

The Infrared Spectrum of Carbon Dioxide. Part I

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Previous work by Fermi and by Dennison has shown that the principal features of the infrared and Raman spectra of carbon dioxide may be explained by taking account of the first order perturbation terms in the potential energy expression. It was not possible to predict the positions of the levels with any high degree of accuracy, however. The present paper extends this work by introducing a second order perturbation. The formula for the second order energy correction of a general linear symmetrical triatomic molecule is initially computed. This formula is then modified in order that it may be applicable to the carbon dioxide molecule in which resonance degeneracy plays an essential rôle. A review is made of the experimental data which determine the positions of the carbon dioxide

vibrational energy levels. These include the results of a recent investigation of absorption bands appearing in the spectrum of Venus, as well as new and as yet unpublished data found by Barker and Wu. In all, twenty levels have been found and out of these, eleven are required to determine the anharmonic constants of the molecule. The remaining nine levels may then be predicted, and their positions are found to agree very accurately with the values obtained experimentally. A table is given showing the positions of a number of CO₂ infrared bands which while accessible to observation have not as yet been reported. The recent work by Langseth and Nielsen on the Raman spectrum of CO₂ is discussed.

INTRODUCTION

IT is now well known that the molecule of carbon dioxide possesses a form which is both linear and symmetrical, the carbon atom lying midway between the two oxygens. The group of normal vibrations of such a system constitute a zeroth order approximate solution to the motion which very satisfactorily explains the general features of the infrared spectrum of the molecule. The respective modes of vibration of the three independent frequencies are indicated schematically in Fig. 1.

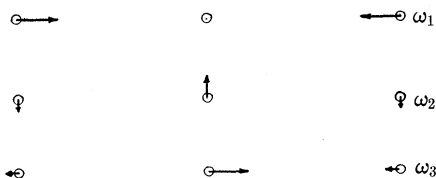


FIG. 1.

The first of these ω_1 corresponds to a symmetrical motion of the oxygen atoms, the carbon atom remaining fixed at the center of mass. This frequency is inactive in the infrared, but will appear strongly in the Raman spectrum and lies at about 7.5μ . In the second frequency ω_2 the carbon

oscillates perpendicularly to the line joining the oxygen atoms, while the distance between the oxygens remains unchanged. ω_2 is a double frequency, active in the infrared, inactive in the Raman spectrum and lies at about 15μ . The unsymmetrical vibration with frequency ω_3 is a motion of the atoms along the figure axis of the molecule in which the carbon moves relative to the center of mass of the oxygens; where again the distance between the latter remains unaltered during the motion. This frequency which is active in the infrared and inactive in the Raman spectrum lies at about 4.7μ .

As has been remarked above, this model fully explains the principal observed features of the spectrum. When, however, the infrared and Raman spectra are examined more carefully, certain details appear which cannot be so simply understood. The Raman spectrum, for example, consists not of one line but of two lines of about equal intensity in the region of 7.5μ . Moreover, many of the combination bands in the infrared deviate from the positions predicted by combination relations by rather large amounts (i.e., approximately 100 waves per cm).

These difficulties have been completely explained by a theory proposed by Fermi¹ and

¹ E. Fermi, *Zeits. f. Physik* **71**, 250 (1931).

somewhat amplified by Dennison.² The explanation depends upon the fact that in carbon dioxide the frequency ω_1 is almost exactly equal to $2\omega_2$. The degeneracy thus introduced produces a first order perturbation which on the one hand changes the identity of the levels, allowing two Raman lines rather than one to appear. On the other hand, the perturbation yields a first order correction to the energy (of the order of 100 waves per centimeter) which accounts for the positions of the combination bands.

The infrared and Raman spectra of the carbon dioxide molecule are known with great accuracy, the errors in the positions of the bands being in the neighborhood of 1 or 2 waves per centimeter. The positions of the combination bands predicted by Fermi's theory fail to agree with the observed positions by amounts of the order of 10 to 20 waves per centimeter. Clearly, these discrepancies must be due to the second order corrections to the energy of which no account was taken in Fermi's theory. It is the purpose of the present paper to introduce this second order correction, and to show that with its aid the positions of the observed lines may be predicted with an error no greater than the experimental one. This procedure will allow a determination of the anharmonic force constants which will prove to be of great importance in determining the general form of the potential function of the carbon dioxide molecule.

ANALYSIS

In presenting the analysis we shall use the coordinates q, z, r and φ which were first introduced and fully described by Dennison³ in the discussion of the molecule YX_2 . q measures the relative separation of the oxygen atoms, z the displacement of the carbon atom from the center of mass of the oxygens measured parallel to the line of the latter, while r and φ are the polar coordinates of the carbon in a plane at right angles to the line of the oxygens, the origin of coordinates lying at the intersection.

It proves convenient to introduce the dimensionless variables σ, ξ, ρ and φ instead of q, z, r and φ which are related to them in the following manner:

$$\begin{aligned}\sigma &= 2\pi[\omega_1 m/2h]^{1/2}q, & \xi &= 2\pi[\omega_3 \mu/h]^{1/2}z, \\ \rho &= 2\pi[\omega_2 \mu/h]^{1/2}r, & \varphi &= \varphi.\end{aligned}$$

The Hamiltonian representing the vibrational motion may be readily obtained.⁴ The symmetry of the molecule conditions that the Hamiltonian must be an even function of z and r and independent of φ .⁵

In accordance with the series of approximations to be made on the system, the Hamiltonian may be expanded in a power series in λ , a parameter of smallness.

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

These functions may be quite readily obtained:

$$\begin{aligned}H_0 &\equiv (2\pi^2/h)\{2\omega_2 p_\sigma^2 + \omega_3 p_\xi^2 + \omega_2 p_\rho^2 + (\omega_2/\rho^2)p_\varphi^2\} + (h/2)\{2\omega_2 \sigma^2 + \omega_2 \rho^2 + \omega_3 \xi^2\}, \\ \lambda H_1 &\equiv (2\pi^2 \Delta/h)p_\sigma^2 + h\{(\Delta/2)\sigma^2 + a\sigma^3 + b\sigma\rho^2 + c\sigma\xi^2\}, \\ \lambda^2 H_2 &\equiv (\omega_3/2\omega_2 I)\rho^2 p_\xi^2 + h\{d\sigma^4 + e\rho^4 + f\xi^4 + g\sigma^2\rho^2 + h\sigma^2\xi^2 + i\rho^2\xi^2\}.\end{aligned}$$

The first order perturbing energy λH_1 contains two classes of terms. The first class represents the fact that ω_1 is not exactly equal to $2\omega_2$, and is proportional to the quantity $\Delta = \omega_1 - 2\omega_2$. In addition to these terms comes the contribution

² D. M. Dennison, Phys. Rev. **41**, 304 (1932).

³ D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

⁴ A general treatment of the carbon dioxide molecule would involve the use of a Hamiltonian containing rotational coordinates in addition to the vibrational coordinates. Such a treatment would allow us to obtain not only the rotational energy, but also the interaction between rotation and vibration. This problem will be

from the anharmonic potential; namely, all those terms cubic in the coordinates which fulfill the necessary symmetry conditions.

The second order energy may likewise be divided into two parts, the first of which

reported in a later paper; for the present we restrict ourselves to predicting the centers of the absorption bands.

⁵ Actually the symmetry of the system demands merely that H shall be an even function of z and independent of φ . The fact that we take H to be an even function of r also implies that we assume that H is analytic.

$([\omega_3/2\omega_2 I]\rho^2 \mathcal{P}_\xi^2)$ embodies the circumstance that for finite amplitudes of vibration, the molecule deviates slightly from strict linearity. The second part contains the quartic terms of the anharmonic potential of vibration. The solution of the system in zeroth and first approximations has been described in detail elsewhere,² and for our present purpose it will suffice to add only a few points to the results already obtained.

The solution of the zeroth order wave equation may be written in the form

$$\{\partial^2/\partial\rho^2 + (1/\rho)(\partial/\partial\rho) + (1/\rho^2)(\partial^2/\partial\varphi^2) + [(2E/h\omega_2) - \rho^2]\}\Psi_{\rho\varphi} = 0$$

is satisfied by the function (here given in normalized form)

$$R_{(\rho)}^{V_2 l e^{\pm i l \varphi}} = (k!)^{\frac{1}{2}} \{(l+k)!\}^{-\frac{1}{2}} \pi^{-\frac{1}{2}} \rho^l e^{-\rho^2/2} L_{l+k}^l(\rho^2) e^{\pm i l \varphi},$$

where $k = (V_2 - l)/2$. $L_{l+k}^l(\rho^2)$ is the associated Laguerre polynomial of argument ρ^2 , from whose properties it will be comparatively easy to evaluate the necessary matrix elements.

The zeroth order energy constant W_0^n depends only upon the quantum numbers $2V_1 + V_2$ and V_3 , thus showing that in this order of approximation the system is degenerate with respect to the quantum numbers V_1 , V_2 , l . We shall let n represent the former ones and t the additional quantum numbers necessary to define the wave function Ψ_{nt} .

The first order energy constant W_1^{nt} is got by equating the secular determinant $|(H_1)_{nt}^{n't'} - W_1 \delta_{t't}|$ to zero and solving for the roots w_1 . $W_1^{n\tau}$ depends upon the quantum numbers V_1 , V_2 , V_3 , and upon l^2 . It is thus independent of the

$$\Psi_{nt} = \Psi_{(\sigma)}^{V_1} \Psi_{(\xi)}^{V_3} R_{(\rho)}^{V_2 l e^{\pm i l \varphi}}.$$

$\Psi_{(\sigma)}^{V_1}$ and $\Psi_{(\xi)}^{V_3}$ are the well-known Hermitian orthogonal functions with the arguments σ and ξ , respectively. The remaining part $R_{(\rho)}^{V_2 l e^{\pm i l \varphi}}$ has been described as a two-dimensional Hermitian orthogonal function expressed in polar coordinates.³ Since various matrix elements of powers of the coordinates will be required, it will be advantageous to examine this expression in greater detail. It may be shown that the differential equation defining it; namely,

algebraic sign of $\pm l$. This last degeneration is not removed even by the perturbing potential $\lambda^2 H_2$, for $\lambda^2 H_2$ is not a function of the coordinate φ . The appropriate stabilized wave functions for the new levels produced by the first order perturbation are the properly chosen linear combinations $\Psi_{n\tau} = \sum_t C_{\tau t} \Psi_{nt}$, where the $C_{\tau t}$ are given by the first minors of the secular determinant for $W_1^{n\tau}$.

The second order correction to the energy is now determinable in the usual way; that is,

$$W_2^{n\tau} = (H_2)_{n\tau}^{n\tau} + \sum_{n't'}' \{(H_1)_{n\tau}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\},$$

where the dash on the summation sign indicates the omission of those terms for which $n' = n$. This may be expanded into the form:

$$W_2^{n\tau} = \sum_i C_{\tau i}^2 [(H_2)_{ni}^{ni} + \sum_{n't'}' \{(H_1)_{ni}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\}] + \sum_i \sum_j C_{\tau i} C_{\tau j} [(H_2)_{ni}^{nj} + \sum_{n't'}' \{(H_1)_{ni}^{n't'}\} \{(H_1)_{n't'}^{nj}\} / \{W_0^n - W_0^{n'}\}],$$

where the l_1 , l_2 , etc., are the several sets of the degenerate quantum numbers which identify the members of the stabilized wave function. In the case of a triatomic, linear, symmetrical molecule which is not subject to resonance degeneracy, the second order energy constant is given by

$$W_2^{nt} = (H_2)_{nt}^{nt} + \sum_{n't'}' \{(H_1)_{nt}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\}.$$

Unlike the resonance case, in which n comprises

$2V_1 + V_2$ and V_3 , n here refers to V_1 , V_2 , and V_3 as separate entities. The sum in W_2^{nt} is somewhat richer in terms than the corresponding sum

$$\sum_{n't'}' \{(H_1)_{nt}^{n't'}\}^2 / \{W_0^n - W_0^{n'}\}$$

in $W_2^{n\tau}$ because of the absence of the resonance phenomenon. Apart from this difference (which proves to be unimportant), it appears that the second order energy constant for the carbon

dioxide molecule may be expressed as a sum of second order energy constants for the nonresonant type of molecule multiplied by the quantities $C_{\tau t_i^2}$, plus terms which cannot be treated in this fashion and which may be called cross products. A very considerable simplification would be effected in the systematics of the problem if it could be shown that the cross products vanish. For, W_2^{nt} modified by the deletion of terms required by the resonance degeneracy is a definite quadratic function of the quantum numbers; namely,

$$h\{x_0 + x_1 V_1 + x_2 V_2 + x_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3\},$$

where the coefficients are known functions of the true anharmonic constants (a, b, c, d, e, f, g, h and i), the fundamental frequencies ($\omega_1, \omega_2, \omega_3$), and the moment of inertia I , and will be enumerated at a later point in the paper. It would thus be possible to write:

$$\lambda^2 \overline{W_2^{nr}} = h \sum_i C_{\tau t_i^2} \{x_0 + x_1 V_1 + x_2 V_2 + x_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3\} i.$$

It is obvious that for arbitrarily chosen perturbing potentials λH_1 and $\lambda^2 H_2$, the cross product terms will in general not vanish; and the above equations will not be valid. The perturbing potentials for a molecule of the carbon dioxide type have, however, been assumed to possess certain special properties; namely, they are analytic functions endowed with the geometric sym-

metry of the molecule, λH_1 contains no power greater than the third, and $\lambda^2 H_2$ contains no power higher than the fourth. A detailed study shows that these properties of the potential function cause each of the cross product terms to vanish. The actual proof of this statement will be omitted since the analysis, while quite straightforward, is rather lengthy.

The connection between theory and experiment, and the determination of the anharmonic constants can be facilitated by the consolidation of the energies of the zeroth and second orders. This may be accomplished by means of the relation $\sum_i C_{\tau t_i^2} = 1$. For, from this it follows at once that $W_0^n = \sum_i C_{\tau t_i^2} W_0^n$, and hence that

$$W_0^n + \lambda^2 W_2^{nr} = h \sum_i C_{\tau t_i^2} \{x' + \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 + x_{23} V_2 V_3\} i;$$

where

$$x' = x_0 + 2\omega_2 + \omega_3/2,$$

$$\nu_1 = x_1 + 2\omega_2, \quad \nu_2 = x_2 + \omega_2, \quad \nu_3 = x_3 + \omega_3.$$

ω_2 and ω_3 are the zeroth order simple harmonic frequencies which are the solution to the problem of small vibrations.

Omitting the cumbersome details of obtaining the matrix elements⁶ and summing them, the functional dependence of the coefficients may be given as follows. (As listed here the relationships are appropriate for the nonresonant type of triatomic, linearly symmetric molecules, such as CS₂, and their adaption to CO₂ is achieved by first discarding all terms containing the denominator $\omega_1 - 2\omega_2$, and then replacing ω_1 by $2\omega_2$.)

$$\begin{aligned} x' &= \omega_1/2 + \omega_2 + \omega_3/2 + 3d/4 + 3f/4 + 2e + g/2 + i/2 + h/4 + (11a^2/8 + b^2/2 + c^2/2 + 3ab/2 \\ &\quad + 3ac/4 + bc/2)/\omega_1 + b^2/2(\omega_1 + 2\omega_2) + c^2/4(\omega_1 + 2\omega_3) + h\omega_3/16\pi^2 I\omega_2, \\ \nu_1 &= \omega_1 + 3d/2 + g + h/2 - 3a(9a/8 + b + c)/\omega_1 - 3a^2/8\omega_1 - b^2/2(\omega_1 + 2\omega_2) + b^2/2(\omega_1 - 2\omega_2) \\ &\quad - 3c^2/8(\omega_1 + 2\omega_3) + c^2/4(\omega_1 - 2\omega_3), \\ \nu_2 &= \omega_2 + 3e + g/e + i/2 - b(b + 3a/2)/\omega_1 - b^2/4(\omega_1 + 2\omega_2) + h\omega_3/16\pi^2 I\omega_2, \\ \nu_3 &= \omega_3 + 3f/2 + h/2 + i - c(c + 6a + 4b)/4\omega_1 - 3c^2/8(\omega_1 + 2\omega_3) + c^2/8(\omega_1 - 2\omega_3) + h\omega_3/8\pi^2 I\omega_2, \\ x_{11} &= 3(d - 19a^2/4\omega_1)/2, \end{aligned}$$

⁶ In computing the second order energy constant it is necessary to obtain the matrix elements of the various powers of the coordinates σ, ξ and ρ . These may be readily found by referring to the known properties of the Hermitian and Laguerre orthogonal functions. See for example E. Schrödinger, Ann. d. Physik [4] **80**, 437 (1926). Math. appendix, and E. Fues, Ann. d. Physik **80**, 367 (1926).

$$\begin{aligned}
 x_{22} &= 3e/2 - b^2/2\omega_1 - b^2/8(\omega_1 + 2\omega_2) - b^2/8(\omega_1 - 2\omega_2), \\
 x_{33} &= 3f/2 - c^2/2\omega_1 - c^2/8(\omega_1 + 2\omega_3) - c^2/8(\omega_1 - 2\omega_3), \\
 x_{11} &= -e/2 + b^2/8(\omega_1 + 2\omega_2) + b^2/8(\omega_1 - 2\omega_2), \\
 x_{12} &= g - 3ab/\omega_1 - b^2/4(\omega_1 + 2\omega_2) + b^2/4(\omega_1 - 2\omega_2), \\
 x_{13} &= h - 3ac/\omega_1 - 3c^2/8(\omega_1 + 2\omega_3) + c^2/2(\omega_1 - 2\omega_3), \\
 x_{23} &= i + h\omega_3/8\pi^2 I\omega_2.
 \end{aligned}$$

These equations constitute relations between the constants which fix the energy levels (and which we may hope to obtain from observational data), and the anharmonic constants of the molecule. The question now arises as to whether these equations imply any connections between the x 's and ν 's themselves. We have noticed only one such interdependence, but this will prove to be of considerable value. x_{22} and x_{11} are related through the first order perturbation constant b and the normal frequency ω_2 by the expression $x_{22} + 3x_{11} = -3b^2/16\omega_2$ (this is the form in which it applies to the carbon dioxide molecule). $-3b^2/16\omega_2$ can be reduced to a number directly inasmuch as ω_2 is known to be about 667.5 cm^{-1} while the quite precise value of $|b| = 72.5 \text{ cm}^{-1}$ is given by Dennison.² Thus for the CO_2 molecule $x_{22} + 3x_{11} = -1.47 \text{ cm}^{-1}$. The observational data which help to determine the numerical values of the x 's and ν 's are the experimental locations of the infrared vibration-rotation band centers; for, each such position is given theoretically by the difference between two energies of the type:

$$\begin{aligned}
 W_1^{n\tau} + \sum_i C_{\tau i}^2 \{ x' + \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 \\
 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 \\
 + x_{23} V_2 V_3 \}_i.
 \end{aligned}$$

(Because of the perturbations, the energy of the ground state is raised by the amount $\Delta/2 + x'$.) About half of the extensively known band system of CO_2 is to be employed in this evaluation of the coefficients, and the latter will then be used to predict the remaining known bands as well as bands yet undiscovered. None of the difference bands will be used in the solution, since they yield no independent relations, but only combinations of those obtainable from the fundamentals and their overtones. Hence, the equations to be used in solving for the coefficients will be simply those which give the separations of the

energy levels from the ground state, and they have the form:

$$\begin{aligned}
 (W_1^{n\tau} - \Delta/2) + \sum_i C_{\tau i}^2 \{ \nu_1 V_1 + \nu_2 V_2 + \nu_3 V_3 + x_{11} V_1^2 \\
 + x_{22} V_2^2 + x_{33} V_3^2 + x_{1l} l^2 + x_{12} V_1 V_2 + x_{13} V_1 V_3 \\
 + x_{23} V_2 V_3 \}_i =
 \end{aligned}$$

observed position of level, where $W_1^{n\tau}$ depends upon Δ , l and $|b|$.

We proceed to discuss the adaptation of these equations to the problem of the carbon dioxide molecule.

CORRELATION

The data on the infrared spectrum of CO_2 come from several sources. Barker,⁷ and Martin and Barker⁸ have explored the region between 2.7μ and 15μ , mapping a number of bands which range from the $\nu_3 + (\nu_1, 2\nu_2)$ combination bands to the ν_2 fundamental. Recently, Wu and Barker⁹ have discovered the overtone $3\nu_3$, and have succeeded in getting accurate measurements on the bands $\nu_3 + (4\nu_2, 2\nu_2 + \nu_1, 2\nu_1)$ at 2μ and the bands $\nu_3 + (6\nu_2, 4\nu_2 + \nu_1, 2\nu_2 + 2\nu_1, 3\nu_1)$ at 1.6μ . These new data on the 2μ group of bands displace the older work of Schaefer and Philipps¹⁰ whose measurements appear to be in error by approximately one hundred waves per centimeter. This accounts for the very large discrepancy between the calculated positions of these bands (correct to first order) and the values of Schaefer and Philipps as noted by Dennison.²

Making a tentative solution for the x 's and ν 's on the basis of these observations by Barker, Martin and Wu, it has been demonstrated that the three doublet bands photographed by Adams and Dunham¹¹ in the atmosphere of the planet Venus are indeed to be attributed to the CO_2 molecule and are to be identified as $5\nu_3$ and $5\nu_3 + (\nu_1, 2\nu_2)$. Detailed information concerning all of the known bands of carbon dioxide is collected in Table I together with the names of the observers.

In determining the constants, the x 's and ν 's, it would be possible to equate all the observed

⁷ E. F. Barker, *Astrophys. J.* **55**, 391 (1922).

⁸ P. Martin and E. F. Barker, *Phys. Rev.* **41**, 291 (1932).

⁹ To be published in the near future.

¹⁰ Cl. Schaefer and B. Philipps. *Zeits. f. Physik* **36**, 641 (1926).

¹¹ W. S. Adams and T. Dunham, Jr., *Pub. A.S.P.* **44**, 243 (1932).

positions of the levels to their theoretical values and solve the resulting equations by the method of least squares. This method appears to be impractical, however, for two reasons, first because of the great numerical labor involved and second because, as we shall see, the positions of the levels alone are not suitable for determining certain of the constants with any degree of accuracy. Instead the following method was employed.

Two very significant consequences of Dennison's² first order solution are immediately applicable. The first of these is the very accurate value of $|b|$; and the second is the estimate of Δ . Though Δ may be uncertain in this order of approximation, it is nevertheless of a lesser order of magnitude than $|b|$, and hence than W_1^{nr} . It is thus feasible to expand W_1^{nr} in powers of $\Delta/|b|$, retaining no terms beyond the first power. Direct use is made of this knowledge in simplifying the equations discussed below and in obtaining a preliminary value of Δ for the present solution.

Eleven of the most accurately known and most suitably placed bands are selected in setting up the observational equations, and these together with the relation $x_{22} + 3x_{11} = -1.47 \text{ cm}^{-1}$ give twelve equations in the twelve unknowns: $\nu_1\nu_2\nu_3$; $x_{11}x_{22}x_{33}x_{11}$; $x_{12}x_{13}x_{23}$; $\Delta|b|$. Careful examination shows that this group of equations are algebraically inconsistent with any set of real values for the constants. The difficulty can easily be traced to the quantity Δ which is nearly in-

determinate from the energy levels alone. This is because very small changes in the energy levels (of the order of magnitude of the experimental error) cause large fluctuations in Δ , even allowing it to become imaginary. It was thus necessary to find an alternative method for the definition of the numerical value of Δ , or at least of its order of magnitude. This method is furnished by the ratio of intensities of the strong Raman doublet in CO_2 in the neighborhood of 1300 cm^{-1} . The experimental value of this ratio has been given by Dickinson, Dillon and Rasetti¹² as $2/3$. The amplitudes entering into the intensity expressions for the Raman lines are proportional to the constants $C_{\tau i}$; that is, to the amount in which the wave function active for the Raman effect enters into the wave function of the level in question. The ratio of the intensities is therefore equal to the ratio of the squares of $C_{\tau i}$ and may be shown in this case to have the form $(1 - \Delta/2^{\frac{1}{2}}|b|)/(1 + \Delta/2^{\frac{1}{2}}|b|)$. In this way it is found that $\Delta \cong 17 \text{ cm}^{-1}$. With this order of magnitude of Δ serving as a criterion, very small (about $\frac{1}{2} \text{ cm}^{-1}$) but arbitrary corrections were made in the observed positions of some of the eleven energy levels mentioned above. These corrections were maintained as small as possible while keeping Δ near 17 cm^{-1} and $|b|$ close to 72.5 cm^{-1} . The modified and now consistent equations are given below, where we have introduced the notation $\beta = |b|$ and $y = \Delta/\beta$.

- (1) $\nu_2 + x_{22} + x_{11} = 667.9 \text{ cm}^{-1}$,
- (2) $\Delta/2 - \beta(1 + y^2/4)/2^{\frac{1}{2}} + (1 - y/2^{\frac{1}{2}})(\nu_1 + x_{11})/2 + (1 + y/2^{\frac{1}{2}})(2\nu_2 + 4x_{22})/2 = 1268.3$,
- (3) $\Delta/2 + \beta(1 + y^2/4)/2^{\frac{1}{2}} + (1 + y/2^{\frac{1}{2}})(\nu_1 + x_{11})/2 + (1 - y/2^{\frac{1}{2}})(2\nu_2 + 4x_{22})/2 = 1387.9$,
- (4) $2\nu_2 + 4x_{22} + 4x_{11} = 1335.8$,
- (5) $\nu_3 + x_{33} = 2350.1$,
- (6) $\Delta/2 - \beta(1 + y^2/8) + (1 - y/2)(\nu_1 + x_{11} + \nu_2 + x_{22} + x_{12} + x_{11})/2 + (1 + y/2)(3\nu_2 + 9x_{22} + x_{11})/2 = 1933.2$,
- (7) $\Delta/2 + \beta(1 + y^2/8) + (1 + y/2)(\nu_1 + x_{11} + \nu_2 + x_{22} + x_{12} + x_{11})/2 + (1 - y/2)(3\nu_2 + 9x_{22} + x_{11})/2 = 2077.4$,
- (8) $5\nu_3 + 25x_{33} = 11496.5$,
- (9) $\Delta/2 - \beta(1 + y^2/4)/2^{\frac{1}{2}} + (1 - y/2^{\frac{1}{2}})(\nu_1 + x_{11} + 5\nu_3 + 25x_{33} + 5x_{13})/2$
 $+ (1 + y/2^{\frac{1}{2}})(2\nu_2 + 4x_{22} + 5\nu_3 + 25x_{33} + 10x_{23})/2 = 12672.4$,

¹² Dickinson, Dillon and Rasetti, *Phys. Rev.* **34**, 582 (1929).

$$(10) \quad \Delta/2 + \beta(1+y^2/4)/2^{\frac{1}{2}} + (1+y/2^{\frac{1}{2}})(\nu_1 + x_{11} + 5\nu_3 + 25x_{33} + 5x_{13})/2 \\ + (1-y/2^{\frac{1}{2}})(2\nu_2 + 4x_{22} + 5\nu_3 + 25x_{33} + 10x_{23})/2 = 12774.7,$$

$$(11) \quad 4\Delta/3 + (4\nu_2 + 16x_{22} + \nu_3 + x_{33} + 4x_{23})/3 + 2(2\nu_1 + \nu_3 + 4x_{11} + x_{33} + 2x_{13})/3 = 4982,$$

$$(12) \quad x_{22} + 3x_{11} = -1.47.$$

These equations yield the following values for the molecular constants.

$$\begin{array}{lll} \beta = 72.9 \text{ cm}^{-1} & \nu_3 = 2362.8 & x_{11} = -0.74 \\ \Delta = 14.7 & x_{11} = -1 & x_{12} = -2.3 \\ \nu_1 = 1321.7 & x_{22} = +0.74 & x_{13} = -22.1 \\ \nu_2 = 667.9 & x_{33} = -12.7 & x_{23} = -10.9 \end{array}$$

While the twelve equations which have been used are consistent and hence yield unique values for the constants, a closer examination discloses the fact that these constants are not determined with equal accuracy. Small changes in the observed positions of the bands (of the order of the experimental error) would sensibly alter some of them, while leaving others virtually unchanged. ν_1 and ν_2 might be out by as much as one wave per centimeter, but ν_3 is probably accurate to about two-tenths of one wave per centimeter. The anharmonic constants β , x_{33} , $x_{13} + 2x_{23}$, and $x_{22} + 3x_{11}$ are known to within a few tenths of one wave per centimeter. The remaining constants are less precisely determined, in some cases only to order of magnitude.

The positions of any of the vibrational levels of the carbon dioxide molecule may now be computed with the aid of the constants just determined. In Table I we have collected the observational data on the positions of the levels in order to compare them with our calculated results. The identification of the levels is given in column I, while the heights of the energy levels above the ground state, observed and calculated, respectively, are contained in columns II and III. The sources of the experimental data are listed in the last column.

In comparing the calculated and observed locations of the vibrational levels, the latter should be divided into two classes. The first of these contains those bands which are employed in the evaluation of the constants; the discrepan-

TABLE I. *Observed and calculated values for the energy levels in CO₂.*

Identification $V_1 V_2 V_3 l$	Position (cm ⁻¹)		Observer (number indicates reference)
	Calculated	Observed	
0 1 0 1	667.9	667.5	8
0 2 0 0	1286.3	1285.8	8
1 0 0 0	1387.9	1388.4	
0 2 0 2	1335.8	1336.2	8
0 3 0 1	1933.2	1933.5	8
1 1 0 1	2077.4	2077.1	
0 0 1 0	2350.1	2350.1	8
0 2 1 0	3614	3610	7
1 0 1 0	3716	3717	
0 4 1 0	4852	4860	9
1 2 1 0	4982	4982	
2 0 1 0	5109	5110	
0 6 1 0	6078	6079	9
1 4 1 0	6233	6233	
2 2 1 0	6352	6353	
3 0 1 0	6512	6512	
0 0 3 0	6974	6978	9
0 0 5 0	11496.5	11496.5	11
0 2 5 0	12672.4	12672.4	11
1 0 5 0	12774.7	12774.7	

cies in this group are all of the order of the experimental error, and represent the small arbitrary additions used to make the simultaneous equations consistent. The agreement between the calculated and observed values for the remaining nine levels is extraordinarily good, being better than the experimental error in eight instances and poorer in only one (the difference of eight waves per centimeter in the case of the 4860 band of the 2μ group of bands is the only example of inferior agreement). This good agreement which obtains in the second class of levels is genuine and not fortuitous. It is to be considered a substantiation of the method of attack used in the problem, and a verification of the expression

TABLE II. Positions of some bands which ought to be accessible to experiment.

Identification				Calculated position (cm ⁻¹)
V ₁	V ₂	V ₃	l	
0	2	3	0	8188
1	0	3	0	8291
0	3	4	1	11050
1	1	4	1	11193
0	4	5	0	13823
1	2	5	0	13952
2	0	5	0	14080
0	1	6	1	14322
0	6	5	0	14961
1	4	5	0	15115
2	2	5	0	15234
3	0	5	0	15397
0	0	7	0	15917
0	2	7	0	17049
1	0	7	0	17151
0	0	9	0	20236
0	2	9	0	21324
1	0	9	0	21426

for the energy of the carbon dioxide molecule.¹³

In Table II are given the positions of some bands which ought to be accessible to experiment, but which have as yet not been discovered. The bands in the visible and photographic infrared regions of the spectrum will have to be sought in the absorption spectrum of the planet Venus, and such a search is being made by T. Dunham, Jr., at Mount Wilson Observatory. On the other hand, the bands $3\nu_3 + (\nu_1, 2\nu_2)$ should offer no par-

¹³ In a recent paper Langseth and Nielsen (Zeits. f. physik. Chemie **B19**, 427 (1932)), have reexamined the Raman spectrum of gaseous carbon dioxide, using an exposure time of one month. In addition to the four Raman lines previously known, they obtained six very faint lines which should, presumably, be due to transitions starting from the three excited levels in the neighborhood of 1300 cm⁻¹. The observed positions of the six extremely faint lines are: 1241, 1305, 1325, 1344, 1369 and 1433 cm⁻¹. On the other hand, the frequencies of the above-mentioned transitions may be readily computed from our formulae, and eight very faint Raman lines should appear in the following positions: 1166, 1248, 1268, 1288, 1390, 1415, 1426 and 1517 cm⁻¹. It thus appears that of the eight lines

ticular difficulty, and should be as easily observed as the bands at 1.6 μ .

CONCLUSION

The second order energy constant for the carbon dioxide molecule has been computed. It involves eleven constants whose connections with the twelve constants defined by the potential energy is given. It is consequently not possible to obtain the potential energy function from our present results, and recourse must be had to some alternative method. This method consists in an analysis of the interaction between vibration and rotation. It may be shown that the convergence in the fine structure lines of the various absorption bands will yield values for the three constants of the first order potential function; namely, a , b and c . A determination of the entire potential function is thus made possible. This investigation will be the subject of a second paper, to appear, shortly in which, also, an attempt will be made to describe the potential energy of the carbon dioxide molecule by means of a function resembling the Morse potential function for diatomic molecules.

Finally, the writers wish to express their indebtedness and thanks to Professor E. F. Barker and Mr. Ta-You Wu for placing the results of their investigation at our disposal and allowing us to publish a preliminary account of them, and to Dr. T. Dunham, Jr. for his willing and helpful correspondence in connection with the Venus bands.

which should appear, the lines 1268, 1288, 1390 and 1415 blend with the four already known Raman lines; the lines 1166 and 1517 do not fall within the limits of the region covered by the experimental data, while the lines 1248 and 1426 probably correspond to the two observed lines 1241 and 1433. The lines 1241 and 1433 are classified as *ausserordentlich schwach* and hence the discrepancy between the observed and computed values is not to be considered as a serious disagreement. There appears to be no place in the theoretical scheme for the remaining four observed lines, inasmuch as we have been able to find no transitions corresponding to these frequencies. It is perhaps possible that this discrepancy originates in the intrinsic difficulty experienced in recording faint lines through exposures of such extended duration.