POLARIZED RAMAN SPECTRA OF α QUARTZ

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Keywords: Raman spectroscopy, quartz, polarizer, analyzer, raman effect etc.

ABSTRACT. The purpose of this experiment was to observe the Raman shift to assign the symmetry character of the obtained vibrational modes of α -quartz (which has 9 atom per unit cell) using the selection rules for Raman Effect. We observed the Raman spectra varying the polarization of the incoming beam and the orientation of the crystal. And we used monochromatic radiation of argon laser of wavelength 540 nm for our Raman spectroscopy. We observed the intensity of light rotating the polarizer to vertical position from its horizontal position with respect to the plane of the optical table where the laser is placed and measured the Raman spectra over an energy from 50 to 1250 cm^{-1} using the laser power of 1W and an acquisition time of 10 sec. averaging over 2 acquisitions. From our experiment we can see that here is 4symmetry for A_1 which is predicted on our vibrational modes. However for E symmetry mode we have observed 14 vibrational modes but as E is doubly degenerate there should be 16 vibrational modes on the Raman active modes in the α quartz, as we can see that there are two vibration missing, it happens may be due to noise on the surroundings. We got different peaks due to the different intensities and the different orientation of the laser beam hitting the sample on different angle. The different intensities of the peaks for the different orientation might be due to the laser beam hitting the samples at different angles due to differences in the orientation of the surfaces. We also found that the biggest amount of the re-radiated light was vibrating horizontally, i.e. in the same direction as the laser beam hitting the sample.

1. INTRODUCTION:

Raman spectroscopy is an analytical technique used to study vibrational, rotational and other low frequency modes in a sample. It relies on inelastic scattering (Raman scattering) of monochromatic light, usually from a laser in the visible near infrared or near ultraviolet range. The laser interacts with molecular vibrations, phonons or other excitations system resulting in the energy of the laser phonons being shifted up or down the shift energy provides information about the photon modes in the system. The physical properties of α -quartz are found to depend on the impurities. It's an optically active crystal, in which the plane of vibration of the incident light has a continuous rotation as the incident light propagates along the optical axis.¹ It is used in identification of phases, molecular and crystalline symmetries, and characteristic region for different group as in IR etc.²

2. OBJECTIVE OF THIS LAB WORK:

The objective of our lab work is to determine the symmetry character of Raman modes on α quartz. To observe the symmetry character of the sample we have a chart of symmetry and Raman tensor of vibrations in α quartz. It is useful to compare the spectra according to the symmetry character due to vibrational modes.

Table 1: Symmetry and Raman tensor in vibration of α quartz.

symmetry	Number of vibrational modes	Activity	Raman tensor elements					
			R_{xx}	R_{yy}	R_{zz}	R_{xy}	R_{xz}	R_{yz}
A_1	4	R	a	a	b	0	0	0
A_2	4	IR	0	0	0	0	0	0
E_1	8	R+R	c	-c	0	-c	-d	d

The table shows that in α quartz the possible symmetry is on point group D_3 . The point group D_3 has three types of irreducible representations (symmetry) which is referred to as A_1 , A_2 and E (E is doubly degenerate). A group theory analysis of the vibrational modes of α -quartz shows that the 27 modes are divided into 3 acoustic vibrations of symmetry A_2+E and 24 optical vibrations of $4A_1+4A_2+8E$ symmetry. We recall that Raman spectroscopy probes the optical vibrations, the acoustic vibrations being too low in frequency to be observed with usual Raman spectrometers. Only A_1 and E -type vibrations are Raman active while A_2 and E vibrations are infrared active.

3. EXPERIMENTAL PROCEDURE:

In this experiment we used the argon light as a monochromatic radiation of wavelength 540nm. Our experimental procedure was conducted on three ways, we used to ensure the polarization of incoming beam, crystal orientation and scattering due to polarization. We first determined the polarization of the incident beam. The laser beam was vertically polarized and the polarizer which is used on the way of light source was on the horizontal position. Here the polarization is defined to be perpendicular to the propagation direction. A white paper is placed on the other end of polarizer which is used to measure the intensity of the light rotating its position from vertical to horizontal. When the light source hits the sample another kind of rotation can occur by the deflection of a series mirror. For this beam the polarization is rotated and now the source is parallel to the optical table. And that is propagating perpendicular to the optical table. For determining the polarization of light we used the polarizer and the white paper just before the light hits the sample. The observable for different position has been given below:

Table 2: Polarization of the incident radiation.

Polarization position	rotator	Incident polarization after rotator	beam after	Incident polarization after beam	beam
290°		vertical		horizontal	
200°		horizontal		vertical	

This way the experiment was done for several cases and different rotation according to rotator. And due to crystal axis, and propagation axis. And we measured the Raman spectra over an energy from 50 to 1250 cm^{-1} using the laser power of 1W and an acquisition time of 10 sec. averaging over 2 acquisitions. The spectrum information is processed and graphed with software. The spectra are composed of peaks, each peak having a specific intensity. The intensity depends upon the shift in frequency of the transition involved. From the spectra we obtain information about the type of

symmetry that corresponds to the given polarization configuration. By counting the peaks present in the graph one can deduce the symmetry representation that corresponds.

4. RESULT:

Case-I: At First we placed the single crystal of α -quartz with its c-axis aligned towards the horizontal polarization direction. and the polarization of the incoming and out coming light is set to be horizontal which is shown on the figure 1. This configuration corresponds to the $x(zz)x$ in Raman configuration:

Figure1: Configuration for $x(zz)x$ Raman direction.

Figure 2: Spectrum data for $x(zz)x$ polarization configuration.

Table 3: Data for intensity peak of $x(zz)x$ configuration.

peak	frequencies	intensity
1	204.782	374
2	354.727	132
3	464.644	2792
4	1057.16	22

The intensity of the peaks gives information about the symmetry character of the vibrational modes. From the above figure it is clearly see that there are four peak. The spectrum presents four peaks of

different heights. According to table 3 contain four spectrum must correspond to the A_1 symmetry. It will not A_2 because A_2 is for infra-red and which is out of range of our measurement (400 Tz-300GHz). the scattering intensity for this vibration is proportional to

$$I_s \propto |e_i \cdot R \cdot e_s|^2 = \left| \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \right|^2 = \left| \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \begin{pmatrix} 0 \\ 0 \\ b \end{pmatrix} \right|^2 = b^2$$

By observing the value of R_{ZZ} from the table.1, we get the value is b . we get the same result on our observation for A_1 symmetry.

Case -II:

For the second portion of the experiment the c-axis of the crystal remains aligned toward the horizontal polarization direction and the polarization of the incoming and out coming light is changed to be vertical which is shown on the figure 3. This configuration corresponds to the $x(yy)x$ in Raman configuration.

Figure 3: Configuration for $x(yy)x$ direction.

Figure 4: Spectrum data for $x(yy)x$ polarization configuration

From the figure it is shown that there are 11 peaks now according to the table of symmetry of vibration in α -quartz we can say this belong to E symmetry. the peak value has been given below:

Table 4: Data for intensity peak of x(yy)x configuration.

peak	frequencies	intensity
1	129.85	966
2	201.483	61
3	265.823	393
4	343.761	24
5	402.247	118
6	464.009	233
7	508.84	293
8	684.405	24.33
9	809.28	268
10	1152.96	48
11	1218.8	28

the scattering intensity for this vibration is proportional to,

$$I_s \propto |e_i \cdot R \cdot e_s|^2 = \left| \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \begin{pmatrix} c & -c & d \\ -c & -c & d \\ -d & d & o \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \right|^2 = \left| \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \begin{pmatrix} -c \\ -c \\ d \end{pmatrix} \right|^2 = |-c|^2 = c^2$$

Now again from observing the symmetry and Raman tensor in vibrational modes table we get the value for R_{YY} is $-c$. so we get the same result on our experimental value of E symmetry.

CASE-III:

For the third experimental measurement the c-axis of the crystal aligned toward the vertical polarization direction and the polarization of the incoming and out coming light is changed to be vertical which is shown on the figure 5. This configuration corresponds to the z(yy)z in Raman configuration.

Figure 5: Configuration for z(yy)z direction.

Figure 6: Spectrum data for $z(yy)z$ polarization configuration

From the figure we can see that there are 10 peaks so according the vibration mode of α quartz it belongs to E symmetry. it is given the intensity value on below:

Table 5: Data for intensity peak of $z(yy)z$ configuration.

Peak	frequency	intensity
1	129.85	1923
2	198.844	73
3	244.227	30
4	332.13	21
7	684.24	29.57
8	772.607	20
9	1053.07	21
10	1159.29	187

The Raman tensor corresponds to this type of vibration is similar to the previous one and scattered intensity proportional to c^2 and Raman configuration $z(yy)z$ corresponds to the Raman tensor $-c$ for E symmetry.

CASE-IV:

Fourthly the c-axis of the crystal is aligned towards the direction of propagation and the polarization of the incoming and out coming light changed to horizontal which is shown in figure 7. This configuration corresponds to the $z(xx)z$ in Raman configuration.

Figure 7: Configuration for z(xx)z direction

Figure 8: Spectrum data for z(xx)z polarization configuration.

Here is seen that 7 spectrum, now we can say that from the Raman tensor table it is E spectra. The intensity peak is charted below:

Table 5: Data for intensity peak of z(xx)z configuration.

Peak	frequency	Intensity
1	128.517	662
2	202.802	760
3	348.923	56
4	370.177	25
5	465.276	10003
6	673.386	25.36
7	1139.7	31

The proportion of the intensity to the Raman tensor corresponding to E symmetry .the scattering intensity for this vibration is proportional to ,

$$I_S \propto |e_i \cdot R \cdot e_s|^2 = \left| \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} c & -c & -d \\ -c & -c & d \\ -d & d & o \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \right|^2 = \left| \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \begin{pmatrix} -c \\ -c \\ d \end{pmatrix} \right|^2 = c^2$$

The Raman tensor element for the z(xx)z configuration for the E symmetry, Rxx is c. which is exactly same as our experimental value.

5. Conclusion:

The table on the below has shown all observable data of spectrum. The first column of this table is the Raman active modes in the α quartz.

Raman active modes in α quartz	E symmetry	A ₁ symmetry
128	129.405	
207	201.043	204.782
264	255.025	
355	341.604	354.727
394	382.371	
403	402.247	
452		
466	464.431	464.644
508	508.84	
698	684.32	
798	772.607	
811	809.28	
1067	1053.07	1057.16
1081		
1161	1150.65	
1233	1218.8	

From our experiment we can see that here is 4symmetry for A₁ which is predicted on our vibrational modes. And for E symmetry it shows that 14 symmetry which is doubly generated, as we should see 16 vibrational modes according to the Raman active modes in the α quartz, as we can see that there are two vibration missing, it happens may be due to noise on the surroundings. We got different peaks due to the different intensities and the different orientation of the laser beam hitting the sample on different angle.

There is one other thing we were not able to determine all the matrix element, we got just only b^2 and c^2 . For obtaining the value of a^2 we need the higher energy range, For that we need to try the IR spectroscopy to cover higher energy range.

Now we can say that a Raman spectrum gives the detail information about the atoms vibrational modes and the symmetry element of the material and the characteristics region for different groups.

References

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