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The Infrared Absorption Spectrum of Carbon Dioxide

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The complete infrared spectrum of CO_2 may consistently be explained in terms of a linear symmetrical model, making use of the selection rules developed by Dennison and the resonance interaction introduced by Fermi. The inactive fundamental ν_1 appears only in combination bands, but ν_2 at 15μ and ν_3 at 4.3μ absorb intensely.

Resolution of the fundamentals ν_2 and ν_3.—The 15μ band has been resolved into several constituent bands corresponding to absorption by the normal molecule, and by molecules in the first and second excited states. Each band consists of a narrow and intense zero branch, with equally spaced rotation lines on either side. The 4.3μ band has also been resolved, best results following a material reduction in the CO_2 content of the atmospheric path. The line spacing is the same as in the 15μ band, and there is no zero branch. In each case alternate rotation lines are absent, the J values for the normal state all being even. The computed moment of inertia is 70.8×10^{-40} gr cm^2.

Harmonic and combination bands.—No first harmonic bands appear, either for ν_2 or ν_3, but the second harmonic has been observed in each case. The strong pair of doublet bands at 2.7μ are interpreted as combination bands corresponding to $\nu_3+\{\nu_1,2\nu_2\}$ and the bands at 2.0μ and 1.6μ are higher members of the same sequence. The differences $\nu_3-\{\nu_1,2\nu_2\}$ explain the weak absorption maxima observed by Schaefer and Philipps at 9.4μ and 10.4μ. The difference bands $\nu_1-\nu_2$ form a part of the 15μ pattern.

Correlation with Raman spectra.—The Raman lines corresponding to the transitions $0\rightarrow\{\nu_1,2\nu_2\}$ and the weaker pair originating in the first excited state 1_1 of ν_2 fit precisely into the energy level diagram obtained from infrared measurements.

MEASUREMENTS of the absorption due to carbon dioxide were among the earliest observations in infrared spectroscopy,[1] and, as apparatus and methods have gradually improved, these bands have been repeatedly reexamined.[2] Resolution of the rotational structure has not been achieved, however, and even the character of the vibrations has been in doubt until quite recently. Three regions of fairly intense absorption are known; those at 2.7μ and 4.3μ were discovered by Langley, while the band at 14.9μ was first observed by Rubens and Aschkinass. The most complete map of the spectrum from 1μ to 15μ is given by Schaefer and Philipps, and includes many bands of low intensity. These show the curious property that none of the frequencies are either sums or differences of others in the set, which, according to Dennison,[3] indicates a linear symmetrical molecule. Other evidence also suggesting that the three atoms of CO_2 lie on a line has been presented by Eucken[4] from

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[1] Langley, Phil. Mag. **15**, 153 (1883). Rubens and Aschkinass, Astrophys. J. **8**, 176 (1898).

[2] Coblentz, Carnegie Inst. Pub. **35** (1905); Burmeister, Verh. d. D. Phys. Ges. **15**, 589 (1913); E. v. Barh, Verh. d. D. Phys. Ges. **15**, 1150 (1913); Barker, Astrophys. Jour. **55**, 391 (1922); Ellis, Phys. Rev. **26**, 469 (1925); Schaefer and Philipps, Zeits. f. Physik **36**, 641 (1926).

[3] Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[4] Eucken, Zeits. f. Physik **37**, 714 (1926).

a consideration of specific heats, and by Stuart[5] who found no permanent electric moment. However, not all of the experimental evidence has seemed to be consistent with this model. The lowest frequency fundamental, though unresolved, was observed as a broad doublet, instead of a triplet as would have been expected from linear molecules vibrating normally to their axes. Also the 2.7μ band appeared as a pair of doublets of almost equal intensity, the explanation for which has not been obvious.

We are now able to present observations on the two active fundamental bands at resolutions sufficient to reveal the rotational structure. These indicate that the molecule is in fact linear and symmetrical. Moreover, they may be satisfactorily correlated with the Raman lines and the whole series of combination bands, including the pair at 2.7μ, in such a manner as to leave no further doubt about the conclusion.

The mechanical problem of the vibrations and rotations of a symmetrical linear triatomic molecule has been discussed in detail by Dennison.[3] The symmetrical vibration ν_1 of the two extreme atoms along the line connecting them is optically inactive, since no change in electric moment results; it is not observed in the infrared. The symmetrical vibration ν_2 normal to the linear axis necessarily involves changes in electric moment having components along the axis of rotation, and must exhibit P, Q and R branches. It should correspond to the lowest fundamental frequency, observed at 14.9μ. Heretofore this has been reported as a broad doublet band, except in the recent observations by Sleator.[6] The third fundamental vibration ν_3 is an unsymmetrical one involving changes of electric moment normal to the axis of rotation, and giving rise to an intense absorption band at 4.3μ with P and R branches only. On the basis of these assignments the approximate numerical value of ν_1 may be computed. It should lie between ν_2 and ν_3, at a wave-length of about 8μ. The combination relations are particularly characteristic. While $\Delta\nu_1$ may be any integer, the value of $\Delta\nu_2+\Delta\nu_3$ must always be odd. Many possibilities are thus excluded, among them the first harmonic bands. Q branches occur only when $\Delta\nu_2$ is odd. The most intense of the combination bands to be expected are $\nu_3+2\nu_2$ and $\nu_3+\nu_1$, both doublets falling in the neighborhood of 2.7μ.

Most of the equipment used in this investigation has already been described. The grating spectrometer of highest resolution is the one recently used for observations on N_2O.[7] Although very effective for measurements with small absorption cells it cannot conveniently be used with long gas paths for detecting weak bands, nor is it so arranged as to be easily cleared of atmospheric components which absorb very strongly, making observations at certain wave-lengths almost impossible. Fortunately a second instrument was available which could be completely enclosed from source to thermopile. Although equipped with mirrors of shorter focus it gave a resolution sufficient to show the rotational structure of the 4.3μ band when the concentration of

[5] Stuart, Zeits. f. Physik **47**, 457 (1928).

[6] Sleator, Phys. Rev. **38**, 147 (1931).

[7] Plyler and Barker, Phys. Rev. **38**, 1827 (1931).

CO_2 was considerably reduced. This instrument could be filled with almost pure CO_2, or with air practically free of CO_2 as required, though it could not be evacuated. No absorption cells were used. The thermopile was a particularly good one, kindly supplied to us by Dr. Hardy, and, when connected with the Firestone amplifier and recording apparatus,[8] made continuous photographic records possible. We are indebted to Professor Randall for a thin KBr prism (angle 10°) made from a crystal grown under his direction and especially useful for observations beyond 15μ.

THE LOW-FREQUENCY FUNDAMENTAL ν_2

In determining the form of the CO_2 molecule a study of the lowest frequency fundamental band is crucial. Fig. 1 shows a series of energy curves for this region traced from the photographic records obtained with a completely enclosed spectrometer using a coarse grating (960 lines per inch) and 1 mm slits. The narrow and intense zero branch is most striking. The whole case was washed for many hours with air from which the CO_2 had been removed, but a trace of this central maximum still persists in the upper curve. Small measured additions of gas very rapidly increase the intensity of the absorption. The estimated percentage absorbed at the peak has been plotted in Fig. 6 as a function of the equivalent length of path. The curves of Fig. 1 also show the development of the three secondary maxima described by Sleator, which lie at 13.9μ, 15.4μ and 16.2μ.

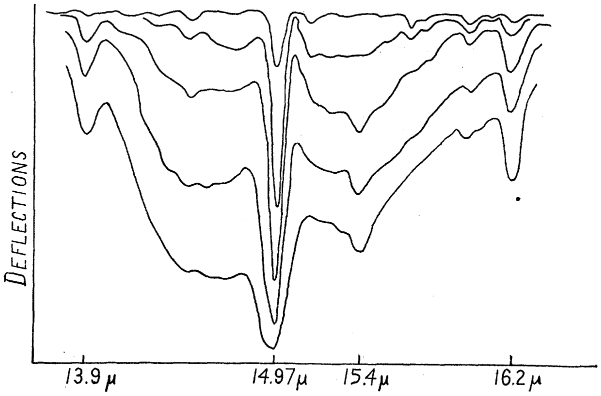

Fig. 1. Development of the 15μ band with increasing amounts of CO_2. Equivalent path lengths in cm at 76 cm pressure: 0.004, 0.05, 0.23, 0.68, 1.58.

Energy curves for this same region under higher resolution are shown in Fig. 2. These were taken with a grating having 1200 lines per inch, used with a thin KBr foreprism. The slits included about 0.45 cm^{-1}. For the central portion the absorbing medium was about six meters of ordinary atmosphere, the equivalent path length in CO_2 being approximately 0.25 cm. The two lateral portions were obtained by increasing the quantity of CO_2 about one hundredfold. The structure of this absorption region is clearly revealed, and

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[8] Firestone, Rev. Sci. Inst. **3**, 163 (1932).

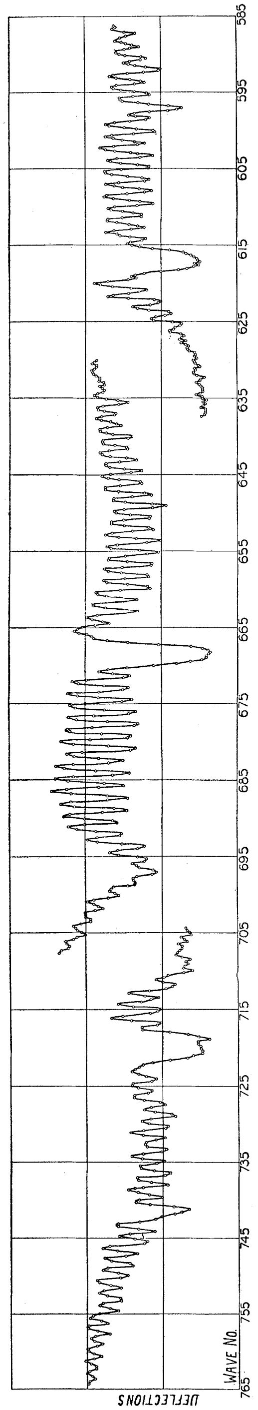

Fig. 2. Fine structure of the 15μ band.

though relatively simple, it is somewhat unusual. In addition to the strong central band with its P, Q and R branches, we find two of the secondary bands already mentioned, similar in structure and symmetrically placed at about ± 50 cm^{-1} from the center. Beyond these on either side and about 20 cm^{-1} farther out another sharp maximum of lesser intensity is found. The symmetry in arrangement and intensities is most striking, and assumes particular interest when the pattern is compared, as in Fig. 3A with the Raman spectrum observed by Dickinson, Dillon and Rasetti.[9] In fact this comparison provides an important means of checking the final interpretation. It should be remarked that the curious dip in the curve at about 697 cm^{-1} upon which the rotation lines are superposed, is not characteristic of CO_2, as it does not appear in the curves of Fig. 1.

Dennison's analysis of the motion associated with the frequency ν_2 assigns to each level two quantum numbers, of which V, the principal one, refers to the vibration state, while the subsidiary number L measures (in units of $h/2\pi$) the angular momentum about the linear axis which is introduced by the two dimensional vibration. Any transition in V is permitted, but L must change by ± 1 when ΔV is odd, and by 0 when ΔV is even. Combinations of these transitions with ν_1 are also possible, and in particular $\nu_1 - \nu_2$ may lie very close to ν_2. As has been shown[10] it is possible to interpret all of the observed CO_2 bands by this scheme, but not without certain curious intensity relations, and no explanation of the symmetry of the pattern is thus provided. Recently a modification has been introduced by Fermi[11] to take account of the interaction between the levels ν_1 and $2\nu_2$. This has been further developed by Dennison,[12] and in his notation has been introduced in the level

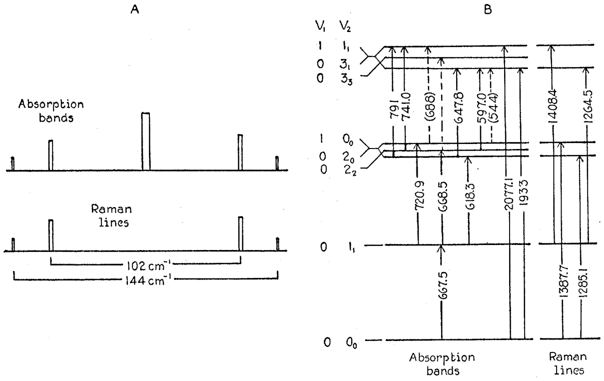

Fig. 3. Vibration levels and transitions involving ν_1 and ν_2.

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[9] Dickinson, Dillon and Rasetti, Phys. Rev. **34**, 582 (1929).

[10] This analysis of the absorption bands and its correlation with the observed Raman spectra, including the weaker transitions originating in the first excited state 1_1, were first reported at the Washington meeting of the Am. Physical Society in May, 1931. Phys. Rev. **37**, 1708 (1931).

[11] Fermi, Zeits. f. Physik **71**, 250 (1931).

[12] Dennison, Phys. Rev. **41**, 304 (1932).

diagram of Fig. 3B. When the carbon atom vibrates along a line normal to the molecular axis it is clear that the two oxygen atoms must swing along arcs so that the distance between them changes slightly, with two minima and two maxima per oscillation; i.e., the motion has a symmetrical component parallel to the axis, with frequency $2\nu_2$. This component alone is, of course, optically inactive. For CO_2 it happens that the frequencies ν_1 and $2\nu_2$ are almost exactly identical, so that a resonance interaction between them produces a pair of combined states (states whose wave functions are linear combinations of those appropriate to ν_1 and $2_0\nu_2$) separated rather widely and almost symmetrically with respect to their unperturbed position, which, of course, would not have been far from the level 2_2. A similar coupling occurs between succeeding pairs of states of like character, such as $3_1\nu_2$ and $\nu_1+1_1\nu_2$.[13]

The motion in the states designated 1_1, 2_2, 3_3 etc., is peculiar since it does not involve changes in the distances between atoms; the molecule is no longer linear but forms a very obtuse triangle which rotates without deformation about an axis parallel to its base. This motion is not coupled with ν_1, for no longitudinal oscillation accompanies it. Further, since there is no change in polarizability of the molecule during the motion, there can be no Raman transitions terminating at these levels.[14] Thus, none of the transitions $0_0\rightarrow 1_1$, $0_0\rightarrow 2_2$ or $1_1\rightarrow 3_3$ is represented in the Raman spectrum.

The explanation of the patterns in Fig. 3A follows at once from this scheme of levels. The two strong Raman lines originate in the state 0_0, and the two weaker ones in the first excited state, as previously suggested.[10] The relative populations of these levels are as 13 to 1 (state 1_1 has a double weight). Infrared transitions to the same final states occur from 1_1 and 2_2 as common initial levels, the population ratio here being 26 to 1. The line $0_0\rightarrow 1_1$ lies almost exactly at the midpoint, its frequency practically coinciding with that determined for $1_1\rightarrow 2_2$ by subtracting 741.0 ($2_2\rightarrow 3_1$) from the Raman frequency 1408.4. This indicates that for ν_2 the anharmonic term is very small, and also that ν_1 and $2\nu_2$ must coincide very exactly. It is not possible to locate the level 3_3 experimentally since the only line in which it is involved ($2_2\rightarrow 3_3$) is completely masked.

The precise determination of the frequencies corresponding to the transitions indicated in Fig. 3 is rendered somewhat difficult by differences in convergence, which shift slightly the maxima of the observed zero branches, sometimes toward higher and sometimes toward lower frequencies. However, utilizing the combination principle, a consistent set of term values has been selected in which the errors probably do not exceed one half of a wave number (except for the level 3_3 which is not observed directly). These term values are listed in Table I, column 3. The positions of the vibration bands computed from them appear in column 4, while columns 5 and 6 show the observed

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[13] As a result of discussions with Professor Kramers during the 1931 Summer Symposium in Ann Arbor we had already reached the conclusion before Fermi's paper appeared, that an interaction of this sort must be invoked to explain the infrared and Raman lines, but details had not been worked out.

[14] Placzek, Zeits. f. Physik **70**, 84 (1931).

wave numbers and the estimated relative intensities. A precise determination of intensities is not possible, for many of the lines are superposed upon a strong background, as in the case of 668.5 and 647.8. Furthermore, the differences in degree of convergence change the contours of the bands sufficiently so that some appear narrow and correspondingly more intense, while others are appreciably broadened. There is a tendency, also, to underestimate the absorption coefficient in regions which are almost opaque, as at the central maximum. It is somewhat surprising that the line at 688.7 has not been clearly revealed, when the corresponding one at 647.7 shows so distinctly. Both lie in regions of strong absorption due to rotation lines of the principal band. The line at 545.1 has also eluded observation although a search for it was made with the coarse grating and a path length of 200 cm of CO_2.

TABLE I. *Term values and vibrational transitions involving* ν_2.

Initial state			Vibration frequency		Relative intensities
V_1	V_2	term value	computed	observed	
			Fundamental bands		
0	0_0	0	667.5	667.5	10,000
0	1_1	667.5	720.9	720.9	250
			668.7	668.5	—
			618.3	618.3	250
0	2_2	1336.2	740.9	741.0	10
			669.5	—	—
			597.3	597.0	10
			791.3	791	1
1	0_0	1285.8	647.7	647.8	7
0	2_0	1388.4	688.7	—	—
			545.1	—	—
0	3_3	2005.7			
1	1_1	1933.5			
0	3_1	2077.1			
			Harmonic bands		
0	0_0		2077.1	2077.1	7
			1933.5	1933	1
			Raman lines		
0	0_0		1388.4	1387.7	15
			1285.8	1285.1	10
0	1_1		1409.6	1408.4	1
			1266.0	1264.5	1

The two second harmonic bands listed in Table I form a part of the absorption region near 4.9μ observed by Schaefer and Philipps. The trace of an energy curve for this region recorded automatically with a 200 cm path of CO_2 is shown in Fig. 5B. In addition to the two maxima listed, other absorption lines appear, probably due to transitions originating in excited states. A further study of this region is contemplated.

The agreement between the Raman frequencies observed by Dickinson, Dillon and Rasetti, and those computed from the term values in Table I may be considered fairly satisfactory, though the differences are somewhat larger than our estimated errors. A better correspondence would result if our frequency scale were uniformly contracted about seven parts in ten thousand. This difference we believe to be considerably greater than our error of calibration.

ROTATIONAL STRUCTURE OF THE BANDS AT 15μ

As is well known, a necessary symmetry property of the wave function Ψ for a diatomic or a linear triatomic molecule with identical extreme atoms excludes either those alternate rotation states for which ψ_R is symmetrical, or those for which it is antisymmetrical, ψ_R being the factor of Ψ affected by an interchange of the identical atoms. It is to be expected, then, that for those vibration states of CO_2 in which $L=0$ the rotational quantum number J may assume only even or only odd values. Which of these sets is excluded depends upon the symmetry properties of the remaining factors of Ψ. When L is not zero the molecule is no longer precisely linear, and J may assume all integral values equal to or greater than L. In those bands involving the transitions 0⟶1 or 1⟶0 in L alternate rotation lines will be completely suppressed and the proper J transitions may be assigned only after it has been decided which are the missing levels. In the absence of zero branches this decision would not be difficult as the frequency interval between the first lines of the positive and negative series would be different for the two cases, but the zero branches are always present, and ordinarily are so broad as to obscure several of the neighboring rotation lines. If their positions could be determined precisely a criterion would be provided for assigning odd and even J values, as is indicated by the band patterns in the lower section of Fig. 4. The band centers at 13.9μ and 16.2μ are particularly favorable for observations of this sort, since, with atmosphere of normal CO_2 content, the central maxima appear weak and very narrow. The adjacent rotation lines are then too weak to be measured, but their positions can be determined, with higher concentrations of CO_2. We find the two zero branches to lie at 720.6 cm^{-1} and 617.9 cm^{-1}, with displacements toward lower frequencies as the concentrations are

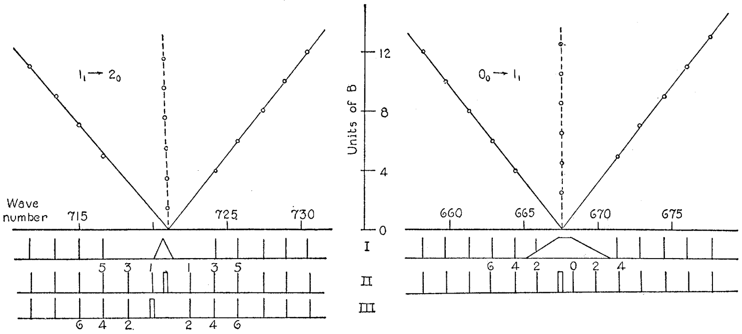

Fig. 4. Comparison of observed and predicted band patterns for $\Delta L = \pm 1$. I. Observed positions of the lines. II. Predicted positions for $\psi_R{}^0$ symmetrical. III. Predicted positions for $\psi_R{}^0$ antisymmetrical.

increased. The rotation lines adjacent to the former, taken from Fig. 2, have been plotted in the upper section of Fig. 4 just above the characteristic band pattern for $\Delta L = -1$, and the position of the zero branch shows clearly that even numbers must be used for the J values of the upper state $(L = 0)$; hence also for the normal state. This is in contrast with the molecule O_2 which, for the nonvibrating state, has only odd J values. It indicates that for CO_2 ψ_R must have the same symmetry as ψ_V. The intersection of the two straight lines falls at 720.9, which is the value given in Fig. 3 as the vertex of the zero branch, and in Table I as the band center. For the other band the coincidence is equally good, the indicated center being 618.3 cm^{-1}. Because of its great intensity we have not determined the position of the strongest zero branch at 14.9μ with equal precision, but since in the initial state (0_0) the J values are even, its frequency may be obtained graphically as on the right of Fig. 4, from the positions of the observed rotation lines. The value so obtained is 667.5 cm^{-1}.

TABLE II. *Wave numbers and wave-number differences in the band at 14.9μ.*

Initial	Observed frequencies		D	D'	$h/4\pi^2cI$	$h/4\pi^2cI'$	ν computed
J	$\Delta J=+1$	$\Delta J=-1$					$\Delta J=0$
4	671.3	664.4	8.4	6.9	0.762	0.765	667.5
6	672.8	662.9	11.5	9.9	0.767	0.762	667.5
8	674.5	661.3	14.8	13.2	0.778	0.777	667.5
10	676.0	659.7	17.8	16.3	0.774	0.777	667.5
12	677.6	658.2	20.9	19.4	0.774	0.776	667.5
14	679.2	656.7	24.1	22.5	0.777	0.777	667.6
16	680.8	655.1	27.2	25.7	0.777	0.778	667.6
18	682.5	653.6	30.4	28.9	0.780	0.781	667.7
20	684.1	652.1	33.6	32.0	0.782	0.780	667.7
22	685.7	650.5	36.7	35.2	0.781	0.783	667.7
24	687.3	649.0	39.8	38.3	0.780	0.782	667.8
26	689.0	647.5	43.0	41.5	0.782	0.783	667.9
28	690.6	646.0	46.2	44.6	0.782	0.783	667.9
30	692.1	644.4	49.0	47.7	0.778	0.783	667.9
32	693.7	643.1	52.2	50.6	0.780	0.780	668.0
34	695.3	641.5	55.4	53.8	0.780	0.780	668.1
36	697.0	639.9	58.5	57.1	0.780	0.783	668.1
38	698.6	638.5	61.6	60.1	0.780	0.781	668.2
40	700.1	637.0	64.6	63.1	0.780	0.780	668.2
42	701.8	635.5		66.3		0.780	668.3
44	703.3						
46	705.2						
48	706.7						

The wave numbers as measured for the various rotation lines are shown in Table II with this assignment of J values. Frequency differences characteristic of the upper and lower vibration states have been obtained in the usual way, i.e.,

$$[J \rightarrow J'] - [(J+2) \rightarrow J'] = [J \rightarrow (J+2)] = (2J'+1)B$$

and

$$[J \rightarrow J'] - [J \rightarrow (J'-2)] = [J' \rightarrow (J'-2)] = (2J+1)B'.$$

These are tabulated under the headings D and D', the primes referring to the upper state. The half interval between rotation lines, $B = h/4\pi^2cI$, is obtained by dividing these differences by the appropriate integers, the results appearing in the 6th and 7th columns. The 8th column shows the positions of the zero branch lines as determined by subtracting $h/8\pi^2 cI$ from the corresponding means of columns 2 and 3. The effect of rotation upon the vibration frequency is seen to be very small. Within the limits of experimental error the positions of the zero branch lines are represented by the formula

$$\nu = 667.5 + 0.00045J^2.$$

Clearly the moment of inertia is affected very little by the change in state of vibration. The mean value of $h/4\pi cI$ is practically 0.780, and consequently $I = 70.8 \times 10^{-40}$ gr. cm^2. Here a little less weight has been assigned to the low rotation states, where larger errors are to be expected. In the same way we find the value $I' = 70.7 \times 10^{-40}$. These results agree very well with the value $I = 70.2 \times 10^{-40}$ obtained from measurements upon rotational Raman spectra by Houston and Lewis.[15] It is to be noted that these authors also reach the conclusion that the J's must be even for the nonvibrating molecule.

Since each of the bands corresponding to absorption from the first vibration state is at least partially obscured by the more intense fundamental, a similar treatment may be applied to them only for the lower rotation states, and much smaller precision is to be expected. The resulting moments of inertia, computed from the wave numbers appearing in Table III are 67.3×10^{-40} for the 13.9μ band, and 73.6×10^{-40} for the 16.4μ band.

TABLE III. *Wave numbers of rotation lines in the bands at 13.9μ and 16.2μ.*

Band at 13.9μ		Initial	Band at 16.2μ	
$\Delta J = +1$	$\Delta J = -1$	J	$\Delta J = +1$	$\Delta J = -1$
—	—	1	—	—
724.2	—	3	620.9	—
725.7	716.6	5	622.8	614.1
727.4	715.0	7	623.9	612.7
728.9	713.5	9	625.3	611.2
730.4	711.7	11		609.6
731.8		13		607.9
733.4		15		606.4
734.9		17		604.8
736.5		19		603.3
738.0		21		601.6
739.5		23		600.1
741.2		25		598.4
744.1		27		596.9
745.5		29		595.3
747.0		31		593.7
748.5		33		592.0
749.9		35		590.5
751.5		37		589.0
753.1		39		587.2
754.6		41		

THE FUNDAMENTAL BAND AT 4.3μ

The absorption associated with the other active fundamental is so intense that near the center of the band observations through ordinary atmos-

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[15] Houston and Lewis, Proc. Nat. Acad. **17**, 229 (1931).

phere are difficult and show very little contrast. Fig. 5C represents a typical set of absorption measurements for this region, plotted against frequencies. The rotation lines are fairly obvious on the low-frequency side of the center, but on the high-frequency side where they are closer together and the absorption is stronger, their positions can be determined only in rough approximation. Table IV shows the average values taken from this and several similar curves, and the corresponding values of $h/4\pi^2cI$ and $h/4\pi^2cI'$. The precision is much less than for the observations given in Table II, but the indicated value for the moment of inertia is practically the same. The values of ν_3 computed as before by averaging the numbers in columns 2 and 3 and subtracting $h/8\pi^2cI$ are shown in column 8. These may be satisfactorily represented by the equation

$$\nu_3 = 2350.1 - 0.0035J^2.$$

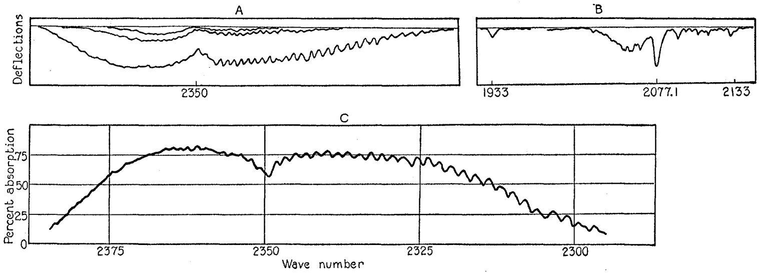

Fig. 5. *A* and *B:* Energy curves traced from automatic records for ν_3 at 4.3μ and $3\nu_2$ at 5μ; *C:* Absorption curve for ν_3 from point by point observations.

TABLE IV. *Wave numbers and wave-number differences in the band at 4.3μ.*

Initial J	Observed frequencies $\Delta J=+1$	$\Delta J=-1$	D	D'	$h/4\pi^2cI$	$h/4\pi^2cI'$	ν computed $\Delta J=0$
0	2350.9	—	2.6		0.867		
2	2352.7	2348.3	5.9	4.3	0.843	0.860	2350.1
4	2354.0	2346.8	8.7	7.2	0.791	0.800	2350.0
6	2355.5	2345.3	12.0	10.2	0.800	0.786	2350.0
8	2356.9	2343.5	15.0	13.4	0.789	0.787	2349.8
10	2358.1	2341.9	18.0	16.2	0.784	0.771	2349.6
12	2359.6	2340.1	21.2	19.5	0.785	0.780	2349.5
14	2361.0	2338.4	24.3	22.6	0.785	0.780	2349.3
16	2362.7	2336.7	27.8	26.0	0.794	0.787	2349.3
18	2364.0	2334.9	31.0	29.1	0.795	0.787	2349.1
20	2365.2	2333.0	33.8	32.2	0.786	0.785	2348.7
22	2366.4	2331.4	36.7	35.0	0.781	0.779	2348.5
24	2367.7	2329.7	40.1	38.0	0.787	0.776	2348.3
26	2369.0	2327.6	43.5	41.4	0.790	0.780	2347.9
28	2370.2	2325.5	46.7	44.7	0.790	0.784	2347.5
30	2371.2	2323.5	49.6	47.7	0.787	0.782	2347.0
32	—	2321.6					
34	—	2319.8					
36	—	2317.9					
38	2375.3	2315.7	61.5	59.6	0.780	0.776	2345.1
40	2376.3	2313.8	64.5	62.5	0.777	0.772	2344.6
42	2377.2	2311.8	67.5	65.4	0.776	0.770	2344.1
44	2378.0	2309.7	70.3	68.3	0.774	0.768	2343.5
46	2378.7	2307.7		71.0		0.765	2342.8

The convergence is larger than for the other band, but not extremely large, and hardly explains the great asymmetry of the emission band. The very strong emission observed beyond 4.4μ[16] is doubtless due in large measure to transitions between states both of which are vibrationally excited.

With the enclosed spectrometer it was possible to remove all traces of this band by washing for many hours with air from which the CO_2 had been removed. A small amount of gas was replaced, and records run with the 7200 line grating and very narrow slits. The rotation structure then showed up clearly on the low-frequency side, but on the high-frequency side was scarcely more distinct than in the plotted curve. Envelopes traced from the photographic records are shown in Fig. 5A, for quantities of CO_2 equivalent to 0.01, 0.02 and 0.11 cm path length at normal pressure. A number of such curves were obtained after adding successively measured amounts of pure CO_2, and from each the percentage absorption at the two maxima was determined. These values are plotted in Fig. 6, curves *B* and *C*.

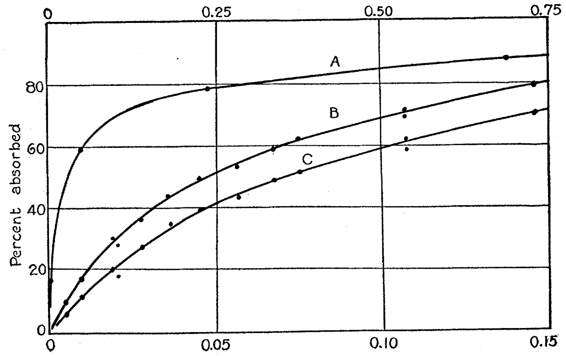

Fig. 6. Dependence of absorption upon path length. Abscissae are equivalent lengths in cm of CO_2 at one atmosphere. *A:* Zero branch of 15μ band, 668 cm^{-1} (upper scale). *B* and *C:* Maxima of 4.3μ band at 2365 and 2340 cm^{-1} (lower scale).

HARMONIC AND COMBINATION BANDS

The preliminary measurements upon the second harmonic of ν_2 in the region near 4.8μ have already been mentioned. These provide precise term values for the pair of interacting levels $\{(\nu_1+1_1\nu_2),3_1\nu_2\}$. With better resolution it may also be possible to identify lines originating in the level 1_2, thus determining the positions of the various compound levels involving 4_0 and 4_2. No first harmonic of ν_3 appears, but the selection rules permit the transition $\Delta V_3=3$, and a weak band has been observed in the proper position, 1.4μ, by Schaefer and Philipps.

The strong double band at 2.7μ has not yet been remeasured, but its character and position are well known. It corresponds to the allowed transitions $\nu_3+\{\nu_1,2\nu_2\}$ where the bracket represents the pair of interacting states at 1285 and 1388 cm^{-1}. Both components are doublet bands, in agreement with the

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[16] Cf. Barker, reference 1.

prediction for $\Delta L = 0$. The fact that their intensities are almost equal again indicates the close resonance between ν_1 and $2\nu_2$, for both of the compound levels must partake about equally of the two component motions. A considerably weaker group of bands appears in the neighborhood of 2μ, and is doubtless to be interpreted as

$$\nu_3 + \{2\nu_1, \nu_1 + 2_0\nu_2, 4_0\nu_2\}$$

but this also remains to be examined in detail. The next member of the same sequence, obtained by adding $\{\nu_1, 2\nu_2\}$ would account for the observed bands near 1.6μ.

With very large amounts of absorbing gas Schaefer and Philipps have also located a pair of bands at 9.4μ and 10.4μ absorbed by molecules already excited to the first pair of interacting levels, and corresponding to the transitions $\nu_3 - \{\nu_1, 2_0\nu_2\}$. There remains the very weak band at 3.28μ, in a position corresponding to $\nu_2 + \nu_3$, a combination which is in apparent contradiction with the rule that $\Delta V_2 + \Delta V_3$ must be odd. If further observation definitely confirms this absorption, and if no other interpretation appears, then the question must be raised whether or not the restriction is absolute.

Thus with one possible exception every observed band is in complete accord with the vibration spectrum predicted by Dennison's rules for a linear symmetrical molecule. The fine structure of the fundamental bands leads also to the conclusion that the molecule must have the linear form O:C:O. Finally the Raman spectra, both vibrational and rotational, may be explained only in terms of the same model. All existing observational data seem now to be consistently correlated.