

## Fourier transform emission spectroscopy of the $B^2\Sigma^+ - X^2\Sigma^+$ system of CN

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Received 7 February 2006; in revised form 29 March 2006

Available online 5 April 2006

### Abstract

The emission spectrum of the  $B^2\Sigma^+ - X^2\Sigma^+$  system of CN has been observed at high-resolution using a Fourier transform spectrometer. The rotational structure of a large number of bands involving vibrational levels  $v = 0-15$  of both electronic states has been analyzed, and improved spectroscopic constants have been determined by combining the microwave and infrared measurements from previous studies. Improved spectroscopic constants for vibrational levels up to  $v'' = 18$  in the  $X^2\Sigma^+$  state and  $v' = 19$  in the  $B^2\Sigma^+$  state have been determined by combining the measurements of the 16–13, 18–17, 18–18, 19–15, and 19–18 bands of Douglas and Routly [Astrophys. J. Suppl. 1 (1955) 295–318] and 17–14 and 17–16 bands of Ito et al. [J. Chem. Phys. 96 (1992) 4195] with our data. The band constants obtained have been used to estimate equilibrium ground state constants for CN.

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**Keywords:** Fourier transform spectroscopy; Emission spectroscopy; Spectroscopic constants

### 1. Introduction

The CN radical has been the subject of extensive studies because of its importance in chemical kinetics, flame diagnostics, and astrophysics. The CN radical is found in many extraterrestrial sources including the Sun [1], stellar atmospheres [2,3], comets [4], dark interstellar clouds [5,6], and diffuse interstellar clouds [7–12]. Recently the lines of CN were identified in spectra of the Red Rectangle nebula (HD 44179) along with those of CH and CH<sup>+</sup> between 3800 Å and 10000 Å [13]. The spectra of the  $A^2\Pi - X^2\Sigma^+$  (red) and  $B^2\Sigma^+ - X^2\Sigma^+$  (violet) transitions of CN can be used to measure the isotopic abundance of C and N in extraterrestrial environments. The CN red system provides a very useful measure of the N abundance in red giant stars.

The laboratory spectra of CN have been known for more than a century and are produced using wide variety of sources such as arcs, flames, active nitrogen afterglows, shock tubes and electrical discharges of all types. Its spectra extend from the vacuum UV to the far infrared. Among the CN transitions, the  $A^2\Pi - X^2\Sigma^+$  and  $B^2\Sigma^+ - X^2\Sigma^+$  systems are most prominent and have been studied extensively. A summary of the previous work on CN available prior to 1992 has been provided in papers by Prasad and Bernath [14,15], in which the observation of the  $B^2\Sigma^+ - X^2\Sigma^+$  [14] and  $A^2\Pi - X^2\Sigma^+$  [15] transitions using a jet-cooled corona excited supersonic expansion source were reported. In those studies an improved set of constants for the  $v = 0-11$  vibrational levels of the  $X^2\Sigma^+$  state,  $v = 0-11$  of the  $B^2\Sigma^+$  state and the  $v = 8-21$  of the  $A^2\Pi$  states of CN were reported. At the same time Rehfuss et al. [16] reported the analysis of many bands of the  $\Delta v = 0$  and  $\Delta v = -1$  sequences of the violet system involving vibrational levels  $v = 0-13$  of the  $B^2\Sigma^+$  and  $X^2\Sigma^+$  states. However they did

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not obtain spectroscopic constants for the  $v = 5, 10,$  and  $12$  vibrational levels because the  $5-5, 5-6, 10-10,$  and  $12-12$  bands are affected by perturbations. Most of the observed perturbations in the  $B^2\Sigma^+$  state are the result of interactions from the lower-lying  $A^2\Pi$  state, although some are also due to the  $a^4\Pi$  state. The perturbations observed in the  $A^2\Pi$  and  $B^2\Sigma^+$  states have been studied in detail [17–23]. Kotlar et al. [17] have performed a deperturbation analysis and provided a set of deperturbed constants for the  $A^2\Pi$  ( $v = 0-12$ ) and  $B^2\Sigma^+$  ( $v = 0-8$ ) states of CN, while Gorbali and Savadatti [18] observed high- $J$  perturbed lines in the  $11-11, 12-12, 13-13,$  and  $14-14$  bands of the  $B^2\Sigma^+ - X^2\Sigma^+$  transition. Ito, Kuchitsu and co-workers have performed an extensive analysis of perturbations in the  $A^2\Pi$  and  $B^2\Sigma^+$  states of CN, and have published a series of papers providing deperturbed spectroscopic constants for the low-lying electronic states of CN [19–24]. The more recent experimental and theoretical studies of CN (since 1992) are summarized below.

The high-resolution spectrum of the  $2-0$  band of the  $A^2\Pi - X^2\Sigma^+$  transition of CN was observed by concentration modulation laser spectroscopy by Liu et al. [25]. In a recent infrared study, diode lasers were used by Hübner et al. [26] to observe the fundamental bands of four isotopic forms,  $^{12}\text{C}^{14}\text{N}, ^{13}\text{C}^{14}\text{N}, ^{12}\text{C}^{15}\text{N},$  and  $^{13}\text{C}^{15}\text{N},$  and spectroscopic constants were determined.

Dagdikian and co-workers [27,28] have applied the technique of optical-optical double resonance to the study of selective rotational energy transfer from individual  $\Lambda$ -doublet levels of the highly rotationally excited  $A^2\Pi$  state. Yang and Dagdikian have also reported the observation of magnetic-dipole transitions in the  $B^2\Sigma^+ - A^2\Pi$  system of CN [29]. In a separate study Nizamov et al. [30] have performed a joint experimental and theoretical study of the  $A^2\Pi \rightarrow X^2\Sigma^+ v_A = 7 \rightarrow v_X = 11$  electronic energy transfer induced by collisions with helium. The collision-induced intramolecular energy transfer from CN ( $X^2\Sigma^+, v''$ ) to CN ( $A^2\Pi$ ) was observed in a molecular beam through the  $A^2\Pi \rightarrow X^2\Sigma^+$  emission by de Moore et al. [31] and the relative vibrational population distribution of CN ( $A^2\Pi, v' = 2-12$ ) was determined. The state-to-state and total rotational energy transfer rate constants and radiative lifetimes have also been measured for the CN ( $B^2\Sigma^+, v = 0, N$ ). An experimental measurement of the electronic-vibrational transition dipole moment for the  $2-0$  band of the  $A^2\Pi \leftarrow X^2\Sigma^+$  transition of CN has been reported by He et al. [32] using a direct time-resolved absorption technique.

In a theoretical study, the dissociation energy of CN has been determined by multi-reference configuration interaction calculations utilizing very large basis sets by Pradhan et al. [33] and a value of  $7.72 \pm 0.04$  eV was found, which compares well with the experimental value of  $7.738 \pm 0.02$  eV obtained by Huang et al. [34]. Ajitha and Hirao [35] have calculated the dipole moments of the  $X^2\Sigma^+$  and  $A^2\Pi$  states of CN at different internuclear distances using the multi-reference coupled cluster (MRCC) linear response approach. In another study, Meléndez

et al. [36] have computed Franck-Condon factors for the  $A^2\Pi - X^2\Sigma^+$  and  $B^2\Sigma^+ - X^2\Sigma^+$  systems of CN.

In the present study we extend the previous work on the  $B^2\Sigma^+ - X^2\Sigma^+$  transition of CN by new high-resolution measurements of bands up to  $v', v'' = 15$  in the  $B^2\Sigma^+$  and  $X^2\Sigma^+$  states. The measurements of the  $16-13, 18-17, 18-18, 19-15,$  and  $19-18$  bands obtained by Douglas and Routly [37] and  $17-14$  and  $17-16$  bands of Ito et al. [24] observed with a grating spectrograph were also included. The previous infrared and microwave measurements were also included in the final fit to obtain an improved set of spectroscopic constants for the  $B^2\Sigma^+$  and  $X^2\Sigma^+$  states.

## 2. Experimental details

The emission spectra of CN (92/02/12 #5) used in the present analysis were recorded on 2/12/1992 using a nitrogen afterglow source. The radicals were excited in a microwave discharge of nitrogen and a trace of  $\text{CH}_4$  and the cell was cooled with liquid nitrogen vapor. The spectra show the signature of diatomic species generated by the physical and chemical interactions of the constituents. Doppler and pressure broadening was minimized, and the observed line width was about  $0.075 \text{ cm}^{-1}$ . Experimental parameters were varied to obtain strong bands and a stable discharge. Molecular lines were produced in profusion, but careful adjustment of nitrogen pumping speed, gas pressure, gas temperature and, particularly, the cooling of the cell using the vapor from liquid nitrogen was required. These spectra have a low-rotational temperature (about 300 K) and a much higher vibrational temperature.

The emission from the discharge was focused on to the entrance aperture of the McMath-Pierce Fourier transform spectrometer (FTS) of the National Solar Observatory at Kitt Peak. The midrange silicon diode detectors and UV beamsplitter limited the band pass to the  $9000-31000 \text{ cm}^{-1}$  spectral region. An unapodized instrumental resolution of  $0.03 \text{ cm}^{-1}$  was set in these experiments. A total of 5 scans were co-added in about 70 min of integration. As the nitrogen afterglow spectra did not contain any atomic lines that could be used as standards for calibration, the spectra below  $25315 \text{ cm}^{-1}$  were calibrated using the strong CN lines of the violet bands common with those obtained in a microwave discharge which were calibrated using Ar I lines from Whaling et al. [38]. In the absence of Ar lines on the higher wavenumber side, the spectra at  $>25515 \text{ cm}^{-1}$  were calibrated using common lines from carbon arc spectra in a similar manner. The absolute accuracy of the calibration is estimated to be better than  $\pm 0.003 \text{ cm}^{-1}$ .

## 3. Observations and analysis

The  $B^2\Sigma^+ - X^2\Sigma^+$  spectra are spread over a large span of wavenumbers and consist of bands belonging to the  $\Delta v = -2, -1, 0, 1,$  and  $2$  sequences. The bands with lower vibrational quanta, particularly in the first four sequences

listed, are complex because of the formation of a head of heads, which result in highly dense rotational structure. In the  $\Delta v = 0$  sequence, bands were identified from 0–0 to 15–15. The bands in the  $\Delta v = 2$  sequence are more open and free from overlapping from the neighboring bands as shown in a portion of the spectrum provided in Fig. 1. The  $v' = 0$ –13 vibrational levels of the  $B^2\Sigma^+$  state are common to several bands from different sequences, while the 14–14 band has a common lower vibrational level with the 12–14 band. The 15–15 band, on the other hand, has a lower vibrational level common only with the 19–15 band observed by Douglas and Routly [37]. Bands with vibrational levels higher than 15 were not observed in our high-resolution FTS spectra. We therefore decided to include the older data recorded at grating resolution for bands with  $v'$ ,  $v'' > 15$  from the papers by Douglas and Routly [37] and Ito et al. [24]. The measurements of lines of the 16–13, 18–17, 18–18, 19–15, and 19–18 bands, taken from the paper of Douglas and Routly [37], were given weights of  $0.05 \text{ cm}^{-1}$ . Since the  $v' = 17$  level is perturbed, the lines of the 17–16 and 17–14 bands taken from the paper of Ito et al. [24] were given weights of  $0.2 \text{ cm}^{-1}$ . In addition, some lines, presumably those most strongly affected by perturbations, were deweighted.

Our spectra are very congested, so the rotational lines in different bands were identified by comparing combination differences from common vibrational bands. The rotational structure of a  ${}^2\Sigma^+ \rightarrow {}^2\Sigma^+$  band consists of four main branches  $R_1$ ,  $R_2$ ,  $P_1$ , and  $P_2$  and two satellite branches  ${}^RQ_{21}$  and  ${}^PQ_{12}$ . The satellite branches are very weak and have been observed for only a few strong bands. The spectral line positions were measured using the data reduction program called DECOMP developed at Kitt Peak by J. Brault. The peak positions were found by fitting a Voigt line shape function to each feature using a nonlinear least-squares procedure. The  $R_1$  and  $R_2$  and  $P_1$  and  $P_2$  branches are split because of the spin rotation interaction in both the  $X$  and  $A$  states. In most of the bands this splitting is well resolved, at least for the higher  $J$  lines. In some bands, however, this splitting has not been observed.

The rotational constants for the individual vibrational levels were determined by fitting the observed line positions to the usual energy level expression for  ${}^2\Sigma$  states obtained with the effective Hamiltonian of Brown et al. [39]. The matrix elements for a  ${}^2\Sigma$  Hamiltonian are listed by Douay et al. [40]. The constants  $T_v$ ,  $B_v$ ,  $D_v$ ,  $\gamma_v$ , and  $\gamma_{Dv}$  were deter-

mined for most of the lower vibrational levels of the  $X^2\Sigma^+$  state, while additional higher order effective constants such as  $H_v$ ,  $L_v$ ,  $\gamma_{Hv}$ , and  $\gamma_{Lv}$  were also required for the perturbed states in order to minimize the standard deviation of the fit. The rotational lines were given suitable weights depending on the signal-to-noise ratio and extent of blending. The term energy for  $v'' = 15$  was estimated based on the intervals in the vibrational levels with  $v'' \leq 14$  and  $v'' = 16$ –18 obtained from the fit, and was fixed in the final fit. The term value for the  $v'' = 15$  vibrational level obtained in this manner ( $27856.2 \text{ cm}^{-1}$  relative to  $v'' = 0$ ) is expected to be accurate to  $\pm 1 \text{ cm}^{-1}$ .

The rotational lines of the  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  bands of CN were measured by S. P. Davis, L. Wallace, J. Brault, and R. Engleman and have been published as a National Solar Observatory Technical Report [41]. This report includes atlases, line lists, and analyses of the CN spectra from three different laboratory sources—the carbon arc, microwave discharge, and active nitrogen afterglow discharge. Our analysis was started using the measurements reported in the NSO report [41] with the aim of obtaining an improved set of spectroscopic constants for the  $B^2\Sigma^+$  and  $X^2\Sigma^+$  states. During the analysis, unusually large residuals were observed for transitions where the two spin components were not resolved. This was because these broad lines were measured as single lines, even though some of the doublets were partially resolved. These lines were therefore remeasured and used in our fit. Additional missing high- $J$  lines were also measured and assigned, particularly for some of the more highly excited bands. The rotational constants for the  $X^2\Sigma^+$  and  $B^2\Sigma^+$  states obtained from the final fit are provided in Tables 1 and 2, respectively.

The output of our final band constant fit is provided as a supplementary data file [44]. The initial data set included all of the microwave, infrared, and violet system lines used in our two previous CN papers [14,15], although some of the weights were adjusted in the final fit. To this data set were added the new violet system lines discussed in the present paper as well as the 18 lines of the fundamental band measured by Hübner et al. [26] by diode laser spectroscopy. New infrared observations of the 1–0 to 8–7 vibration–rotation bands have also been made by Horka et al. [45] and these lines were also added. The problem with all of the infrared data is that the spin-splittings are not resolved (or in the case of Hübner et al. [26], the lines were averaged for the few partly resolved cases). In the case

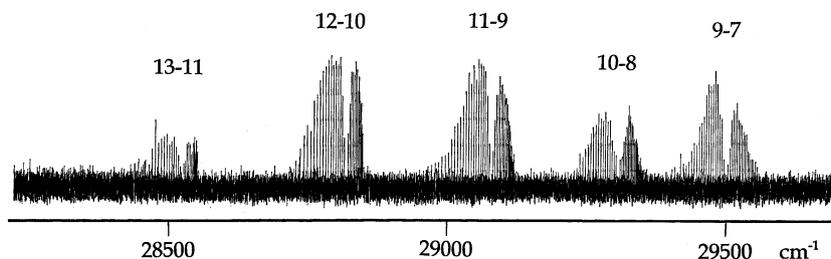


Fig. 1. A compressed portion of the  $\Delta v = 2$  sequence of the  $B^2\Sigma^+ \rightarrow X^2\Sigma^+$  system of CN with some higher vibrational bands marked.

Table 1  
Spectroscopic constants (in  $\text{cm}^{-1}$ ) for the  $X^2\Sigma^+$  state of CN

$v$	$T_v$	$B_v$	$10^6 \times D_v$	$\gamma_v$	$\gamma_{Dv}$
0	0.0	1.891089596(96)	6.39726(64)	$7.25514(52) \times 10^{-3}$	$-1.91(11) \times 10^{-7}$
1	2042.42143(24)	1.873665288(90)	6.40576(60)	$7.17376(74) \times 10^{-3}$	$-1.83(11) \times 10^{-7}$
2	4058.54933(29)	1.856186883(85)	6.41672(60)	$7.0850(12) \times 10^{-3}$	$-1.47(11) \times 10^{-7}$
3	6048.34329(35)	1.83865221(11)	6.42731(56)	$6.9814(12) \times 10^{-3}$	$-1.40(11) \times 10^{-7}$
4	8011.76637(42)	1.82105914(21)	6.44121(73)	$6.8631(14) \times 10^{-3}$	—
5	9948.77554(56)	1.80340409(27)	6.4530(38)	$6.7198(14) \times 10^{-3}$	—
6	11859.32721(61)	1.78568472(29)	6.4651(44)	$6.5417(15) \times 10^{-3}$	—
7	13743.37442(66)	1.76789824(29)	6.4812(46)	$6.3136(14) \times 10^{-3}$	—
8	15600.86884(71)	1.75004020(28)	6.4835(64)	$6.0121(15) \times 10^{-3}$	—
9	17431.75410(77)	1.73210149(27)	6.5334(85)	$5.6133(22) \times 10^{-3}$	—
10	19235.95846(76)	1.71405029(27)	6.6424(73)	$5.2004(74) \times 10^{-3}$	$1.17(25) \times 10^{-6}$
11	21013.2936(11)	1.694997(24)	1.30(15) <sup>c</sup>	$1.424(21) \times 10^{-2}$	$-8.156(75) \times 10^{-5}$
12	22765.7297(11)	1.677358(16)	8.954(75)	$1.3336(21) \times 10^{-1}$	$-2.339(15) \times 10^{-4}$
13	24488.7281(13)	1.659510(16)	6.645(40)	$1.750(17) \times 10^{-2}$	—
14	26185.6934(15)	1.641291(26)	6.58(12)	$1.153(21) \times 10^{-2}$	—
15	27856.2000 <sup>a</sup>	1.622749(62)	6.38(25)	$3.6(1.7) \times 10^{-3}$	$2.83(59) \times 10^{-5}$
16	29500.37(71)	1.6004(23)	4.3(1.8)	—	—
17	31115.064(25) <sup>b</sup>	1.58528(44)	4.2(1.8)	—	—
18	32703.724(20) <sup>b</sup>	1.56699(18)	7.85(36)	—	—

<sup>a</sup> Fixed, see text for details.

<sup>b</sup> These values are relative to the fixed term value for  $v'' = 15$  ( $27856.2 \text{ cm}^{-1}$ ) and any change in this value propagates directly into the  $v = 17$  and 18 term values.

<sup>c</sup> An effective  $H_{11} = -1.011(23) \times 10^{-8} \text{ cm}^{-1}$  was determined.

Table 2  
Spectroscopic constants (in  $\text{cm}^{-1}$ ) for the  $B^2\Sigma^+$  state of CN

$v$	$T_v$	$B_v$	$10^5 \times D_v$	$\gamma_v$	$\gamma_{Dv}$
0	25797.86825(43)	1.9587413(13)	0.660855(81)	$1.7154(52) \times 10^{-2}$	$-8.58(29) \times 10^{-7}$
1	27921.46650(55)	1.9380444(45)	0.67324(29)	$1.8162(82) \times 10^{-2}$	$-1.044(81) \times 10^{-6}$
2	30004.90632(77)	1.916503(10)	0.7021(27)	$1.840(13) \times 10^{-2}$	$-2.51(59) \times 10^{-6}$
3	32045.94678(73)	1.894180(15)	0.7105(60)	$2.453(16) \times 10^{-2}$	$-7.4(1.1) \times 10^{-6}$
4	34041.97036(68)	1.8704809(66)	0.7448(15)	$2.1169(97) \times 10^{-2}$	$-5.18(35) \times 10^{-6}$
5	35990.0970(21)	1.847108(24)	0.9132(54)	$4.31(83) \times 10^{-3}$	$1.691(39) \times 10^{-4}$ , <sup>c</sup>
6	37887.42418(74)	1.8193429(54)	0.8092(11)	$2.5237(87) \times 10^{-2}$	$-8.50(27) \times 10^{-6}$
7	39730.53401(80)	1.790761(12)	1.1054(58)	$6.126(58) \times 10^{-3}$	—
8	41516.64296(84)	1.7621417(59)	0.9040(13)	$3.4942(98) \times 10^{-2}$	$-2.000(32) \times 10^{-5}$
9	43242.98350(93)	1.730285(12)	0.9243(58) <sup>b</sup>	$1.567(11) \times 10^{-2}$	$-1.897(36) \times 10^{-5}$
10	44908.7905(14)	1.697091(90)	4.73(20) <sup>b</sup>	$3.1270(75) \times 10^{-1}$	$-4.287(33) \times 10^{-3}$ , <sup>c</sup>
11	46511.39508(97)	1.6649929(84)	1.0311(21)	$2.138(14) \times 10^{-2}$	$-1.690(50) \times 10^{-5}$ , <sup>c</sup>
12	48053.7300(11)	1.629723(27)	1.798(19)	$-9.15(23) \times 10^{-3}$	$-7.81(22) \times 10^{-5}$
13	49537.3389(13)	1.598042(16)	1.0877(37)	$3.325(22) \times 10^{-2}$	$-2.613(59) \times 10^{-5}$
14	50964.6127(38)	1.56437(49)	9.5(1.4)	$1.159(60) \times 10^{-2}$	—
15	52340.0303(17) <sup>a</sup>	1.532490(75)	1.223(34)	$9.90(18) \times 10^{-2}$	$-4.39(11) \times 10^{-4}$ , <sup>c</sup>
16	53664.4700(98)	1.49988(12)	1.289(22)	$8.4(2.1) \times 10^{-3}$	$5.45(51) \times 10^{-5}$
17	54944.838(690)	1.4656(21)	0.91(16)	$7.2(2.1) \times 10^{-3}$	—
18	56178.130(22) <sup>a</sup>	1.43704(30)	0.83(10)	0.0	—
19	57371.297(14) <sup>a</sup>	1.40806(13)	1.212(26)	0.0	—

<sup>a</sup> These values are determined by (and depend on) the fixed  $v'' = 15$  term value in Table 1. Any change in this term value propagates directly into  $v' = 15$ , 18, and 19.

<sup>b</sup> Effective constants  $H_9 = -1.346(72) \times 10^{-9}$ ,  $H_{10} = 5.28(17) \times 10^{-7}$ , and  $L_{10} = -1.843(55) \times 10^{-9} \text{ cm}^{-1}$  were also determined.

<sup>c</sup> Effective constants  $\gamma_{H5} = -2.244(61) \times 10^{-7}$ ,  $\gamma_{H10} = 3.060(42) \times 10^{-5}$ ,  $\gamma_{L10} = -8.09(15) \times 10^{-8}$ ,  $\gamma_{H15} = 8.67(37) \times 10^{-7} \text{ cm}^{-1}$  were also determined.

of pure rotational transitions, new data for terahertz transitions were published for  $v = 0$  and 1 by Klisch et al. [43], and the lines for  $v = 2-7$  were obtained for our fits from Klisch's Ph.D. thesis [43]. The infrared vibration-rotation lines from the Fourier transform and diode laser measurement are expected to be better than  $\pm 0.005 \text{ cm}^{-1}$  in preci-

sion and were given estimated errors of  $0.005 \text{ cm}^{-1}$  in the final fit. The hyperfine-free microwave measurements for  $v'' = 0-10$  were given weights ranging from  $2 \times 10^{-6}$  to  $5 \times 10^{-6} \text{ cm}^{-1}$  as quoted in Refs. [42] and [43], except for a few blended lines. Since the present Fourier transform spectra were recorded at much higher temperature than

Table 3  
Equilibrium constants (in  $\text{cm}^{-1}$ ) for the  $X^2\Sigma^+$  state of CN

Constants	Values ( $\text{cm}^{-1}$ )
$\omega_e$	2068.6834(11)
$\omega_e x_e$	13.12172(47)
$10^3 \times \omega_e y_e$	-5.412(77)
$10^5 \times \omega_e z_e$	-9.83(43)
$B_e$	1.89978350(83)
$\alpha_e$	0.01737487(93)
$10^5 \times \gamma_e$	-2.430(28)
$10^7 \times \delta_e$	-4.92(23)
$r_e(\text{\AA})$	1.1718073(25)

the corona discharge sources, many more high- $N$  lines were measured especially for the higher vibrational bands as compared to those reported previously [14,16]. The inclusion of vibration–rotation and microwave measurements has provided a precise set of spectroscopic constants for the ground state and has also improved the excited state constants. The pure rotational and infrared transitions also help break correlations between constants of the  $B^2\Sigma^+$  and  $X^2\Sigma^+$  states. The constants obtained in this work provide considerable improvement over the previous values which were determined using relatively low- $N$  rotational lines.

The constants of Tables 1 and 2 were utilized to determine equilibrium constants using the expressions

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

$$B_v = B_e - \alpha_e(v + 1/2) + \gamma_e(v + 1/2)^2 + \delta_e(v + 1/2)^3, \quad (2)$$

All of the vibrational term values of the ground state show evidence of perturbation for  $v = 10$  and above and were therefore deweighted. The final equilibrium constants thus obtained for the  $X^2\Sigma^+$  state are given in Table 3. A similar fit for the  $B^2\Sigma^+$  state did not provide any satisfactory equilibrium constants because of the existence of perturbations in nearly all of the vibrational levels.

#### 4. Results and discussion

The rotational analysis of the  $B^2\Sigma^+ - X^2\Sigma^+$  system of CN began by fitting separately all observed bands having a common excited state vibrational level. This procedure helped us to find the lines affected by perturbations based on their residuals in the fit. From our FTS spectra, we have measured rotational lines up to  $N = 24$  in the 0–0 band in spite of extensive overlapping. We have observed two local perturbations in the  $v = 0$  vibrational level of the  $B^2\Sigma^+$  state. A local perturbation at  $N = 7$  affects only the  $F_1$  spin component while another perturbation observed at  $N = 15$  affects both parity levels. Kiess and Broida [46] suggested that the perturbations observed in the  $v = 0$  vibrational level are a result of interaction with the  $v = 10$  vibrational level of the  $A^2\Pi$  state. We have found that the bands with  $v' = 1, 2, 3,$  and  $4$  of the  $B^2\Sigma^+$  state are free from local perturbations over our observed range of  $N$  values of 19, 23, 18, and 24, respectively.

We have rotationally analyzed the four bands, 5–4, 5–5, 5–6, and 5–7 with the common  $v' = 5$  level of the  $B^2\Sigma^+$  state. As mentioned by Engleman [47] and Rehfuss et al. [16], the  $v' = 5$  level of the  $B^2\Sigma^+$  state is affected by a perturbation. Engleman [47] has reported the analysis of the 5–4 and 5–5 bands, while Rehfuss et al. [16] analyzed the 5–5 and 5–6 bands for the unperturbed low- $N$  lines. In contrast to the previous work, the e-parity rotational levels belonging to the  $v' = 5$  vibrational level are perturbed near  $N' = 11$ , while the f-parity levels do not show signs of perturbation. Thus in our fits we deweighted transitions involving these perturbed levels, although we included ground state combination differences for both spin components. Prasad et al. [14,15] observed very low- $N$  lines ( $N \leq 5$ ) of the 5–4 band with a jet-cooled supersonic expansion source. We have managed to identify rotational lines up to  $N = 24$ , which include a number of levels beyond the perturbation.

Four bands, 6–5, 6–6, 6–7, and 6–8 have been rotationally analyzed with the common  $v' = 6$  vibrational level. The lines of the four bands fit well and the residuals suggest that the  $v' = 6$  level of the  $B^2\Sigma^+$  state is free from local perturbations over the observed range up to  $N = 25$ . Five bands (7–6, 7–7, 7–8, 7–9, and 7–10) with the common  $v' = 7$  vibrational level have been measured and combined in the final fit. Rotational levels of both e- and f-parity are affected by perturbations near  $N = 15$  for  $v' = 7$ . The 8–7, 8–8, 8–9, and 8–10 bands were analyzed and  $v' = 8$  is unperturbed for  $N'$  less than 26.

We have obtained a rotational analysis for six bands having a common vibrational level  $v' = 9$  of the  $B^2\Sigma^+$  state. The rotational lines of the 9–7, 9–8, 9–9, 9–10, 9–11, and 9–12 bands were combined in the final fit. The residuals of the lines indicate that the  $v' = 9$  vibrational level of the excited state is affected by interactions with a nearby state for  $N > 23$ . For the 10–8, 10–9, 10–10, 10–11, and 10–12 bands, we find that  $v' = 10$  is strongly affected by perturbations. The interaction is such that both spin components are separated starting from the lowest  $N'$  values. A portion of the spectrum of the 10–10 band near the band origin is provided in Fig. 2 in which some low- $N$  lines have been marked. Lines with  $N' > 14$  of both parity components are heavily affected and had to be deweighted in

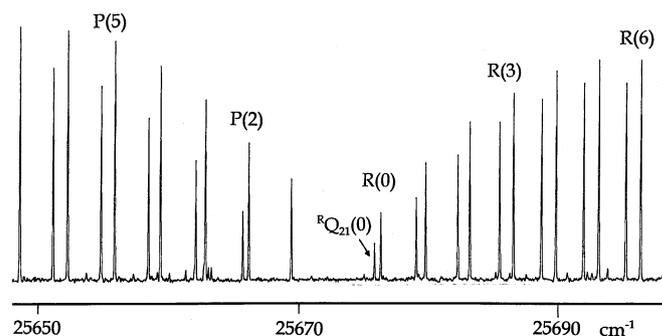


Fig. 2. An expanded portion of the 10–10 band of the  $B^2\Sigma^+ - X^2\Sigma^+$  system of CN showing some low- $N$  lines near the band origin.

Table 4  
Observed perturbations in the  $B^2\Sigma^+$  state of CN

$v, B^2\Sigma^+$	Description	Perturbing state
0	Local perturbations at $N = 7$ in $F_1$ and at $N = 15$ in both $F_1$ and $F_2$ components	$A^2\Pi, v = 10$ [23,46]
5	$F_1$ levels perturbed at $N = 11$ , several lines near perturbation deweighted and $F_2$ levels not perturbed	$A^2\Pi, v = 17$ [45]
7	Both $F_1$ and $F_2$ levels perturbed for $N \geq 15$	$A^2\Pi, v = 20, v = 21$ [23]
9	Both $F_1$ and $F_2$ levels perturbed for $N \geq 23$	$a^4\Pi ?$ [24]
10	Both $F_1$ and $F_2$ levels perturbed for $N \geq 14$	$A^2\Pi, v = 24$ [19]
12	Both $F_1$ and $F_2$ levels perturbed for $N \geq 13$	$A^2\Pi, v = 27; a^4\Pi ?$ [19,24]
13	Local perturbation at $N = 9$ in $F_1$ with $F_2$ levels not perturbed	?
14	Both $F_1$ and $F_2$ levels perturbed for $N \geq 6$	$A^2\Pi, v = 30$ [19,47]
16	Data from Ref. [36]	$A^2\Pi, v = 33$ [47]
17	Data from Ref. [24]	$A^2\Pi, v = 34; a^4\Pi ?$ [24,47]
18	Data from Ref. [36]	$A^2\Pi, v = 36$ [47]
19	Data from Ref. [36]	$A^2\Pi, v = 38$ [47]

the final fit. A number of higher order effective parameters are required for  $v' = 10$  in order to obtain a fit with a reasonable standard deviation. Several of the higher order effective constants such as  $H_v, L_v, \gamma_v, \gamma_{Dv}, \gamma_{Hv}$ , and  $\gamma_{Lv}$  have been determined and they have unusually large magnitudes compared to the other vibrational levels, which is a result of interactions in the excited state.

Of the other higher vibrational levels of the  $B^2\Sigma^+$  state,  $v' = 11, 13$ , and  $15$  are not perturbed over the observed  $N$  range of 23, 20, and 15, respectively, while the  $v' = 12$  and  $14$  levels are perturbed for  $N' > 13$  and  $6$ , respectively, for both spin components. As mentioned earlier, the bands with  $v' > 15$  were not observed in our high-resolution FT spectra. The measurements of bands with  $v' > 15$  were therefore taken from other publications [24,37] and combined with our data to obtain a more complete set of spectroscopic constants. In a relatively recent study of CN, Ito et al. [48] have studied the perturbations observed in the  $v = 14, 16, 17, 18$ , and  $19$  vibrational levels of the  $B^2\Sigma^+$  state and have suggested that  $v = 30, 33, 34, 36$ , and  $38$  vibrational levels, respectively, of the  $A^2\Pi$  state are probably responsible for the perturbations. The lines involving these  $B^2\Sigma^+$  state vibrational levels have relatively large residuals.

The observed perturbations of the different vibrational levels of the  $B^2\Sigma^+$  state are summarized in Table 4, and the likely identities of the perturbing states have also been given based mainly on previous work. We also find one perturbation in the  $X^2\Sigma^+$  state. From our rotational analysis, we conclude that the  $v'' = 11$  vibrational level of the  $X^2\Sigma^+$  state is perturbed near  $N'' = 13$  and this perturbation affects only the  $f$ -parity levels of the lower state. Notice that because of this perturbation additional higher order effective constants such as  $H_v$  and  $\gamma_{Hv}$  are also determined for this vibrational level.

## 5. Conclusion

Emission spectra of the  $B^2\Sigma^+ - X^2\Sigma^+$  transition of CN have been observed using an active nitrogen afterglow source. The rotational structure of a number of bands with  $v = 0-15$  of both the states have been measured and combined with the available microwave and infrared data for

the ground state. The lines measurements for a number of bands with  $v', v'' > 15$  were also taken from the data published by Douglas and Routly [37] and Ito et al. [24] and combined with our data to determine an improved set of spectroscopic constants. Perturbations were noted and suggestions have been made for the possible perturbing states. The  $A^2\Pi - X^2\Sigma^+$  Red System of CN has also been observed and measured [41] with the flowing afterglow source and we are planning a combined A-X and B-X analysis.

## Acknowledgments

We thank M. Dulick and D. Branston of the National Solar Observatory for assistance in obtaining the spectra. The National Solar Observatory is operated by the Association of Universities for Research in Astronomy, Inc., under contract with the National Science Foundation. We thank Thomas Giesen for providing additional pure rotational data for  $v = 2-7$  from the Ph.D. thesis of E. Klisch (and not listed in Ref. [43]), as well as the comments of Holger Mueller. The research described here was supported by funding from the NASA laboratory astrophysics program. Support was also provided by the Natural Sciences and Engineering Research Council of Canada.

## Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect ([www.sciencedirect.com](http://www.sciencedirect.com)) and as part of the Ohio State University Molecular Spectroscopy Archives ([http://msa.lib.ohio-state.edu/jmsa\\_hp.htm](http://msa.lib.ohio-state.edu/jmsa_hp.htm)).

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