The Infrared Spectrum of Carbon Dioxide. Part II

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The interaction between the vibration and rotation of the CO_2 molecule is discussed. It is shown that the fine-structure lines will exhibit a convergence which depends upon certain of the anharmonic potential constants. The convergence factors are compared with the experimental data of the resolved bands and an excellent agreement is found, which leads to a determination of the anharmonic constants. Combining these results with those of Part I, the complete potential function for CO_2 is obtained. A simple analytic function for the potential is proposed which contains but four constants. It is shown that this function agrees satisfactorily with the experimental potential for small displacements. The range of the validity of the analytic function is discussed and one of the heats of dissociation of CO_2 is obtained.

INTRODUCTION

A PREVIOUS paper by this title, Part I,[1] was concerned with an analysis of the vibrational levels of the linear and symmetrical molecule O—C—O. The Hamiltonian governing the vibrational motions of the molecule was shown to have the form,

$$H = H_0 + \lambda H_1 + \lambda^2 H_2,$$

where

$$H_0 \equiv (2\pi^2/h)\{2\omega_2 p_\sigma^2 + \omega_2 p_\rho^2 + \omega_3 p_\xi^2 + (\omega_2/\rho^2) p_\varphi^2\} + (h/2)\{2\omega_2\sigma^2 + \omega_2\rho^2 + \omega_3\xi^2\},$$

$$\lambda H_1 \equiv (2\pi^2\Delta/h) p_\sigma^2 + h\{(\Delta/2)\sigma^2 + a\sigma^3 + b\sigma\rho^2 + c\sigma\xi^2\},$$

$$\lambda^2 H_2 \equiv (\omega_3/2\omega_2 I)\rho^2 p_\xi^2 + h\{d\sigma^4 + e\rho^4 + f\xi^4 + g\sigma^2\rho^2 + h\sigma^2\xi^2 + i\rho^2\xi^2\}.$$

The quantities σ, ρ, and ξ are dimensionless variables corresponding to the normal coordinates q, r, and z, respectively.

A system having the Hamiltonian H_0 was solved rigorously and to this system, λH_1 and $\lambda^2 H_2$ were applied as first and second order perturbations. An expression was thus obtained for the vibrational energy levels $W = W_0 + \lambda W_1 + \lambda^2 W_2$ which was shown to be in excellent agreement with the observed positions of the levels.

The immediate dependence of the energy W was upon eleven derived constants whose connections with the twelve constants of H were given explicitly. Thus the positions of the vibrational levels furnish but eleven data and it is necessary to find some new relation before the twelve constants of the potential energy may be determined. This new relation may be found from an analysis of the interaction between the vibration and rotation of the molecule. It will be shown that this interaction, just as in the case of a diatomic molecule, leads to a convergence in the band lines; that is, to a term in the fine-structure formula proportional to the square of the ordinal number of the line. The analysis, in addition to fixing the values of the twelve energy constants, serves to correlate the convergence factors of all the CO_2 bands which have thus far been resolved.

THE INTERACTION BETWEEN ROTATION AND VIBRATION

The interaction between vibration and rotation can be divided into two parts which may be described in the following way. The centrifugal forces occasioned by the rotation of the molecule pull the atoms away from their old equilibrium positions to new ones in the anharmonic force field. The frequencies with which the atoms oscillate about their new positions of rest differ from the corresponding frequencies of the non-rotating molecule by amounts which are measured by the anharmonicity of the field; that is, in first order by the coefficients a, b and c, and in higher order by d, e, f, g, h and i. It is thus

[1] Adel and Dennison, Phys. Rev. **43**, 716 (1933).

apparent that the frequencies of vibration are slightly dependent upon the rotational state of the molecule, giving rise to a convergence factor in the fine-structure formula. This part of the mutual perturbations may be thought of as the effect of rotation upon vibration.

The reverse phenomenon; namely, the perturbation of rotation by vibration is independent of the anharmonic nature of the force field. To the present degree of approximation, the moments of inertia of the molecule must be considered as functions of the normal coordinates. The consequent periodic fluctuation of the moments of inertia distorts the rotational frequency to a new value. It is clear that this mechanism also induces a convergence of fine-structure lines. It is to be noted that a consequence of the effect of the vibration is to distort the molecule into a slightly asymmetrical rotator with three different, and in this instance variable, moments of inertia.

The three moments of inertia of the molecule depend upon the normal coordinates in the following manner,

$$C=\mu r^2, \quad B=(m/2)(a+q)^2+\mu z^2, \quad A=B+C.$$

The wave equation describing the system may be easily obtained. It consists of two parts. The first of these is independent of the rotation and was the equation treated in Part I. The second part of the wave equation contains terms relating both to the rotation of the molecule and to the interaction between vibration and rotation. It may be written,

$$\begin{aligned}&[\partial^2/\partial\vartheta^2+\cot\vartheta(\partial/\partial\vartheta)+(A_e/C_e+\cot^2\vartheta)\partial^2/\partial\varphi^2\\&\quad+\csc^2\vartheta(\partial^2/\partial\psi^2)-2\cot\vartheta\csc\vartheta(\partial^2/\partial\varphi\partial\psi)\\&\quad+8\pi^2A_eW/h^2]U+(\mu r^2/I)F(\varphi,\vartheta,\psi;\partial^2/\partial\vartheta^2,\\&\quad\partial^2/\partial\varphi^2,\partial^2/\partial\psi^2;\partial^2/\partial\vartheta\partial\varphi,\partial^2/\partial\vartheta\partial\psi,\partial^2/\partial\varphi\partial\psi)U\\&\qquad\qquad=0,\end{aligned}$$

where $1/A_e=\frac{1}{2}(1/A+1/B)$ and $1/C_e=1/C-\frac{1}{2}(1/A+1/B)$. It is evident that the first group of terms constitute the wave equation for a symmetrical rotator with effective moments of inertia A_e and C_e. The remaining terms, grouped as $(\mu r^2/I)F$, have no counterpart in the symmetrical rotator equation and are the purely asymmetrical rotator terms. These terms would introduce effects characteristic of the difference between the energy levels of the symmetrical and asymmetrical rotators. They would give rise to a splitting of the fine-structure lines into multiplets whose separation would be a function of the small coefficient $(\mu r^2/I)$. The bands of CO_2 observed in the Venus atmosphere are very finely resolved but they show no trace of multiplicity or even of unsharpness. We may, therefore, on purely *a priori* grounds discard the group of terms $(\mu r^2/I)F$. An exact analysis, moreover, confirms this conclusion and shows that they will, to the present order of approximation, furnish no contribution to the energy levels.

The wave equation involving the angles ϑ, φ, ψ may now be integrated and we can show that the interaction energy (and hence the convergence) may be considered as due wholly to those terms which mark the difference between the symmetrical rotator with effective moments of inertia A_e and C_e and the rigid, linear model of CO_2 with moment of inertia I. Expanding $1/A_e$ and $1/C_e$ in powers of the normal coordinates we may, upon introduction of the quantum numbers of angular momentum J and l, express the interaction in the form of a perturbing potential energy.

$$V_I=\frac{h^2}{8\pi^2I}[J(J+1)-l^2]\left[\frac{-3q^2}{a^2}+\frac{\mu}{I}(r^2+z^2)+\frac{2q}{a}\right].$$

The most significant term is the one linear in q, for it marks the removal of the oxygen atoms to new positions of equilibrium. As will become evident, it is immediately responsible for the introduction of the anharmonic coefficients a, b and c. The terms, quadratic in q, r and z giving the remainder of the interaction, express the variation of the principal moments of inertia with the phase of vibration.

When considered as a portion of the potential energy of the molecule, V_I is inconsistent with the assumption of normal coordinates because of the presence of the stretching term proportional to q. A transformation must, therefore, be effected from the coordinate q to a normal coordinate x. q and x satisfy the relation $q-x=\delta$, where

$$\delta=(h^2/8\pi^2I)(J(J+1)-l^2)/4\pi^2\omega_2^2(2Im)^{\frac{1}{2}}$$

is the linear displacement of equilibrium. Transforming the cubic anharmonic potential from its dependence upon q to its new dependence upon x, we find the final form of the interaction function to be,

$$V_I = -(h^2/8\pi^2 I)[J(J+1)-l^2][-3(m/2I+\alpha/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})x^2+(\mu/I-\beta/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})r^2 + (\mu/I-\gamma/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})z^2],$$

where

$$\alpha x^3 = a\sigma^3, \quad \beta x r^2 = b\sigma\rho^2, \quad \gamma x z^2 = c\sigma\xi^2.$$

That is to say, we have $V_I = C_1\sigma^2 + C_2\rho^2 + C_3\xi^2$ and as a consequence the correction to the energy of a rotation vibration level can be found from the zeroth order energy of vibration of the molecule by a comparison of the coefficients in V_I with the corresponding coefficients in

$$V_0 = (h/2)(2\omega_2\sigma^2+\omega_2\rho^2+\omega_3\xi^2).$$

In other words, since the contribution of V_0 is

$$h\{2\omega_2(V_1+\tfrac{1}{2})+\omega_2(V_2+1)+\omega_3(V_3+\tfrac{1}{2})\},$$

the contribution of V_I is

$$E_I = (h^2/8\pi^2 I)[J(J+1)-l^2][(V_1+\tfrac{1}{2})\{3h/8\pi^2 I\omega_2+(3h/4\pi^2 m\omega_2)(\alpha/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})\} + (V_2+1)\{-h/4\pi^2 I\omega_2+(h/4\pi^2\mu\omega_2)(\beta/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})\} + (V_3+\tfrac{1}{2})\{-h/4\pi^2 I\omega_3+(h/4\pi^2\mu\omega_2)(\gamma/4\pi^2\omega_2^2(2mI)^{\frac{1}{2}})\}].$$

We have now computed the energy shift of a rotation-vibration level resulting from the interaction between rotation and vibration. To pass from the corrected energy levels to the corrected positions of the fine-structure lines the selection rules for J and l must be introduced. For a parallel band $\Delta J = \pm 1$ and $\Delta l = 0$. Representing by N the ordinal number of the fine-structure line, the correction to the N-th line of a parallel band produced in a transition from the ground state is

$$\Delta\nu = (h/8\pi^2 Ic)[\{PV_1+QV_2+RV_3\}N^2+\{P(V_1+1)+Q(V_2+2)+R(V_3+1)\}N],$$

where P, Q, and R are the respective coefficients of $(V_1+\frac{1}{2})$, (V_2+1), and $(V_3+\frac{1}{2})$ within the bracket [ ] of the above expression for E_I. Similar expressions obtain for the corrections to the fine-structure of a perpendicular band.

The interpretation of $\Delta\nu$ follows at once from a correlation with the empirical expression for the positions of the fine-structure lines in a band. In the empirical formula $\nu = K_0+K_1N+K_2N^2$, K_1 is the major interval between fine-structure lines, while K_2 fixes the convergence which is superimposed upon the spacing determined by K_1. This suggests the division of $\Delta\nu$ into two sections—the one linear and the other quadratic in N. That is to say, the interaction between rotation and vibration not only is the cause of convergence, but it alters the major interval as well. Thus, the measured separation of lines is

$$K_1 = h/4\pi^2 Ic + \text{linear part of } \Delta\nu.$$

The quantity $\Delta\nu$ is, therefore, essential to a precise determination of the moment of inertia of the molecule.

Putting the numerical values of the known constants into $\Delta\nu$, we find:

$$\Delta\nu = 0.390[(0.00175+0.000112a)V_1+(-0.00117+0.0000372b)V_2 + (-0.00033+0.000019c)V_3]N^2+0.390[(0.00175+0.000112a)(V_1+1) + (-0.00117+0.0000372b)(V_2+2)+(-0.00033+0.000019c)(V_3+1)]N.$$

Of the twenty-eight bands which have now been observed in the infrared spectrum of carbon dioxide, only five are sufficiently well resolved for the present analysis. These are the active fundamentals and the three Venus bands. The observed positions are:[2]

$$\nu_2 = 667.5 + 0.780\,N + 0.0005\,N^2; \quad \nu_3 = 2350.1 + 0.780\,N - 0.0035\,N^2;$$

$$5\nu_3 = 11496.5 + 0.769\,N - 0.0153\,N^2; \quad 5\nu_3 + (\nu_1, 2\nu_2)\begin{cases} 12672.5 + 0.769\,N - 0.0150\,N^2 \\ 12774.7 + 0.769\,N - 0.0156\,N^2. \end{cases}$$

(For sources of data see Part I.)

The band ν_2 possesses the theoretical convergence: $0.390(-0.00117 + 0.0000372b)N^2$. From the vibrational analysis of Part I the value 72.9 cm^{-1} was obtained for $|b|$. Obviously the convergence demands that b be positive and the value $b = 72.9$ cm^{-1} yields the convergence factor $+0.0006\ N^2$, in excellent agreement with the observed value $+0.0005\ N^2$.

Of the two bands ν_3 and $5\nu_3$, the photographic one, $5\nu_3$, is the more accurately resolved. For this reason $5\nu_3$ will be used to compute the value of c which will then serve to predict the convergence of the fundamental ν_3. From the equation

$$0.390(-0.00033 + 0.000019c)5\ N^2\ cm^{-1} = -0.0153\ N^2\ cm^{-1}$$

the value $c = -202.1$ cm^{-1} is found. The calculated convergence $-0.0031\ N^2$ agrees very well with the measured value $-0.0035\ N^2$ for the ν_3 fundamental.

The convergences for the combination bands at 12,672.5 and 12,774.7 cm^{-1} are given by the respective linear combinations:

$$\{0.43[0.390(0.00175 + 0.000112a)] + 0.57(0.00120) - 0.0153\}N^2$$

$$\{0.57[0.390(0.00175 + 0.000112a)] + 0.43(0.00120) - 0.0153\}N^2$$

since the resonance degeneracy of the molecule described in Part I must be taken into account. Equating the first expression to the observed datum $-0.0150\ N^2$, the value -36.2 cm^{-1} for the anharmonic constant a is found. When this is substituted into the second expression the value $-0.0153\ N^2$ is obtained, which may be compared with the observed constant $-0.0156\ N^2$.[3]

The moment of inertia of CO_2 may be determined from any of the resolved infrared bands. It appears, however, that the $5\nu_3$ band should yield the most reliable value since it is the most accurately resolved band. In making the computation the correction arising from the convergence factor must be applied to the coefficient of N in the fine-structure formula. The observed major interval of the $5\nu_3$ band is 0.769 cm^{-1}. It follows that:

$$0.769\ N = hN/4\pi^2 Ic - 0.0031(V_3 + 1)N,$$

where $V_3 = 5$. We obtain $I = 70.1 \times 10^{-40}$ gram cm^2, a value which is in good accord with the value 70.2×10^{-40} as determined from the rotational Raman effect of CO_2.[4]

The Potential Energy Function of CO_2

The analysis of the interaction between rotation and vibration has yielded values for the coefficients a and c. Combining these data with the x's and ν's it becomes possible to determine the remaining anharmonic coefficients; namely, d, e, f, g, h, i. The equations used in this evaluation are given on pages 719 and 720 of Part I and are simply the connections between the constants of the vibrational energy and the constants of the vibrational potential. The results of this calculation are listed in Table I, together with the zeroth and first order constants of the potential.

ω_1, ω_2, ω_3, b, and c are the most accurately known of the twelve constants, with a probable

[2] Due to the fact that the oxygen nucleus has zero spin, half of the fine-structure lines of CO_2 are missing. The above formulae represent the observed positions of the lines when N takes on the values $+1$, $+3$, $+5$, $+7$, R-branch; -2, -4, -6, -8, P-branch.

[3] We are very much indebted to Professor E. F. Barker for the following information. He has recently resolved the two infrared bands $\nu_3 - (\nu_1, 2\nu_2)$ at 10μ, and from the convergence factors which he obtains, the two values of a -38.6, -36.6 may be computed. We shall adopt the mean value -37.0.

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

TABLE I.

ω_1 1361 cm^{-1}	a −48.8	d 7.8, 5.3	g −9.9
ω_2 673	b 72.9	e 2.0	h 7.7
ω_3 2378	c −202.1	f 2.4	i −12.3

error of about ½ percent. The value of a is probably known to within 5 percent while the remaining constants may well be in error by as much as 10 percent to 15 percent. Two values are given for d, one obtained from the constant x_{11} and the other from the expression for ν_1. We should regard the latter determination as the more accurate. It is to be noted that the least accurately known constants are the smallest in magnitude; namely, the coefficients of the second order potential. The behavior of the molecule, however, is determined chiefly by the zeroth and first order potentials. Consequently, we believe that the potential energy of the carbon dioxide molecule for small displacements will be represented to within a few wave numbers by the data in Table I. An attempt will now be made to approximate this potential energy by means of an analytic function with a fewer number of constants.

It seems probable that each of the two oxygen nuclei are bound to the carbon nucleus by a force field having a potential minimum. The success of the Morse potential function for diatomic molecules suggests that we connect the carbon with each of the oxygens by a Morse function. The constants of these two functions will, of course, be identical. The valencies of the two oxygen atoms are satisfied by the carbon atom and we might accordingly expect that the two oxygen atoms will repel one another. From analogy with the repulsion forces of homopolar atoms we shall attempt to approximate this potential by an expression of the form Ae^{-Bq}. Thus,

$$V=[De^{-2\alpha(r_1+\epsilon)}-2De^{-\alpha(r_1+\epsilon)}]+[De^{-2\alpha(r_2+\epsilon)}-2De^{-\alpha(r_2+\epsilon)}]+Ae^{-Bq}.$$

The distances between the nuclei are given by $a/2+r_1$, $a/2+r_2$, and $a+q$, as shown in Fig. 1,

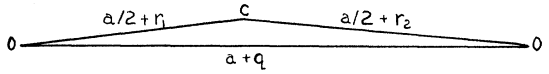

FIG. 1. Configuration of the carbon dioxide molecule.

and completely define the configuration of the system. The quantities r_1 and r_2 are connected with the normal coordinates by the relations

$$r_1=q/2+r^2/a+z, \quad r_2=q/2+r^2/a-z$$

and V may be rewritten as follows, where $y=q/2+r^2/a$,

$$V=2De^{-\alpha(\epsilon+y)}\cosh 2\alpha z-4De^{-\alpha(\epsilon+y)}\cosh \alpha z+Ae^{-Bq}.$$

The equilibrium condition

$$\partial V/\partial q=\partial V/\partial r=\partial V/\partial z=0 \quad \text{at} \quad q=r=z=0$$

yields the relation $2\alpha^2\epsilon D=AB$. ϵ can thus be evaluated in terms of α, D, A and B, and the potential V is seen to depend upon these four parameters only.

For the purpose of comparison with the terms of the series potential already obtained for CO_2, we must expand $V(r_1r_2q)$ about the point $q=r=z=0$, and all terms through the quartic must be retained. Powers of ϵ higher than the first may be neglected, and the expansion yields the following term by term comparison,

$$\pi^2m\omega_1^2=\tfrac{1}{2}\{AB^2+D\alpha^2(1-3\alpha\epsilon)\},$$
$$2\pi^2\mu\omega_2^2=4\epsilon D\alpha^2/a,$$
$$2\pi^2\mu\omega_3^2=2D\alpha^2(1-3\alpha\epsilon),$$
$$a=\{(D\alpha^3/4)[(7\alpha\epsilon/3)-AB^3/6]\}R^3,$$
$$b=\{2D\alpha^2(1-3\alpha\epsilon)/a\}RS^2,$$
$$c=\{D\alpha^3(7\alpha\epsilon-3)\}RT^2,$$
$$d=\{AB^4/24+(D\alpha^4/96)(7-15\alpha\epsilon)\}R^4,$$
$$e=\{2D\alpha^2(1-3\alpha\epsilon)/a^2\}S^4,$$
$$f=\{D\alpha^4(7-15\alpha\epsilon)/6\}T^4,$$
$$g=\{D\alpha^3(7\alpha\epsilon-3)/2a\}R^2S^2,$$
$$h=\{D\alpha^4(7-15\alpha\epsilon)/4\}R^2T^2,$$
$$i=\{2D\alpha^3(7\alpha\epsilon-3)/a\}S^2T^2, \text{ where}$$
$$R=(1/2\pi)[h/m\omega_2]^{\frac{1}{2}},$$
$$S=(1/2\pi)[h/\mu\omega_2]^{\frac{1}{2}},$$
$$T=(1/2\pi)[h/\mu\omega_3]^{\frac{1}{2}}.$$

For the determination of α, D, B and A, it is desirable to employ the four best known of the

constants $\omega_1 \cdots i$. ω_1, ω_2, ω_3 and c are evidently the data required. (The constant b is unsuited for the fourth relation as will be seen in the general discussion to follow.) In this way we obtain,

$$\alpha = 1.81\text{A}^{-1}, \quad B = 1.086\text{A}^{-1}, \quad \epsilon = 0.061\text{A}.$$

$$D = 168350 \text{ cm}^{-1}, \quad A = 62600 \text{ cm}^{-1}.$$

By using these values, the remaining anharmonic constants can be predicted and the suitability of the generalized Morse function will be indicated by the agreement between these values and the corresponding ones obtained earlier in the paper. The comparison is contained in Table II.

TABLE II.

	Infrared analysis	Generalized Morse function
a	-37.0 cm^{-1}	-36 cm^{-1}
b	72.9	102
d	5.3, 7.8	1.1
e	2.0	4.6
f	2.4	4.1
g	-9.9	-8.9
h	7.7	12.4
i	-12.3	-17.7

The agreement shown in Table II is, in several respects, satisfactory. The anharmonic constants are correctly given by $V(r_1r_2q)$ as regards order of magnitude and as regards algebraic sign. It is apparent, however, that their numerical values diverge by amounts which are certainly in excess of the experimental errors. Perhaps the principal objection to the function we have chosen is that it belongs to the class of central force potentials which have, in the past, shown themselves to be incapable of describing the potential functions of polyatomic molecules. There are certain consequences of the central force assumption which are completely independent of the restricted form $V(r_1r_2q)$. This assumption imposes certain restrictions upon the anharmonic constants which are listed below:

$$b/\omega_3^2 = 2\pi^2\mu RS^2/a; \quad e/\omega_3^2 = 2\pi^2\mu S^4/a^2$$

$$i/g = 4T^2/R^2; \qquad f/h = 2T^2/3R^2.$$

It is because b is already specified by the central character of the forces that it may not be used in determining the constants of the generalized Morse function.

The fact that the four relations given above are not accurately fulfilled by the actual constants of the molecule proves that the true force function cannot be wholly central in character. On the other hand, the fact that they are approximately fulfilled leads us to the belief that to this extent the potential energy of CO_2 can be represented by a central force function such as $V(r_1r_2q)$.

Our purpose in introducing $V(r_1r_2q)$ was to find a function which possesses definite physical significance and whose constants might be evaluated from the infrared data. The function we have chosen does fairly well represent the potential energy of CO_2 for small displacements of the particles. The question now arises as to whether it will also furnish some measure of the potential for large displacements and of the heats of dissociation of the molecule.

Suppose, for example, that we consider the dissociation of CO_2 into CO and O, where we must suppose that the products of the dissociation are probably not in the normal state. For this purpose we assume that one of the oxygen atoms is slowly removed to infinity; the distance between the remaining C and O remaining constant. This can be accomplished by letting q and z become infinite while preserving the relation $z = q/2$. The energy required for this operation is $D - A$, but the residual CO molecule is not in its normal state since $a/2$ is no longer its equilibrium distance, but rather $(a/2) - \epsilon$. The heat of dissociation is thus equal to

$$2De^{-\alpha\epsilon} - De^{-2\alpha\epsilon} - A.$$

Upon substituting the values of the constants, we obtain for the heat of dissociation 103,750 cm^{-1} or 300 calories/mol. In order to compare this figure with an experimental determination of the heat of dissociation we would require more detailed information about the excited states of CO and O than appears to be now available.