COMPARISON OF THE INFRA-RED ACTIVITIES OF THE FOUR RAMAN-INACTIVE VIBRATIONS IN α-QUARTZ

By BISHAMBHAR DAYAL SAKSENA AND SHANTI SWARUP BHATNAGAR

(*Department of Physics, University of Allahabad, Allahabad, India*)

1. INTRODUCTION

THE modes of vibration of α-quartz have been analysed by one of us (Saksena, 1940). The unit cell of α-quartz contains six silicon and six oxygen atoms, each silicon atom being shared between two cells. This corresponds to the molecular formula $3 SiO_2$. There are 27 modes of vibration of this group of which three are translational and the remaining 24 are internal modes. As α-quartz belongs to the point-group D_3, these modes are divided into three classes A, B and E, of which A is totally symmetric, B anti-symmetric and E doubly degenerate. The 24 modes are divided as follows—namely 4 in class A, 4 in class B, and 8 in class E. Class A is active in Raman effect only, class B in infra-red only and class E in both. For class B, the change of electric moment occurs only along the optic axis of the crystal which is taken as the z-axis, the other two, namely the electrical and mechanical axes, being called the x-axis and y-axis respectively. From the reflection experiments of Rubens, Reinkobar and others, reference to whose work may be found in the paper mentioned above, Saksena took the frequencies falling in class B as 1149 ($8 \cdot 7 \mu$), 777 ($12 \cdot 87 \mu$), 508 ($19 \cdot 7 \mu$), 364 ($27 \cdot 5 \mu$). The percentage of reflection is 90 for $19 \cdot 7 \mu$, 88 for $8 \cdot 7 \mu$, 67 for $27 \cdot 5 \mu$ and 40 for $12 \cdot 87 \mu$. If the percentage of reflection be supposed to represent the intensities of these vibrations it would appear that $19 \cdot 7 \mu$ and $8 \cdot 7 \mu$ are the strongest and very nearly of the same intensity, next in order is $27 \cdot 5 \mu$ and the weakest is $12 \cdot 87 \mu$. There is no data for the intensities of these frequencies in absorption but as the maxima in reflection generally agree with those in absorption, the above will also represent the intensities in absorption.

The intensity of a fundamental v_i in absorption is proportional to $v_i \left(\dfrac{dM}{d\xi} \right)^2$ (Herzberg, 1943) where $\dfrac{dM}{d\xi}$ represents the change in dipole moment with the normal mode of vibration ξ. To a first approximation the changes of dipole moment produced by the displacement of atoms of a molecule in a given normal mode may be associated with the stretching

and bending of individual bonds and the effect may be summed up for all the bonds in the molecule. Wolkenstein (1945) has shown that the principle of additive bond contribution is in accord with the qualitative data of absorption intensities in a number of simple cases. In the case of bending vibrations there is no change in the bond moment as the bond distances remain practically unaltered. The change of dipole moment during the vibration can be calculated directly from the bond moments and displacement of atoms. Bell (1948) has in this way found the moment of C–H bond from the intensities of the C–H bending vibrations. In the case of stretching vibrations there is no agreed theoretical basis for calculating the changes of dipole moment. Rollefson and Havens (1940) consider it highly probable that the charge on an atom is not constant during a vibration.

In calculating the piezo-electric constants of α-quartz (Saksena, 1948), it was supposed that during an elastic deformation the electric moment arises from a change of bond distances and bond angles on strain. It should be justifiable to make a similar assumption in calculating the electric moment during the infra-red vibration, for both the processes, namely the elastic deformation and infra-red vibration, take place sufficiently slowly for the electron cloud to adjust itself to changed conditions. Saksena (1944) has calculated the elastic constants and the infra-red frequencies of α-quartz by using the same force constants. The observations made in the preceding paragraph lend additional support to this view because the Si–O bonds in quartz are largely covalent in nature. In this paper we have compared the intensities of the four infra-red active modes of class B of α-quartz. We have no data on the absolute intensities of the four vibrations, namely $8 \cdot 7 \mu$, $12 \cdot 87 \mu$, $19 \cdot 7 \mu$ and $27 \cdot 5 \mu$, but qualitatively the observed and the calculated intensities are in good agreement.

2. METHOD

There are six silicon and six oxygen atoms in the unit cell of α-quartz. Each silicon atom is linked to four oxygens and each oxygen has two silicon atoms as near neighbours. Thus at each silicon atom there are four Si–O bonds but as each silicon is linked to two cells there are twelve Si–O bonds in each unit cell. There are also just 12 positive and 12 negative charges, as each silicon carries a charge of $+ 4$ units and each oxygen a charge of $- 2$ units. Each Si–O bond may therefore represent a sharing of charge $k.e$ units where k is in the neighbourhood of unity. If all the bonds be treated as equivalent, each will have the same value k, otherwise, due to symmetry, six of them will have a value k_1, and the other six a value k_2. We may now calculate the moment produced by the stretching and bending of a bond.

A change of length Δr along the bond direction would give a moment $ke.\,\Delta r$ in that direction. The electric moment is directed from the silicon to the oxygen atom so that a negative value of Δr gives a moment opposite in direction. If a Si–O bond of length r is displaced from its original position by an angle $\Delta\theta$ such that the oxygen has moved a distance $r.\,\Delta\theta$, the moment produced at right angles to the bond direction is $ker.\,\Delta\theta$. This is the moment due to bending of the bond and it may be put as $ke\,(\delta_0 - \delta_{si})$, where δ_0 and δ_{si} represent the displacements of oxygen and silicon atoms. The direction of this moment, which is normal to the Si–O bond, is such that there is a transport of negative charge due to the motion of the oxygen atom away from the silicon atom. The electric moment therefore appears in the direction leading from oxygen to silicon atom normal to the bond. If x_1, y_1, z_1 are the co-ordinates of the silicon atom and x_2, y_2, z_2 of the oxygen atom and if $x_1 + \Delta x_1$, $y_1 + \Delta y_1$, $z_1 + \Delta z_1$, and $x_2 + \Delta x_2$, $y_2 + \Delta y_2$, $z_2 + \Delta z_2$, represent their displaced positions then since

$$\delta_{si} = \sqrt{\Delta x_1{}^2 + \Delta y_1{}^2 + \Delta z_1{}^2}$$

and

$$\delta_0 = \sqrt{\Delta x_2{}^2 + \Delta y_2{}^2 + \Delta z_2{}^2}$$

the resolved parts of the bending moments along the axis of the crystal are $ke\,(\Delta x_2 - \Delta x_1)$, $ke\,(\Delta y_2 - \Delta y_1)$, and $ke\,(\Delta z_2 - \Delta z_1)$ in a direction pointing from oxygen to silicon atom. Bell has used an equivalent expression

$$\mu_e = \mu_{CH}\,\Sigma\,(x_H - x_C),$$

where μ_e is the effective moment for infra-red absorption, μ_{CH} the moment of the C–H bond and x is the displacement of the given atom.

For finding the resultant moment we have to sum up the resolved parts of the stretching and the bending moments due to all the bonds in the unit cell. It is shown in a later section that the resolved parts of both the stretching and bending moments along the x and y directions of the crystal are zero. The net moment arises only along the optic axis.

3. Normal Modes of Vibration

In order to find the displacements of atoms we shall first obtain the normal modes of vibrations. The displacements of atoms in any given mode ν may be found out by equating the maximum value of the potential energy of the unit cell for the given mode equal to $h\nu$.

The frequencies of the four modes falling in class B have been calculated by Saksena in an earlier paper (Saksena, 1945). It was shown that if α, β, γ, δ are the displacements in the four symmetry modes

$$A \rightarrow m_0^{\frac{1}{2}}(z_1 + z_2 + z_3 + z_4 + z_5 + z_6) - m_{si}^{\frac{1}{2}}(z_7 + z_8 + z_9 + z_{10} + z_{11} + z_{12})$$

$$B \rightarrow y_2 + y_4 + y_6 - y_1 - y_3 - y_5$$

$$C \rightarrow y_8 + y_{10} + y_{12} + y_7 + y_9 + y_{11}$$

$$D \rightarrow x_7 + x_9 + x_{11} - x_8 - x_{10} - x_{12}$$

where the numbers 1 to 6 represent silicon atoms and 7 to 12 oxygen atoms and x, y, z have their usual significance, the potential energy is given by

$$2V = 6 (a\delta^2 + b\gamma^2 + c\beta^2 + d\alpha^2 + 2e\delta\gamma + 2f\delta\beta + 2g\delta\alpha + 2h\gamma\beta + 2i\gamma\alpha + 2j\alpha\beta)$$

and the kinetic energy by

$$2T = 6 (16\dot{\delta}^2 + 16\dot{\gamma}^2 + 14 \cdot 15\dot{\beta}^2 + 36 \cdot 3\dot{\alpha}^2)$$

and we have then

$$\left.
\begin{aligned}
(a - 16\lambda^2)\delta + e\gamma + f\beta + g\alpha &= 0 \\
e\delta + (b - 16\lambda^2)\gamma + h\beta + i\alpha &= 0 \\
f\delta + h\gamma + (c - 14 \cdot 15\lambda^2)\beta + j\alpha &= 0 \\
g\delta + i\gamma + j\beta + (d - 36 \cdot 3\lambda^2)\alpha &= 0.
\end{aligned}
\right\} \quad (1)$$

The frequencies are given by the determinant

$$\begin{vmatrix}
(a - 16\lambda^2) & c & f & g \\
e & (b - 16\lambda^2) & h & i \\
f & h & (c - 14 \cdot 15\lambda^2) & j \\
g & i & j & (d - 36 \cdot 3\lambda^2)
\end{vmatrix} = 0 \quad (2)$$

If Δ_1, Δ_2, Δ_3, Δ_4 are the minors of this determinant the last three equations of (1) give

$$\frac{\delta}{\Delta_1} = \frac{-\gamma}{\Delta_2} = \frac{\beta}{\Delta_3} = \frac{-\alpha}{\Delta_4}. \quad (3)$$

Using $k = 5 \cdot 01 \times 10^5$ dynes, $k_1 = 1 \cdot 056 \times 10^{-11}$ dynes,

$k_2 = 1 \cdot 315 \times 10^{-11}$ dynes, $k_3 = - \cdot 8992 \times 10^5$ dynes,

we get

$$\Delta_1 = - 8218 \cdot 32 \, \lambda^6 + 10343 \cdot 5206 \, \lambda^4 - 3534 \cdot 523 \, \lambda^2 + 300 \cdot 5203$$

$$\Delta_2 = 330 \cdot 4278 \, \lambda^4 - 17 \cdot 8368 \, \lambda^2 - 43 \cdot 8367$$

$$\Delta_3 = - 660 \cdot 1373 \, \lambda^4 + 482 \cdot 5524 \, \lambda^2 - 60 \cdot 8692$$

$$\Delta_4 = - 843 \cdot 3173 \, \lambda^4 + 452 \cdot 0957 \, \lambda^2 - 54 \cdot 8316$$

The frequencies calculated with the above force constants are 1160, 809, 489, 149.

The values of Δ_1, Δ_2, Δ_3, Δ_4 for various frequencies are given by:

TABLE I

Frequency	λ^2	Δ_1	Δ_2	Δ_3	Δ_4
1160	·7889	−85·4664	147·6901	−90·9871	−222·9697
809	·3833	2·3943	− 2·1607	27·1189	− 5·4266
489	·1403	−11·8003	−40·0419	− 6·8744	− 8·5191
149	·01096	263·0134	−44·0195	−55·6597	− 49·9779

The four normal modes are given by

$$\left(\frac{36\cdot3}{16}\right)^{\frac{1}{2}} \alpha_i A + \left(\frac{14\cdot15}{16}\right)^{\frac{1}{2}} \beta_i B + \gamma_i C + \delta_i D \qquad [i = 1, 2, 3, 4]$$

As the modes are orthogonal, they satisfy the relations of the type

$$\frac{36\cdot3}{16} \alpha_1\alpha_2 + \frac{14\cdot15}{16} \beta_1\beta_2 + \gamma_1\gamma_2 + \delta_1\delta_2 = 0.$$

Using (3) the normal mode may also be written as

$$- (36\cdot3)^{\frac{1}{2}} \frac{\Delta_4}{\Delta_1} A + (14\cdot15)^{\frac{1}{2}} \frac{\Delta_3}{\Delta_1} B - (16)^{\frac{1}{2}} \frac{\Delta_2 C}{\Delta_1} + (16)^{\frac{1}{2}} D$$

4. DISPLACEMENTS OF ATOMS

It may be seen that each normal mode is a linear combination of the four symmetry modes with different amplitudes and different masses. As may be seen from the expressions of kinetic energy, $6 \times 36\cdot3$, $6 \times 14\cdot15$, 6×16, 6×16, are the effective oscillating masses in the four modes. The remaining term gives the amplitude. Thus if δ be the amplitude in the symmetry mode D, $-\frac{\Delta_2}{\Delta_1} \delta$ is the amplitude in the mode C, $\frac{\Delta_3}{\Delta_1} \delta$ is the amplitude in the mode B and $-\frac{\Delta_4}{\Delta_1} \delta$ in the mode A. To calculate the value of δ for each frequency we take the maximum value of the potential energy as $h\nu$ and with the help of (3) calculate δ. The results in units of $(10)^{-10}$ cm. are shown in Table II.

TABLE II

Frequency	α	β	γ	δ	$\Delta r_{1,7}$	$\Delta r_{2,7}$
1160	−1·422	·5805	·9426	·5455	−2·533	2·6804
809	·5948	2·972	·2368	·2623	−2·024	−1·867
489	− ·7391	·5965	−3·474	1·024	1·992	− ·676
149	1·332	−1·484	1·174	7·013	·4268	1·846

The displacement of atoms for various frequencies may be calculated from the four symmetry modes. The displacement along the co-ordinate axes are given in Table III.

TABLE III

Atom	x	y	z
1 – Si	0	β	$\dfrac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
7 – O	$-\dfrac{1.4386}{1.882}\delta + \dfrac{1.214}{1.882}\gamma$	$-\dfrac{1.214}{1.882}\delta - \dfrac{1.4386}{1.882}\gamma$	$-\dfrac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
2 – Si	$\dfrac{\sqrt{3}}{2}\beta$	$-\dfrac{\beta}{2}$	$\dfrac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
8 – O	$\dfrac{.3322}{1.882}\delta + \dfrac{1.853}{1.882}\gamma$	$\dfrac{1.853}{1.882}\delta - \dfrac{.3322}{1.882}\gamma$	$-\dfrac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
3 – Si	$-\dfrac{\sqrt{3}}{2}\beta$	$-\dfrac{\beta}{2}$	$\dfrac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
9 – O	$\dfrac{1.7708}{1.882}\delta + \dfrac{.6389}{1.882}\gamma$	$-\dfrac{.6389}{1.882}\delta + \dfrac{1.7708}{1.882}\gamma$	$-\dfrac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
4 – Si	0	β	$\dfrac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
10 – O	$-\dfrac{1.7708}{1.882}\delta - \dfrac{.6389}{1.882}\gamma$	$-\dfrac{.6389}{1.882}\delta + \dfrac{1.7708}{1.882}\gamma$	$-\dfrac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
5 – Si	$\dfrac{\sqrt{3}}{2}\beta$	$-\dfrac{\beta}{2}$	$\dfrac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
11 – O	$-\dfrac{.3322}{1.882}\delta - \dfrac{1.853}{1.882}\gamma$	$\dfrac{1.853}{1.882}\delta - \dfrac{.3322}{1.882}\gamma$	$-\dfrac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$
6 – Si	$-\dfrac{\sqrt{3}}{2}\beta$	$-\dfrac{\beta}{2}$	$\dfrac{m_O^{\frac{1}{2}}}{m_{Si}^{\frac{1}{2}}}\alpha$
12 – O	$\dfrac{1.4386}{1.882}\delta - \dfrac{1.214}{1.882}\gamma$	$-\dfrac{1.214}{1.882}\delta - \dfrac{1.4386}{1.882}\gamma$	$-\dfrac{m_{Si}^{\frac{1}{2}}}{m_O^{\frac{1}{2}}}\alpha$

The values of α, β, γ, δ are given in Table II.

It may be seen from this table that the sum of the moments due to all the bonds along the x and y direction are zero, *i.e.*,

$$\Sigma_{12}\, ke\, (\delta x_0 - \delta x_{Si}) = 0$$

$$\Sigma_{12}\, ke\, (\delta y_0 - \delta y_{Si}) = 0,$$

where δx and δy are the displacements along the x and y axes of the silicon and oxygen atoms. The moment is only along the z-axis and is directed from oxygen to silicon, *i.e.*, along the positive direction of the optic axis, for according to symmetry mode A the silicon is moving up and the oxygen is moving down along the optic axis. This moment is equal to

$$\alpha \cdot \frac{m_0 + m_{Si}}{m_0^{\frac{1}{2}}\, m_{Si}^{\frac{1}{2}}} = 2\cdot082\alpha \quad \text{per bond.}$$

The total moment is therefore $12\, ke \times 2\cdot082\, \alpha$ and is directed along the positive direction of the optic axis, if α is positive. Thus for various frequencies the moments along the positive direction of the optic axis due to bending moment of all the bonds in the unit cell are given by:

Frequency	1160	489	809	149
Moment	$-5\cdot92$	$-3\cdot077$	$2\cdot477$	$5\cdot546 \times (6ke \times 10^{-10})$

The change in the bond length can be calculated from the relations,

$$1\cdot588\, \Delta r_{1,7} = -\cdot1672\delta - 1\cdot447\gamma - 1\cdot214\beta + 1\cdot311\alpha$$

$$1\cdot588\, \Delta r_{2,7} = \cdot5963\delta + \cdot8935\gamma - \cdot6348\beta - 2\cdot431\alpha$$

where $\Delta r_{1,7} = \Delta r_{3,9} = \Delta r_{5,11} = -\Delta r_{1,12} = -\Delta r_{5,10} = -\Delta r_{3,8}$

$\Delta r_{2,7} = \Delta r_{4,9} = \Delta r_{6,11} = -\Delta r_{2,8} = -\Delta r_{4,10} = -\Delta r_{6,12}.$

The values of $\Delta r_{1,7}$ and $\Delta r_{2,7}$ have already been calculated in Table II.

As the moments along the bonds are directed from silicon to oxygen the direction cosines of the bonds are given in Table IV. The resolved parts along the axes of the stretching bond moments are then $ke.\Delta r.1$, $ke.\Delta r.m$. $ke.\Delta r.n$.

TABLE IV

d.c.	$r_{2,8}$	$r_{2,7}$	$r_{1,7}$	$r_{1,12}$	$r_{6,12}$	$r_{5,11}$	$r_{5,10}$	$r_{4,10}$	$r_{4,9}$	$r_{3,9}$	$r_{3,8}$	$r_{6,11}$
l ..	$-\cdot9858$	$+\cdot1206$	$-\cdot8054$	$-\cdot8054$	$+\cdot1206$	$+1\cdot454$	$-\cdot6488$	$+\cdot8642$	$+\cdot8642$	$-\cdot6488$	$+1\cdot454$	$-\cdot9858$
m ..	$-\cdot4290$	$-1\cdot068$	$+1\cdot214$	$-1\cdot214$	$+1\cdot068$	$+\cdot091$	$+1\cdot305$	$-\cdot6389$	$+\cdot6389$	$-1\cdot305$	$-\cdot091$	$+\cdot4290$
n ..	$-1\cdot168$	$+1\cdot168$	$-\cdot63$	$+\cdot63$	$-1\cdot168$	$-\cdot63$	$+\cdot63$	$-1\cdot168$	$+1\cdot168$	$-\cdot63$	$+\cdot63$	$+1\cdot168$

Summing up for all the bonds in the unit cell we see that the resolved parts of the moments along the x and y axes are zero, *i.e.*,

$$\sum_{}^{12} ke \cdot \Delta r \cdot 1 = 0$$

$$\sum_{}^{12} ke \cdot \Delta r \cdot m = 0.$$

Along the z-axis the moments are:

Frequency	1160	809	489	149
Moment	2·977	−·57	−1·286	$1 \cdot 19 \times (6ke \times 10^{-10})$

This may be visualised in another way also. The negative value of $\Delta r_{1,7}$ for 1160 gives a moment in the direction 7 to 1, *i.e.*, from oxygen to silicon and as the silicon atom is above the oxygen atom its resolved part along the optic axis is along the positive direction. Similarly the positive value of $\Delta r_{2,7}$ gives a moment from silicon to oxygen, and since silicon atom 2 is below the oxygen the resolved part of this moment is also along the positive direction of the optic axis. The two moments are in the same direction and can therefore be added up.

Summing up the moments due to stretching and bending of bonds we get the total moment and the intensities of the absorption bands along the optic axis. The results for the various frequencies are as follows:

Frequency	1160	809	489	149
$\dfrac{dM}{d\xi} =$	−2·943	1·907	−4·363	$6 \cdot 736 \times (6ke \times 10^{-10})$
$I = \nu \left(\dfrac{dM}{d\xi}\right)^2 \propto$	10	2·9	9·3	6·8

We thus see that the weakest line is 809 and that 1160 and 489 are almost of the same intensity. The results are in agreement with the observed intensities of these frequencies.

6. SUMMARY

The electric moments developed during an infra-red vibration have been calculated by supposing that the moments produced may be divided into two parts, one due to bending of bonds and the other due to the stretching of bonds. By taking the stretching moment as $ke \cdot \Delta r$ acting from silicon to oxygen atom where Δr gives the change in bond length, the moments due to all the bonds can be resolved along the axis. It is found that the resolved parts are zero along the x and y directions. The bending moment is given by $ke(\delta_0 - \delta_{Si})$, where δ_{Si} and δ_0 are the displacements of silicon and oxygen

atoms and acts along the direction leading from oxygen to silicon atom normal to the bond. It is again seen by resolving moments along the axes and adding the results for various bonds that the net moment arises only along the optic axis. The two moments then can be added up. It is then seen that the frequencies 1160 and 489 have almost the same intensity and 809 is the weakest.

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