

# THE ANALYSIS OF THE FOURTH POSITIVE SYSTEM OF $^{12}\text{C}^{16}\text{O}$ MOLECULE IN THE NEAR ULTRAVIOLET REGION

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The emission bands of the fourth positive system of CO molecules were photographed in the region 2100 — 2700 Å. A partial rotational analysis of each of the bands has been made in order to perform an exact vibrational analysis. Band origins and vibrational quanta are obtained as a result of this analysis.

## 1. Introduction

The fourth positive system of CO molecules corresponding the  $A^1\Pi - X^1\Sigma^+$  transition is well known. The first vibrational analysis and vibrational constants were given by Estey [1]. The rotational analysis of the easily accesible bands was made by Gerö and Schmid [2-4]. Tilford has extended the number of the observed vibrational levels to the  $v = 23$  in the  $A^1\Pi$  state by observing the  $0-v'$  progression in absorption [5]. Recently Yardley [6] measured the higher vibrational quanta in  $X^1\Sigma^+$  state with high accuracy.

In this work, 35 emission bands of this system were observed in the ultraviolet region 2100 — 2700 Å. The rotational analysis of these bands have been made for small values of the rotational quantum numbers so that the vibrational assignement would be certain. In this way, the recent vibrational analysis has been completed specially for the perturbed and blended bands.

## 2. Experimental

All of the bands were photographed as emission bands by a discharge in a water-cooled Geisslers tube filled with  $^{12}\text{C}^{16}\text{O}$  of 0.5 mm Hg pressure. The spectrum was photographed with a PGS-2 grating spectrograph (VEB C. Zeiss, Jena) in the ninth order with a dispersion of about 0.5 Å/mm on ORWO UV-1 type plates. The iron [7] and the copper [8] lines from the hollow cathode type lamp were used as standards.

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### 3. Results

In the region examined there are other intensive systems, and their presence makes rotational analysis difficult, specially for the weak and perturbed bands. Because of this, the data from other papers [2-5, 9, 10] were used by the present authors. The rotational assignments were made for the  $P$ ,  $Q$  and  $R$  branches in each band for low values of the rotational quantum number  $J$ . The values of  $B_v$  and  $B_{v'}$  were estimated from the combination differences  $\Delta_2 F'(J)$  and  $\Delta_2 F''(J)$ .

The band origins have been calculated by interpolating the  $P$  and  $R$  branches and extrapolating the  $Q$  branch. The comparison of values obtained from both methods permits us to assume that the errors for the unperturbed band origins are less than  $0.1 \text{ cm}^{-1}$ . For origins of the perturbed bands, the error may be larger. The band origins are listed in Table I.

The wave-lengths of the heads can be found in hitherto existing monographical literature [11-13]. Those wave-lengths are given on the basis of some earlier works in which the vibrational analysis was made of the plates obtained in small dispersion. Some of them were not maintained in the later works. In the present work, using more accurately determined band origins and adequate vibrational quanta, one could in doubtful cases decide about the occurrence of these bands in emission. In this way, the bands (9,22), (4,18), (11,23), (7,20), (6,19), (5,18), (4,17), (12,19), (16,25) and (13,21) were not confirmed. The bands (12,23) and (15,25) were not observed, but their presence is possible, nevertheless this region is overlapped by the strong bands of the  $5B$ -system. In addition the bands (10,22) and (13,23) were observed for the first time, and the band (11,21) was observed although the work of Gerö [3] and the monographie [11] do not refer to it.

Using the formula of Jenkins and Mc Kellar [14] with the least-squares method, the vibrational quanta between the respective levels were found. If the same difference in vibrational energy levels corresponds to some of the bands, suitable differences in the wave numbers were averaged. The statistical weights were assumed according to the exactitude of the wave numbers.

The vibrational levels perturbed in rotational states with lower values of  $J(v' = 4, 6, 11)$  were omitted, and for that reason the double vibrational quanta were calculated using the Jenkins and Mc Kellar formulae between following and previous levels. When there are no bands with a common vibrational level, the Jenkins and Mc Kellar method was "diagonally" applied. This application is instanced for the bands (5,13) and (3,12) for the levels  $v' = 3$  and  $v' = 5$ . The considered differences between the corresponding wave numbers of the branches are

$$G'(5) - G'(6) - (B'_5 - B'_3)J(J+1) = \begin{cases} X_{12,13}(J-1) + R_{5,13}(J-1) - R_{3,12}(J-1) \\ X_{12,13}(J) + Q_{5,13}(J) - Q_{3,12}(J) \\ X_{12,13}(J+1) + P_{5,13}(J+1) - P_{3,12}(J+1) \end{cases},$$

where  $X_{12,13}$  are the corresponding differences of wave numbers for branches with a common vibrational level, for example (4,12) and (4,13).

TABLE I

The band origins of the IV-th positive system (in  $\text{cm}^{-1}$ ); the values in the brackets correspond to the averaged band origins)

$\nu''$ $\nu'$	12	13	14	15	16	17	18	19	20	21	22	23	24
3	45101.87 (45102.02)												
4	46479.95	44649.83	42845.17										
5		45991.89 (45992.06)	44187.29 (44187.33)	42408.25 (42408.28)	40654.47 (40654.57)								
6			45494.84	43715.82	41962.23	40233.63							
7				44990.75 (44990.81)	43237.19 (43237.10)	41508.62 (41508.72)	39805.60 (39805.59)						
8					44476.99 (44476.99)	42748.56 (42748.61)	41045.51 (41045.48)	39367.55 (39367.49)					
9						43954.50 (43954.50)	42251.45 (42251.37)	40573.44 (40573.38)	38920.57 (38920.46)	37292.65 (37292.53)			
10								41744.64 (41744.66)	40091.75 (40091.74)	38463.81 (38463.82)	36860.84 (36860.78)		
11									41229.55	39601.63	37998.70		
12											39102.66 (39102.77)		
13												38593.92	37040.44

The intercepted vibrational quanta are listed in Tables II and III with respect to the values given previously [4–6]. Also, the values  $\Delta B$  are shown as the by-product of the calculation of the vibrational quanta.

TABLE II

The data for  $X^1\Sigma^+$  state (in  $\text{cm}^{-1}$ )

$v''$	$\Delta G''$		$B''_{v_1} - B''_{v_2}$	
	After Yardley [6]	This work	After Gerö [4]	This work
12	1830.24	$1830.15 \pm 0.04$	0.0173	$0.0170 \pm 0.0004$
13	1804.64	$1804.57 \pm 0.02$	0.0179	$0.0177 \pm 0.0002$
14	1779.14	$1779.05 \pm 0.06$	0.0179	$0.0177 \pm 0.0007$
15	1753.71	$1753.71 \pm 0.02$	0.0165	$0.0175 \pm 0.0003$
16	1728.38	$1728.38 \pm 0.03$	0.0178	$0.0174 \pm 0.0003$
17	1703.13	$1703.12 \pm 0.01$	0.0166	$0.0175 \pm 0.0002$
18	1677.99	$1678.01 \pm 0.03$	0.0180	$0.0176 \pm 0.0004$
19	1652.92	$1652.87 \pm 0.02$	0.0178	$0.0173 \pm 0.0003$
20	1627.93	$1627.96 \pm 0.06$	0.0171	$0.0176 \pm 0.0007$
21	1603.03	$1602.96 \pm 0.06$	0.0171	$0.0185 \pm 0.0008$
22	—	—	—	—
23	—	—	0.0174	$0.0164 \pm 0.0011$
24	—	—	—	—

TABLE III

The data for  $A^1\Pi$  state (in  $\text{cm}^{-1}$ )

$v'$	$\Delta G'$		$B'_{v_1} - B'_{v_2}$	
	After Tilford [5]	This work	After Tilford [5]	This work
3	2720.64	$2720.28 \pm 0.09$	0.0469	$0.0479 \pm 0.0010$
5	2582.72	$2582.53 \pm 0.03$	0.0481	$0.0483 \pm 0.0003$
7	1239.90	$1239.89 \pm 0.03$	0.0245	$0.0243 \pm 0.0005$
8	1205.58	$1205.89 \pm 0.02$	0.0245	$0.0238 \pm 0.0002$
9	1171.33	$1171.28 \pm 0.05$	0.0253	$0.0250 \pm 0.0006$
10	2241.85	$2241.99 \pm 0.05$	0.0495	$0.0519 \pm 0.0008$
12	—	—	—	—

The accuracy of the vibrational quanta received from the Jenkins and Mc Kellar method is one order higher, than that of the band origins. Therefore, it seems, that the compensating procedure of the band origins was purposeful. To this effect, the mean value of the wave number of the 7 — 17 transition was derived from all the observed and unperturbed band origins by considering the obtained vibrational quanta for both electronic states (the choice of this transition is gratuitous but 7 — 17 transition was chosen taking into account its central place in our band group). On the basis of this mean

value of this transition and with the help of the reverse proceeding, the mean band origins were calculated and listed in Table I.

In addition, a detailed vibrational analysis, like that of the fourth positive system, has been recently undertaken in isotopic molecules of the carbon monoxide.

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