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ROTATIONAL ANALYSIS OF THE $\tilde{B}$ — $\tilde{X}$ BANDS OF ISOTOPIC CO^+

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Abstract: Emission spectrum of the $\tilde{B}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ (2180 — 2800 Å) transition of $^{13}C\,^{18}O^+$ molecules excited in a hollow — cathode discharge tube has been photographed on a 6.4 m Ebert spectrograph. From (0,1), (2,4), (0,3), (1,4), (2,5) and (3,6) bands the rotational constants Be, De and r_e were derived.

1. Introduction

In the electronic spectrum of the CO^+ molecule four electronic systems commonly known as First negative ($\tilde{B}^2\Sigma^+ - \tilde{X}^2\Sigma^+$), Baldet-Johnson ($\tilde{B}^2\Sigma^+ - \tilde{A}^2\Pi_i$), Comet-tail ($\tilde{A}^2\Pi_i - \tilde{X}^2\Sigma^+$) and Marchand-D Incan-Janin ($^2\Delta_r - \tilde{A}^2\Pi_i$) were identified[1,2]. The analysis of the First negative system of the ordinary molecule has been subject to comprehensive study by a few authors[3-6]. Janjić[7] examined this system of isotopic $^{12}C\,^{18}O$ and gave the vibrational and rotational analysis.

The paper[8] is concerned with the vibrational analysis of the B—X system of $^{13}C^{18}O$, $^{13}C^{16}O^+$ and $^{12}C^{18}O^+$ molecules.

In the present paper we have succeded in photographing, at high resolution, the first negative system of $^{13}C^{16}O^+$ and $^{13}C^{18}O^+$ molecules, together with rotational analysis of bands, leading to the determination of molecular parameters.

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2. *Experimental procedures*

The emission spectrum has been obtained in a hollow-cathode discharge tube which was essentially the same as that described in the papers[9,10]. In brief, a hollow-cathode discharge tube with iron electrode, after degassing, was initially filled with $^{13}C^{16}O$ (70% of ^{13}C) under a pressure of approximately 5 mm Hg, the electric current was passed through it for a few hours. After a small quantity of ^{13}C carbon was deposited on the electrodes, the tube was evacuated and oxygen containing 93% of the isotope $^{18}O_2$ was introduced. The cathode glow was obtained by using DC current of 80 mA. The spectrum was photographed in first order of a 6.4 m plane grating Ebert spectrograph (Disp. 1.2 Å/mm). Exposures of 45 minutes were found sufficient to obtain well developed hands on Kodak I-O plates. Iron lines from a DC arc were superposed as the reference spectrum. The plates were measured on an IZA-2 Abbe comparator. The comparator readings were fed to a CDC-3600 computer, and the wave numbers of the rotational lines were obtained using a computer program. We have estimated the errors of the lines to 0.05 cm^{-1}.

3. *Results and discussion*

The system consists of well developed sequences of the bands degraded to the red. The structure of the isotopic bands, which are the same as that of ordinary molecule, may be seen in Fig. 1, where (2,4) band of $^{13}C^{18}O^+$ molecule is shown. From the analysis of $^{12}C^{16}O^+$ and $^{12}C^{18}O^+$ bands of this system[5-7] it is konwn that the bands belong to $^2\Sigma^+ - {}^2\Sigma^+$ transition, although doublet

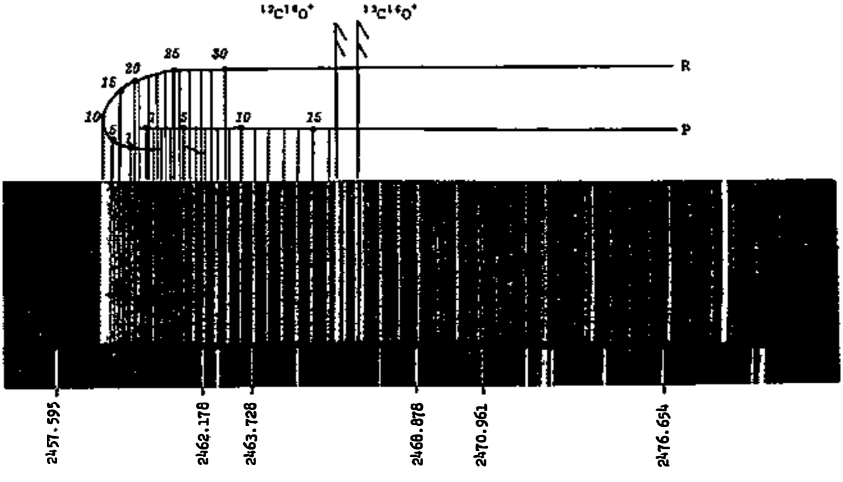

Fig. 1. Rotational structure of (2,4) band of $^{13}C^{18}O^+$.

structure is not resolved in our spectrograms. The bands are degraded to the red and thus the R-branches from the heads. From a close study of the spectrum it was found that the only bands (0,1), (2,4), (0,3), (1,4), (2,5) and (3,6) with the head of the bands at $\lambda\lambda$ — 2293.90, 2458.98, 2530.63, 2556.46, 2584.23 and 2613.84 Å respectively were relatively free from overlapping and therefore suitable for rotational analysis. The wave number and assignment of the rotational lines are given in Table 1.* In all bands the lines are sharp and well defined.

TABLE 1.

WAVE NUMBERS AND ROTATIONAL LINE ASSIGNMENTS OF THE BANDS OF $^{13}C^{18}O^+$ [cm^{-1}].

N	Band (0,1)		Band (2,4)		Band (0,3)	
	R(*N*)	P(*N*)	R(*N*)	P(*N*)	R(*N*)	P(*N*)
1	43563.98	43554.79	40642.16	40632.06	3983.80	....
2	567.12	550.75	644.86*	628.1t	487.04*	39472.08
3	568.60*	546.27	646.07	488.14	488.14	468.48
4	570.92	541.59	640.21	619.14	490.92	464.17
5	752.48	526.54	649.27*	614.31	493.11	459.14
6	574.88	531.16	651.18	608.89	495.25	455.30
7	576.77	....	....	603.25	496.99	450.42
8	....	....	....	597.40	498.67	445.34
9	....	....	....	593.94	499.90	440.04
10	43581.65 H	....	40655.02 H	589.25	....	434.42
11	....	....	....	582.75	....	428.66
12	....	....	....	575.94	....	422.74
13	....	....	....	568.73	....	416.49
14	....	....	....	561.26	39503.38 H	410.13
15	43573.48	....	40649.27	553.44	—........	403.36
16	573.13	....	647.25	545.44	....	396.56
17	569.94	....	644.86	536.89	39501.19	389.37
18	568.60	....	643.40	....	500.14	382.01
19	565.46	....	640.40	....	499.02	374.37
20	561.52	....	637.53	....	497.62	366.54
21	558.71	....	634.03	....	496.02	358.32
22	556.90	....	630.37	....	494.19	....
23	552.69	....	626.31	....	492.05	....
24	548.27	....	621.83	....	489.72	....
25	543.80	....	617.25	....	487.04	....
26	538.79	....	612.26	....	480.67	....
27	533.48	....	606.98	....	477.36	....
28	....	....	601.40	....	475.64	....
29	....	....	595.04	....	469.92	....
30	....	....	590.96	....	....	....
31	....	....	584.35	....	....	....

H — Head of the Band
*— overlapped

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* The line structre in one of the bands (2,4) is shown in Fig. 1.

TABLE 1. (cont.)

N	Band (1,4)		Band (2,5)		Band (3,6)	
	R(N)	P(N)	R(N)	P(N)	R(N)	P(N)
1	....	39079.84	38668.24	38661.63	38234.64*	38445.42
2	....	076.04	671.20	658.07	237.27*	221.66
3	....	071.88	673.84	654.04	239.34*	217.71
4	....	967.75	676.29	649.87	241.23*	213.39
5	....	063.42	678.31	645.34	242.92*	208.69
6	....	058.71	680.14*	640.62	244.24*	203.99
7	....	053.78	681.66*	635.55	245.37*	198.73
8	....	048.59	682.77*	630.26	....	193.29
9	....	043.16	683.79*	624.57	....	187.66
10	....	037.43	....	618.83	38246.31 H	181.66
11	....	031.51	....	612.61	....	175.47
12	39104.69 H	025.36	....	606.17	....	168.91
13	....	018.61	38684.82 H	599.54	38245.37	162.77
14	....	012.11	....	592.54	244.24	154.81
15	....	005.21	....	585.45	242.92	147.38
16	39103.01	38997.83	....	577.89	241.23	131.68
17	101.85	990.42	38683.79	570.32	239.34	123.46
18	100.43	982.71	682.77	562.33	237.27	114.86
19	098.85	974.81	681.66	554.04	234.64	107.60
20	096.89	966.51	680.14	545.79	321.82	096.61
21	094.60	957.98	....	537.10	228.62	087.49
22	092.20	....	....	528.19	....	0.7744
23	089.52	....	....	....	....	....
24	086.55	....	....	....	....	....
25	083.20	....	....	....	....	....
26	....	....	38664.73	....	....	....
27	....	....	661.63*	....	....	....
28	....	....	658.07*	....	....	....
29	....	....	654.04*	....	....	....
30	....	....	649.87*	....	....	....

H — Head of the Band
* — overlapped

4. Rotational analysis

The rotational energy levels of a $^2\Sigma^+$ state when spin splitting is neglected are given by the relation

$$F_{1,2}(N) = B_v N(N+1) - D_v N^2 (N+1)^2, \tag{1}$$

where B_v and D_v are rotational constants, and N is quantum number of the total angular momentum. The wave number of P and R branches, which are only present in unresolved $^2\Sigma^+ - {}^2\Sigma^+$ transition, will be given by

$$P(N) = v_0 + F'(N-1) - F''(N), \tag{2}$$

$$R(N) = v_0 + F'(N+1) - F''(N), \tag{3}$$

where v_0 is the band origin.

The rotational formulas derived from these general relations are as follows

$$P(N)\colon\ v_p = v_0 + (B' - B'')N^2 - (B' + B'')N + (D'' - D')N^4 + 2(D' - + D'')N^3, \tag{4}$$

$$R(N)\colon\ v_R = v_0 + (B' - B'')N^2 + (3B' - B'')N + 2B' + (D'' - D')N^4 + + 2(D'' - 3D')N^3. \tag{5}$$

Analysis of the measured bands was in a high degreed facilitated by using the computed spectra. The approximate values of rotational constants were estimated using the relations for isotopic molecules and the constants of the $^{12}C^{16}O^+$. From these values and band origin, calculated from the vibrational isotope effect, the computed rotational spectra have been calculated. These calculated spectra have been used for the pieced out the P and R branches and rotational quantum number assignment for the measured lines.

TABLE 2.

The Rotational Constants of $^{13}C^{18}O^+$ [cm^{-1}]

$B^2\Sigma_+$	$X^2\Sigma^+$
$B_0 = 1.6118$	$B_1 = 1.7925$
$B_1 = 1{,}5725$	$B_3 = 1.6897$
$B_2 = 1.5335$	$B_4 = 1.6778$
$B_3 = 1.5217$	$B_5 = 1.6617$
$B_e = 1.6313$	$B_6 = 1.5979$
$\alpha_e = 0.0368$	$B_e = 1{,}7454$
$D_e = 6.4\ 10^{-6}$	$\alpha_e = 0.0234$
$r_e = 1.17_0$ Å	$D_e = 4.7\ 10^{-6}$
	$r_e = 1.13_1$ Å

One of the branches and numbering have been determined by use of numerical method of obtaining molecular constants. The rotational constants B_v, for the upper and lower state and bands origin v_0, were calculated by solving medium — size systems of linear equations by the least squares method, using a computer program. The D_e constants have been calculated by using the relation $D_e = 4\,B_e^3/\omega_e^2$ ($B'_e = 1.6313$; $\omega'_e = 1645.7$; $B''_e = 1.7454$; $\omega''_e = 2110.2$). The values of these constants are summarized in Table 2.

5. Vibrational analysis

The origin of the bands have been calculated together with rotational constants. The values obtained are collected in Table 3. The vibrational equilibrium constants, calculated from these values of v_0 are: $v_e = 45874.86$; $\omega'_e = 1656.23$; $\omega''_e = 2113.97$; $\omega'_e x'_e = 26.58$; $\omega''_e x''_e = 14.72$ cm^{-1}.

TABLE 3.

The Origins of the $^{13}C^{18}O^+$ bands

v'	v''					
	1	2	3	4	5	6
0	43558.51		39477.93			
1				39084.43		
2				40634.65	38668.24	
3						38227.33

These values for the origins of the $^{13}C^{18}O^+$ bands agree well with that calculated using isotopic relations$^{11)}$ and corresponding values$^{12)}$ of $^{12}C^{16}O^+$.

In conclusion it should be mentioned that the experimental results reported here give the unambiguous evidence that CO^+ is the emitter of the observed bands. The success and practical importance of the method for computation a synthetic spectrum of isotopic species depends on the availability of the corresponding data. In this case of CO^+ molecule, where the data for investigated electronic system of the ordinary molecule are known, the method was wery useful.

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ROTACIONA ANALIZA $\tilde{B} - \tilde{X}$ TRAKA IZOTOPSKOG CO$^+$

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Sadržaj

Emisioni spectar $\tilde{B}^2\Sigma^+ - \tilde{X}^2\Sigma^+$ (2180 — 2800 Å) prelaza $^{13}C^{18}O^+$ molekula ekscitiran u cevi za pražnjenje sa šupljom katodom, snimljen je na 6.4 m Ebert difrakcionom spektrografu. Iz analize (0,1), (2,4), (0,3), (1,4), (2,5) i (3,6) traka dobijene su rotacione konstante Be, De i r_e.