^{-1}$.

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version of the PGOPHER program and R.S. Ram for help in acquiring the spectrum from the National Solar Observatory archive.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jms.2014.06.006>.

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