

Rotation-Vibration Spectra of Diatomic and Simple Polyatomic Molecules with Long Absorbing Paths

XI. The Spectrum of Carbon Dioxide (CO₂) below 1.25 μ *

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The spectrum of CO₂ in the photographic infrared has been studied with absorbing paths up to 5500 m. Thirteen absorption bands were found of which eleven have been analyzed in detail. One of these is due to C¹⁸O₂. From the band origins of the C¹²O₂ bands improved values for some of the anharmonic constants of the molecule have been derived.

The study of the rotational structure of the photographic infrared CO₂ bands has yielded considerably improved values for the rotational constants. The new values are $B_{000}=0.3902_0$ cm⁻¹, $\alpha_1=+0.00109$, $\alpha_2=-0.00073$, $\alpha_3=+0.00307$ cm⁻¹. From these the following equilibrium values of rotational constant, moment of inertia, and internuclear distance are obtained:

$$B_e=0.3915_5 \text{ cm}^{-1}, \quad I_e=71.46_3 \times 10^{-40} \text{ gm cm}^2, \quad r_e=1.1600_5 \times 10^{-8} \text{ cm}.$$

By taking account of the effect of Fermi resonance, excellent agreement of the observed $B_{[v]}$ values with those calculated from the α_i and B_e is obtained.

The l -type doubling in the states 01'0, 11'3, and 03'3 has been determined. The agreement of the splitting constants q with those obtained from theory is satisfactory.

A. INTRODUCTION

THE infrared spectrum of CO₂ has been studied exhaustively by a large number of investigators. However, most of this work has been restricted to the fundamentals and low overtone and combination bands. Until recently very little had been done on the photographic infrared spectrum of CO₂ other than the observation of three CO₂ bands at 8689, 7883, and 7820 Å in the spectrum of the planet Venus by Adams and Dunham,¹ and the observation of the first of these in the laboratory at high pressure by Adel and Slipher.² Just as for N₂O (paper VI of this series³), very long absorbing paths are needed in order to obtain the photographic infrared spectrum of CO₂.

The present investigation was initially undertaken mainly with a view to comparing laboratory and planetary spectra under as nearly similar conditions as possible. This aspect of the problem has been discussed to some extent in a previous paper.⁴

In the present work the main object has been the detailed analysis of all the observed photographic infrared CO₂ bands and the derivation from them of new improved rotational constants of the molecule. In the case of CO₂, unlike that of N₂O, the moment of inertia is sufficient to determine the geometrical parameters, namely, the one internuclear distance $r(\text{C}-\text{O})$. An

approximate value for $r_0(\text{C}-\text{O})$, the effective internuclear distance in the lowest vibrational level, has been known for many years. A value for $r_e(\text{C}-\text{O})$, the equilibrium internuclear distance, was derived by one of us⁵ from the infrared data known in 1944. It is now known that the older infrared data are subject to slight systematic errors due to insufficient standards available at the time. In the present paper we have re-evaluated all the data published since 1944 and have compared the rotational constants of CO₂ derived from them with those newly obtained from the photographic spectra which we believe to be somewhat more accurate.

B. EXPERIMENTAL

The absorption tube was the 22-m tube described in paper I of this series.⁶ By means of a White mirror system up to 250 traversals through this tube were obtained corresponding to a path length of 5500 m. This long path length was obtainable only in the region below 8800 Å. In the extreme photographic region at 12 000 Å on account of the lower plate sensitivity only 24 traversals could be used corresponding to a path length of 530 m. Pressure broadening in CO₂ at 1 atm is quite appreciable. Therefore for most measurements, spectra taken at pressures of $\frac{1}{3}$ atm were used. Only for the weakest bands was it found profitable to use higher pressures of up to 2 atm. The very faint head at 7158.6 Å was detectable only at 10 atm pressure.

The spectra below 8800 Å were taken in the second order, those above 8800 Å in the first order of the Yerkes 21-ft grating spectrograph (dispersion 1.25 and 2.5 Å/mm, respectively). Second-, third-, and fourth-order Fe

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¹ W. S. Adams and T. Dunham, *Publ. Astron. Soc. Pacific* **44**, 243 (1932).

² A. Adel and V. M. Slipher, *Phys. Rev.* **46**, 240 (1934).

³ G. Herzberg and L. Herzberg, *J. Chem. Phys.* **18**, 1551 (1950).

⁴ G. Herzberg, in G. P. Kuiper's *The Atmospheres of the Earth and Planets* (University of Chicago Press, Chicago, 1949), first edition, p. 346; (1952), second edition, p. 406. See also a preliminary note on the photographic infrared spectrum by G. Herzberg and H. Verleger, *Phys. Rev.* **48**, 706 (1935).

⁵ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

⁶ H. J. Bernstein and G. Herzberg, *J. Chem. Phys.* **16**, 30 (1948).

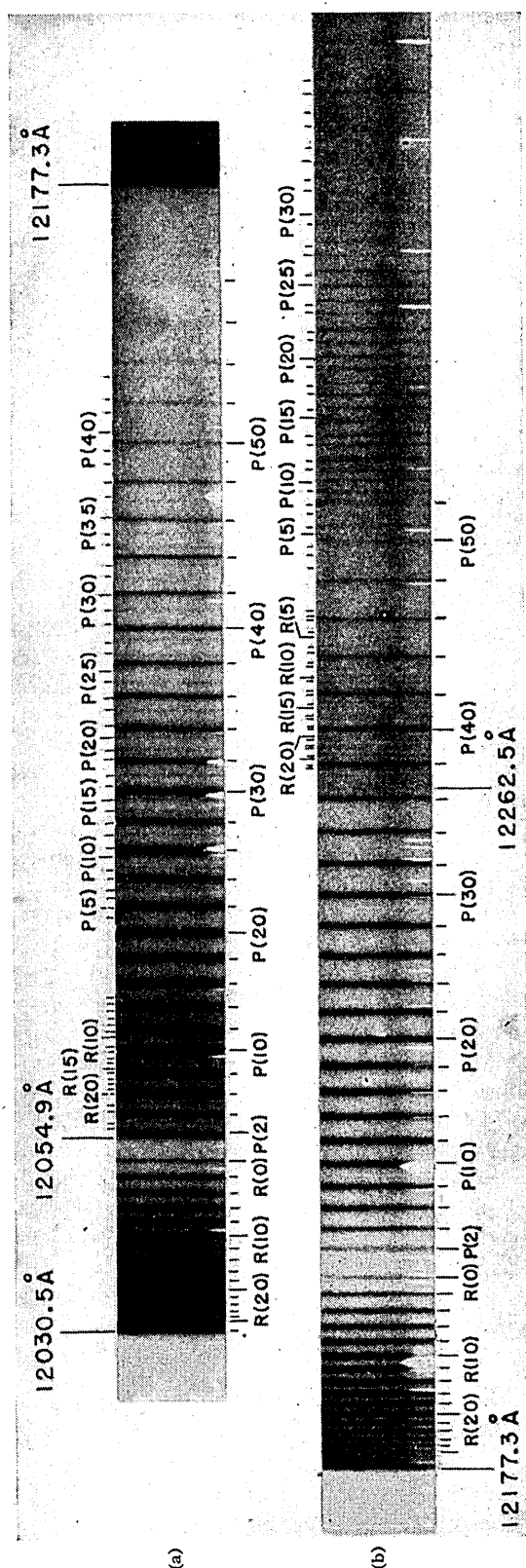


Fig. 1. CO₂ bands near 12 000 Å obtained with an absorbing path of 530 m at 1 atmos (1st order, 21-ft grating). (a) The bands $\nu_1 + 3\nu_2$ and $\nu_1 + \nu_2 + 3\nu_3 - \nu_2$. (b) Bands $\nu_1 + 3\nu_2 + 3\nu_3$ and $\nu_1 + \nu_2 + 3\nu_3 - \nu_2$. The staggering in the "hot" bands above each strip. Lines of main bands are marked below, those of "hot" bands above each strip. The staggering in the "hot" bands is exaggerated in the leading lines.

lines were used as standards. From comparison of independent measurements of one and the same band on different plates, it is estimated that the relative positions of unblended lines of medium or higher intensity have been obtained to an accuracy of $\pm 0.02 \text{ cm}^{-1}$. In the extreme photographic region, above 12 200 Å, where the intensity of the continuous background is inadequate, the accuracy may be appreciably less. In the whole region, because of the possibility of a very slight shift between absorption and comparison spectrum, the absolute accuracy is not as high as the relative accuracy within each band, and is probably of the order $\pm 0.08 \text{ cm}^{-1}$.

C. OBSERVED SPECTRUM

The number of photographic infrared bands found for CO₂ is much smaller than that found for N₂O with the same absorbing path. The observed CO₂ bands are listed in Table I. Two earlier spectrograms of the three Venus bands at 7820, 7883, and 8689 Å have been previously reproduced.⁴ The same applies to the band at 10 488 Å which is the strongest of a group of three bands. This group had actually been observed by one of us⁷ in the spectrum of Venus before it was found in the laboratory. In Fig. 1 the two very strong bands at 12 030.5 and 12 177.3 Å and the weaker bands accompanying them are reproduced.

In Table II the wave numbers of the individual lines of all the observed photographic bands are given, with the exception of the bands at 8735.9₅ and 7158.6 Å for which only the heads were observed at high pressure. There are faint indications of "hot" bands (see below) belonging to the bands near 10 500 Å, but they were too weak to be measured. At the extreme end of the photographic region a band due to C¹³O₂ was found. The wave numbers of the lines of this band are given in Table III.

TABLE I. Band heads (λ_h, ν_h), band origins (ν_0), and assignments of CO₂ bands observed in the photographic infrared.

λ_h (air) (Å)	ν_h (vac) (cm ⁻¹)	Estimated intensity	ν_0 (vac) (cm ⁻¹)	Assignment
12 334.2	8 105.3	2	8 089.0 ₆	$2\nu_2 + 3\nu_3$ (C ¹³ O ₂)
12 262.5	8 152.7	8	8 135.95	$3\nu_2 + 3\nu_3 - \nu_2$
12 177.3	8 209.7 ₅	100	8 192.62	$2\nu_2 + 3\nu_3$
12 054.9 ₃	8 293.0 ₉	8	8 276.83	$\nu_1 + \nu_2 + 3\nu_3 - \nu_2$
12 030.4 ₉	8 309.9 ₄	100	8 294.01	$\nu_1 + 3\nu_3$
10 626.7 ₆	9 407.6 ₉	4	9 389.02	$4\nu_2 + 3\nu_3$
10 487.6 ₁	9 532.3 ₃	20	9 517.00	$\nu_1 + 2\nu_2 + 3\nu_3$
10 361.7 ₉	9 648.2 ₀	8	9 631.38	$2\nu_1 + 3\nu_3$
8 688.7 ₉	11 505.9 ₂	1	11 496.43	$5\nu_3$
8 735.9 ₅	11 443.8 ₁	0.05	...	$\nu_2 + 5\nu_3 - \nu_2$
7 882.8 ₃	12 682.3 ₁	0.1	12 672.28	$2\nu_2 + 5\nu_3$
7 820.1 ₁	12 784.0 ₃	0.3	12 774.73	$\nu_1 + 5\nu_3$
7 158.2	13 966.2	0.02	...	$\nu_1 + 2\nu_2 + 5\nu_3$

⁷ G. Herzberg (unpublished): see Astron. J. 52, 147 (1947).

TABLE II. Wave numbers of the lines in the CO₂ bands (ν_{vac} , cm⁻¹).^a

$2\nu_2+3\nu_3$ $\nu_0=8192.62$				$\nu_1+3\nu_2$ $\nu_0=8294.01$				$4\nu_2+3\nu_3$ $\nu_0=9389.02$			
J	R(J)	P(J)		R(J)	P(J)			R(J)	P(J)		
0	8193.39 ₀			8294.77 ₃							
2	94.84 ₇	8191.03 ₁		96.23 ₇	8292.45 ₀			9391.24 ₆	9387.43 ₁		
4	96.25 ₄	89.37 ₇		97.63 ₇	90.78 ₉			92.64 ₂	85.79 ₅		
6	97.58 ₆	87.66 ₅		98.95 ₂	89.05 ₅			94.03 ₇	84.10 ₇		
8	98.85 ₂	85.89 ₄		8300.19 ₆	87.23 ₄			95.32 ₀	82.35 ₁		
10	8200.03 ₀	84.02 ₂		01.34 ₈	85.37 ₃			96.58 ₄	80.50 ₇		
12	01.17 ₀	82.09 ₃		02.44 ₂	83.41 ₉			97.73 ₁	78.61 ₁		
14	02.23 ₅	80.12 ₅		03.44 ₉	81.38 ₁			98.81 ₂	76.67 ₄		
16	03.21 ₄	78.04 ₃		04.38 ₆	79.27 ₅			99.87 ₉	74.65 ₉		
18	04.14 ₀	75.91 ₈		05.25 ₇	77.10 ₁			9400.84 ₀	72.58 ₁		
20	04.99 ₂	73.71 ₀		06.05 ₁	74.83 ₅			01.75 ₆	70.43 ₃		
22	05.76 ₄	71.41 ₅		06.77 ₀	72.51 ₈			02.62 ₂	68.21 ₀		
24	06.47 ₁	69.06 ₄		07.40 ₃	70.09 ₂			03.42 ₈	65.96 ₈		
26	07.09 ₆	66.67 ₁		07.94 ₉	67.62 ₅			04.15 ₁	63.59 ₆		
28	07.66 ₃	64.20 ₄		08.47 ₁	65.06 ₂			04.77 ₁	61.20 ₆		
30	08.14 ₆	61.63 ₅		08.88 ₃	62.43 ₄			05.37 ₇	58.75 ₃		
32	08.59 ₄	59.01 ₀		09.18 ₉ †	59.74 ₂			05.88 ₁	56.23 ₄		
34	08.95 ₄	56.34 ₃		09.46 ₆ †	56.96 ₄			06.37 ₈	53.61 ₅		
36		53.60 ₀			54.10 ₄				50.90 ₀		
38		50.72 ₁			51.17 ₄				48.23 ₇ †		
40		47.83 ₉			48.18 ₉						
42		44.88 ₅			45.09 ₇						
44		41.82 ₆			41.97 ₅						
46		38.73 ₆ *			38.77 ₉						
48		35.59 ₆			35.47 ₀ *						
50					32.11 ₇ †						
52					28.68 ₆ †						
54					25.19 ₃ †						

$2\nu_2+3\nu_3$ $\nu_0=9517.00$				$2\nu_1+3\nu_2$ $\nu_0=9631.38$				$5\nu_2$ $\nu_0=11\ 496.43$			
J	R(J)	P(J)		R(J)	P(J)			R(J)	P(J)		
0	9517.74 ₉			9632.10 ₄ †				11 497.22 ₄ †			
2	19.23 ₆	9515.42 ₂		33.60 ₅ †	9629.80 ₆ †			98.58 ₃	11 494.83 ₀		
4	20.60 ₄	13.76 ₂		35.02 ₂	28.19 ₉			99.87 ₂	93.12 ₆		
6	21.91 ₆	12.02 ₁		36.35 ₄	26.47 ₇			11 501.03 ₃	91.28 ₈		
8	23.15 ₃	10.20 ₆		37.60 ₁	24.63 ₀			02.07 ₂	89.32 ₉		
10	24.29 ₉	08.31 ₁		38.78 ₁	22.76 ₃			02.97 ₈	87.24 ₅		
12	25.37 ₄	06.34 ₉		39.90 ₁	20.83 ₆			03.76 ₈	85.04 ₆		
14	26.37 ₄	04.31 ₃		40.95 ₅	18.83 ₆			04.42 ₆	82.71 ₁		
16	27.27 ₆	02.17 ₃		41.90 ₃	16.75 ₈			04.97 ₇	80.25 ₇		
18	28.12 ₄	9499.97 ₂		42.82 ₁	14.58 ₉			05.40 ₇	77.68 ₈		
20	28.90 ₂	97.69 ₄		43.63 ₂	12.38 ₃			05.69 ₇	74.98 ₈		
22	29.57 ₇	95.33 ₅		44.38 ₃	10.07 ₂				72.17 ₁		
24	30.18 ₃	92.92 ₂		45.08 ₇	07.71 ₇				69.22 ₈		
26	30.71 ₄	90.39 ₇		45.67 ₅	05.29 ₂				66.16 ₆		
28	31.15 ₆	87.79 ₈		46.21 ₉	02.77 ₂				62.98 ₃		
30	31.52 ₄	85.12 ₆		46.69 ₇	00.16 ₉				59.67 ₂		
32	31.82 ₄ †	82.39 ₁		47.09 ₈ †	9597.57 ₆				56.23 ₆		
34		79.57 ₀			94.85 ₈				52.69 ₀		
36		76.66 ₁			92.06 ₀				49.02 ₀		
38		73.69 ₁			89.20 ₉ †				45.21 ₄		
40		70.61 ₃			86.32 ₉ †				41.27 ₆		
42		67.50 ₄							37.25 ₀		
44		64.30 ₇									
46		61.01 ₁									
48		57.62 ₃									
50		54.22 ₆ †									
52		50.67 ₀ †									

$2\nu_2+5\nu_3$ $\nu_0=12\ 672.28$				$\nu_1+5\nu_2$ $\nu_0=12\ 774.73$			
J	R(J)	P(J)		R(J)	P(J)		
0				12 775.86 ₃			
2				76.93 ₅	12 773.08 ₄		
4	12 675.92	12 668.96*		78.19 ₅	71.43 ₀		
6	676.92*			79.31 ₈	69.59 ₆		
8	678.05*	665.17*		80.37 ₀	67.60 ₃		
10	678.87*	663.08		81.23 ₃	65.50 ₉		
12	679.77	661.08*		82.01 ₉	63.29 ₁		
14	680.51	658.71		82.66 ₆	60.96 ₄		
16	681.09	656.28		83.21 ₈	58.47 ₂		
18	681.56	653.80		83.64 ₃	55.87 ₉		
20	681.90	651.17			53.17 ₈		
22		648.38			50.31 ₆		
24					47.33 ₈		
26					44.24 ₁		
28					41.03 ₅		
30					37.94 ₇		
32					34.23 ₅		
34					30.69 ₆		

$3\nu_2+3\nu_3-\nu_2$ $\nu_0=8135.95$				$\nu_1+\nu_2+3\nu_3-\nu_2$ $\nu_0=8276.83$			
J	R(J)	P(J)		R(J)	P(J)		
0							
1	8137.39						
2	38.25	8134.55					
3	38.74*	33.43					
4	39.54	32.70					8273.62
5	40.24	31.87					72.53*
6	40.98	31.03					71.87
7	41.56	30.12		8282.43			70.95
8	42.22	29.10*					70.12*
9	42.81	28.25		83.42*			69.17
10	43.43	27.32		84.20			68.17
11	43.95	26.37		84.75			67.16
12	44.53	25.51		85.40*			66.22
13	44.91*	24.40		85.82			65.09*
14	45.62	23.46		86.36			64.01
15	46.06	22.32		86.79			63.14
16	46.66	21.36		87.29*			62.10
17	47.05	20.31		87.68			61.00
18	47.54	19.24		88.19			59.78*
19	47.85*	18.05		88.58			58.80
20	48.44	17.05		89.07*			57.68
21	48.62	15.85					56.63
22	49.20	14.80					55.38
23	49.43	13.54					54.14*
24		12.45					53.00
25		11.18					51.69
26		10.08					50.50
27	50.72*	08.68					49.17
28	51.14	07.60					47.84
29		06.22					46.39
30	51.67						45.15*
31		03.51					43.96
32	52.19	02.45*					42.68
33		00.87					41.19
34		8099.74					8239.94
35		98.08					38.39
36		97.05					37.06
37		95.30*					35.49*
38		94.18*					34.23
39							32.13*
40		91.33*					31.21
41		89.35					29.50
42							27.71

TABLE III. Wave numbers of the lines in the C¹³O₂ band (ν_{vac} , cm⁻¹).^a

J	$R(J)$	$P(J)$
0	8090.57	
2	91.33*	
4	92.64	
6	94.18*	8084.12
8	95.30*	82.32
10	96.40	80.44
12	97.42	78.41
14	98.55	76.41
16	99.50	74.32
18	8100.35	72.14
20	01.08	69.86
22	01.79	67.54
24	02.45*	65.15
26	02.93	

^a An asterisk indicates blended lines.

tetrads (resonance between $3\nu_1$, $2\nu_1+2\nu_2$, $\nu_1+4\nu_2$, and $6\nu_2$) or higher polyads. Since the diad ($\nu_1, 2\nu_2$) occurs⁸ at 1388.3 and 1285.5 cm⁻¹, and since $\nu_3=2349.3$ cm⁻¹, the two bands near 12 000 Å represent clearly the diad $3\nu_3+(\nu_1, 2\nu_2)$, and the three bands near 10 500 Å represent the triad $3\nu_3+(2\nu_1, \nu_1+2\nu_2, 4\nu_2)$. The three Venus bands have long been known to be due to $5\nu_3$ and $5\nu_3+(\nu_1, 2\nu_2)$. The remaining very faint band at 7158.6 Å agrees very closely with the position predicted by Herman⁹ for the central component of the triad $5\nu_3+(2\nu_1, \nu_1+2\nu_2, 4\nu_2)$ if account is taken of the separation of the band head from the band origin.

The strongest bands are accompanied by much weaker "hot" bands, that is, transitions for which in both the upper and lower state of the main bands the vibration ν_2 is singly excited. The assignments of all the observed bands are given in the last column of Table I.

In Fig. 2 the vibrational energy levels of CO₂ and the observed transitions are represented in a diagram similar to that for N₂O in paper VI of this series.³ The designation of the vibrational levels is in conformity with that used in reference 5 and first suggested by Mulliken.¹⁰ The selection rules are (disregarding $\Delta, \Phi, \dots$

TABLE IV. Vibrational constants of CO₂.

Designation	Present work	Bands used ^a	Taylor, Benedict, and Strong ^b
ω_3^0	2361.80	$\nu_3, 5\nu_3$	2361.80
x_{33}	-12.50		-12.50
x_{23}	-12.42	$5\nu_3, \nu_2+5\nu_3-\nu_2$	-11.58
x_{13}	-19.17	$\nu_1+\nu_3, \nu_1+3\nu_3$	-21.84
$x_{12}+4x_{22}$	+ 0.68	$\nu_1+3\nu_3, \nu_1+\nu_2+3\nu_3-\nu_2$	+ 0.76
x_{11}	- 2.61	$\nu_1+3\nu_3, 2\nu_1+3\nu_3$	- 2.20
$\omega_1^0+2x_{22}-2g_{22}$	1340.92	$\nu_1+\nu_3$	1341.50

^a In the case of polyads only the first member is given although the complete polyad was used in each case.^b Reference 11.^c From Benedict and Plyler (reference 13).⁸ G. Herzberg, reference 5, p. 274.⁹ R. C. Herman, *Astrophys. J.* **107**, 386 (1948).¹⁰ R. S. Mulliken, *J. Phys. Chem.* **41**, 159 (1937).

states)

$$\Sigma_g^+ \leftrightarrow \Sigma_u^+, \quad \Sigma_g^+ \leftrightarrow \Pi_u, \quad \Sigma_u^+ \leftrightarrow \Pi_g, \quad \Pi_u \leftrightarrow \Pi_g.$$

In agreement with these rules no transitions from the ground state (Σ_g^+) to levels with $(\nu_2+\nu_3)$ an even number have been observed; e.g., the band $4\nu_3$ which would be at 9247 cm⁻¹ is definitely absent.

The vibrational levels of a linear triatomic molecule referred to the lowest level and neglecting the effect of Fermi resonance can be represented by

$$G_0(v_1, v_2, v_3) = \omega_1^0 v_1 + \omega_2^0 v_2 + \omega_3^0 v_3 + x_{11} v_1^2 + x_{22} v_2^2 + x_{33} v_3^2 + x_{12} v_1 v_2 + x_{13} v_1 v_3 + x_{23} v_2 v_3 + g_{22} l_2^2 + \dots, \quad (1)$$

where l_2 is the quantum number of the vibrational angular momentum about the symmetry axis ($l_2 = v_2, v_2-2, \dots, 1$ or 0). The presence of the Fermi resonance between ν_1 and $2\nu_2$ in CO₂ has the consequence that the actual levels within each polyad are shifted compared to the values following from (1). These shifts are determined by secular equations of second, third, $\dots$ order into which enter the coefficient α_{122} of the cubic term $q_1 q_2^2$ of the potential function and the vibrational quantum numbers v_1, v_2 , and l_2 . For this reason no explicit formula for all the energy levels can be given. However, the average of the levels of a polyad follows the same formula as is obtained from (1) for this average.

In a recent paper, Taylor, Benedict, and Strong¹¹ have derived from new infrared measurements revised anharmonic constants of CO₂. The vibrational data obtained in the present paper do not allow of an independent determination of all the anharmonic constants, but they do give independent determinations of a few of these constants and certain combinations of them. These are listed in Table IV together with the constants given by Taylor, Benedict, and Strong. We believe that the new values of x_{23}, x_{13} , and x_{11} are improvements on the values obtained from lower overtone and combination bands.

E. ROTATIONAL ANALYSIS

(a) Determination of Rotational Constants

The determination of the rotational constants of CO₂ from the observed photographic infrared bands is straightforward. The combination differences $R(J-1) - P(J+1) = \Delta_2 F''(J)$ of the bands involving the 00⁰ level are given in Table V. The values referring to the best bands $\nu_1+3\nu_3, \nu_1+2\nu_2+3\nu_3, 2\nu_1+3\nu_3$, and $5\nu_3$ agree in a very satisfactory manner, and have been averaged in the last column of Table V. The $\Delta_2 F''(J)$ values obtained from the bands in the region 1.5 to 4.5 μ , measured by Goldberg, Mohler, McMath, and Pierce,¹² Benedict and Plyler,¹³ and Nielsen and Yao¹⁴ show a

¹¹ Taylor, Benedict, and Strong, *J. Chem. Phys.* **20**, 1884 (1952).¹² Goldberg, Mohler, McMath, and Pierce, *Phys. Rev.* **76**, 1848 (1949).¹³ W. S. Benedict and E. K. Plyler, *J. Research Natl. Bur. Standards* **46**, 246 (1951).¹⁴ A. H. Nielsen and Y. T. Yao, *Phys. Rev.* **68**, 173 (1945).

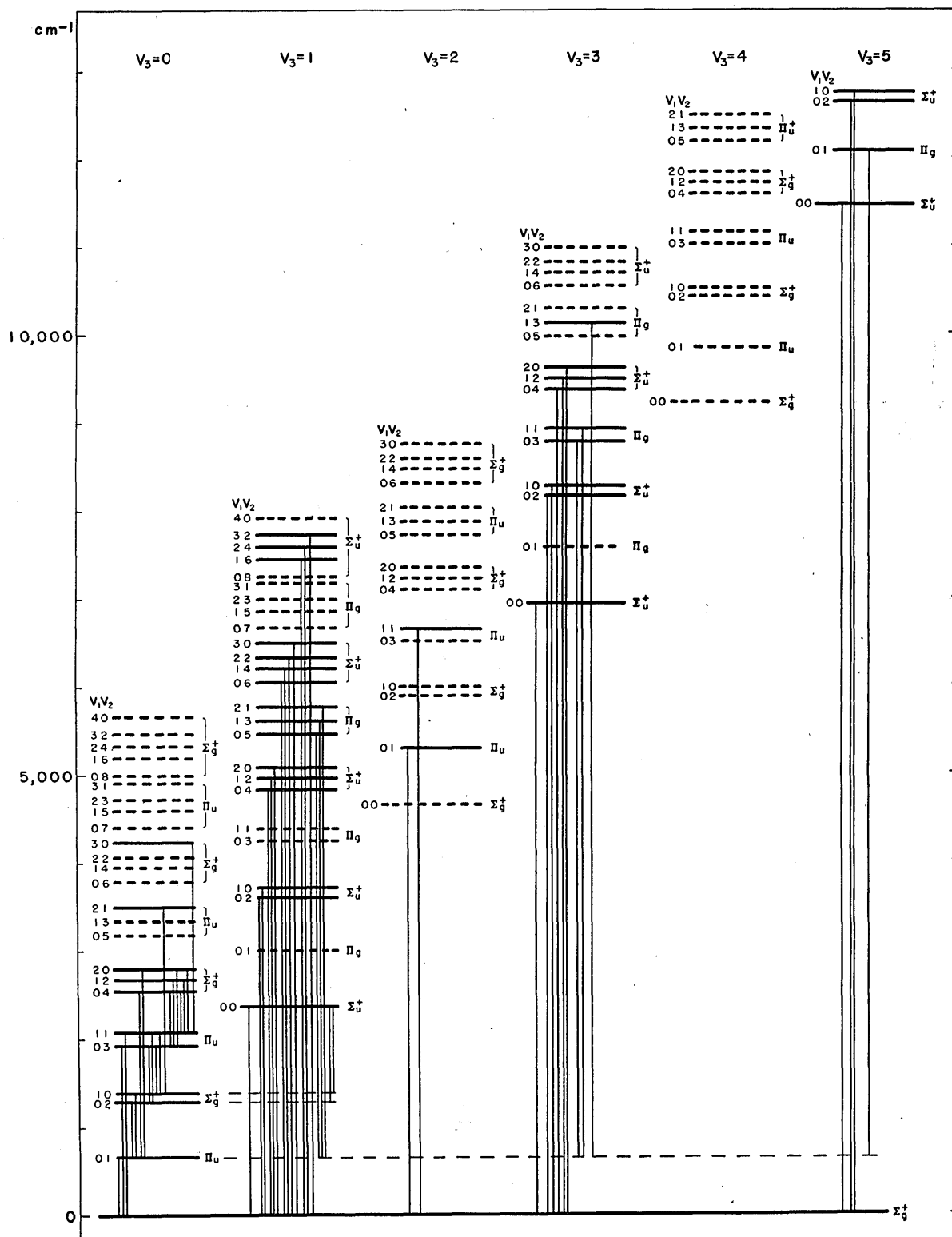


FIG. 2. Vibrational energy levels of the CO₂ molecule. Only Σ^+ and Π levels are shown. Several Δ , Φ , ... levels have been found by Taylor, Benedict, and Strong (see reference 11). They all have $v_3=0$ and are close to the levels 100, 110, 200, 210, and 300 shown in the figure. Observed levels are shown by heavy full lines, predicted levels by broken lines. Observed transitions are indicated by light vertical lines. The bands $\nu_2+2\nu_3$ and $3\nu_2+2\nu_3$ shown in the third column have been found under low dispersion in unpublished work of Herzberg and Kuiper (see reference 4).

TABLE V. Combination differences $\Delta_2 F''(J)$ for the ground state (00⁰) of CO₂.

J	$\Delta_2 F''(J)$ from the individual bands								Mean ^a $\Delta_2 F''(J)$
	$2\nu_2+3\nu_3$	$\nu_1+3\nu_3$	$4\nu_2+3\nu_3$	$\nu_1+2\nu_2+3\nu_3$	$2\nu_1+3\nu_3$	$5\nu_3$	$2\nu_2+5\nu_3$	$\nu_1+5\nu_3$	
1	2.35 ₉	2.32 ₃		2.32 ₇ †	2.29 ₈ †	2.39 ₄ †		2.77 ₉	2.32 ₃
3	5.47 ₀	5.44 ₃	5.45 ₁	5.46 ₈ †	5.40 ₇ †	5.45 ₇		5.50 ₅	5.45 ₃
5	8.58 ₉	8.58 ₂	8.53 ₅	8.58 ₅	8.54 ₅	8.58 ₄		8.59 ₉	8.57 ₄
7	11.69 ₂	11.71 ₈	11.68 ₆	11.71 ₀	11.72 ₄	11.70 ₉	11.75*	11.71 ₅	11.71 ₅
9	14.83 ₀	14.82 ₃	14.81 ₃	14.84 ₂	14.83 ₈	14.82 ₇	14.97*	14.86 ₁	14.83 ₃
11	17.93 ₂	17.92 ₉	17.97 ₃	17.95 ₀	17.94 ₅	17.93 ₂	17.79*	17.94 ₇	17.93 ₉
13	21.04 ₅	21.06 ₁	21.05 ₇	21.06 ₁	21.06 ₆	21.05 ₇	21.06	21.05 ₅	21.06 ₁
15	24.18 ₇	24.17 ₄	24.15 ₃	24.20 ₁	24.19 ₉	24.16 ₉	24.23	24.19 ₄	24.18 ₆
17	27.29 ₆	27.28 ₅	27.29 ₃	27.30 ₄	27.31 ₄	27.28 ₉	27.29	27.33 ₉	27.29 ₈
19	30.43 ₀	30.42 ₂	30.40 ₇	30.43 ₀	30.43 ₈	30.41 ₉	30.39	30.46 ₅	30.42 ₇
21	33.57 ₇	33.53 ₃	33.54 ₆	33.56 ₇	33.56 ₀	33.52 ₆	33.52		33.54 ₇
23	36.70 ₀	36.67 ₃	36.65 ₄	36.65 ₅	36.66 ₆				36.66 ₆
25	39.80 ₀	39.77 ₈	39.83 ₂	39.78 ₆	39.79 ₅				39.78 ₆
27	42.89 ₂	42.88 ₇	42.94 ₅	42.91 ₆	42.90 ₃				42.90 ₂
29	46.02 ₈	46.03 ₇	46.01 ₃	46.03 ₀	46.05 ₀				46.03 ₉
31	49.13 ₆	49.14 ₁	49.14 ₃	49.13 ₃	49.12 ₁				49.13 ₉
33	52.25 ₁	52.21 ₆ †	52.26 ₆	52.25 ₄ †	52.24 ₂ †				52.23 ₈ †
35	55.35 ₄	55.36 ₂ †	55.41 ₈						55.36 ₂ †

^a Only the data from the bands $\nu_1+3\nu_3$, $\nu_1+2\nu_2+3\nu_3$, $2\nu_1+3\nu_3$, and $5\nu_3$ have been included in the mean. Data from weak (†) and blended (*) lines have been omitted in the averaging.

larger scatter¹⁵ and were therefore not used in the averages. From the $\Delta_2 F''(J)$ values of Table V the following rotational constants were obtained:

$$B_{000} = 0.3902_0 \text{ cm}^{-1}, \quad D_{000} = 0.12 \times 10^{-6} \text{ cm}^{-1}.$$

The limit of error of B_{000} is estimated to be $\pm 0.0001_0$, that of D_{000} is $\pm 0.04 \times 10^{-6}$. The $\Delta_2 F''(J)$ values of the "hot" bands were similarly treated, but are of course not as accurate as those of the main bands. Therefore, for the 01⁰ level D was assumed to be equal to D_{000} . Different B values are obtained for the even (c) and odd (d) rotational levels of the 01⁰ II state on account of l -type doubling (see below). We find

$$B_{010}^{(c)} = 0.3912_3 \text{ cm}^{-1}, \quad B_{010}^{(d)} = 0.3905_8 \text{ cm}^{-1}.$$

The B_v values of the upper states of the bands were obtained from the combination sums. One has

$$R(J) + P(J) = 2\nu_0 + (2B' - 4D') + 2(B' - B'' - 6D')J(J+1) - 2(D' - D'')J^2(J+1)^2. \quad (2)$$

Plotting $R(J) + P(J)$ against $J(J+1)$ after addition of $aJ(J+1)$, where a is an approximate value for $2(B'' - B')$, straight lines were obtained. Since there was no indication of curvature, $D' - D''$ can be assumed to be close to zero. Thus, the slope of the straight line gives directly $B' - B''$ and therefore B' while the intercept gives ν_0 . The ν_0 values have already been included in Table I. The B_v values obtained in this way are given in Table VI.

In order to give an impression of the accuracy obtained, Fig. 3 gives a plot of the deviations of the observed band lines from those calculated from the constants of Table VI for the band $\nu_1+2\nu_2+3\nu_3$. It is seen that most observed lines are within $\pm 0.01 \text{ cm}^{-1}$ of the calculated.

¹⁵ This is also shown by the appreciable scatter of the B'' values obtained by Goldberg *et al.* for different bands without the use of combination differences.

Table VI also includes $B_{[v]}$ values obtained by us in the way described above from the bands measured by Goldberg *et al.*,¹² Benedict and Plyler,¹³ and Nielsen and Yao,¹⁴ adopting the B_{000} and B_{010} values here obtained for the lower states of their bands.

In the absence of perturbations the $B_{[v]}$ values are given by the formula

$$B_{v_1 v_2 v_3} = B_e - \alpha_1(v_1 + \frac{1}{2}) - \alpha_2(v_2 + 1) - \alpha_3(v_3 + \frac{1}{2}), \quad (3)$$

where B_e is the rotational constant for the equilibrium position, i.e.,

$$B_e = \frac{h}{8\pi^2 c I_e} = \frac{h}{16\pi^2 c m_O r_e^2}. \quad (4)$$

Here I_e is the equilibrium moment of inertia, r_e the equilibrium internuclear distance, and m_O the mass of the oxygen atom.

If the Fermi resonance is taken into account, Eq. (3) no longer represents the individual $B_{[v]}$ values of levels that form Fermi polyads. Nevertheless it still gives the correct average of the $B_{[v]}$ values of a given polyad. With this in mind the α_i can be obtained from various polyads (and monads). A good fit is obtained with

$$\alpha_1 = +0.00109, \quad \alpha_2 = -0.00073, \quad \alpha_3 = +0.00307 \text{ cm}^{-1}.$$

The mean $B_{[v]}$ values for each polyad calculated with these α_i values are given in the fourth column of Table VI and should be compared with the observed mean values given in the third column or, in the case of monads, with the B_v values of the second column. The agreement for the photographic infrared bands is within $\pm 0.00003 \text{ cm}^{-1}$ which is well within the accuracy of the $B_{[v]}$ determination. The deviations are larger (up to ± 0.00020) for the bands in the farther infrared.

Using the above α_i values one finds from (3) and B_{000} ,

$$B_e = 0.3915_5 \text{ cm}^{-1}.$$

TABLE VI. Rotational constants B_v of CO_2 .

Level v_1 v_2 v_3			$B_{v_1v_2v_3}$, observed (cm^{-1})		$B_{v_1v_2v_3}$, calculated			
			Individual values	Means of polyads	Monads and means of polyads	Observed-calculated	Individual values of polyads	Observed-calculated
0	0 ⁰	0	0.3902 ₀		0.39020	0 assumed		
0	1 ¹	0	0.3909 ₀		0.39093	-0.0000 ₃		
0	2 ⁰	0	0.3906 ₀					
1	0 ⁰	0	0.3903 ₀	0.3904 ₅	0.39039	+0.0000 ₆	0.39059	+0.0000 ₁
0	0 ⁰	1	0.3872 ₀		0.38713	+0.0000 ₇	0.39018	+0.0001 ₂
0	2 ⁰	1	0.3873 ₃					
1	0 ⁰	1	0.3871 ₇	0.3872 ₈	0.38732	-0.0000 ₄	0.38752	-0.0001 ₄
0	4 ⁰	1	0.3880 ₃				0.38711	+0.0000 ₆
1	2 ⁰	1	0.3864 ₉	0.3873 ₅	0.38750	-0.0001 ₅	0.38838	-0.0003 ₀
2	0 ⁰	1	0.3874 ₉				0.38661	-0.0001 ₅
0	5 ¹	1	0.3886 ₇				0.38747	+0.0000 ₂
1	3 ¹	1	0.3874 ₇		0.38823	...	0.38900	-0.0003 ₃
2	1 ¹	1	...				0.38765	-0.0001 ₈
0	6 ⁰	1	0.3887 ₉				0.38799	
1	4 ⁰	1	0.3866 ₃	0.3874 ₉	0.38769	-0.0002 ₀	0.38930	-0.0005 ₁
2	2 ⁰	1	0.3864 ₇				0.38699	-0.0003 ₃
3	0 ⁰	1	0.3880 ₃				0.38650	-0.0000 ₃
0	2 ⁰	3	0.3815 ₀	0.3811 ₅	0.38118	-0.0000 ₃	0.38795	+0.0001 ₃
1	0 ⁰	3	0.3808 ₀				0.38139	+0.0001 ₁
0	3 ¹	3	0.3822 ₂	0.3819 ₄	0.38191	+0.0000 ₃	0.38096	-0.0001 ₆
1	1 ¹	3	0.3816 ₅				0.38215	+0.0000 ₇
0	4 ⁰	3	0.3823 ₁				0.38166	-0.0000 ₁
1	2 ⁰	3	0.3804 ₇	0.3813 ₅	0.38136	-0.0000 ₁	0.38224	+0.0000 ₇
2	0 ⁰	3	0.3712 ₇				0.38047	+0.0000 ₀
0	0 ⁰	5	0.3748 ₅		0.37485	0 assumed	0.38137	-0.0001 ₀
0	2 ⁰	5	0.3756 ₀	0.3750 ₆	0.37504	+0.0000 ₂	0.37525	+0.0003 ₅
0	0 ⁰	5	0.3745 ₂				0.37482	-0.0003 ₀

This value may be compared with 0.3906 cm^{-1} obtained by one of us⁵ from earlier infrared measurements and 0.3920 cm^{-1} obtained by Goldberg *et al.*¹² from measurements of the bands in the region 1.5 to 2.1μ . In view of the better standards available in the photographic infrared, we believe that the new B_e value has a higher degree of accuracy.

Using the recent fundamental constants of DuMond and Cohen,¹⁶ one finds from B_e the following values of the moment of inertia and internuclear distance in the equilibrium position:

$$I_e = 71.46_8 \times 10^{-40} \text{ gm cm}^2,$$

$$r_e = 1.1600_5 \times 10^{-8} \text{ cm},$$

and similarly from B_{000} for the effective values in the lowest vibrational level:

$$I_0 = 71.71_5 \times 10^{-40} \text{ gm cm}^2,$$

$$r_0 = 1.1620_5 \times 10^{-8} \text{ cm}.$$

According to Adel and Dennison¹⁷ the $B_{[v]}$ values of a Fermi diad are given by

$$\begin{aligned} B_n &= a^2 B_n^0 + b^2 B_i^0, \\ B_i &= b^2 B_n^0 + a^2 B_i^0, \end{aligned} \quad (5)$$

where B_n^0 and B_i^0 are the unperturbed $B_{[v]}$ values as obtained from (3) and where a and b are the fractional contributions of the unperturbed to the perturbed eigen-

functions. Similarly, one has in the case of a triad

$$\begin{aligned} B_i &= a_{ii}^2 B_i^0 + a_{ij}^2 B_j^0 + a_{ik}^2 B_k^0, \\ B_j &= a_{ji}^2 B_i^0 + a_{jj}^2 B_j^0 + a_{jk}^2 B_k^0, \\ B_k &= a_{ki}^2 B_i^0 + a_{kj}^2 B_j^0 + a_{kk}^2 B_k^0, \end{aligned} \quad (6)$$

and corresponding equations for tetrads and higher polyads. Adel and Dennison¹⁷ and Goldberg *et al.*¹² have given the coefficients for diads, triads, and tetrads on the assumption of a certain set of vibrational constants. Even though this set has now been slightly revised by Taylor, Benedict, and Strong,¹¹ it appears of interest to use Dennison's coefficients for an evaluation of the individual $B_{[v]}$ values from the B_e and α_i values derived above. The result is given in the sixth column of Table VI. The $o-c$ values are rather larger than for the means of the polyads. Particularly in the case of the diads there appears to be a systematically increasing difference.

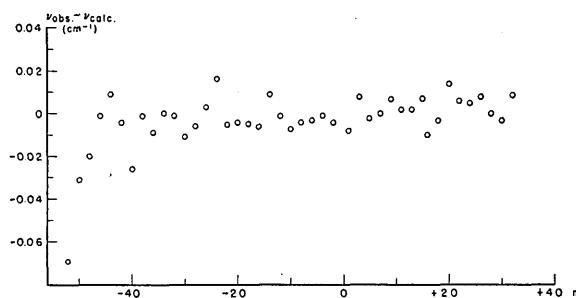


FIG. 3. Deviations of the lines in the band $\nu_1 + \nu_2 + \nu_3$ from those calculated with the constants of Table VI. On the abscissa m is plotted which is $J+1$ for the R branch and $-J$ for the P branch.

¹⁶ J. W. M. DuMond and E. R. Cohen, Phys. Rev. 82, 555 (1951).

¹⁷ A. Adel and D. M. Dennison, Phys. Rev. 44, 99 (1933).

TABLE VII. *l*-type doubling constants for CO₂.

Level			<i>q</i> (observed)		<i>q</i> (calculated)
<i>v</i> ₁	<i>v</i> ₂	<i>v</i> ₃	Goldberg <i>et al.</i>	Present work	
0	1 ¹	0	0.00050 ₅	0.00065	0.00061
2	1 ¹	1	...	...	0.00116
1	3 ¹	1	0.00080	0.00122	0.00109
0	5 ¹	1	0.00130	0.00158	0.00141
1	1 ¹	3	...	0.00077	0.00086
0	3 ¹	3	...	0.00093	0.00097

This is in all probability due to a variation of the interaction parameter W_{ni} (Dennison's $b/\sqrt{2}$) with v_3 , not taken into account in the elementary theory. Such a dependence has already been postulated by Taylor, Benedict, and Strong¹¹ to explain the vibrational splittings in various polyads. At this stage it does not appear profitable to pursue this matter further.

The data on C¹³O₂ (Table III) are of lower accuracy than those of C¹²O₂. Combining the data here obtained for the band $2\nu_2 + 3\nu_3$ and those of Goldberg *et al.* for $\nu_1 + 2\nu_2 + \nu_3$ and $4\nu_2 + \nu_3$ we obtain

$$B_{000}(\text{C}^{13}\text{O}_2) = 0.3903_7 \text{ cm}^{-1}.$$

(b) *l*-Type Doubling

The vibrational double degeneracy of levels with $l \neq 0$ of linear molecules is removed with increasing rotation by the interaction of rotation and vibration. Thus *l*-type doubling results.¹⁸ The magnitude of the splitting for levels with $l=1$ is given by

$$\Delta\nu = qJ(J+1),$$

where q differs somewhat for different Π levels.

In the case of CO₂, since the spin of the O nuclei is zero, alternate levels are missing in each set of rotational levels. For Π states this means that the odd levels are missing in one *l*-type doubling component and the even levels are missing in the other. Thus the characteristic staggering arises in $\Pi - \Pi$ bands.¹⁹ This is clearly seen in the spectrogram Fig. 1. The *l*-type doubling also accounts for the difference between the B_{010} value obtained from the *P* and *R* branches of the fundamental ν_2 and the B_{010} value obtained from the $\Pi - \Pi$ bands. The latter are averages of $B_{[v]}^{(e)}$ and $B_{[v]}^{(d)}$ (as listed in Table VI), the former is $B_{[v]}^{(d)}$. Indeed the B_{010} value obtained from the measurements of ν_2 by Martin and Barker²⁰ is 0.3906_5 cm^{-1} (adjusting the value given in reference 5 to the new B_{000} value) which agrees very satisfactorily with $B_{010}^{(d)}$ given above.

The precise value of q in a given case is most readily obtained as the difference of the two $B_{[v]}$ values, $B_{[v]}^{(e)}$ and $B_{[v]}^{(d)}$, corresponding to the even and odd rotational levels. The resulting q values are given in Table VII. The individual values of $B_{[v]}^{(e)}$ and $B_{[v]}^{(d)}$ are

obtained from Table VI by adding or subtracting $\frac{1}{2}q_{[v]}$ to or from the appropriate $B_{[v]}$ value. Since the q values were obtained as the differences of $B_{[v]}^{(e)}$ and $B_{[v]}^{(d)}$ their accuracy is of the same order as that of $B_{[v]}$ which implies a rather high percentage error.

De Heer and Nielsen²¹ have given formulas for the q values of the levels of a triad, and similar formulas for the levels of a diad can be readily obtained from their paper. In Table VII the theoretical values based on these formulas are given in the last column. The agreement between the new q values and the calculated ones is probably within the accuracy of the determinations.

F. DISCUSSION AND CONCLUSION

It is gratifying to note that in the present case for which Fermi resonance can be fully taken into account the agreement between observed and calculated $B_{[v]}$ values is very much better than in the cases of N₂O and HCN previously treated. In these latter molecules the constants W_{ni} determining the magnitude of Fermi interaction have not yet been evaluated. Moreover in these cases more possibilities for Fermi perturbations exist since on account of the lower symmetry of the molecule there are fewer restrictions for Fermi interactions (e.g., $2\nu_1$ may perturb ν_3 in N₂O but not in CO₂).

As mentioned above, in CO₂, unlike N₂O, the rotational constants of one isotopic molecule, C¹²O₂, suffice to determine the geometrical structure. If sufficient data were available on C¹³O₂ to extrapolate to the equilibrium rotational constants, an independent check on the assumption of the equality of equilibrium internuclear distances in isotopic molecules could be obtained. Frequently, for lack of sufficient data, particularly in microwave spectroscopic work, it is assumed that the effective internuclear distances r_0 in the lowest vibrational level are the same in isotopic molecules. If this were the case in C¹²O₂ and C¹³O₂ the B_0 values would have to be the same. Actually $B_0(\text{C}^{13}\text{O}_2)$ is slightly greater than $B_0(\text{C}^{12}\text{O}_2)$ as is to be expected on account of the smaller zero point energy. To be sure $B_0(\text{C}^{13}\text{O}_2)$ is not as accurate as $B_0(\text{C}^{12}\text{O}_2)$ and the difference is only slightly greater than the probable error.

In order to make further progress in the interpretation of the details of the CO₂ spectrum, it will be important that the fine structure of the bands studied by Taylor, Benedict, and Strong be investigated. In this way the variation of the Fermi interaction parameter with v_1, v_2, v_3 could be established and the variation of the $B_{[v]}$ of the polyads be understood in more detail.

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¹⁸ G. Herzberg, *Revs. Modern Phys.* **14**, 219 (1942).

¹⁹ For a more detailed explanation see Fig. 111, p. 389 of ref. (5) and the accompanying discussion.

²⁰ P. E. Martin and E. F. Barker, *Phys. Rev.* **41**, 291 (1932).

²¹ J. de Heer and H. H. Nielsen, *J. Chem. Phys.* **20**, 101 (1952).