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ROTATIONAL ANALYSIS OF THE $B^2\Sigma^+$ - $X^2\Sigma^+$ BANDS OF $^{12}\text{C}^{18}\text{O}^+$

Key words: Rotational analysis, carbon monoxide ion, molecular constants

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Abstract

The emission spectrum of the $B^2\Sigma^+$ - $X^2\Sigma^+$ (First Negative) system of the molecular ion $^{12}\text{C}^{18}\text{O}^+$ have been photographed at a resolution sufficient to observe the spin splitting of the lines with $N > 18$. Four bands, 0-1, 0-3, 1-4 and 2-5, have been rotationally analyzed and the molecular constants of the $B^2\Sigma^+$, $v = 0, 1, 2$ and $X^2\Sigma^+$, $v = 1, 3, 4, 5$ have been obtained.

Introduction

The electronic spectra of the neutral molecule CO and molecular ion CO^+ have been the objective of investigations for a long time (for a summary of the literature trough 1979, see Ref. 1-4). However, because of both these species are of great astrophysical interest, they are retained up to now in the group of the most extensively spectroscopically studied diatomic molecules.

The $B^2\Sigma^+$ - $X^2\Sigma^+$ (First negative) system, which is the objective of our study, is one of the four known emission band system of CO^+ ion arising from transitions between excited states $C^2\Delta_r$, $B^2\Sigma^+$, $A^2\Pi$ and the ground state $X^2\Sigma^+$.

Pesic et al [5] have studied the isotope displacement in the vibrational structure of the $^{12}\text{C}^{18}\text{O}^+$ relative to that of the $^{12}\text{C}^{16}\text{O}^+$ and $^{13}\text{C}^{18}\text{O}^+$ bands. The system was rotationally analyzed in the following isotopomers, viz., $^{12}\text{C}^{16}\text{O}^+$ [6,7,8], $^{12}\text{C}^{18}\text{O}^+$ [9], $^{13}\text{C}^{16}\text{O}^+$ [7,10] and $^{13}\text{C}^{18}\text{O}^+$ [11].

The only observation of the rotational structure of the $^{12}\text{C}^{18}\text{O}^+$ was made by Janic et al [9] but under dispersion used, the spin splitting of the lines has not been observed in any of the recorded bands. Therefore, this observation clearly merited a reinvestigation of the rotational structure of the B - X system. We have photographed the spectrum between 200 and 300 nm at a resolution superior to what was employed before. Based on this, the new rotational analysis has been performed. The results are presented in this paper.

Experimental

The molecular ion $^{12}\text{C}^{18}\text{O}^+$ has been excited in the cathode glow of a discharge tube with water-cooled carbon hollow cathode. A dc voltage of 800 V has been applied between the electrodes of the discharge tube at a current of 250 mA. After several trials, the partial pressure of helium in the range of 700 and 800 Pa and that of oxygen-18 of approximately 133 Pa, have been found to be optimum for producing a strong $^{12}\text{C}^{18}\text{O}^+$ emission. The spectrum was photographed using Ilford HP5 emulsion on a 6.4 m Czerny-Turner spectrograph in the tenth order (disp. 0.012 nm/mm), near blaze wavelength. Overlapping orders of the spectrum have been eliminated with Carl Zeiss order sorter. The exposure time ranged between 2 and 3 hours with a 30 μm spectrograph slit width. Iron atomic lines from an iron-neon hollow-cathode lamp, whose wavelengths were taken from [12], have been used for calibration. The line positions have been determined using a measuring microscope and reduced to vacuum wavenumbers in the usual way. The uncertainty of the measurements is estimated to be $\pm 0.02 \text{ cm}^{-1}$.

Results and Discussion

The bands of the $B-X$ system of CO^+ ion are very net. The present work concern only with four intense bands, 0-1, 0-3, 1-4 and 2-5, having the heads at 229.654, 254.007, 256.671 and 259.516 nm, respectively. Because the bands belong to the $^2\Sigma^+ - ^2\Sigma^+$ transition, one expects the four main branches in each band R_{11ee} , R_{22ff} , P_{11ee} and P_{22ff} , and two weak satellite branches, R_{Q21fe} and P_{Q12ef} , which are usually are not seen on the spectrograms.

As the bands are red-degraded, the heads are formed in R branches. However, since the spin splitting in the present study was detected only for the lines with $N > 18$, the unresolved R_{11ee} and R_{22ff} lines (with low N values) have formed a single head in each band instead theoretically predicted two. Since commercial $^{18}\text{O}_2$ used in experiments contained traces of $^{16}\text{O}_2$, the band heads of $^{12}\text{C}^{16}\text{O}^+$ have appeared on the spectrograms too. However, due to large isotope displacements of the $^{12}\text{C}^{18}\text{O}^+$ bands relative to $^{12}\text{C}^{16}\text{O}$ bands [5], the overlapping spectral regions of both isotopomers are restricted to small part of the bands. This facilitates assignment of the lines using data from [6] and [7] for $^{12}\text{C}^{16}\text{O}^+$ and known isotope relations [13] with the displacement constant $\rho = [\mu(^{12}\text{C}^{16}\text{O}^+)/\mu(^{12}\text{C}^{18}\text{O}^+)]^{1/2} = 0.97584$.

About 300 lines for all four bands have been measured and assigned up to N around 37. They are given in Table 1. The assignment has been checked using the standard procedure [14]. Direct fitting of the measured lines has been performed by computer program employing the least-squares method. A standard $^2\Sigma$ energy level expressions, Hund's case (b), have been used in the fit of the upper and lower rotational levels:

$$F(N) = B_v N(N+1) - D_v [N(N+1)]^2 \quad \left. \begin{array}{l} +1/2 \gamma N \quad e \text{ level} \\ -1/2 \gamma (N+1) \quad f \text{ level} \end{array} \right\}$$

where $N = J-1/2$ and $N = J+1/2$ for e and f (F_1 and F_2) levels, respectively.

Resulting set of molecular constants for each band obtained in the final calculation, in which the lines with $\nu_{\text{obs}} - \nu_{\text{cal}}$ larger than three standard deviations have been excluded, are collected in Table 2 together with those reported in [7].

TABLE 1

Wavenumbers and Rotational Assignment for the $B^2\Sigma^+ - X^2\Sigma^+$ Bands of $^{12}C^{18}O^+$

N	0 - 1 band			0 - 3 band		
	R _{11ee}	R _{22ff}	P _{11ee}	P _{22ff}	R _{11ee}	R _{22ff}
0	43511.07(-03)		43504.00(-03)		39334.00(-13)	39326.98(-09)
1	514.17(-02)		500.00(-05)		337.14(-15)	323.21(-03)
2	516.97(00)		495.61(-01)		340.08(-11)	319.06(-02)
3	519.39(-05)		490.97(-01)		342.65(-21)	314.67(01)
4	521.58(-01)		485.95(-07)		345.16(-11)	310.23(-20)
5	523.37(-06)		480.67(-08)		347.52(08)	305.19(04)
6	524.91(-04)		457.09(-08)		349.20(-15)	300.11(08)
7	526.15(-01)				350.89(14)	294.72(05)
8	526.98(-08)				352.30(-15)	
9	527.56(-01)		463.01(-06)		353.59(-04)	289.15(09)
10	527.89(-01)		456.53(-02)		354.46(-10)	283.29(08)
11			449.64(-08)		355.20(-05)	277.22(10)
12	527.65(16)				355.80(11)	270.85(07)
13	526.96(17)		435.04(-08)			264.29(08)
14	525.76(-02)		427.18(-17)			257.42(02)
15	524.39(-06)		419.17(-10)			250.33(-02)
16	522.72(-08)		410.74(-13)			243.04(-02)
17	520.75(-08)					235.47(-07)
18	518.67(14)		393.05(-05)		353.32(08)	227.71(-07)
19	515.87(-05)		383.70(-07)		352.07(08)	219.75(-05)
20	512.93(-04)		374.08(-04)		350.48(-02)	211.38(-20)
21	509.74(04)		364.08(-04)		348.78(00)	203.07(-06)
						202.86(-16)

N	1 - 4 band				2 - 5 band			
	$R_{11\infty}$	R_{22ff}	$P_{11\infty}$	P_{22ff}	$R_{11\infty}$	R_{22ff}	$P_{11\infty}$	P_{22ff}
0	38928.77(02)							
1	391.83(-01)	38921.77(-01)						38495.14(08)
2	934.69(01)		917.90(00)					491.26(04)
3	937.24(-01)		913.77(00)					487.09(-01)
4	939.52(-03)		909.39(01)					482.68(-01)
5	941.55(-05)		904.76(03)					478.04(03)
6	943.29(-09)		899.90(08)					473.04(00)
7	944.79(-11)		894.62(-02)					467.77(-02)
8	946.07(-08)							462.23(-03)
9	947.25(12)		883.49(-03)					456.41(-03)
10			877.48(-08)					450.34(00)
11			871.28(-06)					443.86(-10)
12	948.65(15)							437.26(-03)
13			858.00(-12)					430.29(-05)

(continued)

Table 1. Continued

N	1 - 4 band				2 - 5 band			
	R_{11ee}	R_{22ff}	P_{11ee}	P_{22ff}	R_{11ee}	R_{22ff}	P_{11ee}	P_{22ff}
14			851.02(-10)		518.02(-08)		423.08(-03)	
15			843.83(-02)		517.02(-09)		415.54(-05)	
16			836.22(-10)		515.73(-10)		407.74(-05)	
17			828.44(-09)		514.18(-08)		399.62(-07)	
18	38943.85(-10)	38943.73(-09)	820.41(-06)		512.28(-12)		391.24(-08)	
19	942.22(-02)	942.04(-06)	812.11(-04)		510.12(-13)		382.57(-08)	
20	940.41(016)	939.96(-14)	803.59(03)		507.70(-11)		373.61(-08)	
21	937.94(-04)	937.76(-07)			504.99(-08)		364.34(-11)	
22	935.39(-05)	935.15(-13)	38785.74(16)	38785.60(15)	501.99(-04)		354.78(-14)	
23	932.62(01)	932.37(-08)	776.33(14)	776.03(-03)	38498.78(08)	38498.51(-03)	38344.98(02)	
24	929.58(08)	929.22(-11)	766.58(05)		495.14(07)	494.88(-02)	38335.38(41)	334.84(00)
25	926.21(10)	925.93(-01)	756.61(01)	756.41(-04)	491.26(11)	490.95(-02)	324.43(01)	
26	922.54(10)	922.24(-02)	746.37(-02)	746.09(-15)	487.09(17)	486.74(00)	313.88(02)	313.62(-09)
27	38918.58(-10)	38918.31(02)	735.88(-04)	735.87(11)	482.68(29)	482.12(-08)	38280.00(03)	302.76(06)
28			725.10(-07)	724.89(-12)	477.61(05)	477.26(-11)		
29			714.07(-08)	713.86(-12)	472.52(09)	472.11(-11)		
30					467.01(03)	466.69(-09)		
31			691.44(17)	691.09(00)	461.29(05)	460.95(-07)		
32			679.50(09)	679.29(07)	38455.18(00)	38454.86(-10)		
33			667.47(19)	667.17(09)				
34			654.91(05)	654.61(-05)				
35			642.06(-10)	641.76(-19)				
36								
37			38615.94(-03)	38615.63(-06)				

TABLE 2

Molecular Constants (in cm^{-1}) of the $B^2\Sigma^+$ and $X^2\Sigma^+$ States of $^{12}\text{C}^{18}\text{O}^+$

Band $\nu' - \nu''$	Origin T_0	B $B^2\Sigma$	B $X^2\Sigma$	$D \times 10^6$ $B^2\Sigma$	$D \times 10^6$ $X^2\Sigma$	B $B^2\Sigma$	γ $X^2\Sigma$
0-1	43507.68(2) 43510.23	1.7002(6) 1.6964	1.8563(1) 1.8523	8.21(2) 7.0	6.27(3) 6.5	0.0155	0.0087 * **
0-3	39330.72(2) 39330.66	1.7002(8) 1.6964	1.8238(7) 1.8178	7.30(7) 7.0	9.84(6) 6.5	0.0150	0.0087 * **
1-4	38925.39(2) 38925.32	1.6757(7) 1.6744	1.8062(6) 1.8013	10.72(6) 7.0	8.57(5) 6.5	0.0165	0.0087 * **
2-5	38498.62(3) 38498.66	1.6395(5) 1.6484	1.7805 1.7843	4.98(40) 7.0	3.07(5) 6.0	0.0160	0.008 * **

The numbers in parentheses represent one standard deviation in the last digits of the constants. * This work; ** Ref.[9].

The centrifugal distortion constants $D_{\nu'}$ and $D_{\nu''}$ are order of 10^{-6} but have to be mentioned that the obtained values are somewhat limited because of lack of data for high N values. The spin splitting constant γ for ground state (last column in Table 2) are that determined from microwave spectrum of the $^{12}\text{C}^{18}\text{O}^+$ ion [14] and it was kept fixed in calculation. The γ constants for the upper states have been evaluated and they are given in Table 2. Because we have not been able to detect the difference in intensity of the resolved R and P lines, the sign of the constant has been accepted that given in [7] and [8].

As seen from Table 2, there is a good agreement in positions of the band origins obtained in this work and those given by Janic et al [9] with exception for 0-1 band, but there are significant discrepancies in the values of rotational constants $B_{\nu'}$ and $B_{\nu''}$. This is due to differences between our and Janic's rotational quantum number assignment of the lines and limited accuracy attainable

in earlier work in which moderate dispersion and iron arc lines have been used as reference lines.

For the purpose to verify obtained data, we have recalculated the constants of Misra et al [7] and Haridas et al [8] for the $^{12}\text{C}^{16}\text{O}^+$ ion using the known isotopic relations. The constants calculated in this manner show a good agreement with our results. Therefore, one can conclude that the present analysis, including first observation of spin splitting in rotational structure of the analyzed bands, has led to improved set of molecular constants of the $^{12}\text{C}^{18}\text{O}^+$ for the B and X electronic states involved in transition.

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