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The Analysis of the Vibration-Rotation Band ω_3 for $C^{12}O^{16}{}_2$ and $C^{13}O^{16}{}_2$

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The vibration-rotation band ω_3 for normal and isotopic CO_2 has been completely remeasured with a 7200 line-per-inch grating and the rotation lines of both bands are completely resolved. Identification of the rotation lines up to $J=90$ in the P branch and $J=56$ in the R branch for the band in normal CO_2 was made, while for the isotopic band they are identified to $J=94$ in the R branch and to $J=44$ in the P branch. The combination principle was applied to the new data and new values of the band centers and the rotational constants B_{000}, B'_{001}, and α_3 have been determined. These new values are compared with those obtained from the earlier data.

I. INTRODUCTION

In connection with the investigation of ω_2 of CD_3Cl at 2285 cm^{-1}, it was observed that the rotation lines of the isotopic CO_2 band, with which it overlaps, were completely resolved. As it was apparent that the resolution of the lines was much better than in the earlier work[1] on normal and isotopic CO_2, it was deemed worthwhile to reinvestigate the region of ω_3 for both molecules exhaustively.

The bands were observed on a prism-grating spectrometer with a two-meter-focus collimating mirror employing a 7200 line-per-inch replica grating made by R. W. Wood. Under ordinary conditions the amount of CO_2 in the atmosphere is so great that no transmission of radiant energy occurs in the most intense portions of ω_3 for normal CO_2. In order to map these regions it was found necessary to place large trays of Ascarite in the spectrometer and seal all cracks in the enclosing box with scotch tape. This device so reduced the CO_2 content of the air within the box that about 40 percent of the energy was now transmitted in the most intense regions.

The spectrometer slits were set to include a spectral interval of about 0.25 cm^{-1}, and the galvanometer deflections were read at frequency intervals of 0.07 cm^{-1}. These deflections were plotted as ordinates *versus* the angular position of the grating with respect to the central image as abscissae. The angle scale was later converted into a scale of frequencies in cm^{-1} by the usual relation $\nu\ (cm^{-1}) = K_\nu\ (cm^{-1}) \csc\theta$, where K_ν is the instrument constant corrected to vacuum. K_ν was determined from this relation by making a great many observations on the angular position of an intense green line of the mercury spectrum in the sixth order.

At least three complete sets of observations were made on the two bands in this region. The angular position of each line was determined from about 10 or 12 observations and in most cases are accurate within ± 0.07 cm^{-1}. The exceptions occur where a line of normal and isotopic CO_2 overlap. In the R branch of the normal CO_2 band, where the lines are closest together because of the convergence, lines separated by only 0.8 cm^{-1} were completely resolved. Where the overlapping occurs, lines separated by as little as 0.2 cm^{-1} were consistently, though not completely, resolved.

II. EXPERIMENTAL RESULTS

The Vibration ω_3 for Normal CO_2

In Fig. 1 is shown the graphical representation of ω_3 for $C^{12}O^{16}{}_2$ with galvanometer deflections plotted as ordinates and frequencies in cm^{-1} as abscissae. It may be seen that the resolution of the rotational structure is complete. The faint lines appearing as satellites and in between the main absorption peaks are real, as they have been repeated in all the measurements. Those lines not attributable to $C^{13}O^{16}{}_2$ may be caused by ω_3 of $C^{12}O^{16}O^{18}$, the center of which should lie in this region of the spectrum. Assignment of J values has been possible to $J=90$ in the P branch and to $J=56$ in the R branch. The J value given is

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[1] P. E. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932); D. M. Cameron and H. H. Nielsen, Phys. Rev. **53**, 246 (1938); A. H. Nielsen, Phys. Rev. **53**, 983 (1938).

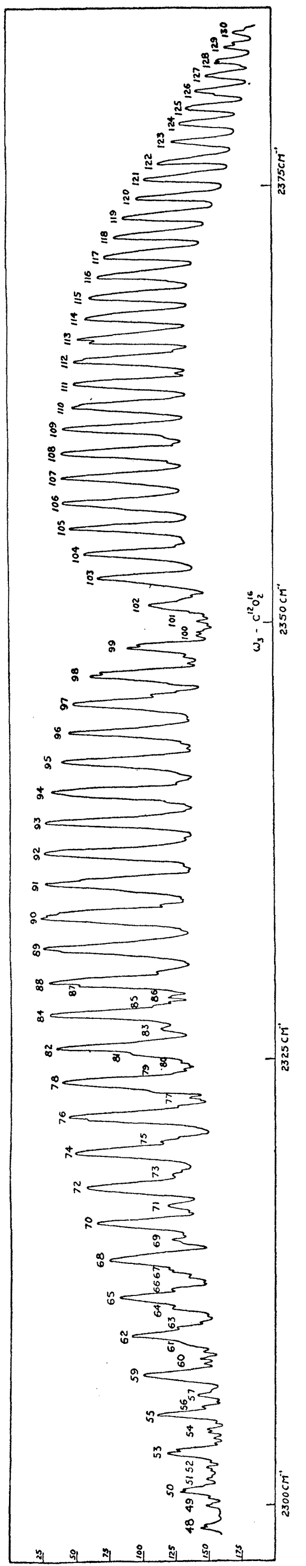

FIG. 1. Vibration-rotation band ω_3 for normal CO_2. Line numbers refer to Table I.

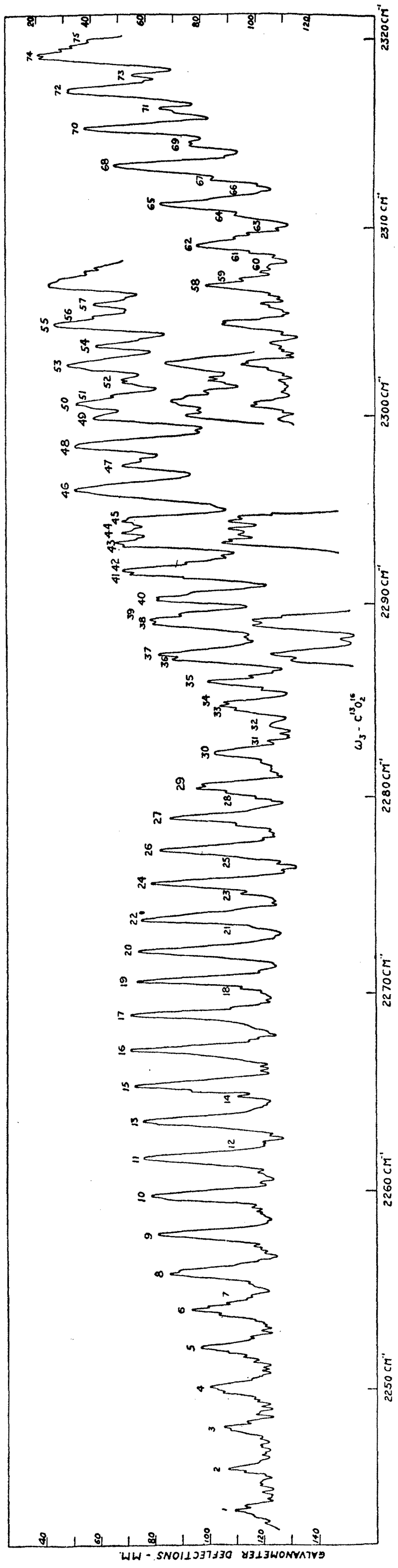

FIG. 2. Vibration-rotation band ω_3 for isotopic CO_2. Line numbers refer to Table II.

TABLE I. The rotation lines of ω_3 for $C^{12}O^{16}_2$.

Line No.	Identification	Positive branch (cm^{-1}) ν(obs.)	ν(calc.)	diff.	Line No.	Identification	Negative branch (cm^{-1}) ν(obs.)	ν(calc.)	diff.
102	*R*(0)	2350.73	2350.72	+.01					
103	*R*(2)	2352.27	2352.23	+.04	99	*P*(2)	2348.41	2348.36	+.05
104	*R*(4)	2353.77	2353.74	+.03	98	*P*(4)	2346.78	2346.76	+.02
105	*R*(6)	2355.20	2355.23	−.03	97	*P*(6)	2345.09	2345.15	−.06
106	*R*(8)	2356.75	2356.69	+.06	96	*P*(8)	2343.38	2343.50	−.12
107	*R*(10)	2358.11	2358.12	−.01	95	*P*(10)	2341.75	2341.83	−.08
108	*R*(12)	2359.59	2359.53	+.06	94	*P*(12)	2340.03	2340.13	−.10
109	*R*(14)	2360.91	2360.91	.00	93	*P*(14)	2338.37	2338.42	−.05
110	*R*(16)	2362.27	2362.27	.00	92	*P*(16)	2336.63	2336.68	−.05
111	*R*(18)	2363.61	2363.61	.00	91	*P*(18)	2334.90	2334.91	−.01
112	*R*(20)	2364.94	2364.91	+.03	90	*P*(20)	2333.06	2333.11	−.05
113	*R*(22)	2366.24	2366.20	+.04	89	*P*(22)	2331.26	2331.30	−.04
114	*R*(24)	2367.49	2367.46	+.03	88	*P*(24)	2329.40	2329.45	−.05
115	*R*(26)	2368.75	2368.70	+.05	84	*P*(26)	2327.49	2327.58	−.07
116	*R*(28)	2369.90	2369.91	−.01	82	*P*(28)	2325.70	2325.69	+.01
117	*R*(30)	2371.09	2371.09	.00	78	*P*(30)	2323.80	2323.78	+.02
118	*R*(32)	2372.24	2372.25	−.01	76	*P*(32)	2321.88	2321.84	+.04
119	*R*(34)	2373.39	2373.39	.00	74	*P*(34)	2319.88	2319.87	+.01
120	*R*(36)	2374.51	2374.51	.00	72	*P*(36)	2317.93	2317.87	+.06
121	*R*(38)	2375.62	2375.58	+.04	70	*P*(38)	2315.86	2315.86	.00
122	*R*(40)	2376.55	2376.65	−.10	68	*P*(40)	2313.85	2313.82	+.03
123	*R*(42)	2377.73	2377.69	+.04	65	*P*(42)	2311.77	2311.75	+.02
124	*R*(44)	2378.71	2378.70	+.01	62	*P*(44)	2309.68	2309.66	+.02
125	*R*(46)	2379.71	2379.68	+.03	59	*P*(46)	2307.54	2307.55	−.01
126	*R*(48)	2380.60	2380.65	−.05	56	*P*(48)	2305.41	2305.41	.00
127	*R*(50)	2381.57	2381.59	−.02	53	*P*(50)	2303.26	2303.24	+.02
128	*R*(52)	2382.47	2382.50	−.03	50	*P*(52)	2301.06	2301.05	+.01
129	*R*(54)	2383.32	2383.38	−.06	48	*P*(54)	2298.93	2298.83	+.10
130	*R*(56)	2384.21	2384.25	−.04	46	*P*(56)	2296.57	2296.59	−.02
					44	*P*(58)	2294.29	2294.33	−.04
					41	*P*(60)	2292.02	2292.04	−.02
					38	*P*(62)	2289.75	2289.73	+.02
					36	*P*(64)	2287.48	2287.39	+.09
					34	*P*(66)	2285.12	2285.03	+.09
					31	*P*(68)	2282.55	2282.64	−.09
					28	*P*(70)	2280.31	2280.22	+.09
					25	*P*(72)	2277.79	2277.79	.00
					23	*P*(74)	2275.29	2275.32	−.03
					21	*P*(76)	2272.84	2272.83	+.01
					18	*P*(78)	2270.56*	2270.32	+.24
						P(80)	*	2267.79	
					14	*P*(82)	2265.10	2265.21	−.11
					12	*P*(84)	2262.62	2262.64	−.02
						P(86)	*	2260.02	
						P(88)	*	2258.39	
					7	*P*(90)	2254.68	2254.73	−.05

that for the ground state.[2] In the region where the *P* branch of normal CO_2 and the *R* branch of the isotopic molecule overlap, the positions are somewhat less accurately known, and identification is therefore a little more difficult and uncertain. In Table I are listed the observed frequencies, corrected to vacuum, of the lines in ω_3 of normal CO_2 with the assigned *J* values. Each line in Fig. 1 is numbered and can be identified by referring to Table I. In adjacent columns of Table I are found the line frequencies computed with the use of constants determined from the data. It may be seen that the mean difference is less than 0.01 cm^{-1}. The lines in Table I marked with an asterisk are either unobserved or somewhat in error because of overlapping with the isotopic band.

The Vibration ω_3 for Isotopic CO_2

Figure 2 shows the graphs of the galvanometer deflections *versus* the frequencies in cm^{-1} for ω_3

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[2] The nuclear spin of the oxygen atoms is zero, and for this reason the part of the wave function depending on the nuclear spin is always symmetrical to an interchange of the two identical oxygen atoms. As a result of the exclusion principle, which requires that the total wave function shall belong to a certain class, only the levels characterized by even *J* values are present in the normal state. The effect is that every other line in the spectrum is absent, i.e., only *R*(*J*) and *P*(*J*) with even values of *J* will occur.

TABLE II. The rotation lines of ω_3 for $C^{13}O^{16}_2$.

Line No.	Identification	Positive branch (cm⁻¹)			Line No.	Identification	Negative branch (cm⁻¹)		
		ν(obs.)	ν(calc.)	diff.			ν(obs.)	ν(calc.)	diff.
33	$R(0)$	2284.91	2284.92	−.01					
35	$R(2)$	2286.44	2286.44	.00	30	$P(2)$	2282.67	2282.56	+.11
37	$R(4)$	2287.84*	2287.95	−.11	29	$P(4)$	2280.95	2280.98	−.03
39	$R(6)$	2289.51	2289.43	+.08	27	$P(6)$	2279.35	2279.38	−.03
40	$R(8)$	2290.81	2290.88	−.07	26	$P(8)$	2277.72	2277.70	+.02
42	$R(10)$	2292.31	2292.31	.00	24	$P(10)$	2275.99	2276.04	−.05
43	$R(12)$	2293.72	2293.72	.00	22	$P(12)$	2274.23	2274.34	−.11
45	$R(14)$	2294.99	2295.09	−.10	20	$P(14)$	2272.62	2272.62	.00
46	$R(16)$	2296.57	2296.45	+.12	19	$P(16)$	2270.70*	2270.47	+.23
47	$R(18)$	2297.88	2297.77	+.11	17	$P(18)$	2269.24	2269.10	+.14
48	$R(20)$	2299.02	2299.07	−.05	16	$P(20)$	2267.30	2267.30	.00
49	$R(22)$	2300.35	2300.25	+.10	15	$P(22)$	2265.52	2265.47	+.05
51	$R(24)$	2301.43*	2301.60	−.17	13	$P(24)$	2263.67	2263.62	+.05
52	$R(26)$	2302.35*	2302.82	−.47	11	$P(26)$	2261.78	2261.75	+.03
54	$R(28)$	2304.15*	2304.02	+.13	10	$P(28)$	2259.69	2259.85	−.16
55	$R(30)$	2305.19	2305.18	+.01	9	$P(30)$	2257.98	2257.91	+.07
57	$R(32)$	2306.40	2306.36	+.04	8	$P(32)$	2256.00	2255.95	+.05
58	$R(34)$	2307.45	2307.46	−.01	6	$P(34)$	2253.93	2253.98	−.05
60	$R(36)$	2308.54	2308.55	−.01	5	$P(36)$	2252.05	2251.97	+.08
61	$R(38)$	2309.42*	2309.63	−.11	4	$P(38)$	2249.97	2249.95	+.02
63	$R(40)$	2310.62	2310.67	−.05	3	$P(40)$	2247.96	2247.89	+.07
64	$R(42)$	2311.51*	2311.67	−.16	2	$P(42)$	2245.93	2245.82	+.11
66	$R(44)$	2312.58*	2312.69	−.11	1	$P(44)$	2243.83	2243.70	+.13
67	$R(46)$	2313.52*	2313.65	−.13					
	$R(48)$	*	2314.86						
69	$R(50)$	2315.08	2315.05	+.03					
	$R(52)$	*	2315.96						
71	$R(54)$	2316.89	2316.83	+.06					
	$R(56)$	*	2318.07						
73	$R(58)$	2318.90	2318.90	.00					
	$R(60)$	*	2319.70						
75	$R(62)$	2320.50	2320.47	+.03					
	$R(64)$	*	2321.19						
	$R(66)$	*	2321.91						
	$R(68)$	*	2322.60						
77	$R(70)$	2322.90	2322.93	−.03					
	$R(72)$	*	2323.89						
79	$R(74)$	2324.34*	2324.21	+.13					
80	$R(76)$	2324.80*	2324.99	−.19					
81	$R(78)$	2325.51*	2325.65	−.14					
	$R(80)$	*	2326.17						
83	$R(82)$	2326.77	2326.79	−.02					
	$R(84)$	*	2327.17						
	$R(86)$	*	2327.64						
85	$R(88)$	2328.22	2328.15	+.07					
86	$R(90)$	2328.51	2328.46	+.06					
	$R(92)$	*	2328.83						
89	$R(94)$	2329.18	2329.19	−.01					

of the isotopic molecule. Several lines have been redrawn from other data in Fig. 2 to show how well small details were reproduced from one set of observations to another. Because of the overlapping of the two bands, the lines are not as completely resolved nor quite as accurately known in the R branch of this band as in the P branch or as in ω_3 of the normal molecule. Assignment of J values to lines has, however, been possible to $R(94)$ and to $P(44)$ with a few exceptions where the overlapping precluded the observation of the individual lines. The observed frequencies are listed in Table II with the appropriate J value for the lower state.[2] The lines in Fig. 2 are numbered and can be identified by referring to Table II. The line frequencies computed from constants determined from the data, are found in adjacent columns in Table II. Because of overlapping with the normal molecule band, a number of lines are either in error or unobserved and are marked with an asterisk. The average difference between the observed and computed frequencies is about 0.02 cm^{-1}.

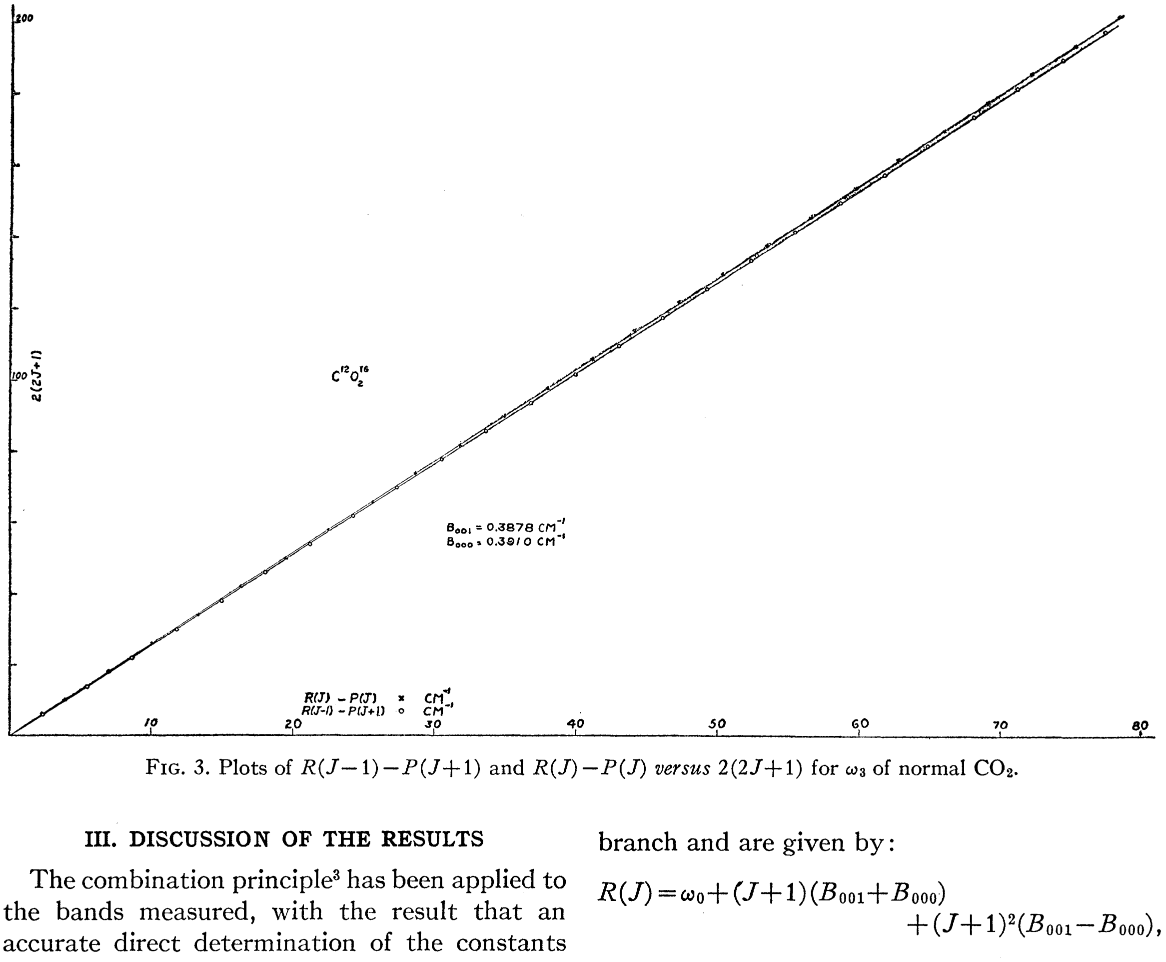

FIG. 3. Plots of $R(J-1)-P(J+1)$ and $R(J)-P(J)$ *versus* $2(2J+1)$ for ω_3 of normal CO_2.

III. DISCUSSION OF THE RESULTS

The combination principle[3] has been applied to the bands measured, with the result that an accurate direct determination of the constants relating to the vibration ω_3 were possible. The energy expressions for the rotational levels in the normal and first excited vibrational states are, respectively:

$$E''/hc = E_{000}/hc + J''(J''+1)B_{000} - J''^2(J''+1)^2D,$$

and (1)

$$E'/hc = E_{001}/hc + J'(J'+1)B_{001} - J'^2(J'+1)^2D.$$

B_{000} and B_{001} are constants ($B = h/8\pi^2Ic$) representing the moments of inertia in the ground and first vibration states, and D is the centrifugal stretching constant. It may be shown for this molecule that, to a good approximation, D may be neglected. The rotation lines on the high frequency side of the band center form the R branch and are given by:

$$R(J) = \omega_0 + (J+1)(B_{001}+B_{000}) + (J+1)^2(B_{001}-B_{000}),$$

while the lines on the low frequency side form the P branch and are given by

$$P(J) = \omega_0 - J(B_{001}+B_{000}) + J^2(B_{001}-B_{000}),$$

where J is the quantum number of total angular momentum in the lowest state, and ω_0 is the band center or the frequency of the $J=0$ line. By combining these relations properly, the following expressions, from which B_{000} and B_{001} emerge, may be obtained:

$$R(J-1) - P(J+1) = 2(2J+1)B_{000}$$

and (2)

$$R(J) - P(J) = 2(2J+1)B_{001}.$$

Figures 3 and 4 show graphs of these two equations with term differences in cm^{-1} plotted as abscissae and $2(2J+1)$ as ordinates for both molecules. The slopes of these lines yield B_{000} and B_{001}, respectively. B_e, the equilibrium value of B,

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[3] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p. 390.

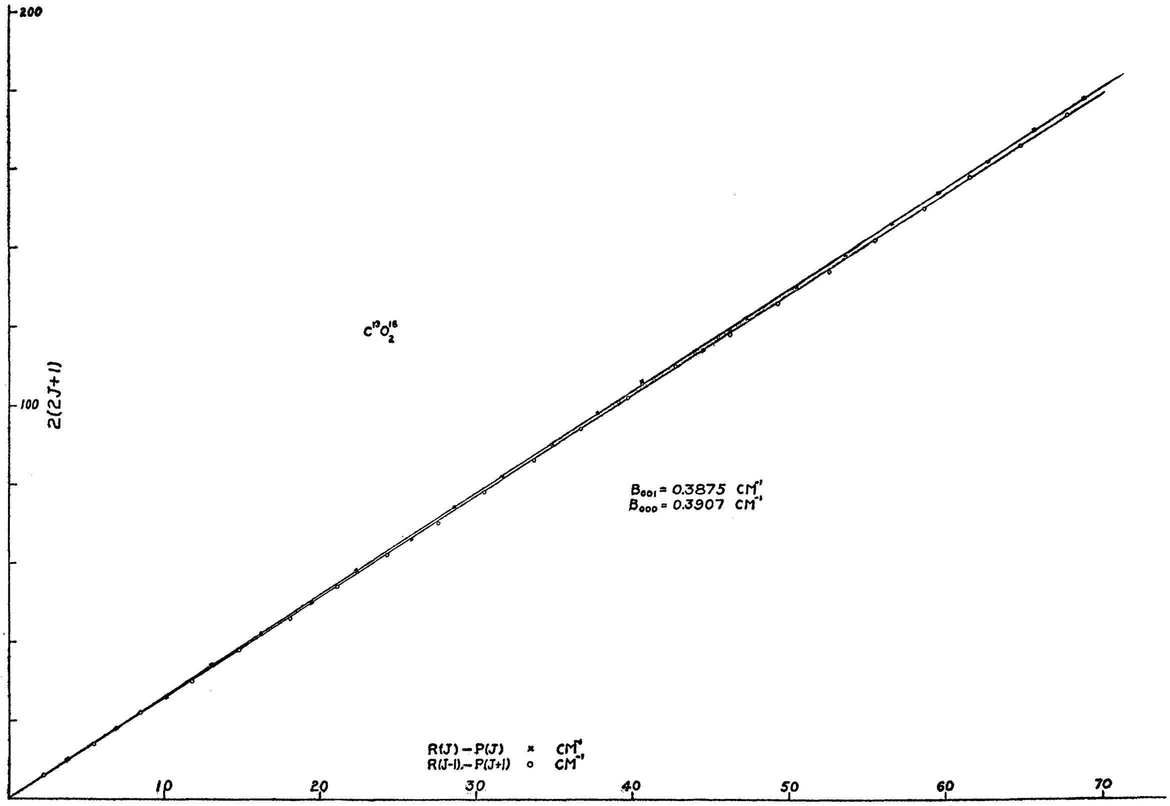

FIG. 4. Plots of $R(J-1)-P(J+1)$ and $R(J)-P(J)$ *versus* $2(2J+1)$ for isotopic CO_2.

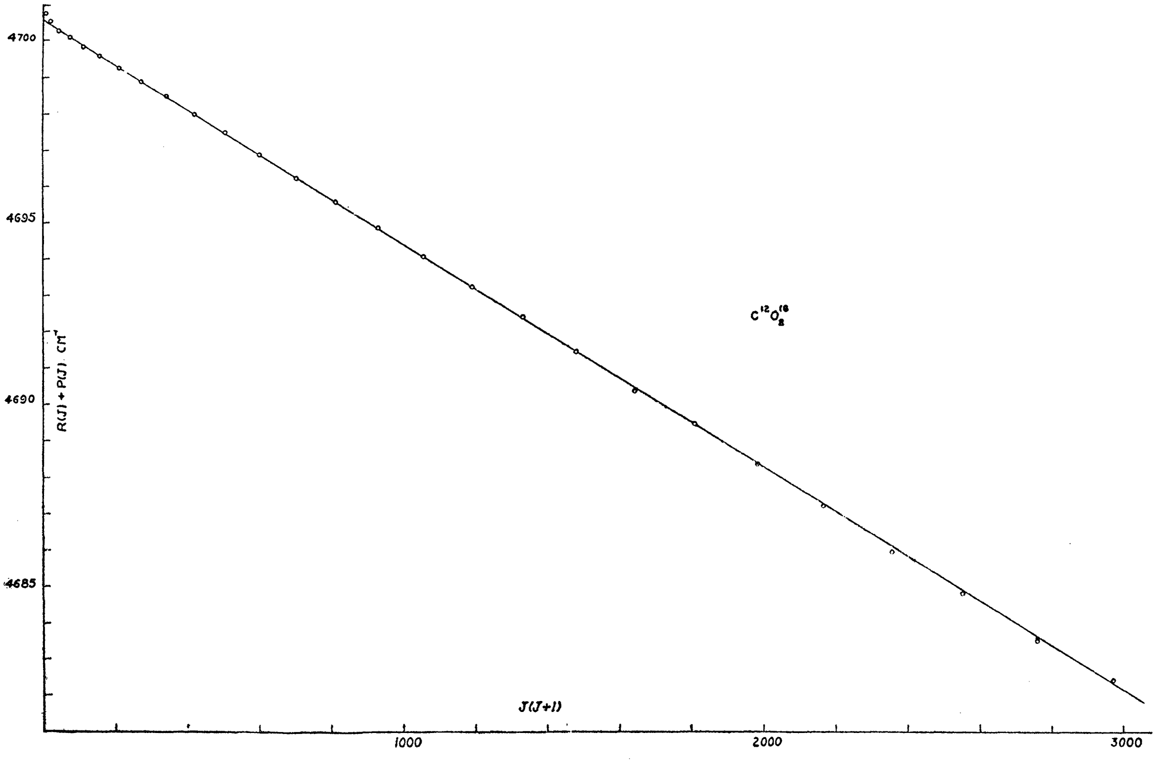

FIG. 5. Plot of $R(J)+P(J)$ *versus* $J(J+1)$ for normal CO_2.

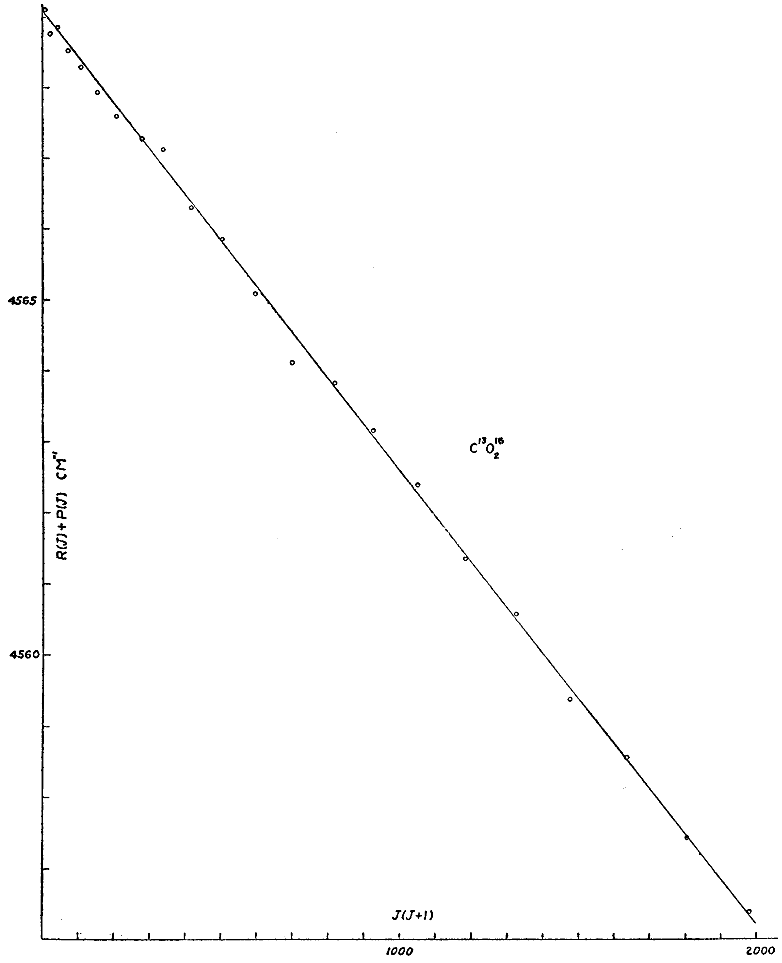

FIG. 6. Plot of $R(J)+P(J)$ *versus* $J(J+1)$ for isotopic CO_2.

and the equilibrium internuclear distances may be obtained from B_{000} and B_{001} and the convergence factors α_1, α_2, α_3 with the relation:

$$B_v = B_e - \alpha_1(v_1+\tfrac{1}{2}) - \alpha_2(v_2+1) - \alpha_3(v_3+\tfrac{1}{2}). \quad (3)$$

The frequency, ω_0, of the $J=0$ line may be obtained from another combination relation, namely:

$$R(J)+P(J) = 2(\omega_0+B_{001}) + 2J(J+1)(B_{001}-B_{000}). \quad (4)$$

When $R(J)+P(J)$ in cm^{-1} is plotted *versus* $J(J+1)$, as in Figs. 5 and 6, a straight line results, the intercept of which is $2(\omega_0+B_{001})$ and the slope of which is $2(B_{001}-B_{000})$ or $-2\alpha_3$. The values of the various constants obtained from the present data follow in Table III.

IV. CONCLUSION

The B_{000} and B_{001} found in columns 1 and 2 of Table III are obtained directly as the slopes of the curves in Figs. 3 and 4, and the differences between these values give α_3 or $B_{000}-B_{001}$ in column 3. Another value of α_3, found in column 4, is obtained directly from the slopes of the curves given in Figs. 5 and 6. From a theoretical relation for α_3 given by Nielsen[4] and utilizing values of the vibrational frequencies of ω_1, ω_2, ω_3, the potential energy constant c given by Dennison,[5] and a value of B_e, the computed value of α_3, found in column 5, was obtained. It may be seen that these determinations of α_3 are in excellent

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[4] A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943).

[5] D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

TABLE III. Values of the constants relating to ω_3 for $C^{12}O^{16}_2$ and $C^{13}O^{16}_2$.

	B_{000} (cm^{-1})	B_{001} (cm^{-1})	α_3 (cm^{-1}) i.e., (B_{000}–B_{001}) from Col. 1–Col. 2	α_3 (cm^{-1}) from Figs. 5 and 6	α_3 (cm^{-1}) calc. from reference (4)	ω_0 (cm^{-1}) band center
$C^{12}O_2^{16}$	0.3910	0.3878	0.0032	0.0031	0.0031	2349.93
$C^{13}O_2^{16}$	0.3907	0.3875	0.0032	0.0032		2284.14

agreement with each other, but do not agree with $\alpha_3 = 0.0029$ cm^{-1} given by Herzberg.[6] The combination principle applied to Martin and Barker's[1] data on ω_2 yields a value for B_{000} of 0.3903. This is in reasonably good agreement with the value in Table III. The value $B_{000} = 0.3895$ cm^{-1} given by Herzberg[6] appears to be low. When the combination principle is applied to Barker and Adel's data[7] on $\nu_3 - (\nu_1, 2\nu_2)$ it yields values for B_{001} of $B_{001} = 0.3861$ cm^{-1} (10.41μ band) and $B_{001} = 0.3862$ cm^{-1} (9.40μ band), respectively. The values of B_{001} from Barker and Adel's data, although in agreement with each other, are not consistent with the B_{001} listed in Table III, found from the present data on ω_3.

It may also be seen from Table III that the constants B_{000}, B_{001}, and α_3 for normal CO_2 are very nearly equal to the values of these constants for the isotopic molecule. This is rather good evidence that the equilibrium moment of inertia and internuclear distance and the force constants are the same for the two molecules.

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[6] G. Herzberg, reference 3, p. 394–395.

[7] E. F. Barker and A. Adel, Phys. Rev. **44**, 185 (1933).