

THE  $E^1\Pi-A^1\Pi$  SYSTEM BANDS IN  $^{13}\text{C}^{16}\text{O}$  AND  $^{12}\text{C}^{18}\text{O}$  MOLECULES\*

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The emission bands of the  $E^1\Pi-A^1\Pi$  transition in isotopic CO molecules have been obtained at high resolution and analysed. The bands 0-1, 0-2 and 0-1 were obtained for  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}$  molecules respectively. A complete rotational analysis of these bands was performed and the fundamental constants of the  $E^1\Pi$  state, i. e. the rotational, vibrational and  $A$ -doubling constants were calculated. The values of the band origins for all the bands of both molecules have been computed as well. The distance between the  $v = 0$  level in the  $E^1\Pi$  state and the  $v = 0$  level in the  $B^1\Sigma^+$  state has been especially accurately calculated for all isotopic molecules analysed so far.

## 1. Introduction

The  $E^1\Pi$  electronic state in the CO molecule can be investigated in two ways. The absorption transition between the  $E^1\Pi$  and  $X^1\Sigma^+$  states can be used for the first way [13, 16] and the  $E^1\Pi-A^1\Pi$  transition in the emission spectrum for the second one [7, 8]. Since both kinds of the transitions were analysed in high resolution some constants for the  $E^1\Pi$  state, i. e. — rotational,  $A$ -doubling constants and vibrational quantum —  $\Delta G_{1/2}$  were found [7, 13, 16]. Besides, a strong interaction has been observed between the  $E^1\Pi$  and some nearby Rydberg states. All previously reported results referred only to the ordinary, i. e.  $^{12}\text{C}^{16}\text{O}$  molecule, excluding fragmentary analysis of the  $E^1\Pi-X^1\Sigma^+$  transition in the  $^{13}\text{C}^{16}\text{O}$  molecule, reported by Tilford, Vanderslice and Wilkinson [16]. The information available about the  $E^1\Pi$  state was insufficient for certain calculations and analysis of the CO molecule [3, 11, 17]. Moreover, because of the interaction of this state with the nearby electronic states, the isotopic relations for the molecular constants did not hold exactly [4]. Therefore, to get further information about the  $E^1\Pi$  state, the authors attempted to obtain the  $E^1\Pi-A^1\Pi$  transition in isotopic molecules. The 0-1 and 0-2 bands were analysed in the  $^{13}\text{C}^{16}\text{O}$  molecule and the 0-1 band — in  $^{12}\text{C}^{18}\text{O}$ .

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## 2. Experimental procedure

The bands of the  $E^1\Pi-A^1\Pi$  transition have been obtained in the emission spectrum from Geissler type lamps filled with the appropriate isotopic species. The spectrum of the  $^{13}\text{C}^{16}\text{O}$  molecule has been found in a lamp filled with gaseous carbon dioxide enriched in 95%  $^{13}\text{C}$ . The spectrum of the  $^{12}\text{C}^{18}\text{O}$  molecule was obtained by using a lamp with

TABLE I  
0-1 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

| $J$ | $R_c$     | $R_d$      | $P_c$       | $P_d$      |
|-----|-----------|------------|-------------|------------|
| 2   |           | 26738.785* |             | 26720.116* |
| 3   | 26744.887 | 744.656    | 26718.513** | 718.513**  |
| 4   | 751.579   | 751.223    | 717.708**   | 717.607**  |
| 5   | 759.015   | 758.556    | 717.708**   | 717.607**  |
| 6   | 767.181   | 766.571    | 718.389**   | 718.066**  |
| 7   | 776.074*  | 775.303*   | 719.787     | 719.334    |
| 8   | 785.749   | 784.790    | 721.927     | 721.342*   |
| 9   | 796.118   | 794.943    | 724.805     | 724.043    |
| 10  | 807.252   | 805.833    | 728.436     | 727.483    |
| 11  | 819.100   | 817.439    | 732.745*    | 731.637    |
| 12  | 831.697   | 829.859    | 737.893     | 736.610    |
| 13  | 845.052   | 26843.965  | 743.775     | 26743.291* |
| 14  | 859.225   | 855.873    | 750.455     | 747.770    |
| 15  | 26874.596 | 870.502    | 26758.355   | 754.912    |
| 16  | 887.840   | 885.704*   | 764.091     | 762.694**  |
| 17  | 904.834*  | 901.627    | 773.591     | 771.154    |

TABLE II  
0-2 band lines of  $^{13}\text{C}^{16}\text{O}$  (in  $\text{cm}^{-1}$ )

| $J$ | $R_c$       | $R_d$      | $P_c$       | $P_d$       |
|-----|-------------|------------|-------------|-------------|
| 3   | 25329.648** | 25329.449* | 25303.374** | 25303.374** |
| 4   | 336.506     | 336.176*   | 302.678**   | 302.638**   |
| 5   | 344.138     | 343.697    | 302.790**   | 302.638**   |
| 6   | 352.529     | 351.986*   | 303.719     | 303.374**   |
| 7   | 361.713     | 361.091*   | 305.399     | 305.069     |
| 8   | 371.675*    | 370.523    | 307.819     | 307.082     |
| 9   | 382.384     | 381.099    | 311.077     | 310.235     |
| 10  | 393.863     | 392.378    | 315.053     | 314.047     |
| 11  | 406.119     | 404.404    | 319.855     | 318.604     |
| 12  | 419.182     | 417.173    | 325.388*    | 323.940     |
| 13  | 433.015     | 430.703    | 331.739     | 329.998     |
| 14  | 447.625     | 444.985    | 338.878     | 336.857     |
| 15  | 462.989     | 460.006    | 346.768     | 344.396     |
| 16  | 479.158     | 475.796    | 355.449     | 352.789     |
| 17  | 496.084     | 492.319*   | 364.909*    | 361.918**   |

TABLE III

0-1 band lines of  $^{12}\text{C}^{18}\text{O}$  (in  $\text{cm}^{-1}$ )

| $J$ | $R_c$       | $R_d$       | $P_c$      | $P_d$      |
|-----|-------------|-------------|------------|------------|
| 2   | 26740.773** | 26740.654** | 26722.068* | 26722.068* |
| 3   | 746.717**   | 746.511*    | 720.527**  | 720.527**  |
| 4   | 753.388**   | 753.080     | 719.666**  | 719.666**  |
| 5   | 760.854**   | 760.335*    | 719.666**  | 719.485**  |
| 6   | 768.968*    | 768.359     | 720.322*   | 719.996    |
| 7   | 777.811     | 777.055     | 721.746    | 721.316*   |
| 8   | 787.432     | 786.469     | 723.876    | 723.292    |
| 9   | 797.772     | 796.615     | 726.762    | 725.988    |
| 10  | 808.854     | 807.503     | 730.349*   | 729.474*   |
| 11  | 820.695*    | 819.223     | 734.725    | 733.769    |
| 12  | 833.262     | 26829.505   | 739.816*   | 26736.617  |
| 13  | 846.735     | 843.657*    | 745.846    | 743.373    |
| 14  | 26861.667*  | 857.479     | 26753.388  | 749.766    |
| 15  | 873.980*    | 871.910     | 758.116    | 756.798    |
| 16  | 889.867     | 887.074*    | 766.584    | 764.544    |

graphite electrodes, filled with oxygen enriched to about 40%  $^{18}\text{O}$ . Pressure in the lamps was about 6 Tr. The bands were obtained at 0.54 Å/mm–0.78 Å/mm linear reciprocal dispersion, using Th standard lines as a comparison spectrum. Other conditions of excitation, expositions and the method of measurement have been described earlier [7].

Calculated values of the wave numbers of the lines for the 0-1 and 0-2 bands in the  $^{13}\text{C}^{16}\text{O}$  molecule and 0-1 band in  $^{12}\text{C}^{18}\text{O}$  are listed in Tables I-III.

### 3. Results and discussion

The calculation of the constants and analysis of the results were performed by two methods: in the first method only the lines of the  $E^1\Pi-A^1\Pi$  transition were used, and in the second one line combinations of the  $E^1\Pi-A^1\Pi$  and  $B^1\Sigma^+-A^1\Pi$  transitions were used.

The rotational constants of the  $E^1\Pi$  state in the direct method of calculation were found by combining the  $R_c$  branch with the  $P_c$  one and the  $R_d$  branch with the  $P_d$  one. From the combinations found from both the 0-1 and 0-2 bands in the  $^{13}\text{C}^{16}\text{O}$  molecule and from the 0-1 band in  $^{12}\text{C}^{18}\text{O}$ , the rotational term differences  $\Delta_2 F'_c(J)$  and  $\Delta_2 F'_d(J)$  were determined. Using them, the following rotational constants were computed on the basis of the least-squares method:  
for  $^{13}\text{C}^{16}\text{O}$  molecule:

$$B_{0c} = (1.8775_7 \pm 0.0002_2) \text{ cm}^{-1},$$

$$B_{0d} = (1.8664_0 \pm 0.0002_3) \text{ cm}^{-1},$$

$$D_{0c} = (5.3_6 \pm 0.5_0) \times 10^{-6} \text{ cm}^{-1},$$

$$D_{0d} = (4.6_2 \pm 0.5_3) \times 10^{-6} \text{ cm}^{-1},$$

and for  $^{12}\text{C}^{18}\text{O}$ :

$$\begin{aligned} B_{0c} &= (1.8697 \pm 0.0009) \text{ cm}^{-1}, \\ B_{0d} &= (1.8593_3 \pm 0.0003_3) \text{ cm}^{-1}, \\ D_{0c} &= (3.5 \pm 2.2) \times 10^{-6} \text{ cm}^{-1}, \\ D_{0d} &= (5.4 \pm 0.9) \times 10^{-6} \text{ cm}^{-1}. \end{aligned}$$

The band origins for the  $E^1\Pi-A^1\Pi$  transition were calculated by a direct combination of the wave numbers of lines. In the 0-1 bands, perturbed band origins were found from  $R(J-1)+P(J)$  sums, calculated for low rotational quantum numbers. The unperturbed 0-2 band origin was found from  $g_{PR}(J)$  and  $g_{\overline{PR}}(J)$  relations [2]. The following constants were computed:

for  $^{13}\text{C}^{16}\text{O}$ :

$$\begin{aligned} \sigma_{01} &= (26725.431 \pm 0.015) \text{ cm}^{-1}, \\ \sigma_{02} &= (25309.923 \pm 0.014) \text{ cm}^{-1}, \end{aligned}$$

and for  $^{12}\text{C}^{18}\text{O}$ :

$$\sigma_{01} = (26727.328 \pm 0.018) \text{ cm}^{-1}.$$

In the other method of calculating constants, the appropriate lines of the  $E-A$  and  $B-A$  transitions were used according to Jenkins and McKellar formulas [1]. Thus the perturbations in the  $A^1\Pi$  state were eliminated from the lines of the  $E-A$  transition and the calculation of the constants could provide values of higher accuracy. This greater accuracy is possible to obtain from the properties of the same method of combination and also from the possibility of using 0-1 bands, the strongest bands of the  $E-A$  transition. Therefore, besides the bands of the  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}$  molecules, obtained presently, also the band 0-1 of the  $^{12}\text{C}^{16}\text{O}$  molecule, reported before [7], was recalculated in this way. The bands 0-1 of the  $B-A$  transition, necessary for the above combinations, were rephotographed for this purpose using Th standard lines as a calibration spectrum. In the  $c$ -component of  $A$ -doubling, the combinations of  $R_c$  and  $P_c$  branches of the  $E-A$  transition with  $R$  and  $P$  branches of the  $B-A$  transition may be written as follows:

$$\left. \begin{aligned} R_c^{EA}(J-1) - R^{BA}(J-1) \\ P_c^{EA}(J+1) - P^{BA}(J+1) \end{aligned} \right\} = C_{00}^{EB} - B_0^E + (B_{0c}^E - B_0^B)J(J+1) + \dots \quad (1)$$

In the  $d$ -component, the lines of the  $R_d$  and  $P_d$  branches of the  $E-A$  transition were used in combination with the  $Q$  branch of the  $B-A$  transition. After a small transformation one can find the following relations:

$$\left. \begin{aligned} R_d^{EA}(J-1) - Q^{BA}(J-1) - 2B_0^B J \\ P_d^{EA}(J+1) - Q^{BA}(J+1) + 2B_0^B(J+1) \end{aligned} \right\} = C_{00}^{EB} - B_0^E + (B_{0d}^E - B_0^B)J(J+1) \dots \quad (2)$$

The values of  $B_0$  constants for the  $B$  state, necessary on the left side of equation (2), were taken according to [9, 14, 15]. On the right side of both equations, all terms with  $D_0$

constants were omitted, as being negligible for  $J \leq 20$ . The  $C_{00}^{EB} - B_0^E$  differences (equal  $\sigma_{00}^{EB}$ ), as well as  $B_{0x}^E - B_0^B$  differences of the rotational constants, where  $C_{00}^{EB}$  is a distance of the  $v = 0$  vibrational levels in the  $E$  and  $B$  states, and  $B_0^E$  is a real value of the rotational constant  $B_0$  of the  $E$  state, were calculated on the basis of the relations (1) and (2) by means of the least-squares method. Here the  $B_{0d}^E$  constant has been adopted as this real

TABLE IV  
Constants for  $E^1\Pi$  state relative to  $B^1\Sigma^+$  state (in  $\text{cm}^{-1}$ ) calculated from Jenkins and McKellar method

| Constant molecule  | $^{12}\text{C}^{16}\text{O}$ | $^{13}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}$ |
|--------------------|------------------------------|------------------------------|------------------------------|
| $C_{00(c)}^{EB}$   | $6015.742 \pm 0.008$         | $6014.81_6 \pm 0.01_1$       | $6014.67_2 \pm 0.04_1$       |
| $C_{00(d)}^{EB}$   | $6015.78_1 \pm 0.02_6$       | $6014.85_0 \pm 0.01_3$       | $6014.68_5 \pm 0.01_7$       |
| $C_{00}^{EB^a}$    | $6015.75_1 \pm 0.02_9$       | $6014.83_2 \pm 0.01_7$       | $6014.681 \pm 0.006$         |
| $B_{0c}^E - B_0^B$ | $0.01648_4 \pm 0.00004_4$    | $0.01538 \pm 0.00007$        | $0.0151_1 \pm 0.0003_0$      |
| $B_{0d}^E - B_0^B$ | $0.0044_8 \pm 0.0001_5$      | $0.00427 \pm 0.00008$        | $0.0043_0 \pm 0.0001_1$      |

<sup>a</sup> the value calculated from the averaged and weighted  $C_{00(c)}^{EB}$  and  $C_{00(d)}^{EB}$  constants.

TABLE V  
Rotational and  $A$ -doubling constants of the  $E^1\Pi$  state in isotopic CO molecules (in  $\text{cm}^{-1}$ )

| Constant molecule | $^{12}\text{C}^{16}\text{O}$   | $^{13}\text{C}^{16}\text{O}$   | $^{12}\text{C}^{18}\text{O}$   |
|-------------------|--|--|--|
| $B_{0c}$          | $1.96454_3 \pm 0.00005_1^{**}$<br>$1.9645^a$<br>$1.9640_7 \pm 0.0002_3^b$<br>$1.9643^c$                      | $1.8775_7 \pm 0.0002_2^*$<br>$1.8779 \pm 0.0002^{**}$<br>$1.877_3^a$   | $1.8697 \pm 0.0009^*$<br>$1.8704_4 \pm 0.0003_3^{**}$  |
| $B_{0d}$          | $1.9525_4 \pm 0.0001_6^{**}$<br>$1.9521_7 \pm 0.0002_3^b$  | $1.8664_0 \pm 0.0002_3^*$<br>$1.8668 \pm 0.0002^{**}$  | $1.8593_3 \pm 0.0003_3^*$<br>$1.8596_3 \pm 0.0001_7^{**}$  |
| $D_{0c}$          | $6.50 \times 10^{-6}^a$<br>$(4.9 \pm 0.6) \times 10^{-6}^b$<br>$6.5 \times 10^{-6}^c$                        | $(5.3_6 \pm 0.5_0) \times 10^{-6}^{**}$  | $(3.5 \pm 2.2) \times 10^{-6}^{**}$  |
| $D_{0d}$          | $(5.1_0 \pm 0.4_9) \times 10^{-6}^b$   | $(4.6_2 \pm 0.5_3) \times 10^{-6}^{**}$  | $(5.4 \pm 0.9) \times 10^{-6}^{**}$  |
| $q$               | $(12.0_0 \pm 0.1_6) \times 10^{-3}^{**}$<br>$(11.9_0 \pm 0.3_3) \times 10^{-3}^b$<br>$15.0 \times 10^{-3}^d$ | $(11.1_7 \pm 0.3_2) \times 10^{-3}^*$<br>$(11.2_6 \pm 0.1_0) \times 10^{-3}^{**}$<br>$13.8 \times 10^{-3}^d$ | $(10.4 \pm 1.0) \times 10^{-3}^{**}$<br>$10.8_1 \pm 0.3_2) \times 10^{-3}^{**}$<br>$13.6 \times 10^{-3}^d$ |

\* present results, calculated from  $\Delta_2 F'(J)$  differences

\*\* present results, calculated from Jenkins and McKellar method

<sup>a</sup> Tilford, Vanderslice and Wilkinson results [15]

<sup>b</sup> Keça, Knot-Wiśniewska and Rytel results [7]

<sup>c</sup> Ogawa and Ogawa results [12]

<sup>d</sup> calculated from "pure precession" situation [2, 7].



(unperturbed) constant in the  $v = 0$  level of the  $E$  state, because the interactions between the  $E$  and other states modifying its rotational constants are predominant in the  $c$ -component [2, 7]. The results of the computations are presented in Table IV, where the  $C_{00}^{EB}$  values, calculated from  $c$  and  $d$   $A$ -components are given separately.

The rotational  $B_{0x}^E$  constants and the  $A$ -doubling constants  $q$  for the  $E$  state were found from the previously calculated differences  $B_{0x}^E - B_0^B$  irrespectively of  $\Delta_2 F'(J)$  method. Table V lists present and earlier results.

The vibrational constants of the  $E^1\Pi$  state have been computed with the help of the already mentioned  $C_{00}^{EB}$  values in  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{16}\text{O}$  molecules and the vibrational quantum  $\Delta G_{1/2}$  — reported by Ogawa and Ogawa [13]. On the basis of the above data one can obtain the following relations:

for  $^{12}\text{C}^{16}\text{O}$

$$C_{00}^{EB} = \sigma_e^{EB} + \frac{1}{2} \omega_e^E - \frac{1}{4} \omega_e x_e^E - \frac{1}{2} \omega_e^B + \frac{1}{4} \omega_e x_e^B + \dots \quad (3a)$$

$$\Delta G_{1/2} = \omega_e^E - 2\omega_e x_e^E + \dots \quad (3b)$$

and for  $^{13}\text{C}^{16}\text{O}$

$$C_{00i}^{EB} = \sigma_{ei}^{EB} + \frac{1}{2} \varrho \omega_e^E - \frac{1}{4} \varrho^2 \omega_e x_e^E - \frac{1}{2} \varrho \omega_e^B + \frac{1}{4} \varrho^2 \omega_e x_e^B + \dots, \quad (3c)$$

where  $\varrho = (\mu/\mu_i)^{1/2}$  and  $\mu, \mu_i$  are the reduced masses of the  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  molecules, respectively. Equations (3) for  $\omega_e^E$  and  $\omega_e x_e^E$  constants were solved under two different assumptions. The fact that the  $E$  and  $B$  states are Rydberg states [6, 12] and their electronic isotope effects should be similar and small, was taken into account in one of them. Therefore, it was assumed that  $\sigma_e^{EB}$  and  $\sigma_{ei}^{EB}$  values are equal in  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  molecules. Using the vibrational constants of the  $B$  state [15] equations (3) were solved yielding the following constant values:

$$\sigma_e^{EB} = 5971.95 \text{ cm}^{-1},$$

$$\omega_e^E = 2246.85 \text{ cm}^{-1},$$

$$\omega_e x_e^E = 46.53 \text{ cm}^{-1}.$$

Taking into consideration the constant values of the more thoroughly investigated Rydberg states, the same set of equations (3) can be solved under another assumption. Namely, the vibrational constants of the  $B^1\Sigma^+$ ,  $C^1\Sigma^+$  and  $C^3\Pi$  states have quite similar values [5, 10, 15]; and they are as follows:

$$\omega_e \approx 2200 - 2250 \text{ cm}^{-1} \text{ and } \omega_e x_e \approx 36.0 \text{ cm}^{-1}.$$

Therefore, it was assumed that in the  $E$  state, like in the previously mentioned ones the constants have similar values. Under the assumption that  $\omega_e x_e^E = 36.0 \text{ cm}^{-1}$ , the solution of equation (3b) gives  $\omega_e^E = 2225.8 \text{ cm}^{-1}$ .

From attempts to fit thus obtained constants with a complete set of equations (3) and from the analysis of the correlation of all the constants it was possible to notice that the value of the difference  $\sigma_e^{EB}(^{12}\text{C}^{16}\text{O}) - \sigma_{ei}^{EB}(^{13}\text{C}^{16}\text{O})$  should not be greater than  $0.120 \text{ cm}^{-1}$ .

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