



Fourier transform emission spectroscopy of the $A^2\Pi-X^2\Sigma^+$ (red) system of $^{13}\text{C}^{14}\text{N}$ (II)

R.S. Ram ^{a,b,*}, P.F. Bernath ^{a,c}

^a Department of Chemistry, University of York, Heslington, York YO10 5DD, UK

^b Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA

^c Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA

ARTICLE INFO

Article history:

Received 6 March 2012

In revised form 21 March 2012

Available online 3 April 2012

Keywords:

Electronic spectra
Rotational analysis
Free radicals
Solar spectra
Carbon stars

ABSTRACT

High resolution emission spectra of the $A^2\Pi-X^2\Sigma^+$ transition of $^{13}\text{C}^{14}\text{N}$ have been measured in the 15 000–24 000 cm^{-1} region. Molecules were produced by the reaction of $^{13}\text{CH}_4$ and $^{14}\text{N}_2$ in an active nitrogen afterglow discharge. The spectra were recorded using the Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope of the National Solar Observatory. A rotational analysis of 27 bands involving the excited state vibrational levels $v' = 9-22$ and the ground state vibrational levels up to $v'' = 12$ has been obtained. An improved set of spectroscopic constants has been determined for the $v = 0-22$ levels of the $A^2\Pi$ state by combining the present measurements with those reported previously for the $v = 0-8$ vibrational levels of the $A^2\Pi$ state [Ram et al., *Astrophys. J. Suppl. Ser.* 188 (2010) 500] and existing infrared and millimeter-wave measurements of $^{13}\text{C}^{14}\text{N}$. The 6–3, 7–4, 8–5 and 9–6 bands of the $B^2\Sigma^+-A^2\Pi$ transition were also identified in the 23 300–24 000 cm^{-1} region and were included in the final analysis. An experimental line list and calculated term values are provided.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Electronic spectra of CN are known for more than a century through characteristic bands present in the visible and ultraviolet regions. These bands belong to the $A^2\Pi-X^2\Sigma^+$ (red) and $B^2\Sigma^+-X^2\Sigma^+$ (violet) transitions which extend from the near infrared to the ultraviolet regions and are very persistent. This radical is frequently observed in a wide variety of sources such as arcs, electrical discharges, flames and shock tubes and its spectra now extend from the microwave to the vacuum ultraviolet [1].

This radical has been found in a wide range of astronomical sources such as comets [2–5] stars [6,7], the sun [8], circumstellar shells [9,10], interstellar clouds [11,12] and the integrated light of galaxies [13]. The CN lines of the violet system were also identified in the spectra of the Red Rectangle nebula [HD 44179] [14]. The presence of CN in astronomical objects makes it a key species to probe carbon and nitrogen abundances, as well as C and N isotopic ratios. The carbon and nitrogen isotopic abundance ratios give information on nucleosynthesis and chemical evolution in galaxies [15]. Millimeter wave surveys of ^{12}CN and ^{13}CN in dark molecular clouds have shown a Galactic abundance gradient attributed to

chemical evolution [16,17] and also shed light on star formation in galaxies [13].

The $A^2\Pi-X^2\Sigma^+$ (red) and $B^2\Sigma^+-X^2\Sigma^+$ (violet) transitions of CN, in particular, have been extensively studied because of their astrophysical importance. The previous studies of $^{12}\text{C}^{14}\text{N}$ have been summarized in some recent papers on the red [18,19] and violet [19–21] systems of $^{12}\text{C}^{14}\text{N}$ and references to the previous studies on $^{13}\text{C}^{14}\text{N}$ can be found in the recent papers on the red [23] and violet [24] systems of $^{13}\text{C}^{14}\text{N}$. Recently, the high resolution spectra of these two transitions of the $^{12}\text{C}^{15}\text{N}$ isotopologue have been studied by Colin and Bernath [25]. Because of the astrophysical importance of CN, Fay and Wyller [26] have stressed on the need for high resolution measurements of the $^{13}\text{C}^{14}\text{N}$ red system bands near 1 μm and longer wavelengths. A line list commonly used in current astronomical work is that of Plez, as discussed in Hill et al. [27]. This list is drawn from eight separate sources and is inadequate for $^{13}\text{C}^{14}\text{N}$ as has been pointed out by Garcia-Hernandez et al. [28]. There is, therefore, a need for high resolution measurements of CN and its isotopologues to improve the simulation of astronomical spectra and obtain more accurate $^{12}\text{C}/^{13}\text{C}$ abundance ratios.

Hempel et al. [29] have measured the fundamental 1–0 band of $^{12}\text{C}^{14}\text{N}$ and $^{13}\text{C}^{14}\text{N}$, and Hübner et al. [30] have reported the measurements of fundamental bands of $^{12}\text{C}^{14}\text{N}$, $^{13}\text{C}^{14}\text{N}$, $^{12}\text{C}^{15}\text{N}$, $^{13}\text{C}^{15}\text{N}$ isotopologues using tunable diode laser absorption spectroscopy. The millimeter wave studies of the $X^2\Sigma^+$ ground state of $^{13}\text{C}^{14}\text{N}$ were obtained by Bogey et al. [31,32] and pure rotational

* Corresponding author at: Department of Chemistry, University of York, Heslington, York YO10 5DD, UK. Fax: +44 0 1904 432516.

E-mail address: rr662@york.ac.uk (R.S. Ram).

measurements were reported for the $v = 0$ –9 vibrational levels of the ground state [32].

Jørgensen and Larsson [33] have calculated the molecular opacities for the CN, $A^2\Pi-X^2\Sigma^+$ transition at temperatures ranging from 1000 K to 6000 K and rotational lines were calculated for the $^{12}\text{C}^{14}\text{N}$, $^{13}\text{C}^{14}\text{N}$, $^{12}\text{C}^{15}\text{N}$, $^{13}\text{C}^{15}\text{N}$ isotopologues for transitions between vibrational levels $v = 0$ –30 of the ground and excited states using available and extrapolated spectroscopic constants. In a recent theoretical study, Shi et al. [34] 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 $^{12}\text{C}^{14}\text{N}$, $^{13}\text{C}^{14}\text{N}$, $^{12}\text{C}^{15}\text{N}$ and $^{13}\text{C}^{15}\text{N}$.

Recently we have reported on extensive high resolution studies of the red and violet transitions of $^{12}\text{C}^{14}\text{N}$ [21,22] and $^{13}\text{C}^{14}\text{N}$ [23,24] with the aim of providing an accurate line list for the bands, and improved spectroscopic constants and term values for the $A^2\Pi$ and $B^2\Sigma^+$ states of the two isotopologues. For $^{12}\text{C}^{14}\text{N}$ we have reported term values and spectroscopic constants for the $v = 0$ –22 vibrational levels of the $A^2\Pi$ state [21] and $v = 0$ –15 vibrational level of the $B^2\Sigma^+$ and $X^2\Sigma^+$ states [22] from the rotational analysis of a large number of bands. In the case of $^{13}\text{C}^{14}\text{N}$, we have recently reported on the 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 [23] while for the violet system we obtained a rotational analysis of 52 bands involving vibrational levels up to $v = 15$ of the $B^2\Sigma^+$ and $X^2\Sigma^+$ states [24]. These studies have 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 $^{13}\text{C}^{14}\text{N}$ [23].

At the time of our previous study of the $A^2\Pi-X^2\Sigma^+$ transition of $^{13}\text{C}^{14}\text{N}$ [23], we noted the presence of a large number of bands in the 15000–24000 cm^{-1} region which were left unassigned because of their relatively weak intensity and overlapping. After the rotational analysis of these bands, we have extended the red system of $^{13}\text{C}^{14}\text{N}$ to much higher vibrational levels of the $A^2\Pi$ state. Several violet degraded bands present in the 23300–24000 cm^{-1} region have been identified as belonging to the $B^2\Sigma^+-A^2\Pi$ transition of $^{13}\text{C}^{14}\text{N}$, observed for the first time. In this paper we report on the rotational analysis of 27 bands of the $A^2\Pi-X^2\Sigma^+$ transition involving vibrational levels $v = 9$ –22 of the $A^2\Pi$ state and the 6–3, 7–4, 8–5 and 9–6 bands of the $B^2\Sigma^+-A^2\Pi$ transition of $^{13}\text{C}^{14}\text{N}$. In the final fit we have combined our new measurements with our previous measurements of the $A^2\Pi-X^2\Sigma^+$ bands in the 4000–15000 cm^{-1} region [23], the measurements of the $B^2\Sigma^+-X^2\Sigma^+$ bands [24], all red and infrared measurements [29,30] and previous millimeter-wave measurements [31,32] with the aim of providing an accurate line list for all bands, and improved spectroscopic constants and term values for the $v = 0$ –22 vibrational levels of the $A^2\Pi$ state.

2. Experimental

The spectra of $^{13}\text{C}^{14}\text{N}$ used in the present analysis were recorded by J. Brault (deceased) and R. Engleman in 1992 using the Fourier transform spectrometer associated with McMath-Pierce Solar Telescope of the National Solar Observatory located at Kitt Peak. The molecules were produced in a lamp by adding mixture of argon and a trace of $^{13}\text{CH}_4$ to active nitrogen, $^{14}\text{N}_2$, made in a microwave discharge. Spectra in the 2900–31000 cm^{-1} region were recorded in two parts. The 2900–16000 cm^{-1} region was recorded using the CaF_2 beamsplitter, InSb detectors, and RG610 filters while the other 9000–31000 cm^{-1} region was recorded using the UV beam splitter and midrange Si photodiode detectors. The spectra in the two regions were recorded at the respective resolution of 0.016 cm^{-1} and 0.03 cm^{-1} by co-adding 5 and 4 scans, respectively.

The spectra recorded with the active nitrogen source were free from any $^{12}\text{C}^{14}\text{N}$ impurity. The line positions were extracted from the observed spectra using a data reduction program called PC-DE-COMP developed by J. Brault. The peak positions were determined by fitting a Voigt line shape function to each spectral feature. The spectra in the 15000–24000 cm^{-1} region were calibrated by transferring calibration from the $B^2\Sigma^+-X^2\Sigma^+$ bands, since this region of the $A^2\Pi-X^2\Sigma^+$ system is free from any atomic or molecular features suitable for independent calibration. The $B^2\Sigma^+-X^2\Sigma^+$ bands were calibrated using the Ar line measurements by Whaling et al. [35] as corrected by Sansonetti [36]. The precision of measurement is expected to be better than $\pm 0.002 \text{ cm}^{-1}$ for the stronger and unblended lines. However the lower J rotational lines in some branches were blended because of the partially-resolved splitting of the main and satellite branches; the blended and weaker lines have uncertainty of $\pm 0.005 \text{ cm}^{-1}$ or higher.

3. Observations

As was noted in the case of the red system of $^{12}\text{C}^{14}\text{N}$, the spectra recorded using the active nitrogen afterglow discharge have a low rotational temperature ($\sim 300 \text{ K}$) and high vibrational temperatures. This results in the observation of vibrational bands with higher v 's than other sources including a regular microwave discharge, high temperature furnaces and arc sources. In fact we have been able to observe bands with vibrational levels up to $v' = 22$ of the $A^2\Pi$ state and $v'' = 12$ of the $X^2\Sigma^+$ state from the afterglow spectra. Because of low rotational temperatures the rotational lines in different bands were typically observed to J values < 30.5 even in the strongest bands.

A few bands located in the 23300–24000 cm^{-1} region have been identified belonging to the $B^2\Sigma^+-A^2\Pi$ transition while the $A^2\Pi-X^2\Sigma^+$ (red) and $B^2\Sigma^+-X^2\Sigma^+$ (violet) bands are located in the 3500–22500 cm^{-1} and 20000–30000 cm^{-1} regions, respectively. Except for the lower sequence bands, the spectra of the red and violet transitions appear complex because of overlapping of the different sequence bands as well as an irregular intensity pattern in the different sequence bands. The irregular intensity pattern of higher vibrational bands arises because of interactions in the excited state, making it difficult to make any vibrational assignments without a proper rotational analysis. Therefore, most of the bands with reasonable intensity were measured and rotationally analyzed in order to make a vibrational assignment. In total 27 bands with $v' = 9$ –22 excited state vibrational levels were rotationally analyzed. All these bands belong to vibrational sequences ranging from $\Delta v = 5$ to $\Delta v = 11$.

Each band of a $^2\Pi-^2\Sigma^+$ transition consists of two sub-bands, $^2\Pi_{1/2}-^2\Sigma^+$ and $^2\Pi_{3/2}-^2\Sigma^+$ because the $A^2\Pi$ state belongs to Hund's coupling case (a). Since the $A^2\Pi$ state of $^{13}\text{C}^{14}\text{N}$ is inverted, the $^2\Pi_{3/2}$ component lies below the $^2\Pi_{1/2}$ component. Following the traditional convention these two components are labeled as F_1 and F_2 , respectively. With the selection rule $\Delta J = 0, \pm 1$, each sub-band consists of three main and three satellite branches depending on whether the $X^2\Sigma^+$ levels are F_1 or F_2 . Therefore, the $^2\Pi_{3/2}-^2\Sigma^+$ sub-band consists of P_{11} , Q_{11} , R_{11} , P_{12} , Q_{12} and R_{12} branches and the $^2\Pi_{1/2}-^2\Sigma^+$ sub-band consists of P_{22} , Q_{22} , R_{22} , P_{21} , Q_{21} and R_{21} branches. An illustrative energy level diagram of a $^2\Pi-^2\Sigma^+$ transition can be found in a paper, for example, on the Comet-tail system of CO^+ [37]. This method of labeling the branches has been adopted in the previous studies of the $A^2\Pi-X^2\Sigma^+$ transition of $^{12}\text{C}^{14}\text{N}$ [38] and $^{13}\text{C}^{14}\text{N}$ [39]. Some of the satellite branches are much weaker than the main branches and have not been identified in some bands due to weak intensity and unresolved splitting from the main branches. A description of the assigned bands is provided in the following sections.

Download English Version:

<https://daneshyari.com/en/article/5414938>

Download Persian Version:

<https://daneshyari.com/article/5414938>

[Daneshyari.com](https://daneshyari.com)