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The Vibrational Levels of Linear Symmetrical Triatomic Molecules

By David M. Dennison
University of Michigan

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The theory proposed by E. Fermi of the energy levels of molecules of the CO_2 type is discussed. It is shown that this assumes a particularly simple form when expressed in the coordinates used by Dennison for describing such molecules. When there exist no integral or nearly integral relations between the vibrational frequencies the first order energy correction λW_1 caused by the anharmonic forces vanishes leaving only the second order term $\lambda^2 W_2$. When, however, two of the fundamental frequencies are commensurable, certain of the energy levels coincide thus becoming degenerate. This degeneracy may be removed by the anharmonic forces in which case there appears a first order energy constant λW_1 different from zero. The value of λW_1 is computed explicitly for certain of the lower energy states and it appears that the only levels which interact under the influence of the resonance are those having the same value of the azimuthal quantum number l. From this it follows that the selection rules are not affected by the existence of the resonance. Finally it is shown how the first order term λW_1 goes over into the second order term $\lambda^2 W_2$ as the resonance between the frequencies becomes less and less exact. When these results are applied to the CO_2 spectrum it is found that the resonance between ν_1 and $2\nu_2$ is almost perfect and consequently the energy levels can only be ordered with the help of the first order term λW_1. For CS_2 on the other hand the difference between ν_1 and $2\nu_2$ is so large that the effect of the resonance on the positions of the energy levels may be disregarded.

WITHIN the last few months two important contributions have been made to our knowledge of the carbon dioxide molecule and its infrared spectrum. The first of these was contained in a paper by E. Fermi[1] and was intended in the first instance to explain the Raman spectrum of CO_2.The second, by P. E. Martin and E. F. Barker,[2] is reported in the foregoing paper and consists of an experimental study of the fine structure of certain of the infrared bands. It is proposed in the present paper to discuss Martin and Barker's results in the light of Fermi's theory and to relate both to the earlier work of Dennison[3] on the general properties of symmetrical molecules of the type YX_2.

It can no longer be doubted that the carbon dioxide molecule in its normal electronic state possesses a form which is both linear and symmetrical. Two sets of independent data prove this. The fact that the fine structure lines of the parallel type band at 4.3μ and of the perpendicular type band at 15μ both are linearly spaced in frequency and have the same spacing constant shows that the CO_2 molecule must be linear. The fact that alternate fine structure lines of these bands have zero intensity shows that the mole-

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

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

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

cule must have the form O=C=O and not O=O=C. The second reason for believing that CO_2 is both linear and symmetrical is that it has been shown that the vibrational levels of such molecules are connected by rather unusual selection rules which permit only certain of the overtone bands to appear. A study of all the known infrared bands of CO_2 reveals that just the permitted overtones and no others are observed.

In discussing the positions of the vibrational levels of the molecule YX_2, the notation proposed by Dennison[3] will be used as well as the same coordinates. The internal or vibrational degrees of freedom are four in number since of the total $3n$ or 9 degrees of freedom, three may be associated with translation of the system as a whole and two (not three, since the molecule is linear) with rotation of the system. The coordinates of the vibrational motion are chosen as z, q, r and ϕ. z is the displacement of the Y atom along the figure axis relative to the center of gravity of the X atoms. q is the displacement of the X atoms, from their equilibrium position, relative to each other. r is the displacement of the Y atom $\perp$ to the figure axis relative to the line joining the X atoms and ϕ is the angle this latter displacement makes in a plane $\perp$ to the figure axis.

The kinetic energy of the system (internal) may be readily computed and is,

$$T = (m/4)\dot{q}^2 + (\mu/2)(\dot{z}^2 + \dot{r}^2 + r^2\dot{\phi}^2)$$

where m is the mass of an X atom and μ is the reduced mass $2mM/(M+2m)$.

We assume that the potential energy U possesses a symmetry which corresponds with the geometric symmetry of the molecule. That is, U must be an even function of z, an even function of r and independent of the angle ϕ.

We assume that the potential function may be developed after λ, a parameter of smallness so that $U = U_0 + \lambda U_1 + \lambda^2 U_2$. The function U_0 contains all the permissable terms which are quadratic in the coordinates, U_1 all the cubic terms and U_2 all the quartic terms. It is usual to let the constants of U_0 contain the normal frequencies ν_1, ν_2 and ν_3 so that it has the form,

$$U_0 = \pi^2\nu_1^2 mq^2 + 2\pi^2\nu_2^2\mu r^2 + 2\pi^2\nu_3^2\mu z^2.$$

The wave function which results from using a wave equation based on T and U_0 has been already described by Dennison.

$$\psi = \psi_{(\sigma)}{}^{V_1}\psi_{(\xi)}{}^{V_3}R_{(\rho)}{}^{V_2 l}e^{\pm il\phi}$$

where $\psi_{(\sigma)}{}^{V_1}$ and $\psi_{(\xi)}{}^{V_3}$ are the well-known Hermitian orthogonal functions.

$$R_{(\rho)}{}^{V_2 l} = \rho^l e^{-\rho^2/2}\sum_{k=0}^{V_2-l} a_k\rho^k$$

where

$$a_{k+2} = \frac{2k + 2l - 2V_2}{(k+2)(k+2+2l)}a_k.$$

The dimensionless variables σ, ξ and ρ, replace the coordinates q, z and r and are related to them by the following expressions,

$$\sigma = 2\pi[\nu_1 m/2h]^{1/2} q$$
$$\xi = 2\pi[\nu_3 \mu/h]^{1/2} z$$
$$\rho = 2\pi[\nu_2 \mu/h]^{1/2} r.$$

It will prove convenient to write the energies T and U in terms of these variables.

$$\begin{aligned} T &= (h/8\pi^2)\{\dot{\sigma}^2/\nu_1 + \dot{\xi}^2/\nu_3 + (\dot{\rho}^2 + \rho^2\dot{\phi}^2)/\nu_2\} \\ U_0 &= (h/2)\{\nu_1\sigma^2 + \nu_3\xi^2 + \nu_2\rho^2\} \\ \lambda U_1 &= \lambda h(a\sigma^3 + b\sigma\rho^2 + c\sigma\xi^2) \\ \lambda^2 U_2 &= \lambda^2 h(d\sigma^4 + e\rho^4 + f\xi^4 + g\sigma^2\rho^2 + i\xi^2\sigma^2 + j\rho^2\xi^2). \end{aligned}$$

The quantities λ, a, $\cdots j$ are constants which characterize the anharmonic nature of the potential function. It will be noted that the condition that U must possess a symmetry which corresponds to the geometric symmetry of the molecule, greatly reduces the number of terms appearing in U_1 and U_2. Thus of the ten cubic terms which may be formed with three variables, only three actually appear in U_1.

The energy constant W of the system may be developed in powers of λ so that $W = W_0 + \lambda W_1 + \lambda^2 W_2$. The zero^th order term W_0 has of course the form,

$$W_0/h = \nu_1(V_1 + \tfrac{1}{2}) + \nu_2(V_2 + 1) + \nu_3(V_3 + \tfrac{1}{2})$$

where V_1, V_2, and V_3 are the quantum numbers appearing in the expression for the wave function. Since the number l does not appear in W_0, the system is in this approximation (V_2+1) fold degenerate.

The terms W_1 and W_2 which arise from the anharmonic nature of the potential function may be readily computed using perturbation theory methods. In the usual case when the frequencies ν_1, ν_2 and ν_3 are incommensurable, this leads to the following result.

$$\begin{aligned} \lambda W_1 &= 0 \\ \lambda^2 W_2/h &= x_0 + x_1V_1 + x_2V_2 + x_3V_3 + x_{11}V_1^2 + x_{22}V_2^2 + x_{ll}l^2 \\ &\quad + x_{33}V_3^2 + x_{12}V_1V_2 + x_{13}V_1V_3 + x_{23}V_2V_3 \end{aligned}$$

x_0, $\cdots x_{23}$ are a set of constants[4] which are related to the anharmonic constants a, $\cdots j$.

The important contribution of Fermi consists in an investigation of the system when two of the frequencies bear a commensurable or nearly commensurable relation to each other. He has been able to show that when $\nu_1 \cong 2\nu_2$ the first order energy constant λW_1 no longer vanishes and may exert a very considerable influence in the energy levels. We propose to make clear just how this result obtains and how it may be correlated with the observed infrared spectrum of CO_2.

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[4] Dennison (reference 3) in giving the formula for $\lambda^2 W_2$ stated that the constant x_{ll} was equal to $-\frac{1}{3}x_{22}$. Unfortunately this statement is incorrect except in the special case where $\lambda U_1 = 0$. In general an independent constant x_{ll} must be introduced.

It will become evident from the analysis that when $\nu_1 \cong 2\nu_2$, λW_1 depends solely upon the anharmonic term $b\sigma\rho^2$ while if ν_1 were approximately twice ν_3, λW_1 would depend entirely upon $c\sigma\xi^2$. For CO_2 as well as CS_2 it is the former condition which holds and we may therefore confine our attention to the term $b\sigma\rho^2$.

We shall first carry out the computation, assuming first that no commensurable relation exists between ν_1 and ν_2. It is possible to ignore the existence of the vibration ν_3 since its coordinate ξ does not enter the part of U_1 we are considering. In fact we may without loss of generality confine ourselves to the case where $\lambda U_1 = \lambda h b\sigma\rho^2$ and $\lambda^2 U_2 = 0$. The usual methods of perturbation theory then give

$$\lambda W_1 = \lambda U_{1V_1V_2l}^{V_1V_2l}$$

$$\lambda^2 W_2 = \lambda^2 \sum_{V_1'V_2'} \left(U_{1V_1'V_2'l}^{V_1V_2l} \right)^2 \Big/ \left(W_0^{V_1V_2} - W_0^{V_1'V_2'} \right)$$

where $U_1{}_{V_1'V_2'l}^{V_1V_2l}$ is the matrix element of U_1.

The general expression for the perturbation energy has been slightly simplified since we take only those matrix elements of U_1 which are diagonal in l and omit the corresponding integration over ϕ. This is permissible since the function U_1 is independent of ϕ and therefore all the matrix elements which are nondiagonal in l automatically vanish. It is supposed that ψ^{V_1} and $R^{V_2 l}$ are properly normalized.

It is clear that the matrix elements of U_1 which are diagonal in V_1 must vanish since $(\psi^{V_1})^2$ is an even function of σ while the function U_1 is odd. Evidently then $\lambda W_1 = 0$. The computation of $\lambda^2 W_2$ is somewhat tedious but quite straight-forward and leads to the following result.

$$\lambda^2 W_2 = -\frac{\lambda^2 b^2 h}{8} \left\{ \frac{V_2^2 + 4V_1V_2 - l^2 + 4V_1 + 4V_2 + 4}{\nu_1 + 2\nu_2} + \frac{V_2^2 - 4V_1V_2 - l^2 - 4V_1}{\nu_1 - 2\nu_2} + \frac{4(V_2 + 1)^2}{\nu_1} \right\}.$$

The expression for $\lambda^2 W_2$ which has been obtained is valid except in the region where ν_1 and $2\nu_2$ are approximately equal. In this case $\lambda^2 W_2$ becomes of higher order of magnitude and the whole method of the perturbation theory which has been used breaks down. A new method must then be employed which leads to the result that when $\nu_1 \cong 2\nu_2$, a first order perturbation energy λW_1 exists.[5]

We begin by letting the unperturbed system be one where ν_1 and $2\nu_2$ are exactly equal, thus making a number of the previously distinct energy levels coincide. It is possible as before to ignore the vibration ν_3 and its coordinate ξ and to introduce the single anharmonic term $\lambda U_1 = \lambda h b\sigma\rho^2$. To this however

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[5] We may remark that λW_1 and $\lambda^2 W_2$ will be given by the above expressions even when $\nu_1 \cong 2\nu_2$ for the particular states where the quantum numbers bear the relation $V_2^2 - 4V_1V_2 - l^2 - 4V_1 = 0$. This conclusion is borne out by the results of the ensuing investigation.

must be added a term involving $\Delta = \nu_1 - 2\nu_2$ to take account of the fact that in the final or perturbed system ν_1 is only of the same order but not necessarily equal to $2\nu_2$. The problem may then be treated in a manner similar to that used by Fermi, namely by the standard method of perturbations of a degenerate system.[6]

The unperturbed system may be characterized by T_0 and U_0 and the effect of the perturbation grouped into the two terms T_1 and λU_1.

$$
\begin{aligned}
T_0 &= (h/8\pi^2\nu_2)(\dot{\sigma}^2/2 + \dot{\rho}^2 + \rho^2\dot{\phi}^2) \\
U_0 &= (h\nu_2/2)(2\sigma^2 + \rho^2) \\
T_1 &= (\Delta h/32\pi^2\nu_2^2)\dot{\sigma}^2 = -(\Delta h/2)(\partial^2/\partial\sigma^2) \\
\lambda U_1 &= \lambda h b \sigma \rho^2 + \Delta h \sigma^2/2.
\end{aligned}
$$

The unperturbed system having the kinetic and potential energies T_0 and U_0 respectively possesses an energy constant $W_0/h = \nu_2(2V_1 + V_2 + 2)$. The unperturbed system is thus degenerate in two ways, first because as before W_0 is independent of the quantum number l and second because the energy does not depend upon V_1 and V_2 separately but only upon the function $2V_1 + V_2$.

To find the first order perturbed energy of a degenerate system, the secular determinant must be constructed and set equal to zero.

$$
\left| A_s^r - \lambda W_1 \delta_s^r \right| = 0.
$$

The roots of this determinant λW_1 furnish the required perturbed energies. The quantity A_s^r is the matrix element of the perturbing function $T_1 + \lambda U_1$.

The quantum numbers for any one secular determinant must belong to the same value of W_0, that is $2V_1 + V_2 =$ a constant. We may simplify the expression for A_s^r by noting two properties of the system. (a) All the elements which are nondiagonal in l vanish since $T_1 + \lambda U_1$ is independent of the angle ϕ. (b) The wave function ψ^{V_1} satisfies the differential equation $(d^2\psi^{V_1}/d\sigma^2) + (2V_1 + 1 - \sigma^2)\psi^{V_1} = 0$ and therefore $(T_1 + \lambda U_1)\psi^{V_1} = \{\lambda h b \sigma \rho^2 + \Delta h (V_1 + \frac{1}{2})\}\psi^{V_1}$. Combining these properties with the other known properties of the unperturbed wave functions, we may express all the nonvanishing elements of A_s^r as follows,

$$
\begin{aligned}
A_{V_1 V_2 l}^{V_1 V_2 l} &= \Delta h (V_1 + \tfrac{1}{2}) \\
A_{V_1 - 1\, V_2 + 2\, l}^{V_1\ V_2\ l} &= -\lambda h b (V_1)^{1/2}[(V_2 + 2)^2 - l^2]^{1/2}/2^{3/2}.
\end{aligned}
$$

The secular determinant may now easily be constructed for any value of $2V_1 + V_2$. The coordinate system we have used allows the determinant to be evaluated very simply since, because the elements A_s^r which are nondiagonal in l all vanish, the determinant may be factored into a set of determinants each corresponding to a particular value of l. Thus if $2V_1 + V_2$ equals 4, the

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[6] While our computation is quite equivalent to that performed by Fermi and leads to the same result we feel that a real advantage is secured by our use of the coordinates σ, ρ and ϕ. Not only is the calculation much simpler but it is found that the final results may be presented in a very natural form which allows a clear understanding of their interrelations.

original determinant is of 9th order. It can be factored into three determinants of order 3, 2, 2, 1 and 1 corresponding to $l=0$, $+2$, -2, $+4$ and -4 respectively.

The explicit solutions of the secular determinant for the smaller values of the quantum members are presented in Table I.

TABLE I.

V_1	V_2	l	$\lambda W_1/h$
0	0	0	$\Delta/2$
0	1	± 1	$\Delta/2$
1	0	0	$\Delta\pm[\Delta^2/4+(\lambda b)^2/2]^{1/2}$
0	2	0	
0	2	± 2	$\Delta/2$
1	1	± 1	$\Delta\pm[\Delta^2/4+(\lambda b)^2]^{1/2}$
0	3	± 1	
0	3	± 3	$\Delta/2$
2	0	0	$(\lambda W_1)^3-(9/2)\Delta h(\lambda W_1)^2 -[3(\lambda hb)^2-(2\ 3/4)\ (\Delta h)^2]\lambda W_1 -(1\ 5/8)\ (\Delta h)^3+(1\ 1/2)\ (\lambda bh)^2\Delta h=0$
1	2	0	
0	4	0	
1	2	± 2	$\Delta\pm[\Delta^2/4+(3/2)\ (\lambda b)^2]^{1/2}$
0	4	± 2	
0	4	± 4	$\Delta/2$

The degeneracy that originally existed in the unperturbed system has been to a considerable extent removed by the perturbing potential and the identities of the levels have been somewhat changed. When two or more levels are connected by lines in the above table, we mean that the original degeneracy of the levels has been removed. The wave functions which are appropriate for describing these new undegenerated levels are linear combinations of the wave functions of the degenerate levels. The coefficients in the linear combinations are given by the first minors of the secular determinant in question.

We should now like to show how the energy constant of second order $\lambda^2 W_2$ which is appropriate for the case $\nu_1 \neq 2\nu_2$ goes over into the first order constant λW_1 when $\nu_1 \mathrel{\hat{=}} 2\nu_2$. In order to compare these two expressions, values of $\Delta=\nu_1-2\nu_2$ must be chosen which are small compared with $\nu_1+2\nu_2$ but which are large compared with the anharmonic constant λb. The leading term of $\lambda^2 W_2$ is then $-\lambda^2 b^2 h(V_2^2-4V_1V_2-4V_1-l^2)/\Delta$ while the expressions for λW_1 may be developed. Thus the energy levels of the states (100) and (020) become $(3/2)\Delta h+\lambda^2 b^2 h/2\Delta$ and $(1/2)\Delta h-\lambda^2 b^2 h/2\Delta$. The terms $(3/2)\Delta h$ and $(1/2)\Delta h$ when added to the W_0 of the degenerate system ($\nu_1=2\nu_2$) are just equal to the W_0 of the undegenerate system and the remaining terms $\pm\lambda^2 b^2 h/2\Delta$ are just equal to $\lambda^2 W_2$ when we substitute the appropriate values of the quantum numbers. A similar agreement is found between λW_1 and $\lambda^2 W_2$ for all the other levels which have been computed.

This analysis leads to a criterion as to the method to be used in correlating the energy levels of such a system. When $|\Delta| \leq |\lambda b|$ we must treat the system as degenerate and use the first order energy constant λW_1. A second order constant $\lambda^2 W_2$ could also be added and would probably have the usual form (i.e., a quadratic function of the quantum numbers). When $|\Delta| \gg |\lambda b|$, λW_1 becomes equal to one of the terms of $\lambda^2 W_2$ and consequently we may order the levels with the aid of the second order constant $\lambda^2 W_2$ alone. The difference between these cases will be brought out in our discussion of the CO_2 and CS_2 spectra.

Finally it will be observed that the selection rules proposed by Dennison for the symmetrical triatomic molecules apply equally well to the degenerate system and to the nondegenerate system for which they were derived. The states of the degenerate system which combine and lose their identity possess wave functions having the same quantum numbers l and V_3 and having numbers V_2 which differ by an even integer. The selection rules depend upon whether the changes ΔV_2, ΔV_3 and Δl are odd or even integers and these changes will be the same (i.e., odd or even) for all the levels of a related group. The wave functions of a related group all have the same symmetry character with regard to an interchange of the two equal atoms.

Discussion of the CO_2 Spectrum

Let us now consider the energy levels of the CO_2 molecule as determined by the observations of Martin and Barker. If the assumption is made that the system is nearly degenerate ($|\Delta| \ll |\lambda b|$), the energy may be expressed as $W_0 + \lambda W_1$ and the second order terms $\lambda^2 W_2$ may be neglected. This identification will allow us to compute from three of the levels Δ and λb (thus checking the assumption as to the degeneracy) and then to predict the positions of the remaining levels. The difference between the predicted and observed positions of these levels will be a measure of the neglected term $\lambda^2 W_2$. The results of this correlation are collected in Table II where the lowest state (000) is taken to have zero energy.

Table II.

V_1	$\nu_2 = 667.5$ cm^{-1} V_2	l	$\lambda b = \pm 72.5$ cm^{-1} Observed level	$\Delta = +4.2$ cm^{-1} Computed level
0	0	0	0	0
0	1	1	667.5 cm^{-1}	—
1	0	0	1285.8	—
0	2	0	1388.4	—
0	2	2	1336.2	1335.0
1	1	1	1933.5	1932.1
0	3	1	2077.1	2077.1
0	3	3	—	2004.6
2	0	0	—	2548.0
1	2	0	—	2675.6
0	4	0	—	2799.0

It appears that in CO_2 the resonance between ν_1 and $2\nu_2$ is almost exact so that their difference is small, $\Delta = 4.2$ cm^{-1}. The accuracy with which this constant has been determined is not great. We estimate the error to be of the order of 50 to 100 percent. The value of $|\lambda b|$ on the other hand may be fixed with considerable precision since it depends essentially on the distance between the two strong Raman bands or between certain of the infrared bands. It is probably accurate to at least 1 percent. It will be noted that the sign of λb cannot be determined through the positions of the energy levels.

The overtone bands of CO_2 which have been observed by Barker[7] and others to lie in the region of 2.7μ must be correlated with the sum of the levels (100), (020) and the level $\nu_3 = 2350$ cm^{-1}. The computed values of these overtone frequencies are therefore 3636 and 3738 cm^{-1} while their observed positions are 3610 and 3717 cm^{-1}. The differences, 24 and 21 cm^{-1}, are due to the fact that in the computation we have neglected the second order energy constant $\lambda^2 W_2$. In a similar way the three overtone bands observed by Schaefer and Philipps[8] at about 2μ arise from a combination of the level ν_3 with the levels (200), (120), (040). The computed values of the frequencies are 4898, 5026 and 5149 cm^{-1}, while their observed positions are 4780, 4890 and 5010 cm^{-1}. The differences, which are also due to the neglected second order terms, are 118, 136 and 139 cm^{-1} respectively. We should expect these differences to be larger than those for the lower overtone bands but only by a factor of about two. The solution of this difficulty must await the results of further analysis.

Discussion of the CS_2 Spectrum

According to Krishnamurti[9] the Raman spectrum of CS_2 gas consists principally of two strong lines with an intensity ratio of about 5:1 lying at 655.5 and 795.0 cm^{-1} respectively. These may be identified with transitions from the normal state to the two combined levels (100), (020). The frequency ν_1 has been found by Dennison and Wright[10] to lie at 396.8 cm^{-1}. Combining these three data and neglecting as before the second order constant $\lambda^2 W_2$ we may compute $\lambda b = \pm 19.7$ cm^{-1} and $\Delta = -136.7$ cm^{-1}.

These results for λb and Δ show that we are in the region where the resonance between ν_1 and $2\nu_2$ is very poor and where λW_1 is equivalent to one of the terms of $\lambda^2 W_2$. (Since for these values of λb and Δ, the expression $[\Delta^2/4 + (\lambda b)^2/2]^{1/2}$ does not differ appreciably from $\Delta/2 + (\lambda b)^2/2\Delta$.) Consequently we may not neglect $\lambda^2 W_2$ in computing the energy levels. In fact we may consider that λW_1 is included among the terms of $\lambda^2 W_2$ and thus use the general expression $W_0 + \lambda^2 W_2$ alone for correlating the energy levels. This expression involves ten constants while there have been observed only eight Raman and infrared bands. Thus only certain of the anharmonic constants may be obtained and no independent relations are available with which to check the theoretical formula. (Those constants which may be computed are all small and of the correct order of magnitude). These considerations show that our initial computation of λb and Δ was somewhat meaningless. That is to say, while we can determine with accuracy the value of Δ, the difference between ν_1 and $2\nu_2$, the positions of the levels will not furnish us with any clear information as to the value of λb other than its order of magnitude.

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

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

[9] Krishnamurti, Ind. Journ. Phys. **5**, 109 (1930).

[10] D. M. Dennison and N. Wright, Phys. Rev. **38**, 2077 (1931).

In a recent note S. Bhagavantam[11] calls attention to the fact that the Raman line at 795.0 cm^{-1} possesses properties which are characteristic of the inactive frequency ν_1 and which have nothing in common with the frequency ν_2. He therefore prefers to designate this level with the symbol ν_1' rather than with $2\nu_2$ as do Dennison and Wright. This remark by Bhagavantam illustrates very clearly the nature of the line in question. As a Raman line its existence depends wholly on the fact that the level must be described partly with the wave function (100) of the unperturbed inactive frequency ν_1. Thus its character in the Raman spectrum must be similar to ν_1 and there is some justification for calling it ν_1'. However, in ordering all the vibrational levels of the molecule, we have shown that since $|\Delta|$ is large compared with $|\lambda b|$ we may disregard the fact that $\nu_1 \cong 2\nu_2$. Therefore in speaking of the positions of the levels it is more appropriate to speak of this level as $2\nu_2$. The level possesses a wave function partly characteristic of ν_1 and partly characteristic of $2\nu_2$ and consequently its proper designation will depend upon what properties of the spectrum are being considered.

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[11] S. Bhagavantam, Phys. Rev. **39**, 1020 (1932).