THE INTENSITIES OF THE RAMAN LINES IN CARBON DIOXIDE

BY N. S. NAGENDRA NATH AND E. V. CHALAM
(*From the Department of Physics, Andhra University, Waltair*)

Received January 24, 1941

§ 1. *Introduction*

IT is well known that the Raman spectrum of carbon dioxide consists of two strong lines with frequency shifts 1285 cm.$^{-1}$ and 1388 cm.$^{-1}$. The linear symmetrical model of CO_2 has four normal vibrations, one of them being the symmetrical motion of the oxygen atoms along the axis of the molecule with the carbon atom at rest, two others being the doubly degenerate vibration of the carbon atom against the oxygen atoms in a plane perpendicular to the axis of the molecule and the remaining other being the vibration of the carbon atom against the oxygen atoms along the axis of the molecule. Fig. 1 illustrates the normal modes of vibration.

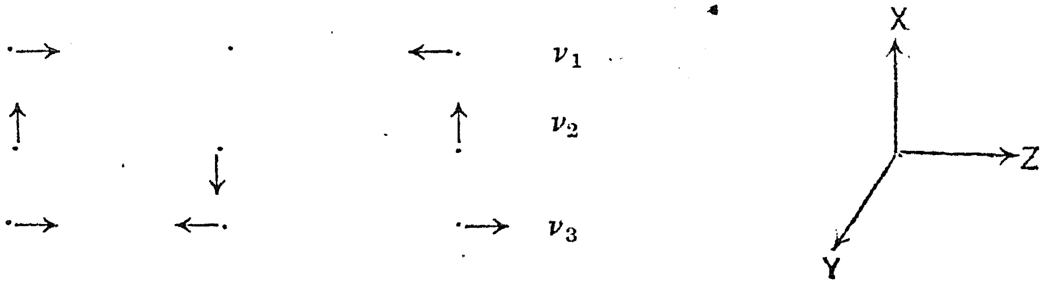

FIG. 1

Amongst the fundamental frequencies only ν_1 is active in the Raman effect, and only ν_2 and ν_3 are active in the infra-red. A simple consideration of the polarisability tensor when the molecule is vibrating with frequency ν_2 or ν_3 shows that their even harmonics only could appear in the Raman effect. Hence in addition to the fundamental frequency ν_1, we could expect $2\,\nu_1$, $2\,\nu_3$ and $2\,\nu_2$ to appear in the Raman spectrum. It may be remarked that the intensity of the former two overtones is mainly governed by the second differential co-efficient of the polarisability of the C–O bond with respect to the internuclear distance. As these overtones have not been reported so far in the experimental literature, we could assume that the higher derivatives of the polarisability of the C–O bond with respect to the internuclear distance are so small as not to give observable effects. But this argument does not apply to $2\,\nu_2$. The intensity of this line is governed by the optical anisotropy of the molecule in the equilibrium configuration and the first derivative of the polarisability of the C–O bond with respect to the internuclear distance. To understand this clearly let us for a moment assume that the polarisabilities of the C–O bonds do not change with respect to the internuclear distance. In such a case no Raman lines will appear except those corresponding to the even harmonics of ν_2 because in the vibration ν_2, the optical anisotropy changes while it does not in the vibrations ν_2 and ν_3. Next, we can also understand the dependence of the intensity of 2 ν_2 on the first differential co-efficient of the polarisability of the C–O bond with respect to the internuclear distance even without the second order coefficients. In the vibration ν_2, the change in the inter-nuclear distance of the C–O bonds is proportional to the square of the distance of the carbon atom from the line joining the oxygens, which distance corresponds to the normal co-ordinate ν_2. Hence, even though the polarisability of the C–O bonds varies linearly as a function of the bond length, it will contribute a second order polarisability in the vibration ν_2.

More generally, the polarisability tensor of a molecule as a function of the normal co-ordinates can be written as

$$\alpha = \alpha_0 + \sum_i \left(\frac{\partial \alpha}{\partial q_i}\right)_0 q_i + \tfrac{1}{2} \sum_{i,j} \left(\frac{\partial^2 \alpha}{\partial q_i \, \partial q_j}\right)_0 q_i \, q_j + \cdots \tag{1}$$

The intensity of the Raman line corresponding to ν_i will depend on $\left(\frac{\partial \alpha}{\partial q_i}\right)_0 q_i$ and that corresponding to 2 ν_i will depend on $\left(\frac{\partial^2 \alpha}{\partial q_i^2}\right)_0 q_i^2$ neglecting the higher order derivatives. The polarisability tensor of the *k*th bond in the molecule can be written as

$$A^{(k)} = A_0^{(k)} + A_1^{(k)} \frac{\Delta r^{(k)}}{a^{(k)}} + \cdots \tag{2}$$

where $\Delta r^{(k)}$ is the change in the internuclear distance $a^{(k)}$. Let us assume that the general expansion (1) is made up of N expansions of the type (2) where N is the number of bonds. This may be assumed to be nearly right because our procedure would be a piece-wise representation of the general expansion of the polarisability of the molecule. If such a procedure is to be adopted, it must not be thought that $\left(\frac{\partial^2 \alpha}{\partial q_i^2}\right)_0$ will not depend on $A_1^{(k)}$ and $A_0^{(k)}$ because in certain normal modes of vibration the variations in the internuclear distances could be quadratic functions of the normal co-ordinates and the ordinary optical anisotropy of the molecule could change even though all A's other than A_0's, are zero.

In the case of CO_2 the variations in the C–O bond lengths are linear functions of the normal co-ordinates corresponding to ν_1 and ν_3 while they depend on the square of the co-ordinate corresponding to ν_2. Because the overtones of ν_1 and ν_3 are not reported so far, we could assume only A_0 and A_1 for the bonds and still account for $2\,\nu_2$. These arguments are really very general. We could thus account for the appearance of overtones of certain modes of vibration even though the overtones of the most symmetrical vibrations are not observed (as in the case of methane and deuteromethanes).

§ 2. *The Polarisability Tensor in Terms of Normal Co-ordinates*

The axes of the molecule are chosen as shown in Fig. 1. The co-ördinates of the oxygen, carbon and oxygen atoms in the equilibrium configuration are $(0, 0, -a)$, $(0, 0, 0)$ and $(0, 0, +a)$ where a is the length of the C–O bond. The oxygen atoms are denoted by the subscripts 1 and 2 and the carbon atom by the subscript 3. Let (x_r, y_r, z_r) be the variations in the co-ordinates of the rth atom. Let m and M be the masses of the oxygen and carbon atoms respectively. Conditions of the constancy of linear and angular momenta require the following constraints among the cartesian variations:

$$\left.\begin{aligned} & m\,(x_1+x_2)+\mathrm{M}x_3=0, \\ & m\,(y_1+y_2)+\mathrm{M}y_3=0, \\ & m\,(z_1+z_2)+\mathrm{M}z_3=0, \\ & \qquad\qquad x_1=x_2, \\ & \qquad\qquad y_1=y_2. \end{aligned}\right\} \tag{3}$$

Following Dennison, the normal co-ordinates can be written as

$$\left.\begin{aligned} q &= z_2-z_1, \\ x &= x_3-\tfrac{1}{2}(x_1+x_2), \\ y &= y_3-\tfrac{1}{2}(y_1+y_2), \\ z &= z_3-\tfrac{1}{2}(z_1+z_2). \end{aligned}\right\} \tag{4}$$

The normal co-ordinate q refers to the vibration with frequency ν_1, the co-ordinates x and y refer to the doubly degenerate vibration with frequency ν_2 and the co-ordinate z refers to the vibration with frequency ν_3.

The variation in the (1–3) bond is given by

$$\begin{aligned} \Delta r_{13} &= \{(x_1-x_3)^2+(y_1-y_3)^2+(z_1-a-z_3)^2\}^{\frac{1}{2}}-a \\ &= \frac{1}{2a}\{(x_1-x_3)^2+(y_1-y_3)^2\}+(z_3-z_1), \end{aligned} \tag{5}$$

retaining terms of the first and second orders only. Similarly

$$\Delta r_{23}=\frac{1}{2a}\{(x_2-x_3)^2+(y_2-y_3)^2\}-(z_3-z_2). \tag{6}$$

The direction cosines of the $(1-3)$ and $(2-3)$ bonds are respectively given by

$$\left.\begin{aligned}(\alpha_{13}, \beta_{13}, \gamma_{13}) &= \frac{1}{a+\Delta r_{13}}(x_3-x_1, y_3-y_1, z_3-z_1+a),\\ (\alpha_{23}, \beta_{23}, \gamma_{23}) &= \frac{1}{a+\Delta r_{23}}(x_3-x_2, y_3-y_2, z_3-z_2-a).\end{aligned}\right\} \tag{7}$$

Let A, B and B be the principal polarisabilities of a C–O bond. Here A and B are functions of the internuclear distance, given by

$$\left.\begin{aligned}A &= A_0 + A_1 \frac{\Delta r}{a},\\ B &= B_0 + B_1 \frac{\Delta r}{a},\end{aligned}\right\} \tag{8}$$

where Δr is the variation in the inter-nuclear distance and A_0 and B_0 the polarisabilities of a C–O bond when $\Delta r = 0$. Higher order terms in (8) will of course be present but for our present discussion their presence is not necessary.

In the presence of an external electric field with components E_x, E_y and E_z, the components of the induced moment in the (1—3) bond are

$$\left.\begin{aligned}M_x &= E_x(B+\alpha^2_{13}\delta_{13}) + E_y\alpha_{13}\beta_{13}\delta_{13} + E_z\alpha_{13}\gamma_{13}\delta_{13},\\ M_y &= E_x\beta_{13}\alpha_{13}\delta_{13} + E_y(B+\beta^2_{13}\delta_{13}) + E_z\beta_{13}\gamma_{13}\delta_{13},\\ M_z &= E_x\gamma_{13}\alpha_{13}\delta_{13} + E_y\gamma_{13}\beta_{13}\delta_{13} + E_z(B+\gamma^2_{13}\delta_{13}),\end{aligned}\right\} \tag{9}$$

where $(\alpha_{13}, \beta_{13}, \gamma_{13})$ are the direction cosines of the (1–3) bond and

$$\delta_{13} = (A_0 - B_0) + (A_1 - B_1)\frac{\Delta\gamma_{13}}{a} \tag{10}$$

Similar expressions hold good for the components of the induced moment in the (2—3) bond.

Using (5), (6) and (7), we get

$$\left.\begin{aligned}\gamma_{13}{}^2 &= 1 - \frac{1}{a^2}\{(x_1-x_3)^2+(y_1-y_3)^2\},\\ \gamma_{23}{}^2 &= 1 - \frac{1}{a^2}\{(x_2-x_3)^2+(y_2-y_3)^2\},\\ \gamma_{13}\alpha_{13} &= \frac{1}{a}(x_3-x_1) - \frac{1}{a^2}(x_3-x_1)(z_3-z_1),\\ \gamma_{23}\alpha_{23} &= -\frac{1}{a}(x_3-x_2) - \frac{1}{a^2}(x_3-x_2)(z_3-z_2),\\ \gamma_{13}\beta_{13} &= \frac{1}{a}(y_3-y_1) - \frac{1}{a^2}(y_3-y_1)(z_3-z_1),\\ \gamma_{23}\beta_{23} &= -\frac{1}{a}(y_3-y_2) - \frac{1}{a^2}(y_3-y_2)(z_3-z_2),\end{aligned}\right\} \tag{11}$$

neglecting terms of the higher order. From (9) the z-component of the total moment induced in both the bonds is

$$\begin{aligned} M_z = {} & E_x \{\alpha_{13}\gamma_{13}(\delta_0 + \delta_1 \Delta r_{13}) + \alpha_{23}\gamma_{23}(\delta_0 + \delta_1 \Delta r_{23})\} \\ & + E_y \{\beta_{13}\gamma_{13}(\delta_0 + \delta_1 \Delta r_{13}) + \beta_{23}\gamma_{23}(\delta_0 + \delta_1 \Delta r_{23})\} \\ & + E_z \{(B_0 + \frac{B_1}{a} \Delta r_{13}) + (B_0 + \frac{B_1}{a} \Delta r_{13}) \\ & \quad + \gamma^2{}_{13}(\delta_0 + \delta_1 \Delta r_{13}) + \gamma_{23}{}^2(\delta_0 + \delta_1 \Delta r_{23})\}, \end{aligned} \tag{12}$$

where

$$\left.\begin{aligned} \delta_0 &= A_0 - B_0, \\ \delta_1 &= (A_1 - B_1)/a. \end{aligned}\right\} \tag{13}$$

Using (11), (5), (6) and the relation $x_1 = x_2$ and $y_1 = y_2$ given by (3) in (12), we get

$$\begin{aligned} M_z = {} & E_x (-\delta_0 + \delta_1) \frac{(x_3 - x_1)(2z_3 - z_1 - z_2)}{a^2} \\ & + E_y (-\delta_0 + \delta_1) \frac{(y_3 - y_1)(2z_3 - z_1 - z_2)}{a^2} \\ & + E_z \left\{ 2 A_0 + A_1 \frac{z_2 - z_1}{a} - (2\delta_0 - A_1) \frac{\rho^2}{a^2} \right\}, \end{aligned} \tag{14}$$

where

$$\rho^2 = (x_1 - x_3)^2 + (y_1 - y_3)^2 = x^2 + y^2. \tag{15}$$

Expressing the cartesian co-ordinates (x_r, y_r, z_r) in terms of normal co-ordinates by means of (4), we get

$$\begin{aligned} M_z = {} & 2(-\delta_0 + \delta_1) \frac{zx}{a^2} E_x + 2(-\delta_0 + \delta_1) \frac{zy}{a^2} E_y \\ & + \left\{ 2 A_0 + A_1 q - (2\delta_0 - A_1) \frac{\rho^2}{a^2} \right\} E_z. \end{aligned} \tag{16}$$

Similarly, we get

$$\begin{aligned} M_x = {} & \left(2 B_0 + B_1 \frac{q}{a} + 2\delta_0 \frac{x^2}{a^2} + B_1 \frac{\rho^2}{a^2} \right) E_x \\ & + 2\delta_0 \frac{xy}{a^2} E_y + 2(-\delta_0 + \delta_1) \frac{xz}{a^2} E_z \\ M_y = {} & 2\delta_0 \frac{yx}{a^2} + (2 B_0 + B_1 \frac{q}{a} + 2\delta_0 \frac{y^2}{a^2} + B_1 \frac{\rho^2}{a^2}) E_y \\ & + 2(-\delta_0 + \delta_1) \frac{yz}{a^2} E_z. \end{aligned} \tag{17}$$

Hence the components of the polarisability tensor are given by

$$\left.\begin{aligned}
a_{xx} &= 2\,B_0 + B_1 \frac{q}{a} + 2\,\delta_0 \frac{x^2}{a^2} + B_1 \frac{\rho^2}{a^2},\\
a_{yy} &= 2\,B_0 + B_1 \frac{q}{a} + 2\,\delta_0 \frac{y^2}{a^2} + B_1 \frac{\rho^2}{a^2},\\
a_{zz} &= 2\,A_0 + A_1 \frac{q}{a} + (A_1 - 2\,\delta_0) \frac{\rho^2}{a^2}.\\
a_{xy} &= a_{yx} = 2\,\delta_0 \frac{xy}{a^2},\\
a_{yz} &= a_{zy} = 2\,(\delta_1 - \delta_0) \frac{yz}{a^2},\\
a_{zx} &= a_{xz} = 2\,(\delta_1 - \delta_0) \frac{zx}{a^2}.
\end{aligned}\right\} \tag{18}$$

where

$$\rho^2 = x^2 + y^2.$$

§ 3. *Matrix Elements of the Polarisability Tensor*

The normal co-ordinates of the vibrations of the CO_2 molecule are q, x, y and z as pointed out in § 1. The vibrational Hamiltonian is given by

$$H = T + V = \tfrac{1}{2}\left\{\frac{m}{2}\,\dot{q}^2 + \mu\,(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + 4\pi^2\left(\frac{m}{2}\,\nu_1^{\,2}\,q^2 + \mu\,\nu^2_{\,2}\,\overline{x^2 + y^2} + \mu\,\nu_3^{\,2}\,z^2\right)\right\}$$

where $\mu = \dfrac{2\,m\,M}{2m + M}$. (19)

It is convenient to employ co-ordinates ρ and ϕ instead of x and y by means of the transformation

$$x = \rho\cos\phi \text{ and } y = \rho\sin\phi \tag{20}$$

The wave function ψ of the vibrating molecule can be written as[2]

$$\psi_{V_1}(q)\,\psi_{V_{2,l}}(\rho)\,\psi_{V_3}(z)\ \exp(\pm\, i\, l\, \phi) \tag{21}$$

where the functions are properly normalised and are orthogonal where V_1 and V_3 are the quantum numbers of the non-degenerate vibrations ν_1 and ν_3, and V_2 and l are the quantum numbers of the doubly degenerate vibration ν_2 with co-ordinates ρ and ϕ. By means of (21), we can calculate the matrix elements of the polarisability tensor (18) for the transitions

$$\left.\begin{aligned}
&(0, 0, 0, 0) \to (1, 0, 0, 0),\\
\text{and } &(0, 0, 0, 0) \to (0, 2, 0, 0),
\end{aligned}\right\} \tag{22}$$

where the four quantum numbers in brackets refer to V_1, V_2, V_3 and l respectively. We will be referring to the transitions (22) simply by

$$\left.\begin{array}{l}(0, 0) \rightarrow (1, 0) \\ (0, 0) \rightarrow (0, 2)\end{array}\right\} \tag{23}$$

omitting V_3 and l on the understanding that V_3 does not change and l is zero and does not change.

For the transition $(0, 0) \rightarrow (1, 0)$ the polarisability tensor (18) is

$$\left.\begin{array}{ccc} B_1 \dfrac{q_1^0}{a} & 0 & 0 \\ 0 & B_1 \dfrac{q_1^0}{a} & 0 \\ 0 & 0 & A_1 \dfrac{q_1^0}{a} \end{array}\right\} \tag{24}$$

where q_1^0 is the matrix element of q for the transition $0 \rightarrow 1$ in V_1. From the theory of the harmonic oscillator

$$q_1^0 = \left(\frac{h}{8\,\pi^2\,\nu_1\,(m/2)}\right)^{\frac{1}{2}}. \tag{25}$$

Similarly for the transition $(0, 0) \rightarrow (0, 2)$, the tensor is

$$\left.\begin{array}{ccc} (B_1 + \delta_0) \dfrac{(\rho^2)_2^0}{a^2} & 0 & 0 \\ 0 & (B_1 + \delta_0) \dfrac{(\rho^2)_2^0}{a^2} & 0 \\ 0 & 0 & (A_1 - 2\,\delta_0) \dfrac{(\rho^2)_2^0}{a^2} \end{array}\right\} \tag{26}$$

where $(\rho^2)_2^0$ is the matrix element of ρ^2 for the transition $0 \rightarrow 2$ in V_2. From the theory of the two dimensional oscillator

$$(\rho^2)_2^0 = \left(\frac{h}{4\,\pi^2\,\nu_2\,\mu}\right)^{\frac{1}{2}}. \tag{27}$$

The spur and the anisotropy of the tensor (24) for the transition $(0, 0) \rightarrow (1, 0)$ are respectively

$$\begin{array}{c} \alpha_1 = \epsilon_1 \dfrac{q_1^0}{a}, \\ \gamma_1^2 = \delta_1^2 \dfrac{(q_1^0)^2}{a^2} \end{array} \tag{28}$$

where

$$\epsilon_1 = (A_1 + 2\,B_1)/3 \text{ and } \delta_1 = A_1 - B_1. \tag{29}$$

The spur and the anisotropy of the tensor (26) for the transition (0, 0) → (0, 2) are respectively

$$\begin{aligned} \alpha_2 &= \epsilon_1 \frac{(\rho^2)^0_2}{a^2}, \\ \gamma_2^2 &= (\delta_1 - 3\,\delta_0)^2 \frac{\{(\rho^2)^0_2\}^2}{a^2}. \end{aligned} \tag{30}$$

The average values of the squares of the tensor components in any fixed frame OXYZ can be calculated by standard methods.

$$\left.\begin{aligned} \overline{\{(\alpha_{ZZ})^{00}_{10}\}^2} &= \alpha_1^2 + \frac{4}{45}\gamma_1^2, \\ \overline{\{(\alpha_{ZX})^{00}_{10}\}^2} &= \frac{1}{15}\gamma_1^2, \\ \overline{\{(\alpha_{ZZ})^{00}_{02}\}^2} &= \alpha_2^2 + \frac{4}{45}\gamma_2^2, \\ \overline{\{(\alpha_{ZX})^{00}_{02}\}^2} &= \frac{1}{15}\gamma_2^2. \end{aligned}\right\} \tag{31}$$

Also

$$\overline{(\alpha_{ZZ})^{00}_{10} \cdot (\alpha_{ZZ})^{00}_{02}}$$

$$= \text{average of the product}$$

$$\{B_1 \cos^2(xZ) + B_1\cos^2(yZ) + A_1\cos^2(zZ)\}\ \{(B_1 + \delta_0)\cos^2(xZ)$$

$$+ (B_1 + \delta_0)\cos^2(yZ) + (A_1 - 2\,\delta_0)\cos^2(zZ)\}\ \frac{q_1^0}{a} \cdot \frac{(\rho^2)^0_2}{a^2}$$

$$= \alpha_1\alpha_2 + \frac{4}{45}\gamma_1\gamma_2 \tag{32}$$

where

$$\gamma_1 = \delta_1 \frac{q_1^0}{a}, \quad \gamma_2 = (\delta_1 - 3\,\delta_0)\frac{(\rho^2)^0_2}{a^2}. \tag{33}$$

Similarly

$$\overline{(\alpha_{zx})^{00}_{10} \cdot (\alpha_{zx})^{00}_{02}} = \frac{1}{15}\gamma_1\gamma_2. \tag{34}$$

§ 4. *Calculation of the Intensities of the Fermi Split Lines*

The appearance of a doublet of comparable intensities instead of a strong line corresponding to ν_1 and a faint line corresponding to $2\,\nu_2$ in the Raman spectrum of CO_2, has been explained by Fermi[3] as due to the accidental degeneracy $\nu_1 \approxeq 2\nu_2$.

Denoting $\nu_1 - 2\,\nu_2$ by Δ, the matrix elements of the polarisability for the observed split lines are, following Placzek,[4]

$$\left.\begin{aligned}[\alpha]^{00}_{10} &= \frac{1}{\sqrt{2x}}\left\{\sqrt{x+|\Delta|}\;(\alpha)^{00}_{10} \pm \sqrt{x-|\Delta|}\;(\alpha)^{00}_{02}\right\}\\ [\alpha]^{00}_{02} &= \frac{1}{\sqrt{2x}}\left\{\sqrt{x-|\Delta|}\;(\alpha)^{00}_{10} \mp \sqrt{x+|\Delta|}\;(\alpha)^{00}_{02}\right\}\end{aligned}\right\} \tag{35}$$

where

$$x = \sqrt{(\Delta^2 + 16\,\mathrm{P}^2)} \tag{36}$$

where

$$\mathrm{P} = \frac{\beta_{12}}{4\pi^3}\sqrt{\frac{h}{(\nu_1 + 2\,\nu_2)^3}}, \tag{37}$$

β_{12} being the anharmonic constant coupling the vibrations with frquencies ν_1 and ν_2. For $\Delta^2 < < \mathrm{P}^2$ the matrix elements are :

$$\left.\begin{aligned}[\alpha]^{00}_{10} &= \frac{1}{\sqrt{2}}\{(\alpha)^{00}_{10} + (\alpha)^{00}_{02}\}\\ [\alpha]^{00}_{02} &- \frac{1}{\sqrt{2}}\{(\alpha)^{00}_{10} - (\alpha)^{00}_{02}\}\end{aligned}\right\} \tag{38}$$

the former corresponding to the higher energy split state and the latter to the lower energy split state. The numbers following square brackets must not be thought of as the quantum numbers because the split states are obtained by linear combinations of the states (1, 0) and (0, 2) obtained when the anharmonicity P is zero.

Using 31 in 38, we have

$$\begin{aligned}\overline{\{[\alpha_{zz}]^{00}_{10}\}^2} &= \tfrac{1}{2}\left[\overline{\{(\alpha_{zz})^{00}_{10}\}^2} + \overline{\{(\alpha_{zz})^{00}_{02}\}^2} + 2\,\overline{\{(\alpha_{zz})^{00}_{10})\;(\alpha_{zz})^{00}_{02}\}}\right]\\ &= \tfrac{1}{2}\left[(\alpha_1 + \alpha_2)^2 + \frac{4}{45}(\gamma_1 + \gamma_2)^2\right]\end{aligned} \tag{39}$$

$$\overline{\{(\alpha_{zx})^{00}_{10}\}^2} = \tfrac{1}{2}\cdot\frac{2}{15}(\gamma_1 + \gamma_2)^2 \tag{40}$$

For unpolarized incident light, the intensity of parallel component of the transversely scattered light is

$$\tfrac{1}{2}\left[(\alpha_1 + \alpha_2)^2 + \frac{7}{45}(\gamma_1 + \gamma_2)^2\right] \tag{41}$$

and that of the perpendicular component is

$$\tfrac{1}{2}\cdot\frac{2}{15}(\gamma_1 + \gamma_2)^2. \tag{42}$$

These intensities are the total intensities of the P, Q and R branches of the vibrational line. If we are interested in the purely vibrational state (*i.e.*,) the

Q branch, the anisotropic scattering in the Q-branch is approximately $\frac{1}{4}$ that of the total anisotropic scattering at ordinary temperatures while the spur scattering has no P and R branches. The intensities of the parallel and perpendicular components of the Q-branch are

$$\left.\begin{aligned} [I_{\|}]^{00}_{10} &= \tfrac{1}{2}\left[(\alpha_1+\alpha_2)^2+\frac{7}{180}(\gamma_1+\gamma_2)^2\right], \\ [I_{\perp}]^{00}_{10} &= \tfrac{1}{2}\cdot\frac{1}{30}(\gamma_1+\gamma_2)^2 \end{aligned}\right\} \tag{43}$$

The aggregate intensity and the depolarisation are respectively given by

$$\left.\begin{aligned} I_1 &= \tfrac{1}{2}\left[(\alpha_1+\alpha_2)^2+\frac{13}{180}(\gamma_1+\gamma_2)^2\right] \\ \rho_1 &= \frac{6(\gamma_1+\gamma_2)^2}{180(\alpha_1+\alpha_2)^2+7(\gamma_1+\gamma_1)^2} \end{aligned}\right\} \tag{44}$$

Similarly the aggregate intensity and the depolarisation of the other split line are

$$\left.\begin{aligned} I_2 &= \tfrac{1}{2}\left[(\alpha_1-\alpha_2)^2+\frac{13}{180}(\gamma_1-\gamma_2)^2\right] \\ \rho_2 &= \frac{6(\gamma_1-\gamma_2)^2}{180(\alpha_1-\alpha_2)^2+7(\gamma_1-\gamma_2)^2} \end{aligned}\right\} \tag{45}$$

From (44) and (45)

$$\frac{I_2}{I_1}=\frac{\rho_1}{\rho_2}\cdot\frac{(1+\rho_2)}{(1+\rho_1)}\cdot\frac{(\gamma_1-\gamma_2)^2}{(\gamma_1+\gamma_2)^2} \tag{46}$$

$$(\gamma_1+\gamma_2)^2=\frac{180\,\rho_1}{6-7\,\rho_1}(\alpha_1+\alpha_2)^2 \tag{47}$$

$$(\gamma_1-\gamma_2)^2=\frac{180\,\rho_2}{6-7\,\rho_2}(\alpha_1-\alpha_2)^2 \tag{48}$$

Using (47) and (48) in (46), we get

$$\frac{I_2}{I_1}=\frac{(1+\rho_2)(6-7\,\rho_1)}{(1+\rho_1)(6-7\,\rho_2)}\left(\frac{\alpha_1-\alpha_2}{\alpha_1+\alpha_2}\right)^2 \tag{49}$$

From (28) and 30)

$$\alpha_1=\epsilon_1\sigma_1, \quad \alpha_2=\epsilon_1\sigma_2 \tag{50}$$

where

$$\sigma_1=q^0_1/a. \quad \sigma_2=(\rho^2)^0_2/a^2 \tag{51}$$

Hence

$$\frac{I_2}{I_1}=\frac{(1+\rho_2)(6-7\,\rho_1)}{(1+\rho_1)(6-7\,\rho_2)}\left(\frac{\sigma_1-\sigma_2}{\sigma_1+\sigma_2}\right)^2 \tag{52}$$

Defining

$$\theta = \frac{\sigma_2}{\sigma_1 + \sigma_2} \text{ and } \phi = \frac{\sigma_2}{\sigma_1 - \sigma_2} \tag{53}$$

and using (50), (51) and (33), we can write the expressions for the depolarisations

$$\rho_1 = \frac{6}{\dfrac{180\,\epsilon_1^{\,2}}{(\delta_1 + 3\,\delta_0\,\theta)^2} + 7}, \quad \rho_2 = \frac{6}{\dfrac{180\,\epsilon_1^{\,2}}{(\delta_1 + 3\,\delta_0\,\phi)^2} + 7} \tag{54}$$

From (52) and (54), we see that the intensity ratio of the split Raman lines and their depolarisations are expressed in terms of σ_1 and σ_2 which are the matrix elements of q and ρ^2 for the required transitions and in terms of δ_0, ϵ_1 and δ_1 where δ_0 is the optical anisotropy of the undisturbed C–O bond, ϵ_1 and δ_1 are respectively the changes in the spur and anisotropy of the bond for doubling the internuclear distance. The expressions (52) and (54) have been derived assuming Δ $(= \nu_1 - 2\,\nu_2)$ to be very small. In case Δ is not small and P and Δ are of the same sign

$$\left.\begin{aligned} \frac{I_2}{I_1} &= \frac{(1+\rho_2)(6-7\,\rho_1)}{(1+\rho_1)(6-7\,\rho_2)}\left(\frac{c_1\,\sigma_1 - c_2\,\sigma_2}{c_2\,\sigma_1 + c_1\,\sigma_2}\right)^2, \\ \rho_1 &= \frac{6}{\dfrac{180\,\epsilon_1^{\,2}}{(\delta_1 - 3\,\delta_0\,\Theta)^2} + 7}, \quad \rho_2 = \frac{6}{\dfrac{180\,\epsilon_1^{\,2}}{(\delta_1 + 3\,\delta_0\,\Phi)^2} + 7} \end{aligned}\right\} \tag{55}$$

where

$$\left.\begin{aligned} c_1 &= \sqrt{x - |\,\Delta\,|}, \quad c_2 = \sqrt{x + |\,\Delta\,|}, \\ \Theta &= \frac{c_1\sigma_2}{c_2\sigma_1 + c_1\sigma_2}, \quad \Phi = \frac{c_2\sigma_2}{c_2\sigma_1 - c_1\sigma_2}. \end{aligned}\right\} \tag{56}$$

Assuming $\Delta^2 \leqslant P^2$ we will now compute the intensity ratio given by (52). We will first estimate σ_1 and σ_2. They are

$$\begin{aligned} \sigma_1 &= \frac{1}{a}\left(\frac{h}{4\,\pi^2\,\nu_1 m}\right)^{\frac{1}{2}} \\ &= 0\cdot03408, \end{aligned} \tag{57}$$

$$\begin{aligned} \sigma_2 &= \frac{1}{a^2}\Bigg(\frac{h}{4\,\pi^2\,\nu_2}\cdot\frac{2m + M}{2mM} \\ &= 0\cdot004266 \end{aligned} \tag{58}$$

assuming $a = 1\cdot16\text{Å}$, $\nu_1 = 1336 \text{ cm.}^{-1}$

$\nu_2 = 667 \text{ cm.}^{-1}$ Hence

$$\frac{\sigma_1}{\sigma_2} = 7\cdot987 \tag{59}$$

Thus

$$\frac{I_2}{I_1} = \frac{(1+\rho_2)(6-7\rho_1)}{(1+\rho_1)(6-7\rho_2)} \times \cdot 6045 \tag{60}$$

If $\rho_1, \rho_2 \ll 1$ or $\rho_1 \approx \rho_2$, then

$$\frac{I_2}{I_1} \approx 0\cdot 6 \tag{61}$$

Bhagavantam's[5] experimental determination gives both ρ_1 and ρ_2 to be nearly equal to 0·2. In this case the intensity ratio would be nearly 0·6. On the other hand taking ρ_1 and ρ_2 to be respectively 0·14 and 0·18 given by Langseth and Nielsen,[6] the intensity ratio would be 0·66 still not far from 0·6 though their depolarisation values are rather different from those determined by Bhagavantam. This is natural since our intensity expression (60) is not very sensitive to ρ_1 and ρ_2 so long as they are nearly equal or both small compared to unity, the former alternative being more plausible. The intensity ratio 0·6 calculated by us is in very good accord with the observed ratios 0·57 by I. Hansen[7] and 0·61 by Langseth and Nielsen and ·5 by Bhagavantam.

We can solve for $\delta_1\,\delta_0$ and ϵ_1/δ_0 by means of equations in (54). The solutions are

$$\left.\begin{aligned} \frac{\delta_1}{\delta_0} &= \frac{3(\theta + k\phi)}{1-k}, \\ \frac{\epsilon_1}{\delta_0} &= \pm 3\left(\frac{6-7\rho_1}{180\rho_1}\right)^{\frac{1}{2}} \frac{k\phi}{1-k} \end{aligned}\right\} \tag{62}$$

where

$$k = \pm\left[\frac{\rho_1(6-7\rho_2)}{\rho_2(6-7\rho_1)}\right]^{\frac{1}{2}} \tag{63}$$

$$\theta = \frac{\sigma_2}{\sigma_1+\sigma_2} = 0\cdot 112, \quad \phi = \frac{\sigma_2}{\sigma_1-\sigma_2} = 0\cdot 1443$$

It may thus be expected that we could determine δ_1 and ϵ_1 and consequently the constants A_1 and B_1 by knowing the experimental values of ρ_1, ρ_2 and δ_0. But it may be seen from our expressions that the determination will be very sensitive to the values of ρ_1 and ρ_2. It has not been found possible to arrive at any definite conclusion about these constants from the available experimental data.

We are thankful to Prof. S. Bhagavantam for his interest in this work.

Summary

The polarisability of a molecule is assumed to be made up of the bond polarisabilities as functions of the inter-nuclear distances. It is pointed out that certain normal co-oridnates could be quadratic functions of some of the variations in the inter-nuclear distances which fact accounts for the appearance of overtone Raman lines assuming only first order variations in the bond polarisabilities. These ideas have been applied to the case of CO_2 and the intensity ratio of the Fermi split lines has been calculated which is in good accord wih experimental observations.

REFERENCES

1.	Dennison	.. *Rev. Mod. Phy.*, 1941, **3**, 280.
2.	——————.	.. *Phy. Rev.*, 1932, **41**, 304.
3.	Fermi	.. *Zeits. f. Phy.*, 1931, **71**, 250.
4.	Placzek	.. *Handbuch der Radiologie*, **6** (2), 323.
5.	Bhagavantam	.. *Ind. Jour. Phy.*, 1931, **6**, 319.
6.	Langseth and Nielsen	.. *Phy. Rev.*, 1934, **46**, 1057.
7.	Hansen	.. *Ibid.*, 1934, **46**, 122.

ERRATA

Page 343, second line of equation (16)—

for $$+\left\{2\,A_0 + A_1\,q - (2\delta_0 - A_1)\,\frac{\rho^2}{a^2}\right\} E_z.$$

read $$+\left\{2\,A_0 + A_1\,\frac{q}{a} - (2\delta_0 - A_1)\,\frac{\rho^2}{a^2}\right\} E_z.$$

Page 350, second line of equation (62)—

for $$\frac{\epsilon_1}{\delta_0} = \pm\, 3\left(\frac{6 - 7\,\rho_1}{180\,\rho_1}\right)^{\frac{1}{2}} \frac{k\,\phi}{1 - k}$$

read $$\frac{\epsilon_1}{\delta_0} = \pm\, 3\left(\frac{6 - 7\,\rho_1}{180\,\rho_1}\right)^{\frac{1}{2}} \frac{k\,(\phi + \theta)}{1 - k}$$