Photoelastic constants of calcite from its first-order Raman spectrum

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A formalism to connect photoelastic constants and Raman intensities of a crystal is developed. The internal coordinates of the crystal are related to the strains and the polarizability derivatives are obtained from Raman intensities and expressions are derived for photoelastic constants of calcite. With Raman intensities taken from the spectra taken by Kondilenko *et al.* [Opt. Spectrosc. <u>40</u>, 402 (1976)], the photoelastic constants are evaluated. They compare favorably with the experimental values determined by Pockel and recently by Nelson and his colleagues. The constants thus evaluated form a 9×9 matrix as the internal coordinates are related to displacement gradients u_{ij} in accordance with Nelson's ideas. As a result of the fact that calcite has only one line in its A_{1g} species, the ratio $(P_{11}+P_{12})/P_{13}$ is found to be independent of the refractive index or Raman intensities of the crystal; the ratio evaluated is 1.007, which may be compared with 1.332 obtained from Pockel's values and with 1.124 from the work of Nelson and collaborators. The ratio P_{13}/P_{33} is dependent entirely on the intensities of A_{1g} line in the yy and zz spectra: we obtained 2.147, as compared with 1.838 of Pockel's and 2.074 of Nelson and collaborators' experimental values.

INTRODUCTION

When a crystal is stressed the strains produced resolve themselves into phonons. Suitable grouping of Raman phonons according to their symmetry manifest themselves as photoelastic constants. This natural connection between Raman intensity and photoelasticity was recognized by Maradudin[1] as early as 1967, who derived an expression for the photoelastic anisotropy $(P_{11}-P_{12}-P_{66})$ of diamond in terms of the intensity of its Raman line. We have

$$P = a_0^2 \frac{\epsilon_0^2}{8\pi} \frac{(P_{11}-P_{12}-P_{66})}{1-(8G/a_0 M v_R^2)} . \tag{1}$$

P is the polarizability change with respect to the frequency v_R, ϵ_0 is the equilibrium dielectric constant, a_0 is the radius of the carbon atom, M is its mass, and G is an expression involving force constants. His calculations were confined to cubic crystals and were not followed up.

Nelson and his colleagues[2-5] gave a comprehensive theory relating intensities of Brillouin components and photoelastic constants. They modified the earlier ideas in two important respects. (1) The strains in a crystal are, in general, not irrotational. This makes the strain tensor unsymmetric. Therefore, they recommended that in place of the symmetric strain tensor elements e_{ij}, one should use the displacements gradients u_{ij}, making the photoelastic constant tensor 9×9 instead of 6×6. They thus differentiated between P_{yzyz} and P_{yzzy} of calcite and ob-

tained the two values separately. (2) For piezoelectric crystals, stress creates electric fields which produce polarizations, and the resulting photoelastic constants, therefore, need not follow the symmetry of the crystal. These ideas seem to have received wide acceptance. Grimsditch and Ramdas,[6] while evaluating the photoelastic constants of rutile, have shown that $P_{ijkl}=P_{jikl}$.

In the traditional methods stress is applied to a crystal until its birefringence is measurably changed and the altered refractive indices determined to evaluate the photoelastic constants. Cordona and his colleagues,[7] while determining these constants for alkali halides at near about their absorption edges, have established a connection to their deformation potentials. They have clearly shown a characteristic difference between the rock-salt- and ceasium-chloride-type crystals.

It is well known that directional Raman spectra of crystals show considerable changes on applying stress leading to change of structure. Inactive modes can appear and very strong lines lose their intensity. Cardona and his colleagues[8] connected these intensity changes to piezobirefringence and evaluated the piezo-optical constants of silicon. Briggs and Ramdas[9] observed splitting of the degenerate lines of Cds upon applying stress and evaluated its deformation potentials. Loudon[10] has developed a theory of Raman intensities of crystals based on deformation potentials and this will be referred to again later. We now develop a relation be-

tween Raman intensities and photoelastic constants of the crystal without applying external stress.

RAMAN INTENSITIES

Raman intensities in molecules are analyzed by Long[11] following the theory of bond polarizabilities first conceived by Eliashevich and Wolkenstein.[12] The polarizability of a molecule was taken to be the sum of the polarizabilities of the constituting bonds. α_{n1} and α_{n2} are polarizabilities along and perpendicular to the nth bond of a molecule. Long then showed that the tensor element

$$\alpha_{xy} = (\alpha_{n1} - \alpha_{n2})\hat{n}x\hat{n}y + \alpha_{n2}\delta_{xy} \ . \tag{2}$$

$\hat{n}x$ and $\hat{n}y$ are the direction cosines of the nth bond and δ_{xy} is Kronecker δ function. As the molecule is oscillating, the bonds get stretched and the inter-bond angles change. Polarizability change due to these two causes is derived by Long. Long's equation is conveniently modified by Kumar et al.[13] as

$$\underline{I}_k = \frac{\delta\alpha_{xy}}{\delta Q_k} = \underline{J}_r \underline{u}' \underline{L} + \underline{J}_\phi \underline{K}_\phi \underline{\mu}\underline{s}' \underline{u}'(\underline{L}^{-1})' \ . \tag{3}$$

The intensity is proportional to $\underline{I}_k^2$. The terminology which is well known is described by these authors. $\underline{J}_r$ and $\underline{J}_\phi$ are derivatives of α_{xy} with respect to stretches of the bonds and their direction cosines and $\underline{K}_\phi$ are derivatives of direction cosines with respect to the displacements of the atoms. $\underline{\mu}$ are the reciprocals of masses of the atoms, $\underline{s}$ are Wilson's[14] s vectors, and $\underline{s}'$ the transpose of the $\underline{s}$ matrix. $\underline{u}$ connects the internal and symmetry coordinates.

Extension of this theory to crystals was initiated by Kumar et al.[13] and theoretical justification was given by Tubino and Piseri.[15] This was followed up for a number of crystals of different symmetry by authors from this laboratory and recently by Domingo and Montero.[16]

There is another theory, referred to earlier by Loudon,[10] based on electron-lattice interactions and deformation potentials. He has obtained formulas connecting polarizability changes and changes of deformation potentials. Although Maradudin[1] was aware of these formulas he chose to use the bond-polarizability model as "the model of electric polarizability we choose, must contain as many parameters as there are pieces of experimental information, no more, no less." Bond-polarizability theory has also the advantage of understanding the properties of the crystal from its molecules and the intensities and photoelastic constants can be derived in terms of physically understandable electrooptical parameters as one obtains for molecules.

PHOTOELASTIC CONSTANTS FROM RAMAN INTENSITIES

Equation (3) can be cast in the matrix form as

$$\underline{I} = \underline{L}'\underline{A} \ . \tag{4}$$

$\underline{A}$ contains the electrooptical constants and $\underline{L}'$ is the transpose of $\underline{L}$ which is related to the symmetry coordinates $\underline{S} = \underline{L}\underline{Q}$. In solving (4) for electrooptical constants two points of uncertainty were faced by the investigators. $\underline{I}$ can have two signs, positive or negative. Hence, one can have a number of possible sets of equations. The elements of $\underline{L}$ are derived from force constants which are generally known to be uncertain. While for molecules one may take additional data from Coriolis interaction constants and rotation distortion constants, for crystals it becomes a real problem to determine reliable force constants.

Authors from this laboratory avoid these problems by writing (4) as

$$\underline{I}'\underline{I} = \underline{A}'\underline{L}\underline{L}'\underline{A} = \underline{A}'\underline{G}\underline{A} \ . \tag{5}$$

This equation at once avoids the sign ambiguity of $\underline{I}$'s and the necessity of determining the elements of $\underline{L}$.

Now, any polarizability tensor element varies as

$$\Delta\alpha_{ij} = \frac{\delta\alpha_{ij}}{\delta Q}\frac{\delta Q}{\delta S}\frac{\delta S}{\delta R}\Delta R$$

$$= \underline{I}'\underline{L}^{-1}\underline{U}\Delta R = \underline{A}'\underline{L}\underline{L}^{-1}\underline{U}\Delta R = \underline{A}'\underline{U}\Delta R \ . \tag{6}$$

$\underline{I}'$ is the transpose of $\underline{I}$. Elements of $\underline{A}$ can be obtained from the Raman-intensity analysis.

The elements $\delta\alpha_{ij}/\delta Q_k$ have this sign ambiguity. For any mode, (4) can be written as

$$\underline{I}_k = A_1\underline{L}_{1k} + A_2\underline{L}_{2k} + \cdots = \underline{A}\,\underline{L}_k \ . $$

The sign of $\underline{I}_k$ is a function of $\underline{A}$ and the sign of the column vector $\underline{L}_k$. $\underline{L}_k$ is multiplied by the relevant $\underline{L}_k^{-1}$ vector of the matrix $\underline{L}^{-1}$, the result being independent of its sign. The row of elements of $\underline{A}$ is the same for all the modes of oscillations of any species and is not directly related to the sign of the elements of $\underline{I}_k$. We thus get rid of the sign ambiguity as well as the uncertainty of evaluating the elements of $\underline{L}$ from force constants.

It is shown in the Appendix that the internal coordinates can be connected to the strains and a general equation of the matrix form

$$\Delta R = \underline{R}\,\underline{l}\,\underline{e} \tag{7}$$

can be derived, so that (6) becomes

$$\Delta\alpha_{ij} = \underline{A}'\,\underline{U}\,\underline{R}\,\underline{l}\,\underline{e} = P'_{ijkl}e_{kl} \ . \tag{8}$$

From the relation $\epsilon = 1 + 4\pi b N\alpha$, ϵ the dielectric constant, α the polarizability tensor, N the number of molecules per unit volume, and b a constant depending on the crystal symmetry, $\underline{P}'$ are calculated in the units of $4\pi bN$. Thus

$$\Delta\epsilon_{ij} = P'_{ijkl}e_{kl} \ . \tag{9}$$

Photoelastic constants are defined as

$$\Delta\underline{\epsilon}^{-1} = \underline{P}\,\underline{e} \ , \tag{10}$$

and from $\underline{\epsilon}\,\underline{\epsilon}^{-1} = \underline{1}$,

$$\Delta\underline{\epsilon}^{-1} = \underline{\epsilon}_0 \Delta\underline{\epsilon}\,\underline{\epsilon}_0 \ , \tag{11}$$

from which one obtains

$$\underline{P}' = \underline{\epsilon}_0 \underline{P}\,\underline{\epsilon}_0 \ . \tag{12}$$

Here $\underline{\epsilon}_0$, the dielectric constant of the crystal in the equilibrium position, is taken as an approximation. Multiplication with the matrix $\underline{\epsilon}_0$ is facilitated if its principal values are taken along the symmetry axes of the crystal. Then (12) becomes (writing $\underline{\epsilon}_0 = \underline{n}^2$, the refractive index)

$$P'_{11} = n_x^4 P_{11},$$
$$P'_{33} = n_z^4 P_{33} \ , \tag{13}$$

and

$$P'_{41} = n_x^2 n_z^2 P_{41} \ .$$

For crystals of calcite symmetry, $P_{11} = P_{22}$, $P_{12} = P_{21}$, etc. Hence, extension of (13) to the other elements of $\underline{P}$ can be easily made.

In this paper we demonstrate Raman-intensity analysis of calcite and show how the elements of $\underline{A}$ of Eq. (8) thus obtained can be used to evaluate the elements of $\underline{P}$.

RAMAN-INTENSITY ANALYSIS OF CALCITE

Calcite is of space-group symmetry D_{3d}^6 with two molecules in the unit cell as shown in Fig. 1. The CO_3 ions in free state are of D_{3h} symmetry with Raman-active modes in A_1, E', and E'' species. A_1 gives the total symmetric stretching. E' contains the asymmetric modes, bending, and translations in the xy (CO_3) plane, while E'' gives rotations R_x and R_y. In the crystal E' and E'' combine into a single E_g species. Then expressions for α'_{ij} for these modes of oscillations are derived in the way explained earlier in one of our papers[17] on $LiNO_3$ (which is of same symmetry). To obtain the expressions for the whole unit cell α'_{ij} for the other molecule are obtained by the proper symmetry operation and the two values are added with proper normalization.

The intensity formulas thus obtained and adopted to $CaCO_3$ are as follows:

For the A_{1g} species,

$$\alpha'_{xx} = \alpha'_{yy} = (3/\sqrt{6})(\alpha'_1 + \alpha'_2)L_{11} \ , \tag{14a}$$

$$\alpha'_{zz} = \sqrt{6}\alpha'_2 L_{11} \ . \tag{14b}$$

For the E_g species,

$$\alpha'_{xx} = -\alpha'_{yy} = \alpha'_{xy} = [(\sqrt{3}/2)\gamma'L_{1i} - \gamma L_{2i}] \ , \tag{14c}$$

$$\alpha'_{xz} = \alpha'_{yz} = \sqrt{2}\gamma L_{3i} \ . \tag{14d}$$

α'_1 and α'_2 are the polarizability derivatives of the C—O bond along and perpendicular to it. $\gamma = (\alpha_1 - \alpha_2)$ and γ' is its derivative.

These formulas include the electro-optical parameters $(\alpha'_1, \alpha'_2, \gamma', \text{ and } \gamma)$ of only the C—O bond. The Ca atom in the unit cell is too far away from the O atoms, hence the polarizability of this Ca—O bond is of no significance.

There are two serious defects in these formulas. (1) Since the CO_3 ion in the crystal retains the symmetry in its free state, E_g splits up into two matrices of orders 3×3 and 1×1 corresponding to E' and E'' in the free state. As we shall see later, this results in the nonappearance of P_{41} and P_{14} which are a result of interaction of the oscillations in E' and E''. (2) The C—O bond is in the xy plane. But P_{13}, P_{31}, and P_{33} which are functions of the strains along the z direction cannot be evaluated as they are the functions of A_{1g} mode, which in this picture does not involve a movement along the z directions.

To understand the interaction between E' and E'' the six calcium atoms around each CO_3 ion and the corresponding Ca—O bonds as shown in Fig. 2 are taken as internal coordinates and their polarizabili-

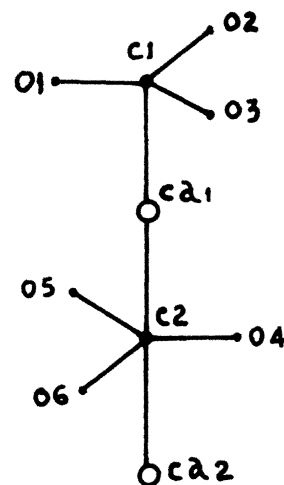

FIG 1. Unit cell of calcite.
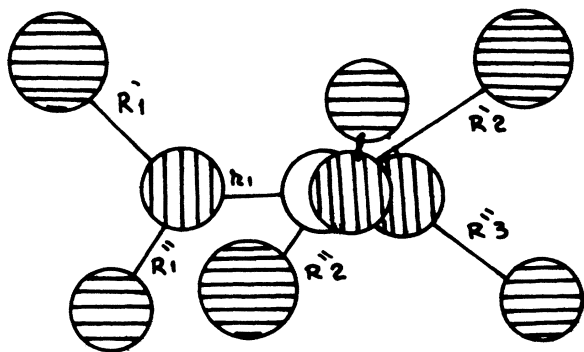
FIG. 2. Carbonate ion connected to Ca ions of the surrounding unit cells. There are three Ca ions above the CO_3 plane and three below. O: carbon atom, ⦿: oxygen atoms, and ⊖: Ca atoms.

ties are considered in deriving the intensity formulas. The first step in this direction is to write down the symmetry coordinates combining these Ca-O and C-O distances. Symmetry coordinates are given in Table I.

Wilson's $\underline{s}$ vectors[14] are calculated and the matrix $\underline{G}$ given by

$$\underline{G} = \underline{u}\,\underline{s}\,\underline{\mu}\,\underline{s}'\,\underline{u}' \tag{15}$$

is shown in Table II. Now, the matrix $\underline{G}$ for E_g is 4×4. Thus E' and E'' vibrations are connected into one species. This is possible if we take the Ca—O bonds outside the unit cell as in Fig. 2. Ca—O

bonds inside the unit cell, if taken, again appear separated in E' and E'' species.

μ_O and μ_C are reciprocals of the masses of the oxygen and the carbon atoms. μ_{Ca} does not come into this picture as the Ca atoms are in the centers of symmetry and hence do not move in the Raman-active modes. r in this table are in angstroms but in deriving the intensity formulas this unit cancels off. Hence, its unit (10^{-8}) is not shown in the table.

Equation (3) contains two quantities $J_r \underline{u}' \underline{L}$ and $J_\phi \underline{K}_\phi \underline{\mu}\,\underline{s}'\,\underline{u}'(\underline{L}^{-1})'$. It may be noted that in Long's original formulation, two approximations were made, the polarizability of any bond is independent of the length changes of the other bonds, and also the changes in the bond angles. This is called the zeroth-order approximation. But in deriving $J_r \underline{u}' \underline{L}$ here we do take these factors into consideration and follow what is called the first-order approximation. In the following equations [(17a) and (17b)] α_1^2 means the polarizability perpendicular to bond 1 and α_2^2 is of bond 2. In the zeroth-order approximation only $\delta\alpha_1^2/\delta r_1$ exists. $\delta\alpha_2^2/\delta r_1$ is the first-order term. This is explained in detail in one of our recent papers.[18] In the second term $(\underline{L}^{-1})'$ elements are converted into $\underline{L}$ elements using $(\underline{L}^{-1})' = \underline{G}^{-1}\underline{L}$. $\underline{G}^{-1}$ elements are obtained by inverting the $\underline{G}$ elements of Table II. Then the two terms are combined into a single term $\underline{A}$, as in Eq. (4).

Then the expressions for α'_{ij} with the use of the formulas (3) are derived and the revised intensity

TABLE I. Symmetry coordinates.

$$S_1^{A_{1g}} = (1/\sqrt{3})\{-(1/\sqrt{3})(r_1 + r_2 + r_3) + (1/\sqrt{3})[(R'_1 + R''_1) + (R'_2 + R''_2) + (R'_3 + R''_3)]\}$$

$$S_{2a}^{E_g} = (1/\sqrt{3})\{(1/\sqrt{6})(2r_1 - r_2 - r_3) - (1/\sqrt{6})[2(R'_1 + R''_1) - (R'_2 + R''_2) - (R'_3 + R''_3)]\}$$

$$S_{3a}^{E_g} = (1/\sqrt{6})[(2\theta_1 - \theta_2 - \theta_3)]$$

$$S_{4a}^{E_g} = -(1/2\sqrt{3})[2(R'_1 + R''_1) - (R'_2 + R''_2) - (R'_3 + R''_3)]$$

$$S_{5a}^{E_g} = (1/1.504)\{R_x - (1.123/2)[(R'_2 - R''_2) - (R'_3 - R''_3)]\}$$

$$S_{2b}^{E_g} = (1/\sqrt{3})\{(1/\sqrt{2})(r_3 - r_2) - (1/\sqrt{2})[(R'_3 + R''_3) - (R'_2 + R''_2)]\}$$

$$S_{3b}^{E_g} = (1/\sqrt{2})(\theta_3 - \theta_2)$$

$$S_{4b}^{E_g} = (-1/2\sqrt{3})[2(R'_1 + R''_1) - (R'_2 + R''_2) - (R'_3 + R''_3)]$$

$$S_{5b}^{E_g} = (1/1.504)\{R_y - (1.123/2)[2(R'_1 - R''_1) - (R'_2 - R''_2) - (R'_3 - R''_3)]\}$$

$$S_{1a} = (1/\sqrt{3})\{-(1/\sqrt{3})(r_1 + r_2 + r_3) - (1/\sqrt{3})[(R'_1 + R''_1) + (R'_2 + R''_2) + (R'_3 + R''_3)]\} = 0^a$$

[a]This is a redundant coordinate. Similar redundant coordinates for S_2 and S_5 can be written down. In the above expressions the normalization factors are obtained from redundant coordinates. a and b refer to the two degenerate types.

TABLE II. G matrix in units of 10^{24}.

$$G_{11} = (\tfrac{4}{3})\mu_O = 0.05$$

$$G_{22} = (\tfrac{4}{3})\mu_O + (\mu_C/2) = 0.075$$

$$G_{33} = (3/r^2)\mu_O + (9/2r^2)\mu_C = 0.208$$

$$G_{44} = \mu_O/2 = 0.019$$

$$G_{55} = (2.05)\mu_O = 0.077$$

$$G_{23} = (3/2r)\mu_C = 0.059$$

$$G_{24} = (\sqrt{2}/\sqrt{3})\mu_O = 0.031$$

$$G_{35} = (1.116/r)\mu_O = 0.033$$

equations involving the polarizability of the Ca—O bonds also are given below.

For the A_{1g} species,

$$\alpha'_{yy} = \alpha'_{xx} = I_{xx} K n_x = A_1 L_{11} , \tag{16a}$$

$$\alpha'_{zz} = I_{zz} K n_z = A'_1 L_{11} . \tag{16b}$$

For the E_g species,

$$-\alpha'_{xx} = \alpha'_{yy} = I^i_{yy} K n_y = A_2 L_{2i} + A_3 L_{3i} + A_4 L_{4i}$$

$$+ A_5 L_{5i} , \tag{16c}$$

$$\alpha'_{xz} = \alpha'_{yz} = I^i_{yz} K (n_y n_z)^{1/2} = A_6 L_{2i} + A_7 L_{3i}$$

$$+ A_8 L_{4i} + A_9 L_{5i} , \tag{16d}$$

where $i = 2,3,4,5$ denotes the frequency. The expressions for A_1, A'_1, A_2, etc. are the following:

$$A_1 = -\frac{\delta}{\delta r_1}(\alpha_{12} + 2\alpha_{22}) - \frac{1}{2}\frac{\delta}{\delta r_1}(\gamma_1 + 2\gamma_2)$$

$$+ (0.2684)\gamma_{Ca-O} , \tag{17a}$$

$$A'_1 = -\frac{\delta}{\delta r_1}(\alpha_{12} + 2\alpha_{22}) - (0.4619)\gamma_{Ca-O} , \tag{17b}$$

$$A_2 = \frac{\gamma'_{C-O}}{2\sqrt{2}} - (0.5828)\gamma_{Ca-O} , \tag{17c}$$

$$A_3 = -\frac{\gamma_{C-O}}{\sqrt{2}} + (0.2489)\gamma_{Ca-O} , \tag{17d}$$

$$A_4 = (0.0944)\gamma_{Ca-O} , \tag{17e}$$

$$A_5 = (-0.3117)\gamma_{Ca-O} , \tag{17f}$$

$$A_6 = (0.8001)\gamma_{Ca-O} - (0.8295)\gamma_{C-O} , \tag{17g}$$

$$A_7 = -(0.3415)\gamma_{Ca-O} + (0.3541)\gamma_{C-O} , \tag{17h}$$

$$A_8 = -(0.7661)\gamma_{Ca-O} + (1.3545)\gamma_{C-O} , \tag{17i}$$

$$A_9 = (0.1077)\gamma_{Ca-O} - (0.7442)\gamma_{C-O} . \tag{17j}$$

TABLE III. Intensities of the Raman lines of calcite.

Spectrum	Species	Frequency ν_i (cm^{-1})	Area A_i	I^2_{ij}
zz	A_{1g}	1088	270	388.6
yy	A_{1g}	1088	1000	1439.2
	E_g	1432[a]	25	51.5
		714	88	73.1
		283	38	8.6
		156	17	1.4
yz	E_g	714	26	21.6
		283	390	87.9
		156	140	11.9

[a]Extrapolated from Fong et al. [J. Chem. Phys. 541, 579 (1971)].

In these expressions four digits are given against each value for the sake of computational consistency. The values are accurate only up to two digits. In deriving these formulas, we have omitted the polarizability derivative of the Ca—O bond as it is mostly of ionic nature.

In deriving Eq. (16) both the molecules are taken into consideration in the way explained earlier.[17] It simply involves multiplying the right-hand side of Eq. (16) by $\sqrt{2}$, the normalization factor. The frequencies are taken from the data published by Kondilenko et al.[19] I_{ij} are calculated from the areas under each of these lines as obtained by these authors. The value of the elements of I are calculated using the formula given by Bernstein[20]

$$(I^i_{xy})^2 = \frac{KA^i \nu_i (1 - e^{-hc\nu_i/kT}) n^2}{(\nu_0 - \nu_i)^4} . \tag{18}$$

K is a constant of proportionality, ν_i is the frequency of the line, ν_0 is the frequency of the exciting line, and $hc\nu_i/kT$ is the usual Botlzmann factor. The frequencies, areas A^i, and the corresponding I'_{xy} excluding n (refractive index) are given in Table III, for ready reference.

Spectra of calcite were taken by Porto et al.[21] in 1966 and recently by Kondilenko et al.[19] The spectra taken by the latter authors show almost the same areas for xx, xy, and yy showing that they were taken under identical conditions. Hence, we have taken the constant of proportionality to be the same for all these spectra and also for yz.

The intensity of a Raman line is proportional to its area. Hence, a sharp line of high peak value can have a lower intensity than a diffuse band. In fact, a diffuse band of low peak value can merge into the background and escape notice. Also, Eq. (18) shows that line of high intensity but of low frequency can have a low I^2 value compared to one of low intensi-

TABLE IV. $\underline{A}'$ and $\underline{U}\,\underline{R}\,l\underline{e}$ matrices. One obtains for $E_g(b)$ similar expressions as for $E_g(a)$.

A	A_{1g}	$E_g(a)$	$E_g(a)$	$E_g(a)$	$E_g(a)$	URle
xx	A_1	A_2	A_3	A_4	A_5	$S_1^{A_{1g}}$ $(1.218)(e_{xx}+e_{yy})+(2.420)e_{zz}$
yy	A_1	$-A_2$	$-A_3$	$-A_4$	$-A_5$	$S_{2a}^{E_g}$ $(0.893)(e_{xx}-e_{yy})-(1.733)e_{yz}$
zz	A_1'					$S_{3a}^{E_g}$ $(1.499)(e_{xx}-e_{yy})$
yz		A_6	A_7	A_8	A_9	$S_{4a}^{E_g}$ $(0.310)(e_{xx}-e_{yy})-(2.122)e_{yz}$
						$S_{5a}^{E_g}$ $(1.355)(e_{xx}-e_{yy})+(2.042)e_{yz}+(0.705)\omega_x$

ty and high frequency. For example, Table III shows that 156 of yz having an area of 140 has $I^2=11.9$ while 714 of area 26 has $I^2=21.6$. This feature is shown clearly in Loudon's[10] formulas also. The band of frequency 1432 of E_g species does not seem to appear in the spectra taken by Kondilenko et al.[21] while Porto et al.[21] just mention it and do not show it in their spectra. We have, therefore, compared the intensity of this band with 714 in the spectra published by Fong et al.[22] and comparing the ratio of their areas in their spectra, computed its value in the yy spectrum here, and used it in our calculations.

PHOTOELASTIC CONSTANTS

In the Appendix we have derived expressions for the internal coordinates R in terms of u_{ij}, the displacement gradients. Then taking the u matrix from Table I, URle is obtained. It may be mentioned that the u elements are multiplied by $\sqrt{2}$ to take both the molecules in the unit cell into account, $U=\sqrt{2}u$; then, taking the A' matrix from Eq. (16), A' and URle are written separately in Table IV.

It is interesting to see that the matrix URle has the same symmetry as the symmetry of the Raman-active tensor elements. The product of A' with this gives $\underline{P}'\underline{e}$, as explained earlier. $\underline{P}'$ has the symmetry of the photoelastic constant matrix as expected. The expressions for $\underline{P}'$ involve the electrooptical con-

stants contained in the elements of $\underline{A}$ of Eq. (17).

The signs against A_2, A_3, A_4, and A_5 in P'_{11} and P'_{12} are opposite, so that $P'_{11}+P'_{12}$ is a function of only A_1, while $P'_{11}-P'_{12}$ is a function of A_2, A_3, A_4, and A_5. It is easily verified that $P'_{11}-P'_{12}=2P'_{66}$. It is also evident that $P'_{11}=P'_{22}$ and $P'_{12}=P'_{21}$.

Similarly, P'_{13} (and P'_{23}) are functions of only A_1, while P'_{31} and P'_{33} are functions of only A'_1. Thus all these major photoelastic constants can be obtained directly from A_1 and A'_1, which are the functions of the total symmetric 1088-cm^{-1} line of this crystal.

P'_{13}, P'_{23}, and P'_{33} are functions of e_{zz} and the direction cosines of the Ca—O bonds outside the unit cell (values of these direction cosines and of the lengths r and R are calculated from the crystal parameters[23] in the usual way, $r=1.28$ Å and $R=2.357$ Å).

From Table IV it is seen that $P'_{11}+P'_{12}=2A_1$ (1.22). Taking P'_{11} and P'_{12} from the experimental data and A_1 from (16a), K, the constant of proportionality, is determined. Then $K^2=5.3\times10^{-6}$ if Nelson's[5] values are taken and 10.8×10^{-6} if Pockel's values (as corrected by Nelson) are taken. They can be used to calculate P'_{13}, P'_{33}, and P'_{31}. The values thus calculated along with the experimental values are shown in Table V. While P'_{13} and P'_{33} compare well with the experimental values, P'_{31} is too small.

It can also be seen that $(P'_{11}+P'_{12})/P'_{13}$ is independent of the refractive index or Raman intensi-

TABLE V. Photoelastic constants.

	Calculated with the use of some values of		Experimental	
	Pockel	Nelson	Pockel	Nelson
P_{13}	0.295	0.208	0.223	0.186
P_{14}	-0.012	-0.011	-0.012	-0.011
$P_{1[4]}$	-0.005	-0.004		
P_{31}	0.107	0.075	0.310	0.241
P_{33}	0.213	0.149	0.188	0.139
P_{41}	-0.019	-0.016	0.0007	-0.036
P_{44}	-0.069	-0.058	-0.069	-0.058
$P_{4[4]}$	-0.017	-0.011		0.047
P_{66}	-0.028	-0.020	-0.0425	-0.0425

TABLE VI. Some ratios of photelastic constants.

		Experimental	
Calculated		Pockel	Nelson
$\dfrac{P'_{11}+P'_{12}}{P'_{13}}=\dfrac{2(1.219)}{(2.420)}=1.007$		1.332	1.124
$\dfrac{P'_{13}}{P'_{33}}=\dfrac{I_{yy}^{A_{1g}}ny}{I_z^{A_{1g}}nz}=2.147$		1.838	2.074

ty. It is purely a function of the crystal parameters. P'_{13}/P'_{33} can be directly obtained from the intensities I_{xx} and I_z and is independent of the electrooptical constants. These ratios are given in Table VI. These peculiarities are entirely due to the A_{1g} species containing only one line. These ratios are functions of A_{1g} lines only.

To evaluate the other constants, however, it is necessary to use the intensity formulas. But, as we have already stated earlier, there are two defects in the formulas (16). I_{yy}^{i} can have a positive or negative sign and the L elements cannot be evaluated with any certainty. Therefore, we take $\sum_i I_{yy}^2$ and

$\sum_i I_{yz}^2$ and use the value of K determined earlier.

A very interesting feature of the equations for $\sum I_{yy}^2$ and $\sum I_{yz}^2$ is that we observe them to be identical whether we take the symmetry coordinate (S_{5a}) to be simply R_x or R_x combined with R's. This is understandable as these expressions contain only constants relating to the crystal.

Then expressions for P'_{44}, P'_{66}, P'_{14}, P'_{41}, and also $P'_{4[4]}$ and $P'_{1[4]}$ (in Nelson's terminology) are obtained from Table III and the Eq. (17). $P_{4[4]}$ is $P_{yz\omega_x}$ and $P_{1[4]}$ is $P_{xx\omega_x}$. These equations are as follows:

$$\sum_i I_{yy}^2 K^2 = n_y^2(67.33)K^2 = \gamma'^2_{C-O}(0.0094)+\gamma^2_{C-O}(0.1035)+\gamma^2_{Ca-O}(0.0205)-\gamma_{C-O}\gamma'_{C-O}(0.0294)$$

$$-\gamma'_{C-O}\gamma_{Ca-O}(0.0186)-\gamma_{C-O}\gamma_{Ca-O}(0.0098),$$ (19a)

$$\sum_i I_{yz}^2 K^2 = n_y n_z(60.73)K^2 = \gamma^2_{C-O}(0.0341)+\gamma^2_{Ca-O}(0.0120)-\gamma_{C-O}\gamma_{Ca-O}(0.0099),$$ (19b)

$$P'_{14}=A_2(-1.7334)+A_4(-2.1228)+A_5(2.0424)=-(0.6129)\gamma'_{C-O}+(0.1731)\gamma_{Ca-O},$$ (19c)

$$P'_{1[4]}=A_5(0.7053)=-(0.2199)\gamma_{Ca-O},$$ (19d)

$$P'_{41}=A_6(0.8935)+A_7(1.4997)+A_8(0.3104)+A_9(1.3539)=(0.1107)\gamma_{C-O}-(0.7973)\gamma_{Ca-O},$$ (19e)

$$P'_{44}=A_6(-1.7334)+A_8(-2.1228)+A_9(2.0424)=(0.4595)\gamma_{C-O}-(2.9572)\gamma_{Ca-O},$$ (19f)

$$P'_{4[4]}=A_9(0.7053)=-(0.5249)\gamma_{C-O}+(0.0759)\gamma_{Ca-O},$$ (19g)

$$P'_{66}=A_2(0.8935)+A_3(1.4997)+A_4(0.3104)+A_5(1.3539)=(0.3159)\gamma'_{C-O}-(1.0606)\gamma_{C-O}-(0.5402)\gamma_{Ca-O}.$$ (19h)

These equations contain three constants to be evaluated γ'_{C-O}, γ_{C-O}, and γ_{Ca-O}. But there are only two intensity equations [(19a) and (19b)].

TABLE VII. Electro-optical constants calculated with the use of values of Pockel and Nelson. The values given below are accurate up to two digits.

$\gamma_{C-O}(yz)$	0.2177	0.1497
γ'_{C-O}	0.1975	0.1758
γ_{Ca-O}	0.1755	0.1423
$\gamma_{C-O}(yy)$	0.1675	0.1224

Therefore it is necessary to take one of the experimental photoelastic constants to determine the three unknowns. We have chosen P_{44} as Pockel and Nelson obtained nearly the same values.

There is another important point. In deriving the intensity formulas, Long assumed that the bonds are of cylindrical symmetry with respect to polarization. But as the present authors have shown earlier for the NO_3 ion[24] (and CO_3 which is of the same symmetry), the N—O bond does not have cylindrical symmetry. Polarization perpendicular to the plane of CO_3, α_3, is different from α_2 in the plane. The
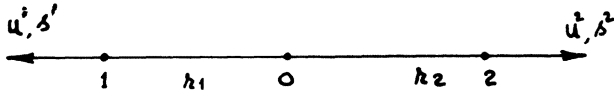
FIG. 3. Stretching between two atoms 1 and 2. u^1 and u^2 are displacements that produce the stretching and s^1 and s^2, Wilson's s vectors. 0 is the origin of the coordinate system.

present authors have shown that for xx-type vibrations, which are in the plane of the CO_3 ion, γ_{C-O} is really $\alpha_1 - \alpha_2$, and while considering yz oscillations involving the rotations, the $C-O$ bonds move in the z direction and γ_{C-O} in this case is $\alpha_1 - \alpha_3$.

So, from $\sum I_{yz}^2$ and P_{44}, $\gamma_{C-O} = (\alpha_1 - \alpha_3)$ and γ_{Ca-O} are calculated. With the use of this value of γ_{Ca-O} in P_{14} and $\sum I_{yy}^2$, γ'_{C-O}, $\gamma_{C-O}(\alpha_1 - \alpha_2)$, and P_{66} are obtained. We see that $\gamma_{C-O}(\alpha_1 - \alpha_2)$ and $\gamma_{C-O}(\alpha_1 - \alpha_3)$ are different. The electro-optical constants thus obtained are given in Table VII and the photoelastic constants in Table V. $P_{4[4]}$ and $P_{1[4]}$ (in Nelson's terminology) are also given in this table.

Since the Raman spectra are of a nonresonance type it is not possible to differentiate between P_{yzyz} and P_{zyyz} and similar expressions for P_{xy} and P_{xz}, as we cannot differentiate between α_{yz} and α_{zy}, etc.

ACKNOWLEDGMENT

APPENDIX: INTERNAL COORDINATES AND STRAINS

It is always instructive and advantageous to understand the properties of a crystal from its constituent molecules. The properties of a molecule are generally related to the chemical bonds and the internal coordinates describing the changes in the bond lengths, bond angles, rotations, etc. Therefore it becomes necessary to relate the strains (and stresses in terms of which the properties of the crystal are understood) to internal coordinates.

Taking the crystal to be a continuous medium the change in the distance between any two points apart is given in books on theory of elasticity[25] as

$$\Delta R = R(e_{xx}l^2 + e_{yy}m^2 + e_{zz}n^2 + e_{yz}mn$$
$$+ e_{zx}nl + e_{xy}lm)$$
$$= R\,le \qquad (A1)$$

(in matrix form). l, m, and n are the direction cosines along the x, y, and z directions. This formu-
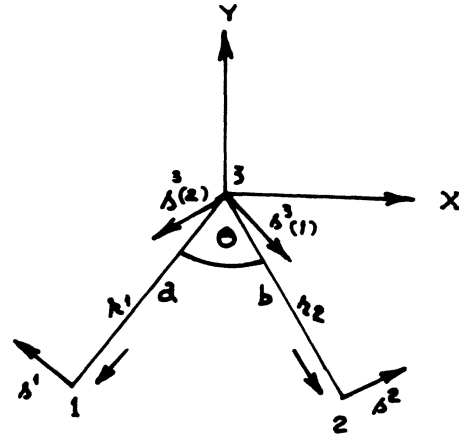

FIG. 4. Change in the angle between two bonds 13 and 23. r_1 and r_2 are lengths of the bonds, e_1 and e_2, are unit vectors along 31 and 32, and s^1, $s^3(1)$, s^2, and $s^3(2)$ are Wilson's s vectors. a and b are points about which rotations of the bonds take place.

la was used for a bond length by early workers[26] to obtain a relationship between force constants and elastic constants. One can find a similar formula for change in angle between two lines also in standard books.[25] But we are not aware of the general formulas for rotation, out-of-plane oscillation, etc. We now attempt at such a derivation that can be generally used for every type of internal coordinate. We start with[27]

$$u_i^k = u_{ij}r_j^k . \qquad (A2)$$

Repetition of j indicates summation. u_i^k is the displacement of the kth atom in the ith (x,y,z) direction. $u_{ij} = \delta u_i / \delta r_j$ are related to strains and r^k is the position vector of atom k. In general $u_{ij} \neq u_{ji}$, but

$$u_{ii} = e_{ii} \qquad (A3)$$

and

$$u_{ij} + u_{ji} = e_{ij} . \qquad (A4)$$

e_{ij} are the strain parameters.

The internal oscillations in a molecule (or crystal) are generated by the displacements of the atoms according to the scheme

$$\Delta R = \sum_k u^k s^k . \qquad (A5)$$

ΔR is any internal coordinate and not necessarily stretching, u^k is the displacement of the kth atom, and s^k is, in general, a unit vector along this displacement. s^k are Wilson's s vectors[14] explained in detail in books on molecular physics.
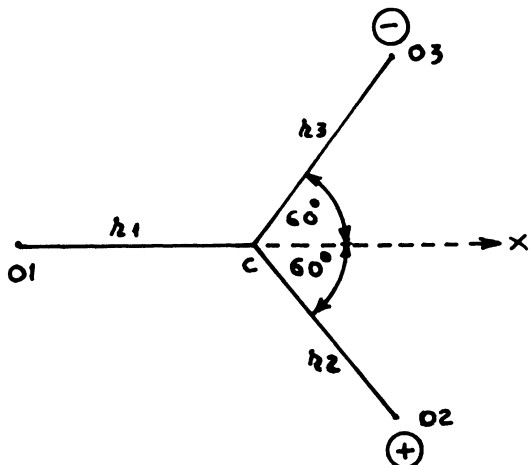
FIG. 5. Rotation of CO_3 about the x axis. O_2 moves along the $+z$ direction and O_3 in the opposite direction.

FIG. 6. Rotation of CO_3 about the y axis. O_2 and O_3 move along the $+z$ direction and O_1 in the opposite direction.

If ΔR is the stretching between two atoms 1 and 2 of a bond, displacements u^1 and u^2 should be along s^1 and s^2 unit vectors, so that $s^1 = -s^2$ (Fig. 3). Taking 0 midway between the atoms as origin, position vectors $r^1 = r^2$. r_j^1 in (A2) is equal to $r^1 1j$, $1j$ being the direction cosine of r^1. Since s^1 and s^2 are in the same direction, $1j$ are the direction cosines of s^1 also. Similarly, $2j$ are the direction cosines of r^2 and s^2.

Now expanding (A2),

$$u_x^1 = (u_{xx}l_1 + u_{xy}m_1 + u_{xz}n_1)r^1 ,$$

$$u_y^1 = (u_{yx}l_1 + u_{yy}m_1 + u_{yz}n_1)r^1 , \tag{A6}$$

$$u_z^1 = (u_{zx}l_1 + u_{zy}m_1 + u_{zz}n_1)r^1 .$$

With similar equations for u_x^2, u_y^2, and u_z^2,

$$\Delta R = u^1 s^1 + u^2 s^2 = (u_x^1 l_1 + u_y^1 m_1 + u_z^1 n_1) + (u_x^2 l_2 + u_y^2 m_2 + u_z^2 n_2)$$

$$= R(e_{xx}l_1^2 + e_{yy}m_1^2 + e_{zz}n_1^2 + e_{yz}m_1 n_1 + e_{zx}n_1 l_1 + e_{xy}l_1 m_1) . \tag{A7}$$

Here, we have set $r^1 = r^2$, $l_1 = l_2$, $m_1 = m_2$, and $n_1 = n_2$; $R = 2r$. l_1, m_1, n_1 are direction cosines of the first bond and $l_2 m_2 n_2$ of the second bond. Equation (A7), found in Ref. 25, is derived in a different way.

Bond angle

Figure 4 shows a molecule 123 in the xy plane. Angle θ increases if the bonds 13 and 23 rotate about their centers a and b. The vectors s^1 and s^2 are given (Ref. 14) as

$$s^1 = \frac{e_1 \cos\theta - e_2}{r \sin\theta} , \quad s^2 = \frac{e_2 \cos\theta - e_1}{r \sin\theta} .$$

e_1 and e_2 are unit vectors along 31 and 32, $s^3(1)$ and $s^3(2)$ relate to atom 3, $s^3(1) = -s^1$, and $s^3(2) = -s^2$. Their direction cosines are obtained by multiplying
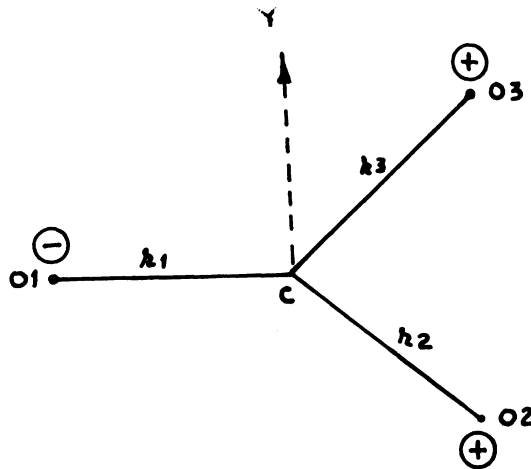
them by e_x and e_y, unit vectors along x and y. Set $r_1 = r_2$ (for simplicity). Then, for bond 13,

$$s_x^1 u_x^1 = (u_{xx}l_1 + u_{xy}m_1)r\frac{l_1\cos\theta - l_2}{r\sin\theta} ,$$

$$s_y^1 u_y^1 = (u_{yx}l_1 + u_{yy}m_1)r\frac{m_1\cos\theta - m_2}{r\sin\theta} ,$$

$$s_x^3 u_x^3 = [u_{xx}(-l_1) + u_{xy}(-m_1)]r\frac{l_2 - l_1\cos\theta}{r\sin\theta} , \tag{A8}$$

$$s_y^3 u_y^3 = [u_{yx}(-l_1) + u_{yy}(-m_1)]r\frac{m_2 - m_1\cos\theta}{r\sin\theta} .$$

We have similar equations for bond 23. Then

$$\Delta\theta = u^1 s^1 + u^3 s^3(1) + u^2 s^2 + u^3 s^3(2) . \tag{A9}$$

Upon simplifying, we get

$$\sin\theta \, \Delta\theta = 2e_{xx}(l_1^2\cos\theta + l_2^2\cos\theta - 2l_1l_2) + 2e_{yy}(m_1^2\cos\theta + m_2^2\cos\theta - 2m_1m_2)$$
$$+ 2e_{xy}(l_1m_1\cos\theta + l_2m_2\cos\theta - l_1m_2 - l_2m_1) \; . \tag{A10}$$

If the molecule is in a general plane, this equation becomes

$$\sin\theta \, \Delta\theta = 2e_{xx}(l_1^2\cos\theta + l_2^2\cos\theta - 2l_1l_2) + 2e_{yy}(m_1^2\cos\theta + m_2^2\cos\theta - 2m_1m_2) + 2e_{zz}(n_1^2\cos\theta + n_2^2\cos\theta - 2n_1n_2)$$
$$+ 2e_{xy}(l_1m_1\cos\theta + l_2m_2\cos\theta - l_1m_2 - l_2m_1) + 2e_{yz}(m_1n_1\cos\theta + m_2n_2\cos\theta - m_1n_2 - m_2n_1)$$
$$+ 2e_{zx}(n_1l_1\cos\theta + n_2l_2\cos\theta - n_1l_2 - n_2l_1) \; . \tag{A11}$$

Rotation of CO_3 about the x axis (R_x)

Rotation of CO_3 about the x axis makes O_2 move up and O_3 move down, indicated by $+$ and $-$ in Fig. 5 along the z axis. The s vectors for rotation are described in an earlier paper.[17] $s^2 = e_z\sin(60°)/r$ and $s^3 = -e_z\sin(60°)/r$. Since the atoms move only along the z direction, s vectors are functions of e_z, the unit vector along the z direction. Then $s_z^2 = \sin(60°)/r$ and $s_z^3 = -\sin(60°)/r$. Since $r_1 = r_2 = r_3 = r$,

$$s_z^2u_z^2 = (u_{zx}l_2 + u_{zy}m_2)r\sin(60°)/r \; ,$$
$$s_z^3u_z^3 = (u_{zx}l_3 + u_{zy}m_3)r - [\sin(60°)/r] \; . \tag{A12}$$

Therefore

$$R_x = s_z^2u_z^2 + s_z^3u_z^3 = \tfrac{3}{2}u_{zy}$$
$$= \tfrac{3}{4}(u_{zy} + u_{yz} + u_{zy} - u_{yz})$$
$$= \tfrac{3}{4}(e_{yz} + \omega_x) \; . \tag{A13}$$

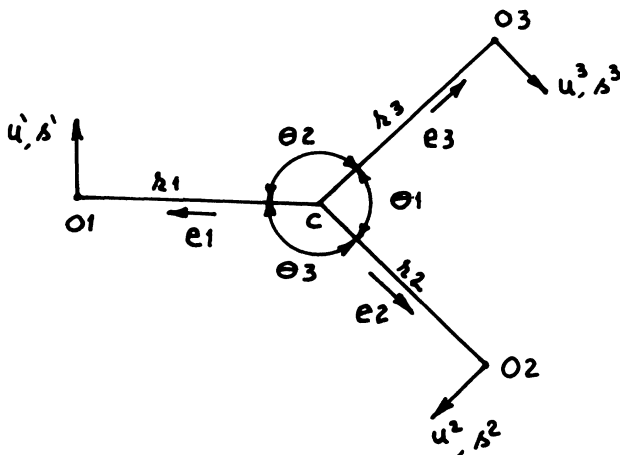$\omega_x = u_{zy} - u_{yz}$ is the rotation about the x axis.

FIG. 7. Rotation of CO_3 about the z axis. $r_1 = r_2 = r_3$ are bond lengths, and e_1, e_2, and e_3 are unit vectors along the bonds. u^1, u^2, and u^3 are displacements necessary to produce the rotations and s^1, s^2, and s^3 are Wilson's s vectors.

Rotation of CO_3 about the y axis (R_y)

Rotation about the y axis is shown in Fig. 6. O_2 and O_3 have to move up while O_1 moves down. The s vectors for this rotation, also described in an earlier paper[17] are $s^1 = -e_z/r$, $s^2 = e_z\cos(60°)/r$, and $s^3 = e_z\cos(60°)/r$ and then by a similar procedure, we obtain

$$R_y = \tfrac{3}{4}(e_{xz} + \omega_y) \; . \tag{A14}$$

Rotation about the z axis is not Raman active. A similar procedure (Fig. 7) shows that

$$s^1 = (e_1\cos\theta - e_2)/r\sin\theta \; ,$$
$$s^2 = (e_2\cos\theta - e_3)/r\sin\theta \; ,$$

and

$$s^3 = (e_3\cos\theta - e_1)/r\sin\theta \; .$$

Then

$$s_y^1u_y^1 = (u_{yx}l_1 + u_{yy}m_1)r(m_1\cos\theta - m_2)/r\sin\theta \; ,$$
$$s_x^2u_x^2 = (u_{xx}l_2 + u_{xy}m_2)r(l_2\cos\theta - l_3)/r\sin\theta \; ,$$
$$s_y^2u_y^2 = (u_{yx}l_2 + u_{yy}m_2)r(m_2\cos\theta - m_3)/r\sin\theta \; ,$$
$$s_x^3u_x^3 = (u_{xx}l_3 + u_{xy}m_3)r(l_3\cos\theta - l_1)/r\sin\theta \; ,$$
$$s_y^3u_y^3 = (u_{yx}l_3 + u_{yy}m_3)r(m_3\cos\theta - m_1)/r\sin\theta \; .$$

Therefore

$$R_z = \underline{s}^1\underline{u}^1 + \underline{s}^2\underline{u}^2 + \underline{s}^3\underline{u}^3$$
$$= \tfrac{3}{2}(u_{xy} - u_{yx}) = \tfrac{3}{2}w_2 \; .$$

TABLE VIII. Direction cosines.

	l	m	n
R_1'	−0.515	0.610	0.603
R_1''	−0.515	−0.610	−0.603
R_2'	−0.271	−0.751	0.603
R_2''	0.786	−0.141	−0.603
R_3'	0.786	0.141	0.603
R_3''	−0.271	0.751	−0.603

It is interesting to see that corresponding to R_z, e_{xy} is zero and we have only ω_z. This is understandable because R_z occurs under the species A_2, which is Raman inactive. There is a close one-to-one correspondence between the symmetry of the strains and the polarizability tensors that produce Raman activity, as both of them are second-order tensors.

The infrared modes do not produce any strains in this crystal. Hence it is not piezoelectric.

The direction cosines of R's can be determined from crystal parameters in the usual way. They are shown in Table VIII. The Rle matrix is formulated similar to (A1) for every one of the internal coordinates and $uRle$ obtained by taking u from Table I.

[1]A. A. Maradudin, Phys. Rev. 166, 1081 (1967).

[2]D. F. Nelson and M. Lax, Phys. Rev. Lett. 24, 379 (1970).

[3]D. F. Nelson and P. D. Lazay, Phys. Rev. Lett. 25, 1187 (1970).

[4]D. F. Nelson and M. Lax, Phys. Rev. B 3, 2778 (1971).

[5]D. F. Nelson, P. D. Lazay, and M. Lax, Phys. Rev. B 6, 3109 (1972).

[6]M. H. Grimsditch and A. K. Ramdas, Phys. Rev. B 22, 4094 (1980).

[7]A. Gavini and M. Cardona, Phys. Rev. 177, 1351 (1969).

[8]M. Chandrasekhar, M. H. Grimsditch, and M. Cardona, J. Opt. Soc. Am. 68, 523 (1978).

[9]R. J. Briggs and A. K. Ramdas, Phys. Rev. B 13, 5518 (1976).

[10]R. Loudon, Proc. R. Soc. London Ser. A 275, 218 (1963).

[11]D. A. Long, Proc. R. Soc. London 217, 203 (1953).

[12]M. Eliashevich and M. W. Wolkenstein, J. Chem. Phys. 9, 101 (1945); 9, 326 (1945).

[13]S. P. Kumar, V. A. Padma, and N. Rajeswara Rao, Indian J. Pure Appl. Phys. 10, 275 (1972).

[14]E. S. Wilson Jr., J. C. Decius, and P. C. Cross, Molecular Vibrations (McGraw-Hill, New York, 1955).

[15]E. Tubino and L. Piseri, Phys. Rev. B 11, 5145 (1975).

[16]C. Domingo and S. Montero, J. Chem. Phys. 74(2), 862 (1981).

[17]S. P. Kumar, V. A. Padma, and N. Rajeswara Rao, J. Chem. Phys. 60, 4156 (1974).

[18]G. Swarna Kumari, K. Ravindranath, and N. Rajeswara Rao, Indian J. Pure Appl. Phys. 20, 167 (1982).

[19]I. I. Kondilenko, P. A. Korotkov, and V. A. Klimenko, Opt. Spectrosc. 40, 402 (1976).

[20]H. J. Bernstein and G. Allen, J. Opt. Soc. Am. 45, 237 (1955).

[21]S. P. S. Porto, J. A. Giordmaine, and T. C. Damen, Phys. Rev. 147, 608 (1966).

[22]M. Y. Fong and M. Nicol, J. Chem. Phys. 54, 579 (1971).

[23]R. W. G. Wyckoff, Crystal Structures (Interscience, New York, 1951), Vol. II, Chap. VII, specifically the table on p. 7.

[24]G. Swarna Kumari and N. Rajeswara Rao, Indian J. Pure Appl. Phys. 19, 326 (1981).

[25]A. E. H. Love, Treatise on the Mathematical theory of Elasticity, 4th ed. (Cambridge University Press, Cambridge, 1952).

[26]H. N. Pandey, Phys. Status Solidi 11, 743 (1965).

[27]M. Born and Kun Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, London, 1954).