Carbon Dioxide in the Infra-Red Solar Spectrum

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(Received August 29, 1949)

Wave-length measurements are given for lines in thirteen vibration-rotation bands of carbon dioxide observed between 1.5μ and 2.1μ in the infra-red solar spectrum and in the laboratory. The observations were made with the McGregor spectrometer and Cashman cell of the McMath-Hulbert Observatory. Among the thirteen bands, seven originate from the ground state and two from the first excited state of $C^{12}O_2^{16}$. The remaining four are identified with ground state transitions in the isotopic molecules $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{18}$.

The rotational constants α_1, α_2, and α_3 have been determined from analysis of the rotational structures. The mean value found for B_{000} is 0.3906 cm^{-1} and for the equilibrium position $B_e = 0.3920$ cm^{-1}.

I. INTRODUCTION

CARBON dioxide is one of the principal absorbers in the earth's atmosphere of solar radiation in the infra-red spectral region from 1.5μ to 20μ. Between 1.5μ and 2.5μ, it is represented by numerous vibration-rotation bands which are grouped at approximately 1.6μ and 2.0μ. Langley[1] recorded two bands at 2.01μ and 2.05μ, which he designated as ω_1 and ω_2. Langley's bands are two of a group of three that result from transitions between the ground state and the triad of excited vibrational levels 04_01, 12_01, and 20_01. The third member of this group, ω_0, occurs at 1.95μ but is partially obscured by water-vapor absorption. Adel[2] later observed all three bands with a resolution higher than Langley's and succeeded in resolving them into their rotational structures.

In addition to the bands at 2μ, Barker and Wu[3] also recorded in the laboratory four weaker unresolved bands of CO_2 at 1.54μ, 1.57μ, 1.60μ and 1.65μ. The 1.6μ bands also arise from the ground state, and terminate in the excited levels 06_01, 14_01, 22_01, and 30_01. According to Adel and Lampland[4] this quartet of bands is represented by a single small absorption in the low resolution prismatic solar spectrum. The bands are plainly visible on Langley's and Abbot's early tracings.

TABLE I. Near infra-red bands of carbon dioxide in the solar spectrum.

Identification	ν_0(obs)	ν_0(calc)	Designation	Disp. (mm/A)	Sec Z
			$C^{12}O_2^{16}$		
2.06μ	4853.48	4852.8	$0\ 0_0\ 0-\begin{cases}0\ 4_0\ 1\\1\ 2_0\ 1\\2\ 0_0\ 1\end{cases}$	3.1	laboratory
2.01μ	4977.78	4981.4		3.1	laboratory
1.96μ	5099.64	5104.3		3.1	laboratory
1.65μ	6075.98	6071.0	$0\ 0_0\ 0-\begin{cases}0\ 6_0\ 1\\1\ 4_0\ 1\\2\ 2_0\ 1\\3\ 0_0\ 1\end{cases}$	2.7	7.0
1.60μ	6227.90	6235.5		4.7	1.1
1.57μ	6349.56	6358.4		4.7	1.2
1.54μ	6503.08	6515.4		2.7	17.4
2.08μ	4807.60	4805.6	$0\ 1_1\ 0-\begin{cases}0\ 5_1\ 1\\1\ 3_1\ 1\\2\ 1_1\ 1\end{cases}$	3.1	1.6
2.01μ	4965.36	4970.5		3.1	2.5
—	—	5131.6		—	—
			$C^{13}O_2^{16}$		
2.10μ	4748.06	4737.8	$0\ 0_0\ 0-\begin{cases}0\ 4_0\ 1\\1\ 2_0\ 1\\2\ 0_0\ 1\end{cases}$	6.2	26.3
2.05μ	4887.30	4892.1		3.1	2.4
—	—	5046.0		—	—
			$C^{12}O^{16}O^{18}$		
2.09μ	4791.22	4797.5	$0\ 0_0\ 0-\begin{cases}0\ 4_0\ 1\\1\ 2_0\ 1\\2\ 0_0\ 1\end{cases}$	6.2	20.4
2.04μ	4904.75	4909.4		3.1	2.4
—	—	—		—	—

The recent installation of a Cashman lead-sulfide cell and an all-reflecting spectrometer in the McGregor tower has made possible the mapping of the near infra-red solar spectrum with a resolution of about 50,000.[5] With this resolution the carbon dioxide bands at 1.6μ and 2.0μ are fully resolved and are well suited for detailed study. In addition to the afore-mentioned bands, several new band structures have been found and identified with the isotopes $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{18}$, as well as with transitions from the first excited vibrational state of CO_2. This paper deals with the measurement and partial analysis of the various CO_2 bands in the solar spectrum between 1.5μ and 2.5μ.

II. OBSERVATIONAL

Table I lists the CO_2 bands that form the subject of the present study. Column one gives the approximate band centers in microns, for convenience of reference. Columns two and three give the observed and calculated frequencies of the band centers in cm^{-1}. Two of the isotopic and excited state bands are so overlaid by other stronger CO_2 bands that it was not possible to measure the band centers nor to assign rotational quantum numbers. Column four gives the quantum numbers involved in the various vibrational transitions. The excited levels enclosed in brackets are in resonance interaction and it is therefore not possible to assign quantum numbers unambiguously to any one level in either group. Column five gives the dispersion of each tracing in mm/A, and column six records the secant of the sun's zenith distance at the midpoint of each tracing.

Reproductions of the ω_0, ω_1, and ω_2 bands are shown in Fig. 1. Although the bands are quite well resolved,

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[1] S. P. Langley and C. G. Abbot, Ann. Astrophys. Obs. Smithsonian Inst. **1**, 127 (1900).

[2] Arthur Adel, Astrophys. J. **97**, 190 (1943).

[3] E. F. Barker and Ta-You Wu, Phys. Rev. **45**, 1 (1934).

[4] Arthur Adel and C. O. Lampland, Astrophys. J. **87**, 198 (1938).

[5] Robert R. McMath and O. C. Mohler, J. Opt. Soc. Am. (to be published).

accurate measurement of many of the components, particularly of ω_0 and ω_1, is hindered both by saturation of the strong lines and by blends with strong lines of water vapor. Although the number of unblended and unsaturated lines in each band appeared to be sufficient for an accurate evaluation of the rotational constants, it seemed desirable as a check to obtain laboratory tracings of the 2μ bands. The source employed for this purpose was a 2000-watt incandescent lamp placed just in front of the entrance slit of the monochromator. CO_2 vapor was generated from dry ice at the bottom of a cylindrical tube, six feet long, placed horizontally inside the spectrometer. The wave-length scale for the laboratory tracings was transferred from the solar tracing by simple superposition of unblended lines of CO_2.

The isotope bands at 2.04μ and 2.05μ, shown in Fig. 2, are the $C^{12}O^{16}O^{18}$ and $C^{13}O_2^{16}$ analogs of ω_1. The C^{13} isotope band corresponding to ω_0 falls in the middle of the ω_1 band and is therefore not observed. Portions of the O^{18} companion to ω_0 are visible on low sun tracings between ω_0 and ω_1, but the band is mostly obscured by water vapor. The isotope bands corresponding to ω_2 are not present on tracings made at high solar altitudes, which is to be expected in view of the relative weakness of ω_2. Both isotope bands do appear, however, on special low sun tracings obtained on September 26–27, 1948, as shown in Fig. 3. The region illustrated in Fig. 3 contains also a combination band of N_2O, centered at 2.13μ, as well as a portion of the 2.08μ excited-state band of CO_2. The latter band is also shown in Fig. 4.

The 1.57μ and 1.60μ bands appear well developed on noon-day tracings (see Fig. 5). The weaker bands at 1.54μ and 1.65μ, however, are ordinarily not present, and low sun tracings are required to bring them out. All four bands are well resolved and suitable for measurement, except for occasional blends, chiefly with solar lines of Fe I, Mg I, and Si I.

III. THE DETERMINATION OF WAVE-LENGTH

The second column of Table II lists the observed wave numbers of individual lines in the various CO_2 bands. An index of refraction for air equal to 1.000272 was adopted to convert all measured wave-lengths to wave number units. The following procedure[5] was employed to establish the wave-length scale. A series of standard lines was selected at intervals of approxi-

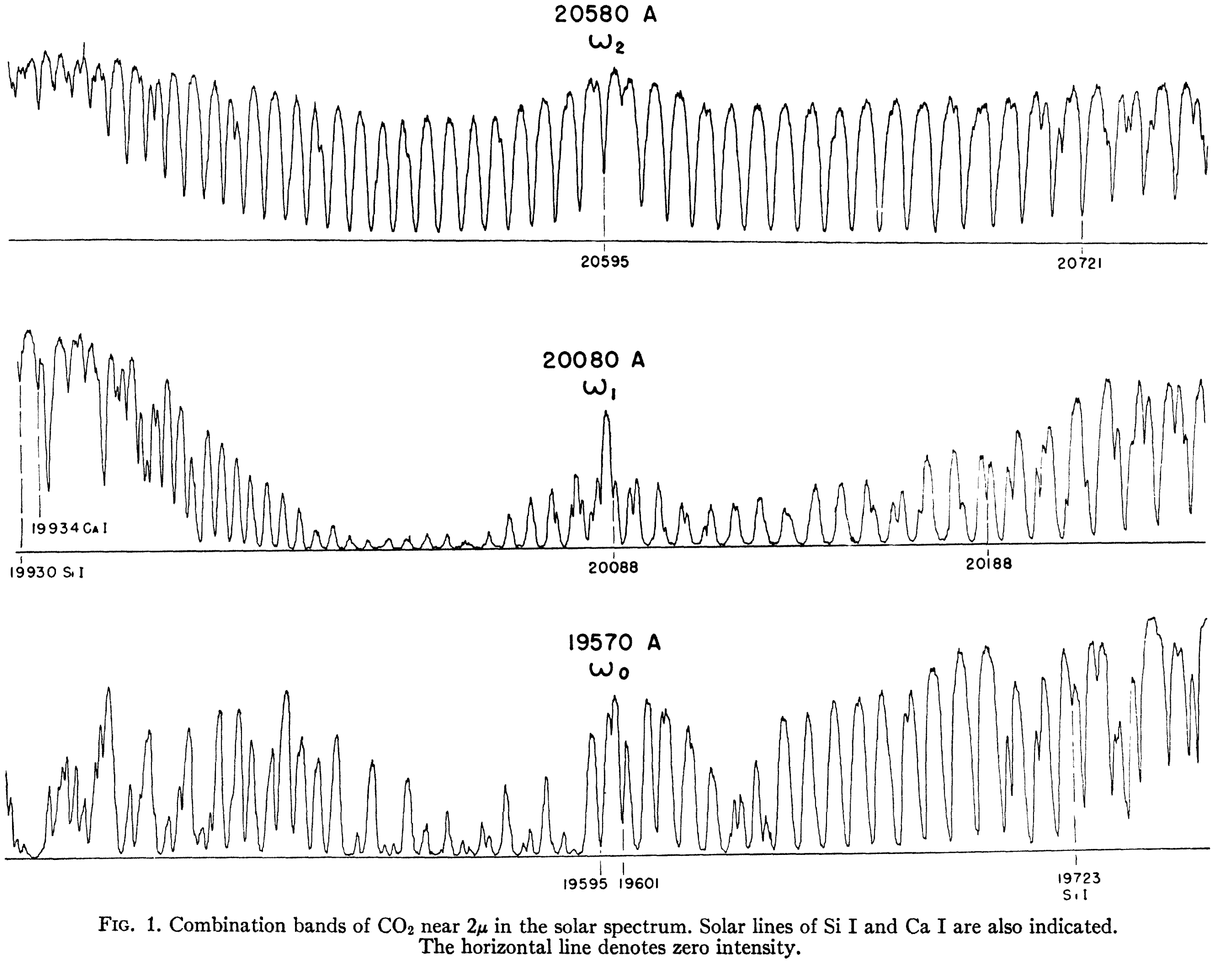

FIG. 1. Combination bands of CO_2 near 2μ in the solar spectrum. Solar lines of Si I and Ca I are also indicated. The horizontal line denotes zero intensity.

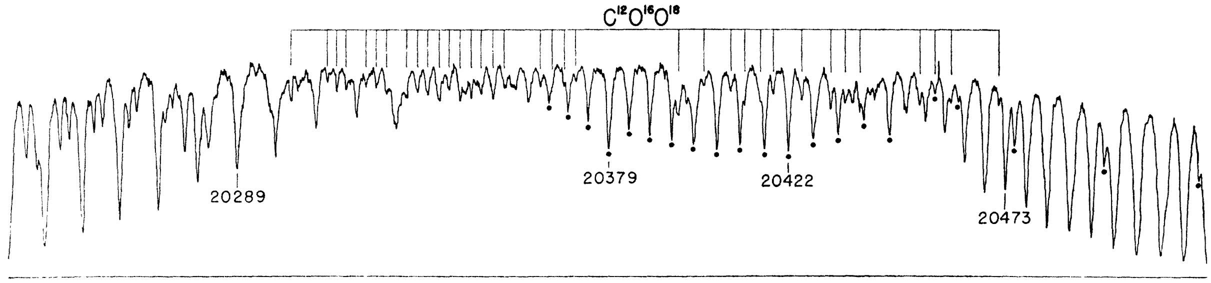

FIG. 2. Isotopic bands of CO_2 in the solar spectrum. The dots indicate lines due to $C^{13}O^{16}$, whereas the vertical lines denote a band of $C^{12}O^{16}O^{18}$. The horizontal lines denote zero intensity.

mately 50A and the wave-length of each line determined with reference to visible Fraunhofer lines in the third- and fourth-order grating spectra. Usually, about three independent determinations were made for each line, the estimated probable error of the mean wave-length being about 0.1A. The dispersion was then calculated from successive pairs of lines and plotted against the wave-length. According to the grating formula as applied to the McGregor spectrometer, the dispersion should increase slowly with wave-length, and in the infra-red the relation should be linear for a spectrum interval of about 2500A. Thus,

$$dx/d\lambda = a + b\lambda, \tag{1}$$

where a and b are constants, and x is the distance in mm from an arbitrary point, in the direction of the dispersion. Integration of Eq. (1) gives the relation between x and λ, *viz.*:

$$x = a\lambda + \tfrac{1}{2}b\lambda^2 + c. \tag{2}$$

For a given wave-length region, the constants a and b were determined from Eq. (1) by least squares and the constant c was adjusted to produce the best fit with the observed wave-lengths of the standard lines. The determination of the wave-length scale for the 1.6μ region is illustrated in Table III and Fig. 6. The measured wave-lengths of the standard lines are given in the first column of Table III and the measured dispersions in the second column. The latter are shown plotted against wave-length in Fig. 6. In general, dispersions were not calculated for line pairs closer than about 50A. The constants of the straight line drawn through the plotted points, determined by least squares, are $a = 3.4829$ mm/A, and $b = 0.00007869$ mm/A^2. The residuals in the third column of Table III are the differences between the observed wave-lengths of column two and those calculated from Eq. (2) with the foregoing constants. On the whole, the quadratic formula gives an excellent representation of the measured standard wave-lengths. The residuals larger than about ±0.05A probably arise from non-uniform motion of the recording paper.

IV. IDENTIFICATIONS OF NEW BANDS

The band centers given in the third column of Table I were calculated from formulas derived by Adel and Dennison.[6] For each band the upper vibrational level is in so called Fermi resonance with two or more neighboring levels. The energies of n such resonating levels are given by the solution of an nth-order determinant. For the triad of levels $\begin{Bmatrix} 2 & 0_0 & 1 \\ 1 & 2_0 & 1 \\ 0 & 4_0 & 1 \end{Bmatrix}$, the deter-

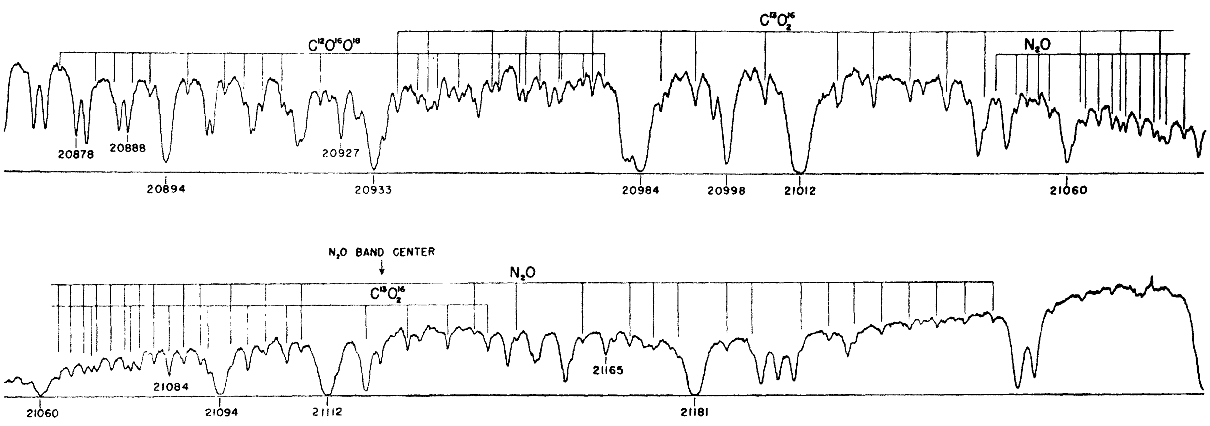

FIG. 3. Bands of $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{18}$ in the solar spectrum. A combination band of N_2O also appears weakly. The horizontal line denotes zero intensity.

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[6] See David M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

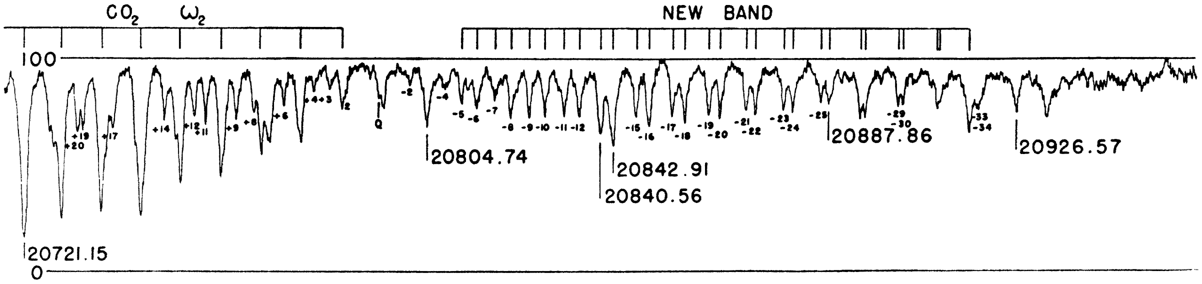

FIG. 4. The excited-state band of CO_2 at 2.08μ in the solar spectrum. The values of m are indicated below unblended lines. The horizontal line denotes zero intensity.

minant has the form

$$\begin{vmatrix} W_{041}-W & -\sqrt{2}b & 0 \\ -\sqrt{2}b & W_{121}-W & -b \\ 0 & -b & W_{201}-W \end{vmatrix} = 0. \quad (3)$$

In Eq. (3), W_{041}, W_{121} and W_{201} are the energies in cm^{-1} of the unperturbed levels, calculable in terms of the potential constants, and $b^2=5081$ cm^{-2}. The potential constants for CO_2 were determined by Adel and Dennison in 1933 from an analysis of all then-existing band centers. A re-analysis of the CO_2 spectrum based on the data of the present investigation undoubtedly would lead to some refinement of the potential constants. Nevertheless, the constants of Adel and Dennison are more than adequate for the calculations needed to establish the identity of isotope and difference bands of CO_2.

The Bands of $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{18}$

The great strength of the ω_0, ω_1, and ω_2 bands of $C^{12}O_2^{16}$ in the solar spectrum suggests that faint bands arising from the same vibrational-rotational transitions in the molecules $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{18}$ should also be present in the spectrum. Since the isotopes are heavier than the ordinary CO_2 molecules, their vibrational frequencies are somewhat lower, actually by 58 to 115 cm^{-1}, than those of $C^{12}O_2^{16}$. In theory, the calculation of band centers for the isotopes of CO_2 would require an entirely new set of potential constants appropriate to the isotopic molecules. As a satisfactory first approximation, however, D. M. Dennison[7] has suggested the following simple modification of the potential constants of CO_2. For the linear symmetrical molecule XY_2, in which the X atom is replaced by an isotope $X^{(i)}$, the following relation holds between the zero-order frequencies of XY_2 and $X^{(i)}Y_2$:[8]

$$\omega_1^{(i)}/\omega_1 = 1;$$

$$f^2 = \left(\frac{\omega_2^{(i)}}{\omega_2}\right)^2 = \left(\frac{\omega_3^{(i)}}{\omega_3}\right)^2 = \frac{1+(2m_Y)/(m_X^{(i)})}{1+(2m_Y)/(m_X)} \quad (4)$$

where ω_1, ω_2, and ω_3 are the zero-order frequencies,

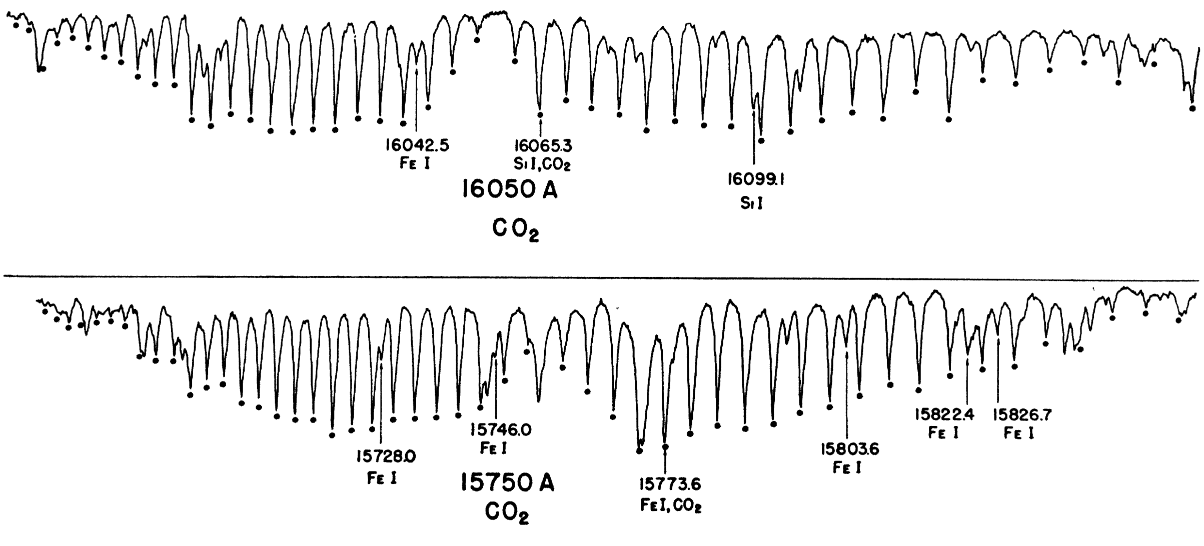

FIG. 5. Combination bands of CO_2 near 1.6μ. The CO_2 lines are indicated by dots and solar lines of Fe I and Si I are also shown. The horizontal line denotes zero intensity.

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[7] D. M. Dennison, private communication.

[8] Gerhard Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 230.

TABLE II. Measured wave numbers of rotational lines of CO_2.

m	ν(obs)	O−C
2.06μ band $C^{12}O_2^{16}$		
+1	4854.27	+0.01
3	4855.83	+0.03
5	4857.29	−0.04
7	4858.82	−0.02
9	4860.33	0.00
11	4861.78	−0.02
13	4863.23	−0.03
15	4864.69	−0.01
17	4866.13	+0.01
19	4867.53	0.00
21	4868.98	+0.06
23	4870.37	+0.08
25	4871.74	+0.09
27	4873.00	+0.01
29	4874.29	−0.02
31	4875.59	−0.02
35	4878.12	−0.05
37	4879.39	−0.03
39	4880.66	0.00
41	4881.86	−0.01
43	4883.05	−0.02
+45	4884.29	+0.03
−2	4851.92	0.00
4	4850.31	−0.03
6	4848.76	+0.03
8	4847.06	−0.06
10	4845.42	−0.06
12	4843.76	+0.03
14	4842.12	−0.05
16	4840.50	+0.01
18	4838.82	−0.01
20	4837.11	+0.04
22	4835.39	+0.05
26	4831.86	+0.04
28	4830.08	+0.04
30	4828.27	+0.03
32	4826.46	+0.03
34	4824.57	−0.02
36	4822.74	−0.01
38	4820.85	−0.03
40	4818.99	−0.02
−42	4817.09	−0.02
2.01μ band $C^{12}O_2^{16}$		
+1	4978.52	−0.04
3	4980.12	+0.03
5	4981.58	−0.06
7	4983.07	+0.02
9	4984.50	+0.02
11	4985.88	−0.01
13	4987.27	+0.01
15	4988.61	0.00
17	4989.90	−0.02
19	4991.15	−0.06
21	4992.42	−0.05
25	4994.88	−0.01
29	4997.20	+0.01
31	4998.32	+0.03
33	4999.39	+0.02
35	5000.39	−0.02
37	5001.44	+0.01
39	5002.45	+0.04
41	5003.40	+0.03
43	5004.30	+0.01
45	5005.17	−0.01
47	5006.05	0.00
49	5006.89	+0.01
+51	5007.66	−0.02
−2	4976.25	+0.03
4	4974.58	−0.04
6	4972.94	−0.05
8	4971.33	0.00
10	4969.62	−0.02
12	4967.93	0.00
14	4966.18	0.00
16	4964.43	+0.03
18	4962.61	+0.01
20	4960.74	−0.02
22	4958.85	−0.05
24	4957.01	0.00
26	4955.11	+0.03
28	4953.11	−0.02
30	4951.17	+0.02
32	4949.16	+0.02
34	4947.12	+0.08
36	4945.00	−0.03
38	4942.93	−0.01
40	4940.82	+0.01
42	4938.69	+0.04
44	4936.50	+0.03
46	4934.28	+0.02
48	4932.06	+0.04
50	4929.71	−0.04
−52	4927.43	−0.02
1.96μ band $C^{12}O_2^{16}$		
+3	5101.94	−0.02
5	5103.51	+0.04
7	5104.97	0.00
9	5106.48	+0.04
11	5107.90	+0.01
13	5109.37	+0.05
15	5110.79	+0.06
17	5112.10	−0.01
19	5113.50	+0.02
21	5114.82	0.00
23	5116.13	+0.01
25	5117.39	+0.05
27	5118.69	−0.03
31	5121.14	−0.07
33	5122.45	+0.03
35	5123.55	−0.05
37	5124.76	−0.01
41	5127.03	−0.01
+43	5128.21	+0.07
−2	5098.01	−0.06
4	5096.45	−0.04
6	5094.84	−0.03
8	5093.22	−0.02
10	5091.58	−0.01
12	5089.94	+0.03
14	5088.26	+0.07
16	5086.58	+0.08
18	5084.79	+0.03
20	5082.99	−0.01
24	5079.35	−0.07
26	5077.55	−0.05
28	5075.74	−0.02
30	5073.93	+0.04
32	5072.02	+0.01
36	5068.13	−0.05
38	5066.20	−0.03
40	5064.29	+0.03
−42	5062.31	+0.04
1.65μ band $C^{12}O_2^{16}$		
+3	6078.26	−0.05
5	6079.81	−0.04
7	6081.37	0.00
9	6082.96	+0.07
11	6084.40	0.00
13	6085.88	−0.01
15	6087.40	+0.03
17	6088.92	+0.08
19	6090.33	+0.03
21	6091.74	0.00
23	6093.19	+0.02
25	6094.56	−0.03
29	6097.35	−0.05
31	6098.77	−0.01
33	6100.11	−0.04
35	6101.56	+0.05
+39	6104.24	+0.05
−2	6074.38	−0.03
4	6072.80	−0.03
6	6071.17	−0.07
8	6069.66	+0.02
10	6068.04	0.00
12	6066.38	−0.03
14	6064.80	+0.02
16	6063.18	+0.04
18	6061.53	+0.04
20	6059.88	+0.04
22	6058.11	−0.05
24	6056.57	+0.09
26	6054.77	−0.02
28	6053.13	+0.04
30	6051.33	−0.04
−32	6049.61	−0.04
1.60μ band $C^{12}O_2^{16}$		
+1	6228.72	+0.05
3	6230.19	0.00
5	6231.67	−0.02
7	6233.14	−0.01
9	6234.58	−0.01
11	6235.98	−0.02
13	6237.38	0.00
15	6238.78	+0.05
17	6240.07	+0.01
19	6241.36	+0.01
21	6242.64	+0.02
23	6243.89	+0.03
25	6245.06	0.00
27	6246.23	−0.01
29	6247.40	0.00
31	6248.49	−0.03
33	6249.59	−0.03
35	6250.68	0.00
37	6251.74	+0.03
39	6252.72	0.00
+41	6253.69	−0.01
−2	6226.35	+0.02
4	6224.72	−0.01
6	6223.06	−0.05
8	6221.43	−0.03
10	6219.77	0.00
12	6218.06	−0.01
14	6216.36	+0.03
16	6214.55	−0.01
18	6212.77	0.00
20	6210.92	−0.02
22	6209.10	+0.01
24	6207.21	0.00
26	6205.33	+0.03
28	6203.36	−0.01
30	6201.44	+0.04
32	6199.44	+0.03
34	6197.40	+0.03
36	6195.33	0.00
38	6193.26	+0.01
40	6191.15	+0.01
42	6188.96	−0.05
1.57μ band $C^{12}O_2^{16}$		
+1	6350.29	−0.04
3	6351.91	+0.05
5	6353.36	+0.01
7	6354.81	0.00
9	6356.23	−0.02
11	6357.64	−0.01
13	6359.02	−0.01
15	6360.39	+0.02
17	6361.69	0.00
19	6362.94	−0.02
21	6364.24	+0.01
23	6365.41	−0.04
25	6366.63	−0.02
27	6367.80	−0.01
29	6368.94	−0.01
31	6370.04	−0.02
33	6371.13	0.00
35	6372.19	+0.01
+37	6373.24	+0.05
−2	6348.08	+0.09
4	6346.47	+0.07
6	6344.78	+0.01
8	6343.08	−0.03
10	6341.40	−0.02
12	6339.71	0.00
14	6337.94	−0.03
16	6336.21	+0.02
18	6334.41	−0.02
20	6332.56	+0.01
22	6330.64	−0.05
24	6328.79	−0.05
26	6326.87	−0.01
28	6324.95	+0.03
30	6322.95	+0.01
32	6320.87	−0.06
34	6318.88	−0.02
36	6316.84	+0.01
38	6314.77	+0.04
40	6312.57	−0.03
42	6310.42	−0.02
44	6308.27	0.00
−46	6306.08	+0.04
1.54μ band $C^{12}O_2^{16}$		
+5	6506.95	+0.08
7	6508.43	+0.05
9	6509.92	+0.05
11	6511.36	+0.01
13	6512.80	0.00
15	6514.20	−0.02
17	6515.65	−0.02
19	6517.05	−0.02
21	6518.49	+0.03
23	6519.89	+0.06
25	6521.21	+0.02
27	6522.53	0.00
29	6523.81	−0.04
31	6525.09	−0.06
33	6526.36	−0.06
35	6527.68	−0.02
37	6528.92	−0.04
41	6531.44	+0.03
+43	6532.68	+0.07
−2	6501.45	−0.02
4	6499.89	+0.02
6	6498.28	+0.01
10	6494.99	−0.03
12	6493.38	+0.01
14	6491.66	−0.04
16	6490.01	0.00
18	6488.33	+0.02

TABLE II.—(*Continued*).

m	ν(obs)	O−C
1.54μ band $C^{12}O_2^{16}$		
20	6486.52	−0.07
22	6484.83	−0.02
24	6483.07	−0.03
28	6479.58	+0.05
30	6477.69	−0.03
34	6474.09	+0.03
36	6472.24	+0.01
38	6470.40	+0.04
−40	6468.51	+0.03
2.08μ band $C^{12}O_2^{16}$		
+3	4809.97	+0.03
4	4810.70	+0.04
6	4812.17	+0.03
8	4813.62	+0.01
9	4814.49	+0.01
11	4815.94	−0.03
12	4816.51	−0.01
13	4817.41	−0.03
14	4817.91	−0.03
16	4819.28	−0.05
17	4820.33	0.00
19	4821.77	+0.02
20	4822.05	−0.01
21	4823.18	+0.02
22	4823.38	−0.01
25	4825.97	+0.03
26	4825.97	−0.02
27	4827.30	0.00
+28	4827.30	+0.04
−2	4806.14	+0.09
4	4804.51	+0.04
5	4803.66	+0.04
6	4802.87	−0.01
7	4802.01	+0.01
8	4801.23	−0.04
9	4800.33	−0.03
10	4799.58	−0.06
11	4798.66	−0.04
12	4797.98	−0.02
15	4795.33	+0.01
16	4794.70	+0.02
17	4793.63	+0.03
18	4793.05	+0.05
19	4791.88	+0.02
20	4791.33	+0.03
21	4790.08	−0.02
22	4789.59	0.00
23	4788.29	−0.02
24	4787.84	−0.03
25	4786.48	−0.03
26	4786.09	−0.04
29	4782.85	+0.01
30	4782.58	−0.03
31	4780.96	−0.02
32	4780.82	−0.01
35	4777.22	+0.03
−36	4777.22	0.00

m	ν(obs)	O−C
2.01μ band $C^{12}O_2^{16}$		
+5	4969.14	−0.04
7	4970.66	0.00
9	4972.08	−0.03
11	4973.49	−0.04
12	4974.13	−0.03
13	4974.91	−0.01
14	4975.50	−0.02
16	4976.82	−0.03
17	4977.66	+0.03
18	4978.17	+0.02
19	4978.97	+0.05
20	4979.45	+0.03
+22	4980.65	0.00
−7	4959.72	0.00
9	4958.07	+0.02
11	4956.36	+0.02
14	4953.81	0.00
16	4952.04	−0.01
18	4950.32	+0.03
20	4948.48	+0.01
22	4946.70	+0.05
23	4945.52	0.00
25	4943.62	+0.01
27	4941.66	−0.03
29	4939.71	−0.02
30	4939.11	0.00
31	4937.74	0.00
32	4937.17	0.00
34	4935.22	+0.01
36	4933.22	−0.01
38	4931.20	−0.03
2.10μ band $C^{13}O_2^{16}$		
+3	4750.40	+0.01
5	4751.94	+0.01
7	4753.45	0.00
9	4754.96	0.00
11	4756.44	−0.02
15	4759.42	−0.02
19	4762.32	−0.02
21	4763.76	−0.02
25	4766.62	0.00
27	4768.01	0.00
29	4769.41	+0.01
31	4770.81	+0.04
35	4773.47	+0.02
+37	4774.76	−0.03
−2	4746.52	+0.02
4	4744.92	0.00
6	4743.33	0.00
8	4741.73	−0.01
10	4740.13	0.00
12	4738.51	0.00
14	4736.87	−0.01

m	ν(obs)	O−C
2.10μ band $C^{13}O_2^{16}$		
20	4731.90	−0.03
22	4730.25	−0.01
−24	4728.60	+0.02
2.05μ band $C^{13}O_2^{16}$		
+3	4889.65	+0.05
5	4891.11	+0.01
7	4892.57	−0.01
9	4894.01	−0.01
11	4895.44	0.00
13	4896.83	0.00
15	4898.20	+0.01
17	4899.52	0.00
19	4900.84	+0.01
21	4902.12	+0.01
23	4903.37	+0.03
25	4904.62	0.00
27	4905.77	−0.01
29	4906.95	0.00
31	4908.09	0.00
33	4909.19	−0.01
+35	4910.33	+0.04
−2	4885.73	−0.01
6	4882.51	−0.01
12	4877.48	0.00
18	4872.18	−0.02
24	4866.66	−0.02
28	4860.88	−0.03
−36	4854.90	+0.02
2.09μ band $C^{12}O^{16}O^{18}$		
+9	4797.65	+0.05
11	4798.95	−0.01
15	4801.65	+0.02
16	4802.25	−0.03
19	4804.26	+0.03
20	4804.84	−0.01
22	4806.08	−0.03
23	4806.69	−0.04
25	4807.93	−0.02
26	4808.56	+0.01
28	4809.76	+0.01
29	4810.33	−0.01
+30	4810.96	+0.04
−3	4788.96	−0.04
5	4787.48	−0.01
8	4785.21	0.00
10	4783.65	0.00
12	4782.09	+0.01
13	4781.30	+0.01
14	4780.51	+0.02

m	ν(obs)	O−C
2.09μ band $C^{12}O^{16}O^{18}$		
15	4779.70	+0.02
17	4778.06	0.00
21	4774.73	−0.02
22	4773.90	−0.02
23	4773.08	+0.01
24	4772.20	−0.02
25	4771.35	−0.02
26	4770.50	−0.01
27	4769.66	+0.02
28	4768.78	0.00
29	4767.91	+0.01
30	4767.02	0.00
−31	4766.15	+0.01
2.04μ band $C^{12}O^{16}O^{18}$		
+4	4907.65	+0.03
5	4908.28	−0.05
6	4909.02	0.00
7	4909.72	+0.01
9	4911.12	+0.05
10	4911.71	−0.03
11	4912.41	+0.01
12	4913.14	+0.08
13	4913.72	+0.01
14	4914.37	+0.01
15	4915.06	+0.09
16	4915.60	−0.03
17	4916.27	+0.01
18	4916.88	0.00
19	4917.49	0.00
21	4918.70	0.00
22	4919.26	−0.04
23	4919.87	−0.02
25	4921.01	−0.04
26	4921.58	−0.04
27	4922.12	−0.07
+31	4924.50	+0.10
−3	4902.53	0.00
4	4901.72	−0.05
6	4900.25	+0.01
8	4898.70	+0.01
9	4897.94	+0.04
10	4897.06	−0.05
11	4896.31	0.00
13	4894.67	−0.01
15	4893.02	−0.01
16	4892.18	0.00
17	4891.33	−0.02
20	4888.83	+0.05
21	4887.86	−0.05
22	4887.03	0.00
23	4886.18	+0.04
−26	4883.44	0.00

and m_X and m_Y are the masses of the atoms X and Y, respectively. The superscript (i) denotes the isotope atom, in this case C^{13}. For $m_X=12$, $m_Y=16$ and $m_X^{(i)}=13$, $f=0.97154$. The potential constants were then altered as follows:

$$\begin{array}{lll} \omega_1^{(i)}=\omega_1 & x_{11}^{(i)}=x_{11} & x_{12}^{(i)}=fx_{12} \\ \omega_2^{(i)}=f\omega_2 & x_{22}^{(i)}=f^2x_{22} & x_{13}^{(i)}=fx_{13} \\ \omega_3^{(i)}=f\omega_3 & x_{33}^{(i)}=f^2x_{33} & x_{23}^{(i)}=f^2x_{23}. \\ & b^{(i)}=f^{\frac{2}{3}}b & \end{array} \tag{5}$$

Similarly, for the linear symmetrical molecule XY_2, in which one of the Y atoms is replaced by $Y^{(i)}$, we have

$$f_1=1-\frac{\Delta m_Y}{4(m_Y+\Delta m_Y)};$$

$$f_2=f_3=1-\frac{m_X}{2(m_X+2m_Y)}\times\frac{\Delta m_Y}{(m_Y+\Delta m_Y)}. \tag{6}$$

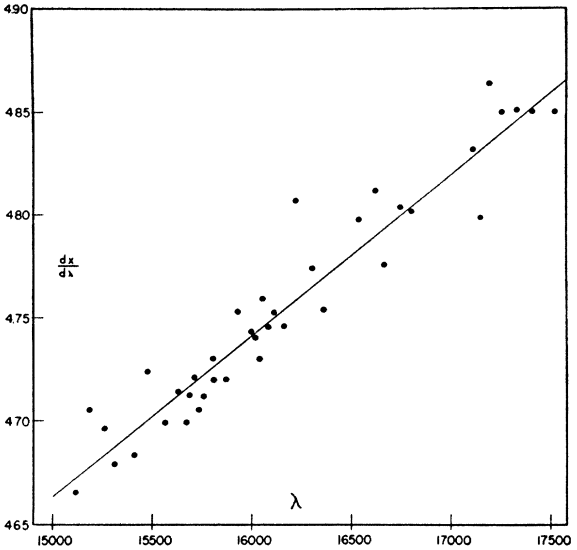

FIG. 6. Variation of dispersion with wave-length on solar tracings in the 1.6μ region. The dots represent individual measurements and the straight line has been determined by least squares.

Equations (6) are valid if the mass difference $\Delta m_Y = m_Y^{(i)} - m_Y$ is small compared with m_Y. For $C^{12}O^{16}O^{18}$ we obtain $f_1 = 0.97222$, and $f_2 = f_3 = 0.99242$. The modified potential constants were then obtained by multiplying ω_1, ω_2, and ω_3 by f_1, f_2, and f_3, respectively; x_{11}, x_{22}, and x_{33} by f_1^2, f_2^2, and f_3^2, respectively; x_{12}, x_{13}, and x_{23} by f_1f_2, f_1f_3 and f_2f_3, and b by $(f_1f_2f_3)^{\frac{1}{3}}$.

The solution of the determinant (3), carried out with the aid of the approximate potential constants for $C^{13}O_2^{16}$ and $C^{12}O^{16}O^{18}$, leads to the values of the band centers in column three of Table I. As a check on the method of calculation, the centers of the 2μ bands of $C^{12}O_2^{16}$ were also computed, the results agreeing exactly with those obtained originally by Adel and Dennison.

Since the ω_1 band is easily the most intense of the 2μ triad, its isotope companions have the highest probability of appearing in the solar spectrum. The calculated centers are, for $C^{13}O_2^{16}$, 4892.1 cm^{-1}, and for $C^{12}O^{16}O^{18}$, 4909.4. As shown in Fig. 2, weak bands are found at 4888.84 cm^{-1} and at 4904.75 cm^{-1}. The negative branch of the $C^{13}O_2^{16}$ band falls on the positive branch of the relatively strong ω_1 band, although several individual components of the former may be recognized. The negative branch of the $C^{12}O^{16}O^{18}$ band is also blended with the positive branch of the neighboring band of $C^{13}O_2^{16}$. It is interesting to note that the lines of the $C^{12}O^{16}O^{18}$ band have approximately one-half the spacing of those of ω_1, whereas the spacing of the $C^{13}O_2^{16}$ band is practically identical with that of ω_1. These facts are precisely in accordance with theory. Because of the identity of the oxygen atoms in ordinary CO_2, and also because the spin of the oxygen nucleus is zero, alternate rotational lines (those arising from antisymmetric levels) are absent. Conversely, since the $C^{12}O^{16}O^{18}$ molecule is not symmetrical, every rotational line appears.

The weakest isotope bands are those corresponding to ω_2, the calculated positions being 4737.8 cm^{-1} for $C^{13}O_2^{16}$ and 4797.5 cm^{-1} for $C^{12}O^{16}O^{18}$. The observed centers are 4748.06 cm^{-1} and 4791.22 cm^{-1}, respectively. Although the discrepancy between the observed and the calculated centers for the $C^{13}O_2^{16}$ band is 10 cm^{-1}, its intensity and spacing render the identification quite conclusive. The C^{13} isotope band corresponding to ω_0 falls in the middle of the positive branch of ω_1 and is not observed. Portions of the O^{18} companion to ω_0 are visible on low sun tracings in the region between ω_0

TABLE III. Determination of wave-length scale.

λ(obs)	$dx/d\lambda$	O−C	λ(obs)	$dx/d\lambda$	O−C
15073.39		+0.17	16126.12		−0.06
	4.665			4.746	
15151.56		+0.19	16195.34		+0.14
	4.705			4.807	
15207.50		−0.20	16241.79		−0.32
15230.50		+0.06	16284.87		−0.04
	4.696			4.774	
15283.37		−0.17	16316.33		−0.07
	4.679			4.754	
15335.45		−0.03	16404.76		+0.13
	4.691				
15376.97		+0.02	16435.22		+0.02
	4.683			4.778	
15438.62		+0.18	16505.12		+0.05
	4.724			4.798	
15501.30		−0.02	16561.85		−0.12
15531.89		+0.02	16589.75		+0.17
	4.699			4.812	
15591.61		+0.08	16645.96		−0.04
	4.714			4.776	
15661.97		−0.01	16681.05		+0.05
	4.699				
15677.57		−0.05	16719.18		+0.02
	4.712			4.804	
15695.80		0.00	16771.44		−0.17
	4.721			4.802	
15719.12		−0.04	16835.75		0.00
	4.705				
15736.08		+0.04	16890.24		+0.06
	4.712				
15769.42		0.00	17081.40		+0.08
	4.730			4.832	
15789.06		+0.03	17138.41		−0.01
	4.720			4.799	
15822.98		+0.04	17156.56		+0.14
				4.864	
15837.78		+0.04	17225.62		−0.06
	4.720			4.850	
15888.67		+0.18	17284.42		−0.18
	4.753				
15960.05		0.00	17302.23		+0.08
				4.851	
15980.88		0.00	17362.16		+0.01
	4.743			4.851	
16002.26		−0.07	17439.84		0.00
	4.741				
16024.45		−0.01	17470.48		−0.04
	4.730			4.850	
16046.48		−0.02	17564.09		0.00
	4.759				
16056.44		−0.03			
	4.746				
16100.98		−0.02			
	4.753				
16126.12		−0.06			

and ω_1, but at long atmospheric paths this region also becomes filled with lines of water vapor.

The Excited-State Bands

Evidence has already been given[9] for the identification of the 2.08μ band as one of the triad of bands originating from the excited vibrational level 01_10 and terminating in the three upper levels $\left\{\begin{matrix} 2 & 1_1 & 1 \\ 1 & 3_1 & 1 \\ 0 & 5_1 & 1 \end{matrix}\right\}$. The calculated center of the band is 4805.6 cm^{-1}, the observed value 4807.60 cm^{-1}. The calculated centers of the remaining two bands of the triad, at 4970.5 cm^{-1} and at 5131.6 cm^{-1}, fall within the strong bands ω_0 and ω_1. Numerous individual lines nevertheless appear to be present and to show the expected doublet pattern. Enough lines of the former band occur to permit a determination of the band center with the aid of the value of B_{010} derived from the 4807.60 cm^{-1} band. The resulting "observed" value is 4965.36 cm^{-1}, in good agreement with theory. It is interesting to note that as predicted by theory, all values of J, both even and odd, occur in the difference bands, in contrast to the ground state bands, where lines arising from levels of even J only are found.

V. EVALUATION OF ROTATIONAL CONSTANTS

The moment of inertia of a polyatomic molecule in any given vibrational energy state may be calculated from well-known formulas in terms of the equilibrium moment of inertia and of n rotational constants, where n is the number of normal vibrational frequencies of the molecule. For CO_2, the rotational constants have been evaluated by Dennison[6] from a discussion of four infra-red bands observed in the laboratory and of three bands observed in the Venus spectrum. New values of the constants were later obtained by Herzberg[10] from a re-discussion of the same observations. It is believed that the new data given in Table II are sufficiently accurate to warrant a re-determination of the rotational constants.

TABLE IV. Constants of least squares solutions.

Band	ν_0	a	b	c
		$C^{19}O_2^{16}$		
2.06μ	4853.48	0.77926	−0.00209	-6.2×10^{-7}
2.01μ	4977.78	0.77722	−0.00371	-7.5×10^{-7}
1.96μ	5099.64	0.77905	−0.00267	-7.8×10^{-7}
1.65μ	6075.98	0.78065	−0.00138	-2.2×10^{-6}
1.60μ	6227.90	0.77614	−0.00357	-1.8×10^{-7}
1.57μ	6349.56	0.77640	−0.00371	-4.1×10^{-7}
1.54μ	6503.08	0.77963	−0.00212	-3.6×10^{-7}
2.08μ J even	4807.62	0.77920	−0.00184	-4.0×10^{-7}
J odd	4807.57	0.77737	−0.00262	-1.0×10^{-6}
2.01μ J even	4965.37	0.78000	−0.00338	-6.9×10^{-7}
J odd	4965.35	0.77870	−0.00371	-3.2×10^{-7}
		$C^{13}O_2^{16}$		
2.10μ	4748.06	0.77980	−0.00142	-2.0×10^{-7}
2.05μ	4887.30	0.77716	−0.00344	-3.5×10^{-6}
		$C^{12}O^{16}O^{18}$		
2.09μ	4791.22	0.73140	−0.00249	-3.8×10^{-6}
2.04μ	4904.75	0.73128	−0.00324	-4.3×10^{-6}

Ground-State Bands

We shall discuss first the analysis of the seven bands that arise from the ground vibrational state of $C^{12}O_2^{16}$. These bands result from transitions of type $\sum_g{}^+ - \sum_u{}^+$ and consequently only those lines occur that originate from lower rotational levels of even J. The wave numbers of the lines in a vibration-rotation band may be represented by the well-known formula:

$$\nu = \nu_0 + am + bm^2 + cm^3, \tag{7}$$

where, for the CO_2 bands under consideration, $m=1$, 3, 5,$\cdots$ for the lines of the positive branch, and $m=-2$, -4, -6,$\cdots$ for those of the negative branch. In Eq. (7), ν_0 is the band center in cm^{-1}, $a=B'+B''$, $b=B'-B''$, and $c=-2(D'+D'')$. The constant $B=h/8\pi^2Ic$, where I is the moment of inertia for the given vibrational state, the single and double primes referring to the upper and lower vibrational states, respectively. The quantity D measures the centrifugal stretching of the molecule.

The constants of Eq. (7) may be determined for each band from the observed wave numbers by the method of combination differences, or by least squares. The latter method was followed in the present investigation, the values of the constants being given in Table IV. The wave numbers calculated from Eq. (7) with these constants yielded the O−C residuals in column four of Table II. From the relations $a+b=2B'$ and $a-b=2B''$, the B-values appropriate to the various vibrational levels were calculated and appear in the third and fifth columns of Table V. For the seven bands originating from the ground state, the values of B'' should in theory be identical. The total spread found is 0.0009 cm^{-1}, which is not surprising in view of uncertainties in the wave-length scales and of the blending

TABLE V. Observed and calculated convergences of CO_2 bands.

Band		Transition		B''(obs)	B''(calc)	B'(obs)	B'(calc)
			$C^{12}O_2^{16}$				
2.06μ			$0\ 4_0\ 1$	0.39068	0.39055	0.38858	0.38852
2.01μ		$0\ 0_0\ 0-$	$1\ 2_0\ 1$	0.39046	0.39055	0.38676	0.38693
1.96μ			$2\ 0_0\ 1$	0.39086	0.39055	0.38819	0.38775
1.65μ			$0\ 6_0\ 1$	0.39102	0.39055	0.38964	0.38931
1.60μ		$0\ 0_0\ 0-$	$1\ 4_0\ 1$	0.38986	0.39055	0.38628	0.38723
1.57μ			$2\ 2_0\ 1$	0.39006	0.39055	0.38634	0.38679
1.54μ			$3\ 0_0\ 1$	0.39088	0.39055	0.38876	0.38809
	(J'' even)			0.39052		0.38868	
2.08μ			$0\ 5_1\ 1$		0.39118		
	(J'' odd)			0.39000		0.38738	
	(J'' even)			0.39169		0.38830	
2.01μ		$0\ 1_1\ 0-$	$1\ 3_1\ 1$		0.39118		
	(J'' odd)			0.39120		0.38750	
—			$2\ 1_1\ 1$	—		—	
			$C^{13}O_2^{16}$				
2.10μ			$0\ 4_0\ 1$	0.39061	—	0.38919	
2.05μ		$0\ 0_0\ 0-$	$1\ 2_0\ 1$	0.39030	—	0.38686	
—			$2\ 0_0\ 1$	—		—	
			$C^{12}O^{16}O^{18}$				
2.09μ			$0\ 4_0\ 1$	0.36694		0.36446	
2.04μ		$0\ 0_0\ 0-$	$1\ 2_0\ 1$	0.36728		0.36400	
—			$2\ 0_0\ 1$	—		—	

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[9] Mohler, McMath, and Goldberg, Phys. Rev. **75**, 520 (1949).

[10] See reference 8, p. 395.

TABLE VI. Squares of the coefficients of CO_2 zero-order wave functions.

i	a_i^2	b_i^2	c_i^2	d_i^2
1	0.4506	0.4399	0.1095	
2	0.3098	0.0260	0.6642	
3	0.2351	0.5352	0.2297	
4	0.3587	0.4394	0.1792	0.0227
5	0.2990	0.0002	0.3309	0.3699
6	0.2159	0.1361	0.1143	0.5337
7	0.1264	0.4243	0.3756	0.0737

of the 1.6μ bands with solar and telluric lines. It is to be noted that the agreement among the B''-values is considerably better for the 2μ bands, which were measured in the laboratory.

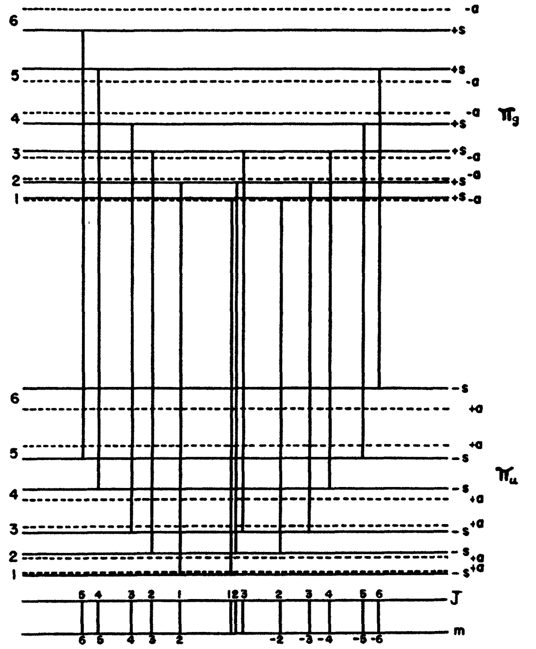

FIG. 7. Schematic energy level diagram and band pattern for Π_u–Π_g transition in CO_2.

The data of Table V may now be employed for the evaluation of the rotational constants of CO_2 and of the equilibrium moment of inertia. Let n_1, n_2, and n_3 be the vibrational quantum numbers of a particular CO_2 state. Then the convergence of the rotational levels is given by[6]

$$B_{n_1n_2n_3}=B_e[1+\alpha_1(n_1+\tfrac{1}{2})+\alpha_2(n_2+1)+\alpha_3(n_3+\tfrac{1}{2})] \quad (8)$$

where B_e refers to the equilibrium position of the molecule and the constants α give the interaction between vibration and rotation. Equation (8) is valid only in the absence of Fermi resonance. For a group of n levels in resonance interaction, the following expressions may be written for the individual levels.[6] Let $B_1{}^0$, $B_2{}^0\cdots B_n{}^0$ be the appropriate values of B in the absence of resonance, as given by Eq. (8). Also, let B_1, $B_2\cdots B_n$ be the actual B values. Then

$$\begin{aligned} B_1&=a_1{}^2B_1{}^0+b_1{}^2B_2{}^0+\cdots \\ B_2&=a_2{}^2B_1{}^0+b_2{}^2B_2{}^0+\cdots \\ &\cdot \quad \cdot \quad \cdot \\ &\cdot \quad \cdot \quad \cdot \\ B_n&=a_n{}^2B_1{}^0+b_n{}^2B_2{}^0+\cdots, \end{aligned} \quad (9)$$

where each summation is carried out over all n levels. The coefficients a, b, c,$\cdots$ are defined as follows. If $\Psi_1{}^0$, $\Psi_2{}^0$,$\cdots$ are the wave functions of the respective unperturbed states, the true wave function for state i is

$$\Psi_i=a_i\Psi_1{}^0+b_i\Psi_2{}^0+\cdots, \quad (10)$$

where the sum of the squares of the coefficients is unity. The coefficients may be determined from the minors of the secular energy determinant, which for the triad of resonating levels

$$\left\{\begin{matrix} 2 & 0_0 & 1 \\ 1 & 2_0 & 1 \\ 0 & 4_0 & 1 \end{matrix}\right\} \quad (11)$$

is given by Eq. (3). A similar determinant may be written for the four resonating levels,

$$\left\{\begin{matrix} 0 & 6_0 & 1 \\ 1 & 4_0 & 1 \\ 2 & 2_0 & 1 \\ 3 & 0_0 & 1 \end{matrix}\right\} \quad (12)$$

that are responsible for the 1.6μ bands. The squares of the coefficients for both sets of resonating levels are given in Table VI, where the index i is 1, 2, and 3 for the triad of levels (11) and 4, 5, 6 and 7 for the quartet of levels (12).

The observed convergences $B'-B''$ of the 1.6μ and 2μ bands are given in the fourth column of Table IV. The theoretical values of $B'-B''$ may be obtained in terms of B_e and the rotational constants from Eqs. (8) and (9). Equating the theoretical and observed convergences and inserting the numerical values of the coefficients of Eq. (9), we obtain an equation for each of the seven bands as follows:

2μ bands

$$B_e(0.6589\alpha_1+2.6822\alpha_2+\alpha_3)=-0.002093; \quad (13)$$
$$B_e(1.3544\alpha_1+1.2912\alpha_2+\alpha_3)=-0.003708; \quad (14)$$
$$B_e(0.9946\alpha_1+2.0108\alpha_2+\alpha_3)=-0.002649; \quad (15)$$

1.6μ bands

$$B_e(0.8659\alpha_1+4.2228\alpha_2+\alpha_3)=-0.001383; \quad (16)$$
$$B_e(1.7717\alpha_1+2.4566\alpha_2+\alpha_3)=-0.003573; \quad (17)$$
$$B_e(1.9658\alpha_1+2.0684\alpha_2+\alpha_3)=-0.003706; \quad (18)$$
$$B_e(1.3966\alpha_1+3.2068\alpha_2+\alpha_3)=-0.002116. \quad (19)$$

Solution of the foregoing equations by least squares gave $B_e\alpha_1=-0.00103$; $B_e\alpha_2=+0.00064$; $B_e\alpha_3=-0.00306$.

In similar fashion, Eqs. (8) and (9) may be employed in obtaining formulas for the average line spacing $B'+B''$, for which the observed values appear in the third column of Table IV. Substitution of the previously calculated $B_e\alpha$ in these formulas yields seven independent determinations of B_e as follows:

Band	B_e	Band	B_e
1.54μ	0.3924	1.96μ	0.3924
1.57μ	0.3915	2.01μ	0.3918
1.60μ	0.3911	2.06μ	0.3921
1.64μ	0.3924	Mean =	0.3920

Finally, the derived values of B_e and α have been employed to obtain the calculated values of B'' and B' in the fourth and sixth columns of Table V. The value $B_e = 0.3920$ yields for the equilibrium moment of inertia $I_e = 71.35 \times 10^{-40}$ g cm², where we have taken $h = 6.624 \times 10^{-27}$ erg sec.

The rotational constants obtained here differ somewhat from those appearing in the literature, as is shown in Table VII. We understand from a private communication, however, that Professor Herzberg has recently secured new results from a study of the photographic infra-red bands of CO_2 which agree more closely with those of this paper. In particular, he obtains $B_{000} = 0.39037$.

Difference Bands

The difference bands originating from the lower level 01_10 are of the type $\Pi_u - \Pi_g$.[11] A schematic energy level diagram for this transition is shown in Fig. 7. Each J-level is split into two sub-levels, the separation $\Delta\nu$ increasing with J according to

$$\Delta\nu = qJ(J+1) \tag{20}$$

where q is a constant. The symmetric levels are represented by solid and the antisymmetric levels by dotted lines. In CO_2 only the symmetric levels are populated. It will be noted that in the Π_u state the lower sub-levels of odd J and the upper sub-levels of even J are symmetric, whereas the converse is true for Π_g. The resulting band will therefore consist of two series of lines, originating, respectively, from lower levels of even and odd J, and characterized by slightly different values of B' and B''. Thus

$$\nu(J_{\text{even}}) = \nu_0 + (B'+B'')_{\text{even}} m + (B'-B'')_{\text{even}} m^2 \tag{21}$$
$$m = +1, +3, +5, \cdots$$
$$-2, -4, -6, \cdots$$

$$\nu(J_{\text{odd}}) = \nu_0 + (B'+B'')_{\text{odd}} m + (B'-B'')_{\text{odd}} m^2 \tag{22}$$
$$m = +2, +4, +6, \cdots \quad -1, -3, -5.$$

Also,

$$B_{\text{even}} - B_{\text{odd}} = q. \tag{23}$$

The constants of Eqs. (21) and (22) were determined by least squares from the wave numbers of the bands observed at 2.01μ and 2.08μ, with the results given in Tables IV and V. Two independent values of q for the ground state may now be obtained by application of Eq. (23). From the 2.01μ band we find $q = 0.00049$ cm⁻¹ and from the 2.08μ band $q = 0.00052$ cm⁻¹, which is to be compared with Herzberg's[10] determination, from other infra-red bands, of $q = 0.00034$ cm⁻¹. Similarly, for the two upper sets of levels, we get $q = 0.00080$ cm⁻¹ and 0.00130 cm⁻¹.

TABLE VII. Rotational constants of CO_2.

	Lake Angelus	Dennison	Herzberg
B_e	0.3920	0.3925	0.3906
B_{000}	0.3906	0.3911	0.3895
$B_e\alpha_1$	−0.00103	−0.00058	−0.00056
$B_e\alpha_2$	+0.000640	+0.00045	+0.00062
$B_e\alpha_3$	−0.00306	−0.00307	−0.0029

The accuracy of the foregoing results is perhaps questionable, in view of the fact that the values of B_{010} derived from the 2.01μ and 2.08μ bands should be identical, whereas actually they differ by about 0.0011 cm⁻¹. The discrepancy is not surprising because relatively few lines in each band are free from blending with other lines of CO_2 or of H_2O. We would nevertheless expect higher accuracy for the determination of q than for the individual values of B.

It is interesting to compare the observed values of B_{010} with the value calculated from Eq. (8). The computed value, $B_{010} = 0.3913$, is to be compared with the mean of the two values determined from each band, *viz.*, 0.3914 for the 2.01μ band and 0.3903 for the 2.08μ band. Further analysis of the Π–Π bands in the laboratory would be highly desirable, especially if the measurements are carried out with a heated sample, and in the absence of water vapor.

Isotope Bands

Four bands arising from isotopes of CO_2 are suitable for analysis, the 2.05μ and 2.10μ bands of $C^{13}O_2^{16}$ and the 2.04μ and 2.09μ bands of $C^{12}O^{16}O^{18}$. All four bands suffer from overlapping by neighboring telluric bands. One result of the blending is to render uncertain the assignment of quantum numbers to the lines of the $C^{12}O^{16}O^{18}$ bands, for which the gap across the band center is twice the mean line spacing, rather than $\frac{3}{2}$ as in the case of symmetrical CO_2. The assignments for the 2.09μ band of $C^{12}O^{16}O^{18}$ are based on the relative line intensities near the apparent band origin. For the 2.04μ band of $C^{12}O^{16}O^{18}$, the center was located with the aid of the value of B_{000} determined from the 2.09μ band.

The B values corresponding to the four isotope bands are given in Table V. The close agreement between the values found for $C^{13}O_2^{16}$ and for $C^{12}O_2^{16}$ is to be expected, since the carbon atom is at the center of mass of the molecule. On the other hand, an elementary calculation indicates that the equilibrium moment of inertia for $C^{12}O^{16}O^{18}$ should be greater than that for $C^{12}O_2^{16}$ by a factor of 1.0605. Assuming that the same ratio holds for the zero vibrational state and adopting $B_{000} = 0.3906$ for $C^{12}O_2^{16}$, we obtain a corresponding value of 0.3683

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[11] See reference 8, p. 389.

for $C^{12}O^{16}O^{18}$, in good agreement with the experimental value 0.3670.

ACKNOWLEDGMENTS

The authors wish to express their thanks to those who have contributed to the success of the above investigation. Dr. D. M. Dennison, of the University of Michigan, has given generously of his advice, while Dr. Frederick H. Seares, of the Mount Wilson Observatory has read the manuscript and made valuable editorial suggestions. Mr. John T. Brodie made many of the observations and Mr. Russel E. Donovan carried out the bulk of the measurement and reduction of the tracings. Finally, the investigation could not have been accomplished without the generous financial assistance of McGregor Fund of Detroit.

PHYSICAL REVIEW VOLUME 76, NUMBER 12 DECEMBER 15, 1949

A Comparison of the *g* Value of the Electron in Hydrogen with That in Deuterium

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(Received August 24, 1949)

The g value of the electron in the ${}^2S_{\frac{1}{2}}$ state of H has been compared with the g value of the electron in the corresponding state of D by the atomic beam magnetic resonance method. The frequencies, f_H, of the transition $(1, 0 \leftrightarrow 1, -1)$ in H, and f_D, of the transition $(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{3}{2}, -\frac{3}{2})$ in D were observed in the same magnetic field and the ratio $(g_J)_H/(g_J)_D$ was computed from the Breit-Rabi formula. The principal uncertainty is caused by the drift of the magnetic field. The average of 36 observations in 4 runs in which f_H and f_D were measured alternately is $(g_J)_H/(g_J)_D = 1.000004 \pm 0.000025$. The average of 3 runs in which the two resonances were observed simultaneously is $(g_J)_H/(g_J)_D = 0.999991 \pm 0.000010$. The uncertainty indicated in each result is the mean deviation of the residuals. We conclude that the g value of the electron when bound to the proton differs from that when bound to the deuteron by less than 0.001 percent.

INTRODUCTION

THIS experiment has as its purpose a comparison of the moment of the electron in the ground state of hydrogen with its moment in the ground state of deuterium.[1] In view of the deviations from the straightforward Dirac theory which occur in the hyperfine structure of the ground state and shift of the $2S$ level in hydrogen, and of the difference of about one part in 4000 between the reduced masses of the electron in H and D, it was considered of interest to measure the ratio of the moments.[2–4] The experiment was performed by measuring the frequency of atomic transitions in a magnetic field large enough to insure a large measure of decoupling of the electron spin from the nuclear spin. The transitions chosen were those amounting essentially to a reorientation of the electron in the external field. The atomic beam magnetic resonance method was used to detect these transitions. Since the magnetic field has not been measured with sufficient accuracy this method suffices only to measure the ratio of the moments and could detect an effect only if it were not common to the two atoms. Absolute values of the moments are not measured in this experiment.

GENERAL DISCUSSION

The ground state of an atom is split into a number of magnetic levels by the combined influence of an external magnetic field and the magnetic interaction between the nuclear spin I and the total electronic angular momentum J. In this experiment the transitions $(1, 0 \leftrightarrow 1, -1)$ in H and $(\frac{3}{2}, -\frac{1}{2} \leftrightarrow \frac{3}{2}, -\frac{3}{2})$ in D have been studied. The quantum numbers (F, m) refer to the low field designation of the states. The field dependence of these transitions is found from the Breit-Rabi[5] formula. The frequencies of the transitions are

$$f_H = \frac{\nu_H}{2}\left[(1+X_H)^{\frac{1}{2}} - (1-X_H) + 2\left(\frac{g_I}{g_J - g_I}\right)X_H\right], \qquad (1)$$

$$f_D = \frac{\nu_D}{2}\left[(1-\tfrac{2}{3}X_D + X_D{}^2)^{\frac{1}{2}} - (1-X_D) + 2\left(\frac{g_I}{g_J - g_I}\right)X_D\right], \qquad (2)$$

where ν_H (or ν_D) is the h.f.s. separation for H (or D) in absolute frequency units. The parameter X, which is proportional to the magnetic field intensity, is given by

$$X = (g_J - g_I)\mu_0 H/\Delta W. \qquad (3)$$

In Eqs. (1)–(3) g_J is the g value of the electron in the ${}^2S_{\frac{1}{2}}$ state, g_I is the g value of the nucleus, ΔW is the

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