FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $B^2\Sigma^+ - X^2\Sigma^+$ (VIOLET) SYSTEM OF ${}^{13}C{}^{14}N$

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ABSTRACT

Emission spectra of the $B^2\Sigma^+ - X^2\Sigma^+$ transition of ${}^{13}C{}^{14}N$ have been observed at high resolution using the Fourier transform spectrometer associated with the McMath–Pierce Solar Telescope of the National Solar Observatory. The spectra have been measured in the 21000–30000 cm⁻¹ region and a total of 52 vibrational bands involving vibrational levels up to v = 15 of the ground and excited states have been rotationally analyzed to provide a much improved set of spectroscopic constants. An experimental line list and calculated term values are provided. The results of the present analysis should prove useful in the identification of additional ${}^{13}C{}^{14}N$ lines in comets and cool stars, and will help in the determination of the ${}^{12}C/{}^{13}C$ abundance ratio.

Key words: comets: general – methods: laboratory – molecular data – stars: abundances – stars: carbon – techniques: spectroscopic

Online-only material: Supplementary data file

INTRODUCTION

Electronic spectra of CN were first measured more than a century ago. Observations of CN now extend from the microwave to the vacuum ultraviolet spectral regions and a number of electronic transitions have been classified. Of these, the $A^2\Pi - X^2\Sigma^+$ (red system) and $B^2\Sigma^+ - X^2\Sigma^+$ (violet system) transitions have been extensively studied because of their astrophysical importance. This radical has been found in a wide range of sources such as comets (Greenstein 1958; Ferrin 1977; Johnson et al. 1983; Fray et al. 2005), stars (Fowler & Shaw 1912; Lambert et al. 1984), the sun (Uitenbroek & Tritschler 2007), circumstellar shells (Wootten et al. 1982; Wiedemann et al. 1991), interstellar clouds (Turner & Gammon 1975; Meyer & Jura 1985), and the integrated light of galaxies (Riffel et al. 2007). The CN lines of the violet system were also identified in the spectra of the Red Rectangle nebula [HD 44179] (Hobbs et al. 2004). The presence of CN in astronomical objects makes it a key probe of carbon and nitrogen abundances, and isotopic ratios. These ratios give information on nucleosynthesis and chemical evolution in galaxies (Wang et al. 2004), and CN also sheds light on star formation in galaxies (Riffel et al. 2007). A millimeter wave survey of ${}^{12}C^{14}N$ and ${}^{13}C^{14}N$ in dark molecular clouds shows a Galactic abundance gradient attributed to chemical evolution (Savage et al. 2002; Milam et al. 2005).

The $B^2\Sigma^+-X^2\Sigma^+$ transition of CN is prominent in the spectra of comets (Greenstein 1958; Ferrin 1977; Fray et al. 2005). There are numerous studies of ${}^{12}C{}^{14}N$ and its isotopologue ${}^{13}C{}^{14}N$ in comets to determine the ${}^{12}C/{}^{13}C$ abundance ratio (Zucconi & Festou 1986; Manfroid et al. 2009). Recently Ritchey et al. (2011) have studied the ${}^{12}C/{}^{13}C$ ratio in diffuse molecular clouds from the $B^2\Sigma^+-X^2\Sigma^+$ transition of CN and the $A^{1}\Pi-X^{1}\Sigma^+$ transition of CH⁺. For most of these studies the isotopic line positions have been estimated from the lines of ${}^{12}C^{14}N$ using approximate isotopic relations, rather than from experimental observations. Some of the recent studies have also been devoted to the determination of the ${}^{14}N/{}^{15}N$ ratio in comets from the study of ${}^{12}C^{14}N$ and ${}^{12}C^{15}N$ molecular lines of the $B^2\Sigma^+-X^2\Sigma^+$ transition. Because of the CNO cycle, the abundance of ¹³C is strongly enhanced in many stars; for example, ${}^{12}C/{}^{13}C$ abundance ratio is 6 for the red supergiant Betelgeuse (Lambert et al. 1984), so there is a need for a detailed experimental line list for ${}^{13}C{}^{14}N$.

The emission bands of the $A^2\Pi - X^2\Sigma^+$ (red) and $B^2\Sigma^+ - X^2\Sigma^+$ (violet) transitions extend from the near infrared to the ultraviolet regions and CN is very persistent because of its large dissociation energy. References to the previous electronic studies can be found in some recent papers on the red (Prasad & Bernath 1992a: Rehfuss et al. 1992) and violet (Rehfuss et al. 1992; Prasad & Bernath 1992b; Ram et al. 2006) systems of ${}^{12}C^{14}N$. In very recent work on the red system of ${}^{12}C^{14}N$ (Ram et al. 2010a), 64 bands involving vibrational levels v'' = 0-12and v' = 0-22 of the ground and excited states were measured and improved spectroscopic constants and term values were provided. The previous spectroscopic studies on ¹³C¹⁴N are summarized in our publication on the $A^2\Pi - X^2\Sigma^+$ transition in which we reported on the high resolution measurements of $^{13}C^{14}N$ in the 4000–15000 cm⁻¹ region (Ram et al. 2010b). Fay & Wyller (1970) stressed the need for high resolution laboratory measurements of ${}^{13}C^{14}N$ bands near 1 μ m because of its presence in stellar atmospheres. In our previous work (Ram et al. 2010b), we reported on the measurements and rotational analysis of 22 bands of the $A^2\Pi - X^2\Sigma^+$ transition involving the v'' = 0-5 and v' = 0-8 vibrational levels. This study provided an extensive set of spectroscopic constants and rotational line positions that were used to show that many unidentified lines in the near-infrared spectra of carbon stars were due to ${}^{13}C^{14}N$.

Jørgensen & Larsson (1990) have calculated the molecular opacities for the CN $A^2\Pi - X^2\Sigma^+$ transition. Rotational lines were calculated up to J = 149.5 for transitions between vibrational levels $0 \le v' \le 30$ and $0 \le v'' \le 30$ using available and extrapolated spectroscopic parameters for the ${}^{12}C^{14}N$, ${}^{13}C^{14}N$, ${}^{12}C^{15}N$, ${}^{13}C^{15}N$ isotopologues. The opacities were calculated for temperatures ranging from 1000 to 6000 K. In a recent theoretical study, Shi et al. (2010) investigated the potential energy curves of the $A^2\Pi$ and $X^2\Sigma^+$ states using high level ab initio calculations and estimated spectroscopic parameters for the four isotopic species ${}^{12}C^{14}N$, ${}^{13}C^{14}N$, ${}^{12}C^{14}N$, and ${}^{13}C^{15}N$.

There are some infrared studies of CN and its minor isotopologues (Hempel et al. 2003; Hübner et al. 2005). Hempel et al. (2003) observe the fundamental 1–0 bands of ${}^{12}C^{14}N$ and ${}^{13}C^{14}N$, while Hübner et al. (2005) reported the fundamental bands of the four isotopologues ${}^{12}C^{14}N$, ${}^{13}C^{14}N$, ${}^{12}C^{15}N$, and ${}^{13}C^{15}N$. Also, there are some millimeter wave studies of ${}^{13}C^{14}N$ (Bogey et al. 1984, 1986) and pure rotational measurements are available for vibrational levels up to v = 9 of the ground state (Bogey et al. 1986).

So far only one publication is available on the $B^2\Sigma^+ - X^2\Sigma^+$ transition of ${}^{13}C{}^{14}N$ (Jenkins & Wooldridge 1938) which provides measurements of just the 0–0, 0–1, and 0–2 bands. In most of the studies of cometary spectra the line lists of minor isotopologues were derived from the line positions of the ${}^{12}C{}^{14}N$ using isotopic relations; these approximate calculations give reasonable predictions, but do not have the accuracy of direct experimental measurements. There is therefore a need for high resolution measurements of minor isotopologues to improve the simulation of astronomical spectra and obtain more accurate ${}^{12}C/{}^{13}C$ abundance ratios.

In this paper, we report on the analysis of 52 bands involving vibrational levels v'' = 0-15 and v' = 0-15 of the ground and excited states of the $B^2\Sigma^+ - X^2\Sigma^+$ transition (except v', v'' = 13). The aim of this study is to provide an accurate line list for all the bands, as well as improved spectroscopic constants and term values. The previous microwave, infrared, and near-infrared measurements were included in our analysis.

2. EXPERIMENTAL

The spectra of ${}^{12}C^{14}N$ radical and its minor isotopologues ${}^{13}C^{14}N$ and ${}^{12}C^{15}N$ have been recorded by J. Brault and R. Engleman at the National Solar Observatory located at Kitt Peak. Several spectra of these species have been collected in the 3000–30000 cm⁻¹ region and archived for future use. The details of the experimental observations are provided in our previous papers on ${}^{12}C^{14}N$ (Ram et al. 2006, 2010a) and ${}^{13}C^{14}N$ (Ram et al. 2010b). The ${}^{13}C^{14}N$ radicals were produced in a microwave discharge lamp by exciting a mixture of argon, ${}^{14}N_2$, and a trace of ${}^{13}CH_4$. The ${}^{13}C^{14}N$ radical was also produced in active nitrogen afterglow discharge experiments. The spectra were recorded using the Fourier transform spectrometer associated with McMath–Pierce Solar Telescope.

The line positions were extracted from the spectra using a data reduction program called PC-DECOMP developed by J. Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature. The spectra were calibrated using the Ar line measurements by Whaling et al. (2002) as corrected by Sansonetti (2007). In the spectra where Ar lines are not present, the calibration was transferred from Ar lines to ¹³C¹⁴N molecular lines. The spectra were brought to the same scale by transferring the calibration using common molecular lines. The precision of measurement is expected to be of the order of ± 0.003 cm⁻¹ or better for the stronger and unblended lines. However, rotational lines of some weaker bands are frequently overlapped by many stronger bands, and the uncertainty in measurement of weaker bands is expected to be somewhat higher.

3. OBSERVATIONS

The spectra of the $B^2\Sigma^+ - X^2\Sigma^+$ transition of ${}^{13}C^{14}N$ are present in the 20000–30000 cm⁻¹ region. The observation of bands at two different effective temperatures (from the two sources)

was quite useful in covering a wide range of vibrational levels ranging from 0 to 15. For example, the spectra observed with the regular microwave discharge consists of only the lower vibrational bands such as 0-2, 0-1, 1-2, 2-3, 0-0, and 1-1, while the spectra observed with the active nitrogen afterglow discharge source consist of very high vibrational bands, up to v = 15 in both the states. The lower vibrational bands were very weakly present in the active nitrogen spectra. Using the spectra recorded with the two sources we have measured the rotational structure of a large number of bands belonging to the $\Delta v = -2$, -1, 0, 1, and 2 sequences. The bands belonging to the $\Delta v = -3$ or $\Delta v \ge 1$ sequences were not observed in the regular microwave discharge. The bands belonging to the $\Delta v = -3$ sequence were also not observed in the active nitrogen afterglow discharge. The bands in the $\Delta v = -3$ sequence are expected to be present in the 20500–20700 cm^{-1} region where much stronger bands of the $A^2\Pi - X^2\Sigma^+$ transition are present, so we made no attempt to find them. In the present work, we have obtained the rotational analysis of 52 bands of the $B^2\Sigma^+ - X^2\Sigma^+$ transition of ${}^{13}C^{14}N$ involving vibrational levels up to v = 15 in the ground and excited states. A description of the assigned bands is provided in the following sections.

3.1. The $\Delta v = -2$, -1 Sequences

The bands located in the 21800–22500 cm^{-1} region belong to the $\Delta v = -2$ sequence. We have measured and assigned the rotational lines of the 0-2, 2-4, 3-5, 4-6, 5-7, 6-8, 7-9, 8-10, 9-11, 10-12, and 12-14 bands. The 1-3 band is very weak in both the spectra and the 11-13 band was not analyzed because of strong perturbation in the lower state. All four expected branches, R1, R2, P1, and P2 were measured in all of the assigned bands. The ground-state constants reported in our previous study (Ram et al. 2010b) were quite useful in the analysis of bands belonging to the $B^2\Sigma^+ - X^2\Sigma^+$ transition. We have identified rotational lines up to J = 41.5 in the 0–2 band, which was observed only in the regular microwave discharge. The active nitrogen source is an ideal source to excite the higher vibrational levels although the rotational excitation is limited to medium J values. For example, we have identified rotational lines only up to J = 31.5 in the strong 8–10 band of the $\Delta v = -2$ sequence from the active nitrogen spectra. Similar observations were made in our previous studies of the $A^2\Pi - X^2\Sigma^+$ transition of ${}^{12}C^{14}N$ (Ram et al. 2010a) and ${}^{13}C^{14}N$ (Ram et al. 2010b). For example, we reported the observation of bands involving vibrational levels up to v = 22 of the $A^2\Pi$ state and v = 12 of the $X^2\Sigma^+$ state in a previous study of the $A^2\Pi - X^2\Sigma^+$ transition of ¹²C¹⁴N (Ram et al. 2010a), but the observations of rotational lines were limited to $J \leq 35.5$ even in very strong bands.

The bands belonging to the $\Delta v = -1$ sequence are located in the 23700–24400 cm⁻¹ region. We have obtained the rotational analysis of the 0–1, 1–2, 2–3, 3–4, 4–5, 5–6, 6–7, 7–8, 8–9, 9–10, 10–11, and 11–12 bands belonging to this sequence. The 0–1, 1–2, and 2–3 bands were measured from the spectra observed with both experimental sources. The 12–13 band could not be assigned because of perturbations in the lower state and the other higher vibrational bands of this sequence were too weak in intensity to analyze. In addition, the lower wavenumber region of this sequence is overlapped with some bands belonging to the $B^2\Sigma^+$ – $A^2\Pi$ transition.

3.2. The $\Delta v = 0$ Sequence

The measurements of the 0–0 and 1–1 bands from both sources were used in the final fit. The $\Delta v = 0$ sequence



Figure 1. Compressed portion of the $\Delta v = 0$ sequence of the $B^2 \Sigma^+ - X^2 \Sigma^+$ transition of ${}^{13}C^{14}N$, with some higher vibrational bands marked.

observed in the afterglow spectra is strongest in intensity and has very extensive vibrational structure. This sequence consists of bands from 0–0 to 15–15 although the intensity of bands does not vary in a regular manner as expected. We have calculated the Franck-Condon factors for this transition using the derived spectroscopic constants and found that observed intensity of bands is not consistent with the calculated Franck-Condon factors. A part of the compressed spectrum of this sequence is provided in Figure 1. It was also noted that the spin splitting in the branches is irregular from one band to the next. The abnormal intensity trend and irregular splitting in different bands is due mainly to interactions in the excited state. We have observed strong perturbations in the v = 2 and v = 7 vibrational levels of the $B^2\Sigma^+$ state in addition to some weaker perturbations in the v = 9, 11, 13, and 14 vibrational levels of this state. Effect of interactions is also seen in the v'' = 12 vibrational levels of the ground state where rotational lines with $N \ge 13$ have to be deweighted. The 13-13 band was not assigned because of perturbations in ground as well as excited vibrational levels (v', v'' = 13). It was found that no branches could be followed in the 13–13 band in spite of a reasonable intensity of this band. On the other hand the structure of the 14–14 and 15–15 bands is quite normal for a ${}^{2}\Sigma^{+}-{}^{2}\Sigma^{+}$ transition. The rotational assignment of these bands was straightforward using combination differences for common vibrational levels from other bands. A part of the spectrum of the 14–14 band is provided in Figure 2. This spectrum appears as a characteristic ${}^{2}\hat{\Sigma}^{+}-{}^{2}\Sigma^{+}$ transition and the spin splitting is resolved from very low J values.

3.3. The $\Delta v = 1$ and 2 Sequences

The bands belonging to these two sequences are located in the 26500–29600 cm⁻¹ region. In the $\Delta v = 1$ sequence we have obtained the analysis of the 3–2, 4–3, 5–4, 6–5, 7–6, 8–7, 9–8, 10–9, 11–10, and 12–11 bands. We were not able to measure rotational lines belonging to the 1–0 and 2–1 bands of this sequence because of weak intensity and strong overlapping from the higher vibrational bands present in the same region. Again the intensity of different bands does not follow the trend expected for a normal transition, based on Franck–Condon factors. For example, the intensity of the 11–10 band is almost two times the intensity of the 10–9 band while the intensity of 12–11 is only 10% the intensity of the 11–10 band. A portion of the 11–10 band is presented in Figure 3. The spin components



Figure 2. Expanded portion of the 14–14 band of the $B^2\Sigma^+-X^2\Sigma^+$ transition of ${}^{13}C{}^{14}N$, with some lines of the R and P branches marked. The spin splitting in the branches is resolved from very low *N* values.



Figure 3. Portion of the 11–10 band of the $B^2\Sigma^+ - X^2\Sigma^+$ transition of ${}^{13}C^{14}N$. The spin splitting is resolved only at high N values ($N \ge 20$).

of the R and P lines of this band are resolved only at relatively high N values ($N \ge 20$) and this contributes to the apparent strength of the band. The 13–12 and other higher vibrational bands are completely absent in this sequence.

We have observed only the 9–7, 10–8, 11–9, 12–10, 13–11, and 14–12 bands of the $\Delta v = 2$ sequence. The intensity of these bands follows the same pattern as observed for the other sequence bands. Again the 13–11 band was not assigned because of perturbations in the excited v = 13 vibrational level.

4. ANALYSIS AND DISCUSSION

We have identified two R and two P branches in all of the analyzed bands. The rotational assignment in the different branches was accomplished by comparing combination differences for bands with common vibrational levels. The spectroscopic constants were determined by fitting the observed line positions using Brown's Hamiltonian (Brown et al. 1979). The matrix elements of a ²Π state are provided, for example, in a paper by Amiot et al. (1981) and for a ²Σ⁺ state by Douay et al. (1988). The rotational lines were given weights based on their signal-to-noise ratio, extent of blending and perturbations. The measurements of all the assigned bands were combined and

Table 1	
Spectroscopic Constants (in cm ⁻¹) for the $X^2\Sigma^+$ Electronic State of ¹³	$C^{14}N$

Constants	v = 0	v = 1	v = 2	v = 3	v = 4	v = 5
$T_{\rm v}$	0.0	2000.085149(41)	3974.971259(45)	5924.620811(64)	7848.99504(10)	9748.05499(16)
$B_{\rm v}$	1.812691744(27)	1.796343167(27)	1.779944752(28)	1.763494607(28)	1.746990615(29)	1.730430483(28)
$D_{\rm v} \times 10^6$	5.87690(11)	5.88535(11)	5.89414(12)	5.90582(22)	5.91420(96)	5.92676(36)
$H_{\rm v} \times 10^{12}$	3.555(16)	3.406(16)	3.148(23)	3.485(93)	1.61(78)	
$\gamma_v \times 10^3$	6.95454(19)	6.87872(19)	6.79449(19)	6.70004(19)	6.59135(19)	6.46270(19)
Constants	v = 6	v = 7	v = 8	v = 9	v = 10	v = 11
$T_{\rm v}$	11621.76333(46)	13470.07579(53)	15292.94640(58)	17090.32689(69)	18862.16381(83)	20608.38452(94)
$B_{\rm v}$	1.713811661(40)	1.697131499(37)	1.680386842(38)	1.663574591(40)	1.6466866(48)	1.6296911(89)
$D_{\rm v} \times 10^6$	5.9397(37)	5.9653(32)	5.9816(34)	6.0039(38)	6.0392(73)	6.101(21)
$\gamma_v \times 10^3$	6.30629(19)	6.11291(19)	5.87123(19)	5.56816(19)	5.322(48)	5.234(70)
Constants	v = 12	v = 13	v = 14	v = 15		
$T_{\rm v}$	22328.8317(12)		25693.7702(25)	27337.33*		
$B_{\rm v}$	1.612239(25)		1.578301(61)	1.561107(67)		
$D_{\rm v} \times 10^6$	5.77(15)		6.58(33)	5.91(16)		
$H_{\rm v} \times 10^9$	-0.84(24)					
$\gamma_{\rm v} \times 10^2$	0.647(15)		2.000(31)	1.64(12)		

Note. Numbers quoted in parentheses are one standard deviation error in the last digits and the asterisk marks a value fixed from extrapolation.

 Table 2

 Spectroscopic Constants (in cm⁻¹) for the $B^2\Sigma^+$ Electronic State of ${}^{13}C{}^{14}N$

Constants	v = 0	v = 1	v = 2	v = 3	v = 4	v = 5
$T_{\rm v}$	25796.91609(55)	27876.71553(65)	29918.08823(80)	31918.96365(58)	33876.8732(10)	35789.24648(71)
$B_{\rm v}$	1.8775261(19)	1.8581488(39)	1.837841(17)	1.8169975(48)	1.794795(21)	1.7719407(92)
$D_{\rm v} \times 10^6$	6.0551(12)	6.1995(43)	6.472(86)	6.4797(69)	6.61(12)	7.121(24)
$H_{\rm v} \times 10^9$			0.27(11)		-1.91(19)	
$\gamma_v \times 10^2$	1.6206(47)	1.7292(73)	0.880(33)	2.0655(83)	1.807(11)	2.911(16)
$\gamma_{\rm Dv} \times 10^5$	-0.0398(47)	-0.119(14)	-0.87(19)	-0.298(20)	-1.052(41)	-1.64(13)
$\gamma_{\rm Hv} \times 10^8$			0.85(27)			0.86(25)
Constants	v = 6	v = 7	v = 8	v = 9	v = 10	v = 11
$T_{\rm v}$	37653.09109(87)	39466.055(12)	41223.65631(87)	42924.93701(94)	44567.85429(87)	46151.3978(10)
$B_{\rm v}$	1.747008(11)	1.720366(83)	1.6936959(76)	1.663375(37)	1.6350244(78)	1.603064(21)
$D_{\rm v} \times 10^6$	7.010(36)	6.43(18)	7.883(20)	5.31(39)	9.150(23)	8.98(15)
$H_{\rm v} \times 10^8$	-0.0768(34)	-0.052(13)	-0.0355(15)	-3.64(11)	0.0098(18)	-0.244(27)
$\gamma_v \times 10^1$	0.2025(13)	1.1358(89)	0.24191(68)	0.0974(28)	0.3393(12)	0.0581(14)
$\gamma_{\rm Dv} \times 10^4$	-0.0828(68)	-3.532(56)	-0.1212(12)	-1.532(44)	-0.2776(55)	-0.0183(56)
$\gamma_{\rm Hv} \times 10^7$	-0.0296(84)	5.27(12)		2.79(16)	0.0977(51)	
$\gamma_{ m Lv} imes 10^{10}$		-2.763(77)				
Constants	v = 12	v = 13	v = 14	v = 15		
$T_{\rm v}$	47676.8577(18)		50557.4048(26)	51919.6407(13) a		
$B_{\rm v}$	1.572482(58)		1.506135(96)	1.478472(73)		
$D_{\rm v} \times 10^5$	1.589(60)		0.14(12)	1.025(20)		
$H_{\rm v} \times 10^7$	0.177(17)		-1.156(44)			
$\gamma_v \times 10^1$	1.9410(98)		-0.1962(40)	0.300(12)		
$\gamma_{\rm Dv} \times 10^3$	-1.554(22)		-0.0955(38)	-0.0256(13)		
$\gamma_{\rm Hv} imes 10^6$	6.59(16)					
$\gamma_{\rm Lv} \times 10^8$	-1.046(36)					

Notes. Numbers quoted in parentheses are one standard deviation error in the last digits.

^a This value is determined by (and is dependent on) the fixed v'' = 15 term value (Table 1). Any change in v'' = 15 term value propagates into the v' = 15 term value.

fitted simultaneously. The available microwave and submillimeter wave measurements of Bogey et al. (1984, 1986) and infrared vibration-rotation measurements by Hempel et al. (2003) and Hübner et al. (2005) were also included in the final fit. The measurements of the 1–0 band by Hempel et al. (2003) and Hübner et al. (2005) were given lower weights than quoted in the papers since the reported rotational line positions were the average of the two spin doublets, although the splitting was partly resolved for many of the lines.

The spectroscopic constants obtained for the ground and excited of ${}^{13}C^{14}N$ are provided in Tables 1 and 2, respectively.

Since no bands involving the v = 13 vibrational level of the ground state could be rotationally analyzed and the 15–15 band does not have any state in common with other bands, the term values for the two lower vibrational levels (i.e., v'' = 13 and 15) were held fixed to the extrapolated values in the final fit. The constants reported in Table 1 show that the ground-state levels are relatively less affected by perturbations compared with the excited state. For the ground state the constants T_v , B_v , H_v and γ_v are required for most of the vibrational levels while for most of the excited vibrational levels the constants T_v , B_v , D_v , H_v , γ_v , γ_{Dv} , and γ_{Hv} are required to minimize the standard deviation of

Table 3 Equilibrium Constants (in cm⁻¹) for the $X^2\Sigma^+$ Electronic State of ${}^{13}C{}^{14}N$

Constants	$X^2 \Sigma^+$			
T _e	0.0			
ω _e	2025.25043(91)			
$\omega_{\rm e} x_{\rm e}$	12.57305(50)			
$\omega_{\rm e} y_{\rm e}$	-0.005772(98)			
ω _e z _e	-0.0000493(60)			
Be	1.82084876(36)			
$\alpha_1 \times 10^2$	-1.630214(36)			
$\alpha_2 \times 10^5$	-2.2805(96)			
$\alpha_3 \times 10^7$	-4.001(72)			
$r_{\rm e}(\rm \AA)$	1.17180546(11)			

Note.	Values	in	parenth	eses	are	one	standard	devia
tion u	ncertair	ntie	s in the	last	digi	ts.		

the fit. For some vibrational levels even higher order constants L_v and γ_{Lv} are also required. The spectroscopic constants obtained for the lower vibrational levels of the ground-state (v = 0-5) agree very well with the values reported in our previous paper (Ram et al. 2010b).

A list of all of the measurements used in the determination of the spectroscopic constants along with the observed—calculated residuals is provided in the online supplementary material (Supplement 1) in the tar package in the electronic edition. The final spectroscopic constants were used to calculate the term values for the observed vibrational levels of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states which are also provided in the online supplementary material (Supplement 2). The term values have been extrapolated to a few higher *J* rotational levels than the observed ones for each vibrational level.

The constants of Tables 1 and 2 have been used to evaluate equilibrium constants for the $X^2\Sigma^+$ and $B^2\Sigma^+$ states using the following expressions:

$$G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \omega_e z_e (v + 1/2)^4$$
(1)

$$B_{v} = B_{e} + \alpha_{1}(v + 1/2) + \alpha_{2}(v + 1/2)^{2} + \alpha_{3}(v + 1/2)^{3}, \quad (2)$$

where ω_{e} , $\omega_{e}x_{e}$, $\omega_{e}y_{e}$, and $\omega_{e}z_{e}$ in Equation (1) are standard vibrational constants while α_1 , α_2 , and α_3 in Equation (2) are non-standard equilibrium rotational constants. The lower vibrational levels of the ground state are free from local perturbations although the v = 12 and 13 vibrational levels of the ground state are affected. While determining the equilibrium vibrational constants we noted that the term values of the v = 10 and 11 vibrational levels also do not fit as well as expected. Therefore the term values for the v > 9 vibrational levels were given lower weights in the determination of the ground-state vibrational constants. The vibrational constants derived in this manner predict the term values of the highest observed vibrational level up to v = 15 to within ± 0.4 cm⁻¹. The rotational constants, however, are less affected by perturbations and the rotational constants of all the observed vibrational levels were used in the determination of the ground-state equilibrium rotational constants. The equilibrium constants for the ground state are provided in Table 3.

In contrast to the ground state, most of the excited state vibrational levels are affected by interactions as was found for the $B^2\Sigma^+$ state of the main isotopologue ${}^{12}C^{14}N$ (Ram et al. 2006). In this case the experimental term values for vibrational levels v > 6 were given lower weights. Even then

Table 4Equilibrium Constants (in cm⁻¹) for the $B^2\Sigma^+$ Electronic State of ${}^{13}C{}^{14}N$

Constants	$B^2\Sigma^+$		
T _e	25752.988(74)		
ω _e	2115.54(18)		
$\omega_{\rm e} x_{\rm e}$	17.243(64)		
$\omega_{\rm e} y_{\rm e}$	-0.4106(63)		
Be	1.88654(11)		
$\alpha_1 \times 10^2$	-1.788(11)		
$\alpha_2 \times 10^4$	-5.63(14)		
$r_{\rm e}(\rm \AA)$	1.151223(34		

Note. Values in parentheses are one standard deviation uncertainties in the last digits.

the excited state vibrational constants were not determined as well as those for the ground electronic state. The derived vibrational constants reproduce the term values for the v = 0-6vibrational levels within ± 0.15 cm⁻¹. For the higher levels, the observed-calculated deviations increase with increasing vibration and for the higher vibrational levels, for example for the v = 14, the deviation is as high as ± 15 cm⁻¹. As in the case of ground state, the excited state rotational constants are less affected by interactions. The equilibrium rotational constants for the $B^2\Sigma^+$ state were determined by giving slight lower weights to the values for the v = 10-15 vibrational levels. The equilibrium constants for the $B^2\Sigma^+$ state are provided in Tables 4. The equilibrium rotational constants of values, $B_{\rm e}^{\prime\prime} = 1.82084876(36) \text{ cm}^{-1} \text{ and } B_{\rm e}^{\prime} = 1.88654(11) \text{ cm}^{-1},$ were derived for the $X^2\Sigma^+$ and $B^2\Sigma^+$ states which provide the equilibrium bond lengths (r_e) of 1.17180546(11)Å and 1.151223(34) Å, respectively, for the two states. These values compare well with the corresponding equilibrium bond lengths $(r_{\rm e})$ of 1.1718073(25) Å for the $X^2\Sigma^+$ state (Ram et al. 2006) and 1.15108(4) Å for the $B^2\Sigma^+$ state (Prasad & Bernath 1992b) of the normal isotopologue, ${}^{12}C^{14}N$. Although the ground state bond lengths of the two isotopologues are identical within experimental error, the small difference in the $B^2\Sigma^+$ state bond lengths may be attributed to the breakdown of the Born-Oppenheimer approximation (i.e., interactions with other states).

Prior to the current work there was only one laboratory measurement of the $B^2\Sigma^+-X^2\Sigma^+$ (violet) system of ${}^{13}C{}^{14}N$ (Jenkins & Wooldridge 1938). These measurements were limited in precision because of the use of a grating spectrograph and by overlapping from the major isotopologue ${}^{12}C{}^{14}N$ also present in the spectra. In contrast the current spectra were free from overlapping by ${}^{12}C{}^{14}N$ for the active nitrogen spectra which provide most of the data for our analysis. The completeness and improved frequency precision of our measurements should aid in the simulation of astronomical spectra, the identification of blended features, the determination of isotopic ratios, and the identification of unassigned lines.

Several vibrational levels of the excited state are affected by perturbations. The most prominent ones are those observed v = 2, 7, and 13 vibrational levels of the $B^2\Sigma^+$ state and the v = 13 vibrational level of the ground state. We observed local perturbations in the *e*-parity level of the $B^2\Sigma^+$, v = 2 vibrational level near N = 6 and most of the lines near the perturbation were given lower weights in the fit. The *f*-parity levels are not perturbed. The perturbation observed in the v = 7 vibrational level affects the lower *J* lines of both *e*- and *f*-parity levels and likewise these lines and some higher *J* lines have to be deweighted. Perturbations were also observed at $N \ge 16$ of v' = 9, $N \ge 20$ of v' = 11, $N \ge 17$ of v' = 12, *e*-parity and $N \ge 13$ of v' = 14, f-parity levels of the $B^2\Sigma^+$ state. Effects of perturbation is also seen in v = 12 vibrational level of the ground state, for which f-parity levels are affected after $N \ge 13$. The branches of bands involving the v = 13 vibrational level of the ground and excited state could not be assigned with certainty because of perturbations in both states. An extensive analysis of the higher vibrational levels of the $A^2\Pi$ state, probably responsible for these perturbations, is currently underway.

The molecular lines of CN are particularly prominent in the spectra of cool carbon stars and lines of ${}^{13}C{}^{14}N$ red system have been identified for decades (Day et al. 1973). The spectra of the cool stars, therefore, provide a severe test for any CN line list. The spectra in the 2.0–2.5 μ m region were previously used by Lambert et al. (1984) for abundance analysis in some carbon stars and a small ${}^{12}C{}^{13}C$ ratio of 4.5 was found for a *J*-type carbon star (WZ Cas). Using our recently published line lists of the red system of ${}^{12}C{}^{14}N$ (Ram et al. 2010a) and ${}^{13}C{}^{14}N$ (Ram et al. 2010b) many more additional lines were identified. The new line lists provided a highly complete set of identifications as well as excellent wavelength agreement between the stellar line positions and the line list.

Zucconi & Festou (1986) have computed synthetic spectra of CN isotopologues using the term values derived from the existing spectroscopic constants of ¹²C¹⁴N and isotopic relations, and demonstrated that several molecular lines of ¹³C¹⁴N and ¹²C¹⁵N are potentially detectable in the spectra of comets obtained with a resolution of 0.1 Å or better. Some recent studies have been devoted to obtaining better values or the ¹²C/¹³C and ¹⁴N/¹⁵N abundance ratios using the spectra of the $B^2\Sigma^+ - X^2\Sigma^+$ transition of CN and its isotopologues in comets. For example, Cochran et al. (2008) observed that all comets have similar carbon and nitrogen ratios and obtained the values of $^{12}C/^{13}C = 91 \pm 21$ and $^{14}N/^{15}N = 141 \pm 29$, whereas Manfroid et al. (2009) reported the average values of $^{12}C/^{13}C = 91 \pm 3.6$ and $^{14}N/^{15}N = 147.8 \pm 5.7$. The present analysis of the $B^2\Sigma^+ - X^2\Sigma^+$ transition provides a large set of precise line positions that can be used for abundance analyses in comets.

6. CONCLUSION

The $B^2\Sigma^+-X^2\Sigma^+$ transition of the ¹³C¹⁴N radical has been investigated at high resolution using spectra recorded with a Fourier transform spectrometer. The rotational structure of 52 bands located in the 20000–30000 cm⁻¹ region has been measured and rotationally analyzed. This analysis provides an improved set of spectroscopic constants for the ground and excited states. The new measurements and spectroscopic parameters from this work should prove helpful in interpreting CN spectra seen in comets and stellar atmospheres.

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