Raman intensity analysis of LaCl₃

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Abstract. Raman intensity analysis of LaCl₃ on lines adopted earlier for crystals like LiNO₃, KNO₃ or YVO₄ is found to be unsuitable for LaCl₃. The rotation of the LaCl₃ pyramids in the unit cell of this crystal is represented by high frequencies, comparable to the internal oscillations of LaCl₃ molecule. The intensity of $R_{2z}$, 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 LiNO₃, the polarisability of bonds like Li—O is found to be negligible.

Keywords. Intensity analysis; symmetry co-ordinates; LaCl₃.

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

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

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 LiNO₃ (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$_{3i}$. The modes of oscillation are distributed as $2A_o+2B_o+1E_{2g}+3E_{2u}+2A_u+2B_u+3E_{1u}+1E_{2u}$ (Murphy et al 1964).

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

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

**Figure 1.** Unit cell of LaCl$_3$

**Table 1.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Nature of the spectrum</th>
<th>Frequency</th>
<th>Assignment</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_o$</td>
<td>$x(zz)y$</td>
<td>212 cm$^{-1}$</td>
<td>Symmetric stretching</td>
<td>0</td>
</tr>
<tr>
<td>$A_g$</td>
<td>$x(zz)y$</td>
<td>180 cm$^{-1}$</td>
<td>Rotation about C-axis</td>
<td>$K_x \times 4.29$</td>
</tr>
<tr>
<td>$A_o$</td>
<td>$x(yy)z$</td>
<td>212 cm$^{-1}$</td>
<td>Symmetric stretching</td>
<td>$K_x \times 11.55$</td>
</tr>
<tr>
<td>$A_g$</td>
<td>$x(yy)z$</td>
<td>180 cm$^{-1}$</td>
<td>Rotation about C-axis</td>
<td>0</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>$x(yy)z$</td>
<td>219 cm$^{-1}$</td>
<td>Asymmetric stretching</td>
<td>$K_x \times 7.908$</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>$x(yy)z$</td>
<td>108 cm$^{-1}$</td>
<td>Bending</td>
<td>$K_x \times 2.134$</td>
</tr>
<tr>
<td>$E_{1g}$</td>
<td>$x(yz)y$</td>
<td>186 cm$^{-1}$</td>
<td>Rotation about X-axis</td>
<td>$K_x \times 4.251$</td>
</tr>
</tbody>
</table>
The frequencies and their assignments are given in table 1. Here $B_g$ is Raman inactive. $A_g$ consists of $\nu_1$, total symmetric stretching and $\nu_2$, 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 $\nu_1$, is very intense. This shows that our approach is totally inadequate.

Another notable feature of the spectrum is that $\nu_2$ (an external oscillation) is comparable to $\nu_1$. 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). Cl—Cl in the pyramid (like 2-3, 3-4, 4-2 and 6-7, 7-8, 8-6), Cl—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)

$$2V = \sum_K \sum_{m,n} \frac{\delta^2 V}{\delta r_{K_aK_b} \cdot \delta r_{K_cK_d}} \delta r_{om}^{K_aK_b} \delta r_{on}^{K_cK_d}$$

Here $r_{K_aK_b}^{om}$ 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 $r$. 

2. Symmetry co-ordinates

Symmetry coordinates representing oscillations of various species can be obtained as

2.1. \( A_s \)

\[
S_1 = \frac{1}{2\sqrt{3}} (102^0 + 103^0 + 104^0 + 506^0 + 507^0 + 508^0 + 102^6 + 103^8 \\
+ 104^8 + 506^8 + 507^8 + 508^8)
\]

*102^o, etc., are written for \( r_{12}^{oo} \), etc., for brevity.
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2.2. E₁₉

\[ S_{2a} = \frac{1}{2\sqrt{3}} (3^\circ 80 + 4^\circ 70 + 6^\circ 31 + 7^\circ 21 + 4^\circ 60 + 2^\circ 80 + 3^\circ 85 + 4^\circ 75 \\
+ 6^\circ 3 + 7^\circ 21 + 4^\circ 65 + 2^\circ 85) \]

\[ S_{3a} = \frac{1}{\sqrt{24}} \left[ 2 \left( 3^\circ 80 - 3^\circ 85 + 4^\circ 70 - 4^\circ 75 \right) - (6^\circ 31 - 6^\circ 31 + 7^\circ 21 \\
- 7^\circ 21 + 4^\circ 60 - 4^\circ 65 + 2^\circ 80 - 2^\circ 85) \right] \cos \delta + \frac{1}{2\sqrt{2}} \left[ (6^\circ 31 - 6^\circ 31 \\
+ 7^\circ 21 - 7^\circ 21) - (4^\circ 60 - 4^\circ 65 + 2^\circ 80 - 2^\circ 85) \right] \sin \delta \]

\[ S_{ab} = \left[ \frac{1}{2\sqrt{2}} (6^\circ 31 - 6^\circ 31 + 7^\circ 21 - 7^\circ 21) - (4^\circ 60 - 4^\circ 65 + 2^\circ 80 - 2^\circ 85) \right] \times \]

\[ \cos \delta - \frac{1}{\sqrt{24}} \left[ 2 \left( 3^\circ 80 - 3^\circ 85 + 4^\circ 70 - 4^\circ 75 \right) - (6^\circ 31 - 6^\circ 31 \\
+ 7^\circ 21 - 7^\circ 21 + 4^\circ 60 - 4^\circ 65 + 2^\circ 80 - 2^\circ 85) \right] \sin \delta. \]

2.3. E₂

\[ S_{4a} = \frac{1}{2\sqrt{6}} \left[ 2 \left( 1^\circ 20 + 1^\circ 20 + 5^\circ 60 + 5^\circ 65 \right) - (1^\circ 30 + 1^\circ 30 + 1^\circ 40 + 1^\circ 40 \\
+ 5^\circ 70 + 5^\circ 75 + 5^\circ 80 + 5^\circ 85) \right], \]

\[ S_{5a} = \frac{1}{2\sqrt{2}} \left[ (1^\circ 40 + 1^\circ 40 + 5^\circ 70 + 5^\circ 80) - (1^\circ 30 + 1^\circ 30 + 5^\circ 70 + 5^\circ 75) \right]. \]

\[ S_{5a} = \frac{1}{2\sqrt{3}} \left[ 2 \left( 3^\circ 40 + 7^\circ 80 \right) - (2^\circ 30 + 2^\circ 40 + 6^\circ 70 + 6^\circ 80) \right], \]

\[ S_{5b} = \frac{1}{2} \left[ (2^\circ 30 + 6^\circ 70) - (2^\circ 40 + 6^\circ 80) \right], \]

\[ S_{6a} = \frac{1}{2\sqrt{3}} \left[ 2 \left( 4^\circ 50 + 1^\circ 80 \right) - (5^\circ 25 + 5^\circ 31 + 7^\circ 11 + 6^\circ 15) \right], \]

\[ S_{6b} = \frac{1}{2} \left[ (5^\circ 31 + 7^\circ 11) - (5^\circ 25 + 6^\circ 15) \right]. \]
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
For instance, in figure 3, the displacements $1^{o}2^{o}$ and $1^{o}2^{o}$ are shown. Since $2^{o}$ and $2^{o}$ are similar atoms in the unit cells 6 and 0, both the displacements are given to both the atoms. Adding the displacement of $2^{o}$ to $2^{o}$ (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 $1^{o}2^{o}+1^{o}2^{o}$, $1^{o}3^{o}+1^{o}3^{o}$ and $1^{o}4^{o}+1^{o}4^{o}$, 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. $A_{g}$

$$
\alpha'_{xx} = \alpha'_{yy} = \left[ \frac{\sqrt{3}}{r_{1}} \sin^{2} 2a \right] (a_{11} - a_{12}) \mu_{Cl} - \frac{8 \sqrt{3}}{r_{3}} \sin \beta \sin \alpha \cos \delta \cos^{3} \beta
$$
\[ \times (a_{21} - a_{22}) \mu_{Cl} \] \[ \times (a_{21} - a_{22}) \mu_{Cl} \] \[ \times (a_{31} - a_{32}) \mu_{Cl} \]

\[ + \left[ \sqrt{3} \sin^2 a \left( a'_{11} - a'_{12} \right) + 2\sqrt{3} \ a'_{12} \right] L_{11} \]

\[ + \left[ \sqrt{3} \sin^2 a \left( a'_{21} - a'_{22} \right) + 2\sqrt{3} \ a'_{22} \right] L_{21}, \]

\[ a'_{zz} = \left[ \frac{-2\sqrt{3}}{r_1} \sin^2 a \left( a_{11} - a_{12} \right) \mu_{Cl} + \frac{16\sqrt{3}}{r_2} \sin \beta \sin a \cos \delta \cos^2 \beta \right. \]

\[ \left. \times (a_{21} - a_{22}) \mu_{Cl} \right] \]

\[ L_{i1}^{-1} \]

\[ + \left[ \sqrt{3} \cos^2 a \left( a'_{11} - a'_{12} \right) + 2\sqrt{3} \ a'_{12} \right] L_{11} \]

\[ + \left[ \sqrt{3} \cos^2 a \left( a'_{21} - a'_{22} \right) + 2\sqrt{3} \ a'_{22} \right] L_{21}. \ i = 1, 2 \]

3.2. \( E_{3g} \)

\[ a'_{y_2} = -\frac{\sqrt{3}}{\sqrt{2}} \cdot \frac{\sin 4\beta}{r_2} (a_{21} - a_{22}) \mu_{Cl} L_{11}^{-1} + \frac{\sqrt{3}}{\sqrt{2}} \cdot \sin 2\beta \left( a'_{31} - a'_{32} \right) L_{11} \]

3.3. \( E_{2g} \)

\[ a'_{x_2} = \left[ \frac{\sqrt{6}}{r_1} \sin^2 a \left( 3 \sin^2 a \mu_{La} - 2 \cos^2 a \mu_{Cl} \right) \left( a_{11} - a_{12} \right) \right. \]

\[ - \frac{3}{\sqrt{2}r_3} \sin a \mu_{Cl} \left( a_{31} - a_{32} \right) \right] L_{11}^{-1} + \left[ \frac{3\sqrt{3}}{2r_3} \left( a_{31} - a_{32} \right) \mu_{Cl} \right. \]

\[ + \frac{3}{r_1} \sin a \left( 2 - \sin^2 a \right) \left( a_{11} - a_{12} \right) \mu_{Cl} \right] L_{13}^{-1} \]

\[ \left. i = 1, 2 \right] \]

\[ - \frac{\sqrt{3}}{\sqrt{2}} \sin^2 a \left( a'_{11} - a'_{12} \right) L_{11} + \frac{\sqrt{3}}{2} \left( a'_{21} - a'_{22} \right) L_{21}. \]

Here, \( r_1 = r_{12}, r_2 = r_{23}, r_3 = r_{33}. \ \ a_{11} \) 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 \( r_3 \). \( a, \beta, \) and \( \delta \) are angles shown in figure 2.

It is interesting to see that the coefficients of \( L^{-1} \) elements in \( A_g \) follow the rule \( a_{xx} + a_{xy} + a_{xz} = 0 \) as expected.

As already stated, an interesting feature of the spectrum of \( \text{LaCl}_3 \) is the large intensity of the line \( v_2 \) compared to \( v_1 \) in \( a_{zz} \) spectrum. This cannot be understood if we do not introduce \( a_{31} \) and \( a_{32} \). Without this, \( v_1 \) would be always stronger than \( v_2 \). Introduction of these additional parameters helps in accounting for intense \( v_2 \) in \( zz \).

It may be mentioned at this stage that though we expect 3 lines in \( E_{2g} \), the spectrum
Raman intensity analysis of LaCl₃ shows only 2 (ν₄ and ν₅). The other line (ν₆) 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 r₁₂, r₂₃ or r₃₈. 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 aₓₓ, 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. aₓₓ, aᵧᵧ and aᵧz are therefore, multiplied by constants K₁, K₂ and K₃. The electro-optical constants (aₓ₁—aₓ₂), (aᵧ₁—aᵧ₂), etc. to be determined are larger (8) than the equations available (7)—four of Aₓ₁, Eₓ₂ and 2 in Eᵧ₂. Ultimately, the number of unknowns is 11 including the proportionality constants and the equations are 7. There are two equations like aₓₓ+aᵧᵧ+aᵧz=0 one each for ν₁ and ν₂. We now try to determine a relation between the Ks. The spectra taken are [following Porto's 1966 notation], x(zz)y for Aₓ₁, x(yy)z for Aᵧ₂, x(yy)y for Eₓ₂, and x(yy)y for Eᵧ₂. Another spectrum x(yy)z contains ν₁ which is prohibited. Hence, it is taken to be defective and is not used. x(zz)y and x(yy)y, and x(yy)y are taken under an identical set-up and hence assumed to be taken under identical conditions. This makes K₂=K₃. According to the selection rules for E₂g, yy spectra should show the same intensity for the common lines. Hence, for any common line ν₄, if Aᵧ₁ is the area in yy spectrum and Aₓ₁ in yy, K₁Aₓ₁=Kᵧ₁Aᵧ₁. This relationship is checked for ν₆. These two equations among Ks 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 aₓₓ 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. Torkinson (1949) suggested neglecting upper half diagonal L elements if the Ls 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. \(A_g\)

\[
\alpha'_{yy} = 11.544789 \, K = 1.0318610 \times 10^{-1} (a_{11} - a_{12}) - 1.7652411 \times 10^{-1} (a_{31} - a_{32}) + 9.8320215 \times 10^{-2} (a'_{11} - a'_{12}) + 4.075027 \times 10^{-1} a'_{13} + 4.0754448 \times 10^{-2} (a'_{21} - a'_{22}) + 1.7524197 \times 10^{-1} a'_{23},
\]

\[
0 = -4.5355917 \times 10^{-2} (a_{11} - a_{12}) + 1.5342966 \times 10^{-2} (a_{21} - a_{22}) + 4.2281506 \times 10^{-2} (a'_{11} - a'_{12}) + 1.7524197 \times 10^{-1} a'_{13} + 9.2717658 \times 10^{-2} (a'_{21} - a'_{22}) + 3.9868102 \times 10^{-3} a'_{23}.
\]

\[
\alpha'_{zz} = 0 = -2.0637221 \times 10^{-1} (a_{11} - a_{12}) + 3.5304822 \times 10^{-1} (a_{21} - a_{22}) + 2.1086226 \times 10^{-1} (a'_{11} - a'_{12}) + 4.075027 \times 10^{-1} a'_{13} + 9.3733073 \times 10^{-2} (a'_{21} + a'_{22}) + 1.7524197 \times 10^{-1} a'_{23}.
\]

\[
5.4489996 \, K = 9.0711835 \times 10^{-2} (a_{11} - a_{12}) - 3.068593 \times 10^{-2} (a_{31} - a_{32}) + 9.0678954 \times 10^{-2} (a'_{11} - a'_{12}) + 1.7524197 \times 10^{-1} a'_{13} + 2.132457 \times 10^{-1} (a'_{21} - a_{22}) + 3.986810 \times 10^{-1} a'_{23}.
\]

4.2. \(E_{1g}\)

\[
\alpha'_{yy} = 5.401620726 \, K = -6.4024497 \times 10^{-2} (a_{31} - a_{32}) + 1.6471028 \times 10^{-1} (a'_{31} - a_{32}).
\]

4.3. \(E_{2g}\)

\[
\alpha'_{yy} = K \times 7.907509903 = 4.5628689 \times 10^{-2} (a_{11} - a_{12}) + 5.1096697 \times 10^{-2} (a_{31} - a_{32}) + 1.1422504 \times 10^{-1} (a'_{11} - a'_{13}) + 3.6028042 \times 10^{-2} (a'_{31} - a'_{32}).
\]

\[
K \times 2.134012 = 1.0440723 \times 10^{-1} (a_{11} - a_{12}) + 6.7186384 \times 10^{-2} (a_{31} - a_{32}) + 2.458657 \times 10^{-2} (a'_{11} - a'_{13}) + 1.3351394 \times 10^{-1} (a'_{31} - a'_{32}).
\]

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
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Involves + or — signs, for each set of values for $A_9$ and $E_{19}$, we get two sets for $E_{2g}$.

<table>
<thead>
<tr>
<th>1st set</th>
<th>2nd set</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a''<em>{12}/a</em>{11}-a_{12}$</td>
<td>$-0.31$</td>
</tr>
<tr>
<td>$a''<em>{14}/a</em>{11}-a_{12}$</td>
<td>$0.91$</td>
</tr>
<tr>
<td>$a''<em>{11}/a</em>{11}-a_{12}$</td>
<td>$5.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>$a''<em>{11}/a</em>{11}-a_{12}$</td>
<td>$4.6 \times 10^{-3}$</td>
</tr>
<tr>
<td>$K_{a_{11}-a_{12}}$</td>
<td>$0.40$</td>
</tr>
</tbody>
</table>

Here $a''_{11}$ and $a''_{12}$ (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.

\[
\gamma
\]

\[
y = -3.8179 \times 10^{-5} = 1.0318 - 0.7006 + 0.8993 - 1.2706 + 0.0186 + 1.0372 \times 10^{-10}
\]

\[
0 = -0.4536 + 0.6089 + 0.3868 - 0.5464 + 0.004249 + 2.3596 \times 10^{-10}
\]

\[
\zeta
\]

\[
0 = -2.0637 + 1.4012 + 1.9288 - 1.2706 + 0.004296 + 1.0372 \times 10^{-10},
\]

\[
-1.8020 \times 10^{-8} = 0.9071 - 1.2179 + 0.8294 - 0.5464 + 0.009772 + 2.3597 \times 10^{-10}
\]

Here, we see that the individual values on the right of these equations are high compared to those on the left. The intensities of $\nu_1$ and $\nu_2$ 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 $\alpha$ and decreases the angle $\beta$ tensor components of any bond 1 are given by Long's (1953) equations. For instance, for bond 1,

\[
(a_{xx})_1 = (a_{11} - a_{12}) 1x^2 + a_{12},
\]

\[
= (a_{11} - a_{12}) \cos^2 \alpha + a_{12}
\]

For bond 2 similarly,

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

Intensity of $\nu_1$ 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


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