

Raman intensity analysis of LaCl_3

N SATYAVATHI and N RAJESWAR RAO

Department of Physics, Osmania University, Hyderabad 500 007

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Abstract. Raman intensity analysis of LaCl_3 on lines adopted earlier for crystals like LiNO_3 , KNO_3 or YVO_4 is found to be unsuitable for LaCl_3 . The rotation of the LaCl_3 pyramids in the unit cell of this crystal is represented by high frequencies, comparable to the internal oscillations of LaCl_3 molecule. The intensity of R_z , rotation about the symmetry axis of the crystal, is higher than the total symmetric line. These two factors show that the two molecules in the unit cell cannot be treated separately. Also, the polarisability of the bonds between atoms connecting the molecules cannot be neglected. The intensity formulae have been derived for this crystal and using the directional Raman spectra, electro-optical constants of the LaCl and Cl—Cl bonds have been evaluated. It is found that while the polarisability of Cl—Cl bond between the molecules, is about 0.4 times that of LaCl bonds, in crystals like LiNO_3 , the polarisability of bonds like Li—O is found to be negligible.

Keywords. Intensity analysis; symmetry co-ordinates; LaCl_3 .

1. Introduction

Raman intensity analysis of crystals has been initiated and a number of crystals have been treated in our laboratory [Kumar *et al* (1972, 1974, 1976), Addepalli *et al* (1976), Padma *et al* (1973)]. In the crystals treated so far, the molecules in the unit cells are well separated so that the forces between them are small compared to the intramolecular forces. Therefore, Raman intensity tensors are derived for any one molecule in the unit cell and the tensor elements for the other molecules are obtained by symmetry operations. Then, the elements for the whole unit cell corresponding to the modes of oscillations under different species are obtained by suitable additions. This procedure is described by the formulae

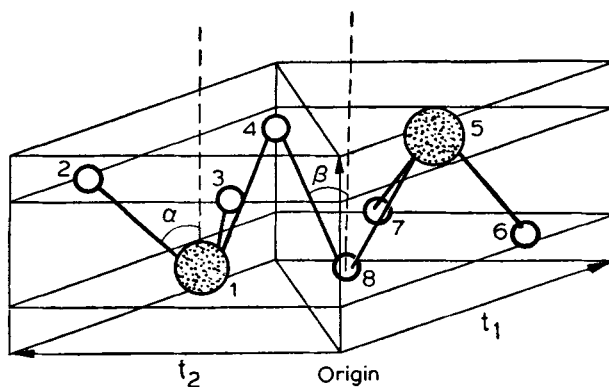
$$\frac{\delta a_{IJ}}{\delta Q} = J_r u' U' L + J_\phi K_\phi \mu s' u' U' L^{-1}. \quad (1)$$

The terminology is described in detail by Addepalli and Rao (1977). Here u connects the internal coordinates and the symmetry coordinates of any molecule in the unit cell. The symmetry coordinates are with respect to the site symmetry of the principal point of the molecule. The symmetry operations on the coordinates of the molecule, gives the symmetry coordinates of the crystal and U connects the crystal and the molecules.

In this procedure, we consider only the internal bonds of the molecule. In crystals like LiNO_3 (Kumar *et al* 1974), the bond between Li and O or between O of one

molecule and of the other in the unit cell are ignored. Polarisability of only the NO bond is taken. The intensity formulae (Raman scattering tensors) have described the directional Raman spectra.

We have initially tried to derive similar formulae for LaCl_3 . This crystal is of symmetry C_{6h}^2 and the directional Raman spectra were taken by Asawa *et al* (1968). The unit cell consists of two molecules of pyramidal symmetry related by inversion (Figure 1). The site symmetry of La atom is C_{3h} . The modes of oscillation are distributed as $2A_g + 2B_g + 1E_{1g} + 3E_{2g} + 2A_u + 2B_u + 3E_{1u} + 1E_{2u}$ (Murphy *et al* 1964).



$$\alpha = 44^\circ, \quad \beta = 43^\circ, \quad \delta = 43^\circ$$

$$r_{12} = 2.9857 \text{ \AA}, \quad r_{38}^* = 3.3551 \text{ \AA}, \quad r_{23}^* = 3.5358 \text{ \AA}$$

Figure 1. Unit cell of LaCl_3 .

Table 1.

Species	Nature of the spectrum	Frequency	Assignment	Intensity
A_g	$x(zz)y$	212 cm^{-1}	Symmetric stretching	0
A_g	$x(zz)y$	180 cm^{-1}	Rotation about C-axis	$K_2 \times 4.29$
A_g	$x(yy)z$	212 cm^{-1}	Symmetric stretching	$K_1 \times 11.55$
A_g	$x(yy)z$	180 cm^{-1}	Rotation about C-axis	0
E_{2g}	$x(yy)z$	219 cm^{-1}	Asymmetric stretching	$K_1 \times 7.908$
E_{2g}	$x(yy)z$	108 cm^{-1}	Bending	$K_1 \times 2.134$
E_{1g}	$x(yz)y$	186 cm^{-1}	Rotation about X-axis	$K_2 \times 4.251$

The frequencies and their assignments are given in table 1. Here B_g is Raman inactive. A_g consists of ν_1 , total symmetric stretching and ν_2 , rotation about C axis (R_z). The intensity formulae have been derived as usual of LaCl_3 pyramids and taking the polarisability of only LaCl . It is found that these formulae do not describe the spectra adequately. The rotations of the molecule about the axis of symmetry R_z is inactive in the Raman spectrum if one takes C_{3v} symmetry. In the C_{6h} symmetry, however, it combines with the total symmetric stretching. Hence, R_z can appear with a small intensity due to interaction between these modes of oscillation. But R_z appears very intense in the zz spectrum where the total symmetric line is absent while in the xx spectrum R_z is absent and the total symmetric stretching ν_1 , is very intense. This shows that our approach is totally inadequate.

Another notable feature of the spectrum is that ν_2 (an external oscillation) is comparable to ν_1 . This shows very high resistance to the rotations of the pyramids LaCl_3 indicating that the two pyramids in the unit cell are strongly bound to each other. The intermolecular forces are not small compared to the intramolecular forces. In the crystals treated by us earlier, e.g. LiNO_3 , polarisability of the intermolecular bonds, for instance between Li and O was neglected. Perhaps, in the present case polarisabilities of such bonds, like between Cl of one pyramid and Cl of neighbouring pyramid cannot be neglected and we now take them into account.

We shall make a departure in describing the internal and external modes of oscillation. *It is reasonable to think that all the modes of oscillation are fundamentally derivable from simple attractions between the atoms.* (This is not to be confused with the assumption of central forces). Modes like bending and rotation are produced by a system of attractions and repulsions between the atoms. So, we shall take the changes in the lengths of bonds like LaCl (like 1-2, 1-3, 1-4 and 5-6, 5-7, 5-8) in (figure 2). $\text{Cl}-\text{Cl}$ in the pyramid (like 2-3, 3-4, 4-2 and 6-7, 7-8, 8-6), $\text{Cl}-\text{Cl}$ between one pyramid and the other (like 3-8, and 4-7). Distances 38 and 48 are slightly different but are taken to be equal as an approximation. Distances like 1-8 between lanthanum of one pyramid and chlorine of the neighbouring pyramid are in one plane. Thus, we have five varieties of bonds, changes in their lengths, producing all the modes of oscillations.

Now, the oscillations in any unit cell are produced not only by the mutual attractions and repulsions of atoms in the unit cell, but also by all the atoms around. The potential energy of any unit cell is, (for harmonic oscillations)

$$2V = \sum_K \sum_{m,n} \frac{\delta^2 V}{\delta r_{K_a K_b}^{om} \cdot \delta r_{K_c K_d}^{on}} \delta r_{K_a K_b}^{om} \delta r_{K_c K_d}^{on}$$

Here $r_{K_a K_b}^{om}$ represents distance between the atom K_a in the zeroth (central) cell and K_b in the m th cell. K gives the numbering of atoms in any unit cell. m and n are the neighbouring unit cell numbers. If we take only the nearest neighbour interactions m and n can be confined to the cells in the immediate neighbourhood. In figure 2 we show the central cell 0 and cells 1, 2, 3, 4. The cell above the plane is 5 and below the plane is 6.

The K s number from 1 to 8 and we take five different types of distances r .

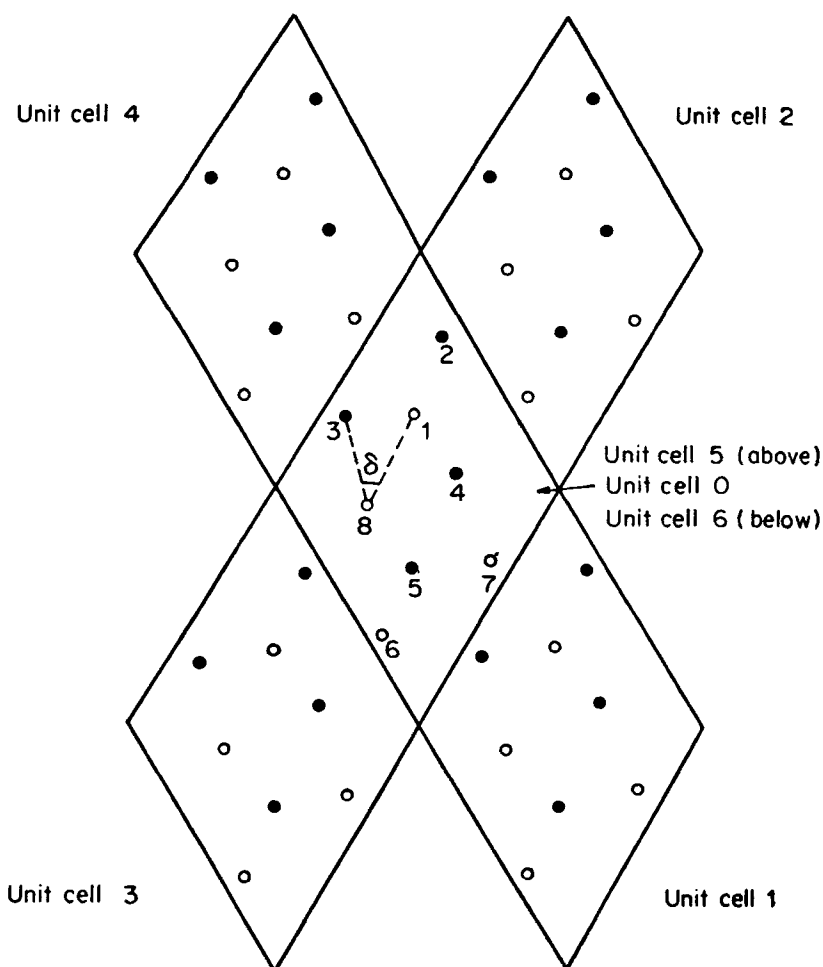


Figure 2. Unit cells of LaCl_3

2. Symmetry co-ordinates

Symmetry coordinates representing oscillations of various species can be obtained as*

2.1. A_g

$$S_1 = \frac{1}{2\sqrt{3}} (1^0 2^0 + 1^0 3^0 + 1^0 4^0 + 5^0 6^0 + 5^0 7^0 + 5^0 8^0 + 1^0 2^6 + 1^0 3^6 + 1^0 4^6 + 5^0 6^6 + 5^0 7^6 + 5^0 8^6)$$

* $1^0 2^0$, etc., are written for r_{12}^{00} , etc., for brevity.

$$S_2 = \frac{1}{2\sqrt{3}} (3^{080} + 4^{070} + 6^{031} + 7^{021} + 4^{360} + 2^{380} + 3^{085} + 4^{075} \\ + 6^{53} + 7^{521} + 4^{365} + 2^{385})^1$$

2.2. E_{1g}

$$S_{3a} = \left[\frac{1}{\sqrt{24}} [2 (3^{080} - 3^{085} + 4^{070} - 4^{075}) - (6^{531} - 6^{531} + 7^{021} \\ - 7^{521} + 4^{360} - 4^{365} + 2^{380} - 2^{385})] \right] \cos \delta + \frac{1}{2\sqrt{2}} [(6^{031} - 6^{531} \\ + 7^{021} - 7^{521}) - (4^{360} - 4^{365} + 2^{380} - 2^{385})] \sin \delta$$

$$S_{3b} = \left[\frac{1}{2\sqrt{2}} (6^{031} - 6^{531} + 7^{021} - 7^{521}) - (4^{360} - 4^{365} + 2^{380} - 2^{385}) \right] \times \\ \cos \delta - \frac{1}{\sqrt{24}} [2 (3^{080} - 3^{085} + 4^{070} - 4^{075}) - (6^{031} - 6^{531} \\ + 7^{021} - 7^{521} + 4^{360} - 4^{365} + 2^{380} - 2^{385})] \sin \delta.$$

2.3. E_2

$$S_{4a} = \frac{1}{2\sqrt{6}} [2 (1^{020} + 1^{026} + 5^{060} + 5^{065}) - (1^{030} + 1^{036} + 1^{040} + 1^{046} \\ + 5^{070} + 5^{075} + 5^{080} + 5^{085})],$$

$$S_{4b} = \frac{1}{2\sqrt{2}} [(1^{040} + 1^{046} + 5^{080} + 5^{085}) - (1^{030} + 1^{036} + 5^{070} + 5^{075})].$$

$$S_{5a} = \frac{1}{2\sqrt{3}} [2 (3^{040} + 7^{080}) - (2^{030} + 2^{040} + 6^{070} + 6^{080})],$$

$$S_{5b} = \frac{1}{2} [(2^{030} + 6^{070}) - (2^{040} + 6^{080})],$$

$$S_{6a} = \frac{1}{2\sqrt{3}} [2 (4^{050} + 1^{080}) - (5^{023} + 5^{031} + 7^{011} + 6^{013})],$$

$$S_{6b} = \frac{1}{2} [(5^{031} + 7^{011}) - (5^{023} + 6^{013})].$$

On plotting these symmetry coordinates, the following (figures 4a and 4b) modes of oscillations are obtained. Since we assume oscillations in various unit cells to be in unison, while plotting the above modes, displacements of similar atoms in different cells are all given to the equivalent atom in the central cell.

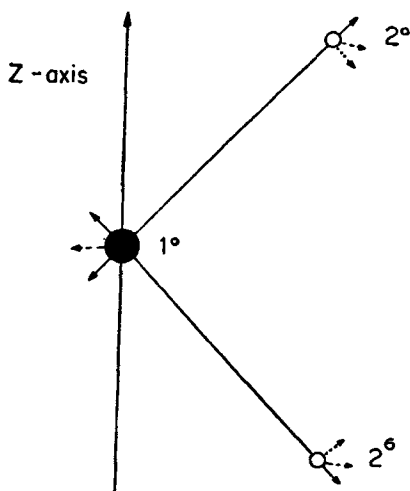


Figure 3. Resultant of displacements



Figure 4a. Modes of oscillations

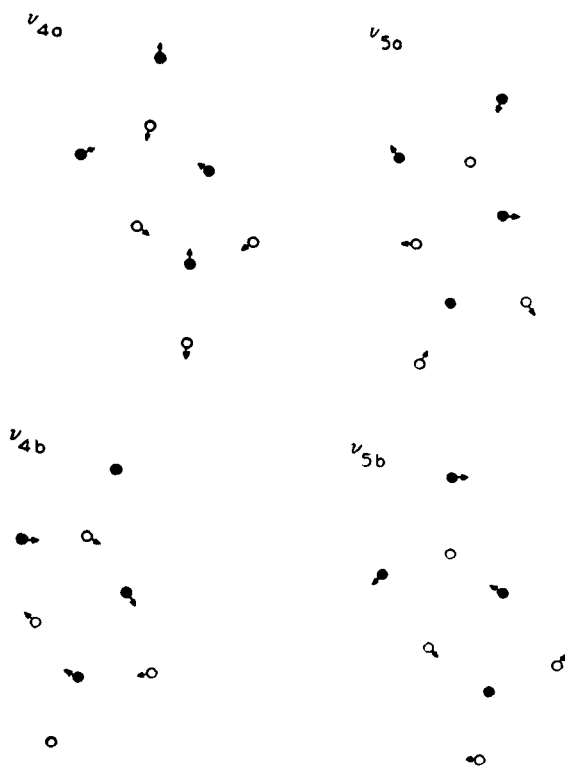


Figure 4b. Modes of oscillations

For instance, in figure 3, the displacements 1^{02^0} and 1^{02^6} are shown. Since 2^8 and 2^0 are similar atoms in the unit cells 6 and 0, both the displacements are given to both the atoms. Adding the displacement of 2^6 to 2^0 (dotted line), the resultant displacement is found to be horizontal. Similarly the resultant displacement of 1 is also horizontal. Adding the three horizontal displacements of 1, due to $1^{02^0} + 1^{02^6}$, $1^{03^0} + 1^{03^6}$ and $1^{04^0} + 1^{04^6}$, one can see that atom 1 remains stationary while 2, 3, 4 spread out in the horizontal plane. One can also imagine that this mode of oscillation is the same in all the unit cells. The symmetry coordinates thus graphically represent the modes of oscillations shown in figure 4.

3. Intensity formulae

In deriving the intensity formulae using polarisabilities of bonds La—Cl and Cl—Cl in the pyramid and also Cl—Cl between two pyramids, i.e., bonds like r_{12} , r_{23} and r_{38} in figure 1, are taken. The formulae derived are:

3.1. A_g

$$\alpha'_{xx} = \alpha'_{yy} = \left[\frac{\sqrt{3}}{r_1} \sin^2 2\alpha (a_{11} - a_{12}) \mu_{\text{Cl}} - \frac{8\sqrt{3}}{r_2} \sin \beta \sin \alpha \cos \delta \cos^2 \beta \right]$$

$$\begin{aligned}
& \times (a_{21} - a_{22}) \mu_{Cl} \left] L_{i1}^{-1} + \frac{\sqrt{3}}{r_2} \sin^2 2\beta (a_{21} - a_{22}) \mu_{Cl} L_{i2}^{-1} \right. \\
& + [\sqrt{3} \sin^2 a (a'_{11} - a'_{12}) + 2\sqrt{3} a'_{12}] L_{1i} \\
& + [\sqrt{3} \sin^2 \beta (a'_{21} - a'_{22}) + 2\sqrt{3} a'_{22}] L_{2i}, \\
\alpha'_{zz} = & \left[\frac{-2\sqrt{3}}{r_1} \sin^2 2a (a_{11} - a_{12}) \mu_{Cl} + \frac{16\sqrt{3}}{r_2} \sin \beta \sin a \cos \delta \cos^2 \beta \right. \\
& \times (a_{21} - a_{22}) \mu_{Cl} \left. \right] L_{i1}^{-1} - \frac{2\sqrt{3}}{r_2} \sin^2 2\beta (a_{21} - a_{22}) \mu_{Cl} L_{i2}^{-1} \\
& + [\sqrt{3} \cos^2 a (a'_{11} - a'_{12}) + 2\sqrt{3} a'_{12}] L_{1i} \\
& + [\sqrt{3} \cos^2 \beta (a'_{21} - a'_{22}) + 2\sqrt{3} a'_{22}] L_{2i}. \quad i = 1, 2
\end{aligned}$$

3.2. E_{1g}

$$\alpha'_{yz} = -\frac{\sqrt{3}}{\sqrt{2}} \cdot \frac{\sin 4\beta}{r_2} (a_{21} - a_{22}) \mu_{Cl} L_{11}^{-1} + \frac{\sqrt{3}}{\sqrt{2}} \cdot \sin 2\beta (a'_{21} - a'_{22}) L_{11}$$

3.3. E_{2g}

$$\begin{aligned}
\alpha'_{xx} = & \left[\frac{\sqrt{6}}{r_1} \sin^2 a (3 \sin^2 a \mu_{La} - 2 \cos^2 a \mu_{Cl}) (a_{11} - a_{12}) \right. \\
& - \frac{3}{\sqrt{2}r_3} \sin a \mu_{Cl} (a_{31} - a_{32}) \left. \right] L_{i1}^{-1} + \left[\frac{3\sqrt{3}}{2r_3} (a_{31} - a_{32}) \mu_{Cl} \right. \\
& + \frac{3}{r_1} \sin a (2 - \sin^2 a) (a_{11} - a_{12}) \mu_{Cl} \left. \right] L_{i2}^{-1} \\
& - \frac{\sqrt{3}}{\sqrt{2}} \sin^2 a (a'_{11} - a'_{12}) L_{1i} + \frac{\sqrt{3}}{2} (a'_{31} - a'_{32}) L_{2i}. \quad i = 1, 2
\end{aligned}$$

Here, $r_1=r_{12}$, $r_2=r_{38}$ and $r_3=r_{23}$. a_{11} is the polarisability of r_1 along its length and a_{12} perpendicular to it. a_{21} , a_{22} and a_{31} , a_{32} are similarly for r_2 and r_3 . α , β , and δ are angles shown in figure 2.

It is interesting to see that the coefficients of L^{-1} elements in A_g follow the rule $\alpha_{xx} + \alpha_{yy} + \alpha_{zz} = 0$ as expected.

As already stated, an interesting feature of the spectrum of LaCl_3 is the large intensity of the line ν_2 compared to ν_1 in a_{zz} spectrum. This cannot be understood if we do not introduce a_{21} and a_{22} . Without this, ν_1 would be always stronger than ν_2 . Introduction of these additional parameters helps in accounting for intense ν_2 in zz .

It may be mentioned at this stage that though we expect 3 lines in E_{2g} , the spectrum

shows only 2 (ν_4 and ν_5). The other line (ν_6) is a relative movement of La and Cl group in the x or y directions. This cannot be constructed from the symmetry coordinates obtained from r_{12} , r_{23} or r_{38} . Its low intensity shows that it is a function of interaction L elements which are low. This again suggests that the frequency also is very low. This line is, therefore, ignored.

4. Intensity analysis

The areas under the various Raman lines in the spectra published by Asawa *et al* (1968) are determined and a_{xx} , etc. are evaluated and given in table 1. It is not known whether the spectra were taken under identical conditions. Therefore, the constants of proportionality may be different for different spectra. a_{xx} , a_{zz} and a_{yz} are therefore, multiplied by constants K_1 , K_2 and K_3 . The electro-optical constants ($a_{11}-a_{12}$), ($a_{21}-a_{22}$), etc. to be determined are larger (8) than the equations available (7)—four of A_g , 1 E_{1g} and 2 in E_{2g} . Ultimately, the number of unknowns is 11 including the proportionality constants and the equations are 7. There are two equations like $a_{xx}+a_{yy}+a_{zz}=0$ one each for ν_1 and ν_2 . We now try to determine a relation between the K s. The spectra taken are [following Porto's 1966 notation], $x(zz)y$ for A_g , $x(yy)z$ for A_g+E_{2g} , $x(yx)y$ for E_{2g} , and $x(yz)y$ for E_{1g} . Another spectrum $x(yx)z$ contains ν_1 which is prohibited. Hence, it is taken to be defective and is not used. $x(zz)y$ and $x(yz)y$, and $x(yx)y$ are taken under an identical set-up and hence assumed to be taken under identical conditions. This makes $K_2=K_3$. According to the selection rules for E_{2g} , yx and yy spectra should show the same intensity for the common lines. Hence, for any common line ν_4 , if A_1 is the area in yy spectrum and A_2 in yx , $K_1A_1=K_2A_2$. This relationship is checked for ν_5 . These two equations among K s add up to 11 equations, to solve for 11 unknowns. But the equations do not contain any numerical terms free from unknowns. Therefore, one can determine only their ratios.

This analysis assumes that it is possible to evaluate L elements. In our analysis of other crystals e.g. Addepalli and Rao (1970), we avoided determination of force constants from which L elements have to be determined using equations, like $I'I=A'GA$ for each species, I is the column vector of a'_{ij} for all frequencies in any species and A the column vector of coefficients of L elements. I' and A' are transposes of I and A . If the electro-optical elements are so few that one equation for each species is sufficient to determine them this procedure is good. It is possible to avoid determination of F elements, from the secular equation. (It may be recalled that F elements in a secular equation are always larger than the frequencies thus introducing uncertainty in their determination). But, when the electro-optical constants are many we are obliged to use all the equations and this uncertainty cannot be avoided.

L elements can also be determined from $LL'=G$. Here since L is an unsymmetrical matrix and G is symmetrical, there are fewer G elements and larger L elements. Torkington (1949) suggested neglecting upper half diagonal L elements if the L s are arranged in the decreasing order of frequency and if some frequencies are large and others small. In the present case the frequencies are of the same order of magnitude and therefore, the upper and lower half L elements also will be of the same order of magnitude. We have now assumed that the L matrix is symmetrical. Then, we have the G equations necessary to evaluate all the L elements. The L elements are thus

calculated and substituted in the intensity equations. The intensity equations now become.

4.1. A_g

$$\begin{aligned} \alpha'_{yy} = 11.544789 \text{ K} &= 1.0318610 \times 10^{-1} (a_{11} - a_{12}) - 1.7652411 \times 10^{-1} (a_{21} - a_{22}) \\ &+ 9.8320215 \times 10^{-2} (a'_{11} - a'_{12}) + 4.075027 \times 10^{-1} a'_{12} \\ &+ 4.0754448 \times 10^{-2} (a'_{21} - a'_{22}) + 1.7524197 \times 10^{-1} a'_{22}, \\ 0 &= -4.5355917 \times 10^{-2} (a_{11} - a_{12}) + 1.5342966 \times \\ &10^{-2} (a_{21} - a_{22}) + 4.2281506 \times 10^{-2} (a'_{11} - a'_{12}) + 1.7524197 \times \\ &10^{-1} a'_{12} + 9.2717658 \times 10^{-2} (a'_{21} - a'_{22}) + \\ &3.9868102 \times 10^{-1} a'_{22}, \\ \alpha'_{zz} = 0 &= -2.0637221 \times 10^{-1} (a_{11} - a_{12}) + 3.5304822 \times \\ &10^{-1} (a_{21} - a_{22}) + 2.1086226 \times 10^{-1} (a'_{11} - a'_{12}) + 4.075027 \times \\ &10^{-1} a'_{12} + 9.3733073 \times 10^{-2} (a'_{21} - a'_{22}) + 1.7524197 \times \\ &10^{-1} a'_{22}, \\ 5.4489996 \text{ K} &= 9.0711835 \times 10^{-2} (a_{11} - a_{12}) - 3.068593 \times 10^{-1} (a_{21} - a_{22}) \\ &+ 9.0678954 \times 10^{-2} (a'_{11} - a'_{12}) + 1.7524197 \times 10^{-1} a'_{12} \\ &+ 2.132457 \times 10^{-1} (a'_{21} - a'_{22}) + 3.986810 \times 10^{-1} a'_{22}. \end{aligned}$$

4.2. E_{1g}

$$\alpha'_{yz} = 5.401620726 \text{ K} = -6.4024497 \times 10^{-3} (a_{21} - a_{22}) + 1.6471028 \times 10^{-1} (a'_{21} - a'_{22}).$$

4.3. E_{2g}

$$\begin{aligned} \alpha'_{yz} = K \times 7.907509903 &= 4.5628689 \times 10^{-2} (a_{11} - a_{12}) + 5.1096697 \times \\ &10^{-2} (a_{31} - a_{32}) + 1.1422504 \times 10^{-1} (a'_{11} - a'_{12}) \\ &+ 3.6028042 \times 10^{-2} (a'_{31} - a'_{32}), \\ K \times 2.134012 &= 1.0440723 \times 10^{-1} (a_{11} - a_{12}) + 6.7186384 \times \\ &10^{-2} (a_{31} - a_{32}) - 2.458657 \times 10^{-2} (a'_{11} - a'_{12}) \\ &+ 1.3351394 \times 10^{-1} (a'_{31} - a'_{32}). \end{aligned}$$

Two more equations using $a_{xx} + a_{yy} + a_{zz} = 0$ are obtained. Now, the a_{ij} values can have + or - signs. We start with A_g and E_{1g} species. These 7 equations contain 7 unknowns including K . Variations of these signs of E_{1g} and A_g ultimately give only two different sets which are by themselves nearly equal. Here we assume that in general intensities in a given species have the same sign. Substituting them in E_{2g} , the other two constants are also evaluated. However, since E_{2g} intensities also

involve + or - signs, for each set of values for A_g and E_{1g} , we get two sets for E_{2g} .

1st set	2nd set
$\frac{\alpha'_{12}}{\alpha_{11} - \alpha_{12}} = -0.31$	-0.29
$\frac{\alpha'_{11} - \alpha'_{12}}{\alpha_{11} - \alpha_{12}} = 0.91$	0.90
$\frac{\alpha'_{22}}{\alpha_{11} - \alpha_{12}} = 5.9 \times 10^{-11}$	-0.2×10^{-8}
$\frac{\alpha'_{21} - \alpha'_{22}}{\alpha_{11} - \alpha_{12}} = 4.6 \times 10^{-8}$	-0.36×10^{-7}
$\frac{\alpha_{21} - \alpha_{22}}{\alpha_{11} - \alpha_{12}} = 0.40$	0.38
$\frac{K}{\alpha_{11} - \alpha_{12}} = -0.33 \times 10^{-8}$	0.46×10^{-8}
$\frac{\alpha_{31} - \alpha_{32}}{\alpha_{11} - \alpha_{12}} = -3.95$ (with $E_{2g} + \text{ve}$)	-3.7
$\frac{\alpha_{31} - \alpha_{32}}{\alpha_{11} - \alpha_{12}} = -3.81$ (with $E_{2g} - \text{ve}$)	-3.9
$\frac{\alpha'_{31} - \alpha'_{32}}{\alpha_{11} - \alpha_{12}} = 1.37$ (with $E_{2g} + \text{ve}$)	1.26
$\frac{\alpha'_{31} - \alpha'_{32}}{\alpha_{11} - \alpha_{12}} = 1.31$ ($E_{2g} - \text{ve}$)	1.34

Here α'_{21} and α'_{22} (polarisability changes with the bond 2 distance) are very small. This means that the polarisability of bond is equal to the sum of the polarisabilities of the two atoms, while for bonds 1 and 3 the intervening electrons are perhaps playing a part.

Substitution of one of the sets into the intensity equations will be very instructive and they are given below.

yy

$$\begin{aligned}
 -3.8179 \times 10^{-2} &= 1.0318 - 0.7006 + 0.8993 - 1.2706 + 0.01867 \\
 &\quad + 1.0372 \times 10^{-10} \\
 0 &= -0.4536 + 0.6089 + 0.3868 - 0.5464 + 0.004249 + 2.3596 \times 10^{-10}.
 \end{aligned}$$

zz

$$\begin{aligned}
 0 &= -2.0637 + 1.4012 + 1.9288 - 1.2706 + 0.004296 + 1.0372 \times 10^{-10}, \\
 -1.8020 \times 10^{-2} &= 0.9071 - 1.2179 + 0.8294 - 0.5464 + 0.009772 \\
 &\quad + 2.3597 \times 10^{-10}
 \end{aligned}$$

Here, we see that the individual values on the right of these equations are high compared to those on the left. The intensities of ν_1 and ν_2 are in fact only due to

difference between large quantities. The orientational effects of bonds 1 and 2 are producing intensities in the opposite direction. Looking at figure 1, spreading of atoms 2, 3, 4 and 6, 7, 8 increases the angle α and decreases the angle β tensor components of any bond 1 are given by Long's (1953) equations. For instance, for bond 1,

$$\begin{aligned} (a_{xx})_1 &= (a_{11} - a_{12}) \cos^2 \alpha + a_{12}, \\ &= (a_{11} - a_{12}) \cos^2 \alpha + a_{12} \end{aligned}$$

For bond 2 similarly,

$$(a_{xx})_2 = (a_{21} - a_{22}) \cos^2 \beta - a_{22}.$$

Intensity of ν_1 is due to the change in a_{xx} ,

$$\Delta(a_{xx})_1 = -2(a_{11} - a_{12}) \cos \alpha \sin \alpha \Delta \alpha.$$

$$\Delta(a_{xx})_2 = -2(a_{21} - a_{22}) \cos \beta \sin \beta \Delta \beta.$$

Since $\Delta \alpha$ and $\Delta \beta$ are of opposite sign, $\Delta(a_{xx})_1$ and $\Delta(a_{xx})_2$ are also of opposite sign. The necessity for taking the intermolecular bond 2 also in deriving the intensity equations is thus clear.

It would have been possible to determine $(a_{11} - a_{12})$ if we had refractive index of the crystal along the z and x axes, as explained in earlier papers (Kumar *et al* 1974, and Satyavathi *et al* 1977). It has not been possible to get this data.

References

- Addepalli V B, Kumar S P, Padma V A and Rajeswar Rao N 1976 *Indian J. Pure Appl. Phys.* **14** 726
 Addepalli V B and Rajeswar Rao N 1977 *Indian J. Pure Appl. Phys.* **15** 157
 Asawa C K, Satten R A and Stafudd O M 1968 *Phys. Rev.* **168** 957
 Damen T C, Porto S P S and Tell B 1966 *Phys. Rev.* **142** 570
 Kumar S P, Padma V A and Rajeswar Rao N 1972 *Indian J. Pure. Appl. Phys.* **10** 272
 Kumar S P, Padma V A and Rajeswar Rao 1974 *J. Chem. Phys.* **60** 4156
 Kumar S P, Ramakoteswar Rao P, Padma V A and Rajeswar Rao N 1976 *Indian J. Phys.* **50** 343
 Long D A 1953 *Proc. Roy. Soc.* **217** 203
 Murphy J, Caspers H H and Buchanan R A 1964 *J. Chem. Phys.* **40** 743
 Padma V A, Kumar S P and Rajeswar Rao N 1973 *Indian. J. Pure. Appl. Phys.* **11** 818
 Satyavathi N, Kumar S P, Padma V A and Rajeswar Rao N (accepted for publication)
 Torkington P 1949 *J. Chem. Phys.* **17** 357