Resolution of the Two Difference Bands of CO$_2$ Near 10μ

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The rotational structure of two absorption bands of CO$_2$ at 9.4μ and 10.4μ has been completely resolved. Both bands have positive and negative branches, but no zero branches. They correspond to transitions up to the state ν_3 from the double state (ν_1, $2\nu_2$), and yield the value 102.8 cm^{-1} for the separation of the two levels. From the intensity distribution of the lines it is clear that J must have only even values in the normal molecule. The line separations and convergences provide a very precise value for the moment of inertia, namely 70.6$\times$10^{-40} gram cm^2. The numerical agreement with predictions from formulae based upon previous measurements with other bands is very satisfactory.

THE form and dimensions of the CO$_2$ molecule are already well known as a result of observations upon infrared absorption bands and Raman spectra. Symmetry and linearity are assured by the vibrational selection rules, and by the character of the rotational fine structure,[1, 2, 3, 4] the latter yielding also the moment of inertia and the interatomic distances. The mechanics of the system, including anharmonic perturbations, rotational and vibrational interactions, and resonance degeneracy has also been very completely treated.[5, 6] The observations here recorded fit precisely into this scheme, providing a check upon its quantitative aspect which is very gratifying. They also yield further information regarding one of the anharmonic constants, and a very precise value for the moment of inertia.

The two absorption bands near 10μ were first observed by Schaefer and Philipps[7] with a one-meter cell containing CO$_2$ at a pressure of 8 atmospheres. They were observed as doublets, and their mean positions were recorded as 9.42μ and 10.42μ. We have examined them with a grating having 2400 lines per inch, using slits only 0.5 cm^{-1} in width, thus obtaining ample resolution for the separation of the rotation lines. The band centers so determined lie at 961.03

cm^{-1} (10.41μ) and 1063.87 cm^{-1} (9.40μ). The absorption cell was a seven meter tube 20 cm in diameter, with windows of thin lacquer films. It was filled by displacement, the concentration of CO$_2$ being about 80 percent.

The bands are shown graphically in Fig. 1, and the measured positions of the individual lines appear in Tables I and II. The ordinal number N is the initial value of J in the negative branch and the final value in the positive branch, i.e., the larger J in each case. The line frequencies are well represented by the equations

$$\nu = 961.03 \pm 0.7765N - 0.00311N^2 \qquad (1)$$
and
$$\nu = 1063.87 \pm 0.7765N - 0.00335N^2 \qquad (2)$$

from which the computed values shown in the tables were obtained. The mean of all residuals is less than 0.04 cm^{-1}. The conditions of observation for these bands are advantageous, not only on account of the high resolution available, but because this region is quite free from atmospheric absorption, and the bands are themselves fairly weak, without complications due to superposition of close neighbors as was the case at 15μ(ν_2).

The two bands arise from absorption by molecules already excited to the double state (ν_1, $2\nu_2$). The initial levels each have a population of about 0.15 percent at room temperature, and their term values are 1285.8 and 1388.4 cm^{-1} respectively. The final state is ν_3, at 2350.1 cm^{-1}. These are the first difference bands to be subjected to high resolution in the infrared. Since the quantum number l is zero both in the

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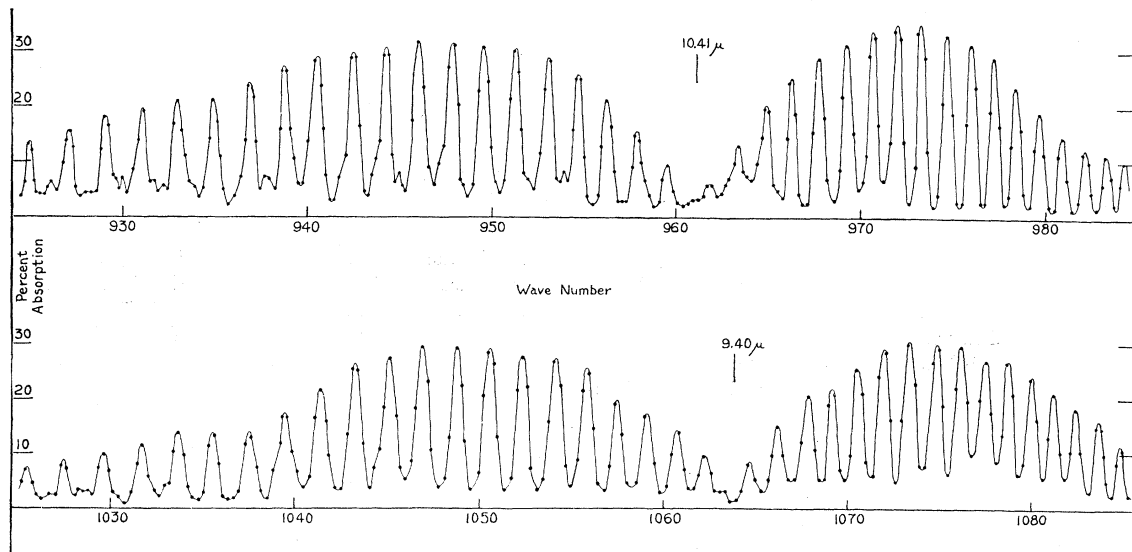[2] Martin and Barker, Phys. Rev. 41, 291 (1932).
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[7] Schaefer and Philipps, Zeits. f. Physik 36, 641 (1926).

FIG. 1. The CO_2 absorption bands $\nu_3 - (\nu_1, 2\nu_2)$.

TABLE I. *The band at 10.41μ.*

	Positive Branch				Negative Branch		
N	ν comp.	ν obs.	dif.	N	ν comp.	ν obs.	dif.
1	961.80	961.76	+0.04	2	959.47	959.43	+0.04
3	963.33	963.33	0	4	957.88	957.79	+0.09
5	964.83	964.87	−0.04	6	956.26	956.20	+0.06
7	966.31	966.34	−0.03	8	954.63	954.61	+0.02
9	967.76	967.78	−0.02	10	952.96	953.03	−0.07
11	969.20	969.24	−0.04	12	951.26	951.25	+0.01
13	970.60	970.68	−0.08	14	949.55	949.53	+0.02
15	971.98	972.00	−0.02	16	947.81	947.85	−0.04
17	973.34	973.30	+0.04	18	946.04	946.06	−0.02
19	974.66	974.68	−0.02	20	944.26	944.28	−0.02
21	975.97	975.98	−0.01	22	942.45	942.47	−0.02
23	977.24	977.20	+0.04	24	940.61	940.56	+0.05
25	978.50	978.43	+0.07	26	938.74	938.76	−0.02
27	979.72	979.71	+0.01	28	936.86	936.90	−0.04
29	980.92	980.93	−0.01	30	934.93	934.94	−0.01
31	982.12	982.12	0	32	932.99	932.98	+0.01
33	983.28	983.30	−0.02	34	931.01	931.04	−0.03
35	984.41	984.39	+0.02	36	929.04	929.07	−0.03
				38	927.02	927.10	−0.08

TABLE II. *The band at 9.40μ.*

	Positive Branch				Negative Branch		
N	ν comp.	ν obs.	dif.	N	ν comp.	ν obs.	dif.
1	1064.65	1064.70	−0.05	2	1062.30	1062.23	+0.07
3	1066.20	1066.17	+0.03	4	1060.71	1060.61	+0.10
5	1067.67	1067.81	−0.14	6	1059.09	1059.03	+0.06
7	1069.14	1069.14	0	8	1057.45	1057.46	−0.01
9	1070.59	1070.55	+0.04	10	1055.77	1055.79	−0.02
11	1072.01	1071.92	+0.09	12	1054.07	1054.15	−0.08
13	1073.41	1073.32	+0.09	14	1052.34	1052.31	+0.03
15	1074.76	1074.77	−0.01	16	1050.59	1050.58	+0.01
17	1076.11	1076.11	0	18	1048.61	1048.76	−0.15
19	1077.41	1077.38	+0.03	20	1047.00	1046.99	+0.01
21	1078.70	1078.69	+0.01	22	1045.16	1045.18	−0.02
23	1079.95	1079.95	0	24	1043.24	1043.28	−0.04
25	1081.19	1081.16	+0.03	26	1041.41	1041.39	+0.02
27	1082.39	1082.37	+0.02	28	1039.51	1039.50	+0.01
29	1083.57	1083.54	+0.03	30	1037.56	1037.57	−0.01
31	1084.72	1084.81	−0.09	32	1035.55	1035.54	+0.01
				34	1033.70	1033.60	+0.10
				36	1031.68	1031.57	+0.11
				38	1029.62	1029.63	−0.01
				40	1027.55	1027.47	+0.08
				42	1025.45	1025.50	−0.05
				44	1023.32	1023.31	+0.01
				46	1021.18	1021.34	−0.16

initial and final levels there are no zero branches, and it is possible to observe the central portion of the pattern, which is completely obscured in the 15μ band. The intensity distribution here makes it perfectly clear that the rotation states have been properly numbered, i.e., that in the upper state $(V_3 = 1)$ the values of J are all odd. They are consequently all even in the unexcited molecule, as determined previously but not so directly.[2]

The interaction between rotation and vibration in the CO_2 molecule has two important consequences. Firstly, it alters the major fine structure interval of the rotation-vibration bands from $h/4\pi^2 Ic$ to

$$(h/4\pi^2 Ic)[1 + \tfrac{1}{2}\{A + 2B + C + \sum_i C^2_{\tau t_i}(AV_1 + BV_2 + CV_3)_i - \sum_j C^2_{\sigma s_j}(AV_1 + BV_2 + CV_3)_j\}],$$

where the $C_{\tau t_i}$ and $C_{\sigma s_j}$ are respectively the coefficients in the stabilized wave functions of the upper and lower vibrational levels involved in the transition.

$$A = (0.00175 + 0.000112a), \quad B = (-0.00117 + 0.0000037b), \quad C = (-0.00033 + 0.000019c),$$

where $a = -36.2$, $b = 72.9$, and $c = -202.1$ cm^{-1} are the coefficients of the cubic anharmonic potential of vibration. The moment of inertia, I, may be computed by equating this expression to the observed fine structure interval. Corresponding to the bands at 1063.87 and 961.03 cm^{-1} we obtain the equations

$$(h/4\pi^2 Ic)[1 + \tfrac{1}{2}\{1.43A + 3.14B + 2C\}] = 0.7765 \text{ cm}^{-1},$$

$$(h/4\pi^2 Ic)[1 + \tfrac{1}{2}\{1.57A + 2.86B + 2C\}] = 0.7765 \text{ cm}^{-1}.$$

Both relations yield the value $I = 70.6 \times 10^{-40}$ gram cm^2.

Secondly, the interaction between rotation and vibration produces a convergence of the fine structure depending upon the square of the ordinal number of the line and given by

$$(h/8\pi^2 Ic)\{\sum_i C^2_{\tau t_i}(AV_1 + BV_2 + CV_3)_i - \sum_j C^2_{\sigma s_j}(AV_1 + BV_2 + CV_3)_j\}N^2.$$

It is thus possible to predict the convergence of the above bands. We find $-0.0034\ N^2$ and $-0.0031\ N^2$ in excellent agreement with the observed values $-0.00335\ N^2$ and $-0.00311\ N^2$.