THE INFLUENCE OF OPTICAL ACTIVITY ON LIGHT-SCATTERING IN QUARTZ

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1. Introduction

In a previous paper, the present writer (1947) has shown how the large rotatory power of quartz in the ultraviolet manifests itself in transverse light-scattering. A plane-polarised beam of intense λ 2537 radiation of a water-cooled magnet-controlled mercury arc traverses a perfectly clear and transparent sphere of quartz along the optic axis. A photograph of its track taken in a direction transverse to it exhibits marked fluctuations in intensity along its length. The effect is obviously due to the incident light vector being alternately parallel and perpendicular to the direction of observation and to the strong polarisation of genuine thermal scattering. In a similar effect observed earlier by Lord Rayleigh (1919) in smoky quartz, the strong Tyndall scattering of visible light by the inclusions present was utilised.

In the present investigation, the light scattered by transparent quartz is analysed spectroscopically and the banding for the individual Rayleigh and the more intense Raman lines recorded separately. Also by the use of a mercury vapour filter placed in the path of the scattered light, the Tyndall scattering of λ 2537 radiation due to inclusions in the crystal is suppressed efficiently and the genuine Brillouin components are recorded. The obliteration of the bands when the incident light traverses a sphere of clear quartz at small angles to the optic axis is also recorded and an explanation given.

2. Experimental Technique

A transparent and practically colourless regular hexagonal crystal of quartz 4 cm. long, kindly lent by Prof. R. S. Krishnan, is employed for the purpose of the experiment. Two ends of it are cut normal to the optic axis. These ends and the sides are all ground and polished. As the crystal contained a few visible inclusions, the best portion is chosen.

The crystal is mounted with its optic axis vertical and one of the hexagonal sides facing the spectrograph. A sealed Z-type horizontal quartz mercury arc is water-cooled and magnet-controlled to give intense λ 2537 radiation. A rectangular aperture of 1 cm. $\times$ 0·5 cm. in front of the arc limits the beam. The light from it is condensed by a quartz lens of focal length 9 cm. for λ 2537 and aperture 4 cm. on one of the end surfaces of the crystal so that the beam traverses vertically along the optic axis. A large double-image prism next to the quartz lens served to polarise the beam, one of the images being screened off at the surface of the crystal. The vertical track of the beam in the crystal is focussed on the slit of a Hilger intermediate quartz spectrograph by a quartz lens. As the lens is not achromatic, its position is adjusted to give the best focus for λ 2537 radiation. With a slit width of 0·14 mm., the spectrum is photographed on a Selochrome plate giving an exposure of the order of 50 hours. A mercury vapour filter is employed in the path of the scattered light to absorb efficiently the Tyndall scattering of λ 2537 radiation and thus, record only the Brillouin components due to it.

3. Results and Discussion

A reproduction from the previous paper is given in Fig. 1 *b*, Plate VII, for comparison and shows clearly the bands in a perfectly clear and transparent sphere of quartz traversed by intense λ 2537 radiation. Owing to its high intrinsic intensity and the operation of λ^{-4} law, only the scattering of λ 2537 radiation is recorded even though no filter is employed in the incident light. Both its Rayleigh and Raman scattering would contribute to the intensity and as is well known, in a clear specimen of quartz, the latter makes as much as one fourth the contribution (Landsberg, 1927; Bhagavantam and Venkateswarulu, 1944). The pictures taken in the present investigation using a spectrograph are reproduced in Figs. 1 (*b*) and 1 (*c*). The complete spectrum [see Fig. 1 (*c*)] shows clearly the variation in the band width for different mercury arc lines. A major portion of their intensity recorded on the plate has its origin in the Tyndall scattering by the few inclusions present in the crystal. This is supported by the non-appearance of the intense 466 cm.$^{-1}$ Raman line (the absolute intensity of which is about 1/5 the intensity of the genuine Rayleigh scattering) excited by any mercury line other than λ 2537. On the other hand, as the λ 2537 radiation has been completely suppressed by the mercury vapour filter, what is observed in its place is the banding due to the Brillouin components arising from thermal scattering.

Fig. 1 (*a*) is a high enlargement of the portion between λ 2537 and the triplet λ 2654. It shows clearly the bands for the Brillouin components of λ 2537 and the two symmetric Raman lines 207 and 466 cm.$^{-1}$ excited by it, while the strong line 128 cm.$^{-1}$ and the weaker 800 (doublet) and 1159 cm.$^{-1}$ lines belonging to the degenerate class E, sub-groups E_1, E_2 and E_3 respectively, show no trace of the banding. It is clear from the work of Saxena (1940) and more recently of Krishnan (1945) that the Raman spectrum of quartz consists in the main of 12 first order lines including two doublets. Of these four lines 207, 357, 466 and 1082 cm.$^{-1}$ lines belong to the symmetric class A which are always completely polarised and should, therefore, show the bands. The rest belong to the degenerate class E divided into three sub-groups depending on their depolarisation values and orientation effects. However, in all sub-groups, as a result of degeneracy the two directions perpendicular to the optic axis are equivalent. This has an important consequence that when light is incident along the optic axis, the scattered intensity would be the same whether the light vector is along or perpendicular to the direction of observation (*vide* Table V of p. 109 of Saxena's paper). This prediction has been beautifully confirmed in the case of quartz for the first time in the present work; the more intense degenerate lines 128, 800 (doublet) and 1159 cm.$^{-1}$ lines showing no trace of the banding. The large optical activity of quartz along the optic axis has been a disturbing factor when it is required to study the effect of polarising an incident beam travelling along that direction. Hence, for such directions, studies have been confined till now to the use of incident unpolarised light. The present arrangement described enables one to make polarisation and intensity measurements using polarised light traversing along the optic axis, and the disturbing factor, namely the optical activity itself is made use of for the purpose. It is interesting to note that some of the degenerate lines, *e.g.*, 800 cm.$^{-1}$ line (E_2 sub-group) and 1159 cm.$^{-1}$ line (E_3 sub-group), have depolarisation values of ∞ and 0 respectively and still show no banding as expected.

The band width for λ 2537 and for the two 207 and 466 cm.$^{-1}$ Raman lines was measured with a glass scale reading to tenths of a millimetre and the reduction produced by the condensing lens and by the spectrograph for λ 2537 along the length of the slit was determined. From this, the actual width, which corresponds to a rotation of 180° of the plane of polarisation of the incident light, was calculated and hence, the rotation per millimetre for λ 2537 deduced. The calculated rotation of 148°·5 per mm. agrees well with the correct value of 148°·6 per mm. It is particularly interesting to note that the band widths of the Raman lines and the exciting line are identical [see Fig. 1 (*a*)]. A Rayleigh line of the same frequency as the 466 cm.$^{-1}$ line excited by λ 2537 would have shown about $\frac{1}{4}$ of a band less in 7 bands and this would have been shown up clearly.

4. Directions inclined to the Optic Axis

As a plane-polarised light beam advances inside a birefringent solid, it undergoes a periodic cycle of changes in its state of polarisation. Hence, its track made visible by the scattered light would exhibit striking fluctuations in intensity along its length. These bright and dark bands have been observed and photographed by the author (1947) using synthetic organic glasses with permanent strains and hence, behaving like very feebly birefringent solids. Now it follows that in a solid showing both optical activity and birefringence, the effect should also be observable. As is well known, quartz has both optical activity and birefringence for directions inclined to the optic axis.

For such directions, the theory of propagation of light in quartz has been dealt with by several workers (Briot, 1863; Gouy, 1885 and Wiener; *vide* Pockel, 1906). Along such directions, two similar elliptically polarised waves but with opposite sense of rotation and lying crossed to each other (*i.e.*, the major axis of one falls on the minor axis of the other) travel unchanged. The axes of the ellipses coincide with the principal planes. Pockels has shown in his book a simple though approximate way of arriving at the ratio of the axes of the vibration ellipses which propagate unchanged and the path difference between the two waves per unit length. If ρ is the rotatory power per unit length along any direction and δ_0 is the path difference due to birefringence alone (if $\rho = 0$), then the actual path difference per unit path between the two elliptic waves is given by

$$\delta = \sqrt{\delta_0{}^2 + (2\rho)^2}$$

and the ratio of the axis χ is given by

$$\chi = \tan\beta \text{ where } \tan\beta = \frac{2\rho}{\delta_0}$$

or

$$\chi^2 = \frac{\delta - \delta_0}{\delta + \delta_0}.$$

Bruhat (1935) has determined recently the rotatory power of quartz for directions parallel and perpendicular to the optic axis for different wavelengths.

For $\lambda\, 2537$ $r_1 = -86°$ per mm. perpendicular to the optic axis

$r_3 = 149°$ per mm. parallel to the optic axis

$$\rho = r_1 \sin^2\phi + r_3 \cos^2\phi$$

where ϕ is the inclination of the ray with the optic axis. The two refractive indices for $\lambda\, 2537$ are

$$n_\epsilon = 1\cdot 60930, \qquad n_\omega = 1\cdot 59830$$

For different values of ϕ the rotation and the path retardation per unit length are given in Table I.

TABLE I

ϕ in degrees	ρ' in degrees/mm.	ρ/π per mm.	$\delta_0/2\pi$ per mm.	$\delta/2\pi$ per mm.	$2\pi/\delta$ in mms.	χ
0	149·0	0·8278	0	0·8278	1·208	1
1	148·93	0·8276	0·01315	0·8277	1·208	0·9784
2	148·7	0·8264	0·05229	0·8281	1·208	0·9387
3	148·4	0·8244	0·1174	0·8327	1·201	0·8677
4	147·9	0·8218	0·2091	0·8480	1·179	0·7774
5	147·2	0·8177	0·3264	0·8804	1·135	0·6775
6	146·4	0·8130	0·4687	0·9383	1·066	0·5778
7	145·5	0·8084	0·6377	1·0296	0·9716	0·4848
7·86	144·6	0·8032	0·8032	1·1359	0·8805	0·4142
8	144·4	0·8019	0·8318	1·1554	0·8655	0·4035
9	143·2	0·7954	1·049	1·3165	0·7498	0·3363
10	141·9	0·7885	1·294	1·5153	0·6601	0·2806
11	140·5	0·7806	1·562	1·7462	0·5726	0·2360
12	138·8	0·7706	1·855	2·0172	0·4958	0·2043
13	137·1	0·7617	2·172	2·3045	0·4340	0·1713
14	135·2	0·7513	2·512	2·6219	0·3814	0·1463
15	133·3	0·7407	2·874	2·9679	0·3369	0·1268
20	131·5	0·6752	5·020	5·0652	0·1974	0·0670
30	90·2	0·5009	10·73	10·7417	0·0931	0·0233
52·69	0	0	27·22	27·22	0·0367	0
90	−86	0·4778	43·37	43·3726	0·0231	0·0055

$2\pi/\delta$ for any value of ϕ gives the periodic distance after which the incident polarised beam proceeding along that direction returns to its original state of polarisation after undergoing a cycle of changes. It is seen, however, from the table that this length changes but little up to 3°. Hence, when light goes along the optic axis convergence angles of the order of 6° can be used, and the bands in transverse light-scattering would still be clear. On the other hand, at say 8° to the optic axis, when the periodic length is appreciably different, it changes so rapidly with the angle that unless the beam is strictly parallel, the rays going at different angles obliterate the banding. These conclusions have been verified in the observations made with the sphere of quartz. The arrangement used has already been described in the earlier paper.

Fig. (2), Plate VII, shows the bands clearly when a fairly wide beam travels exactly along the optic axis. At 4° to the optic axis the bands are still clear and of the same width and are reproduced in Fig. 2 (*b*). At the edge of the track away from the optic axis the banding is just obliterated. At 8° to the optic axis the series of pictures, Figs. 2 (*c*), (*d*) and (*e*) show the effect of narrowing the beam. With a wide beam [Fig. 2 (*c*)] some rays are going very near the optic axis and hence, show the banding while on the other side the bands are obliterated. When the beam is strictly limited, the bands have been completely obliterated. At 10° [Fig. 2 (*e*)] the bands have disappeared even with a fairly wide beam. The maximum convergence of the incident light used is about 8° to 10° while the minimum used is about 2°.

It should be recalled that in a purely optically active solid the banding would be equally clear in any azimuth transverse to the beam. On the other hand, in a birefringent solid without optical activity, the banding would be marked only when both the direction of the incident light vector and that of observation are inclined at 45° to the principal planes. When either direction coincides with the principal plane the banding would disappear. Hence, for directions away from the optic axis, the sphere of quartz is rotated so that the bands would be most marked and yet the banding vanished at 10°. The value of χ in the last column of Table I gives a measure of the azimuth effect if strictly parallel light is used.

It is interesting to note that in the visible say at λ 4358, the ratio of the rotatory power to birefringence of quartz is half that for the ultra-violet λ 2537. Hence, to get equal clarity of the banding, the square of the convergence angles used should be only half as large in the visible compared to the ultra-violet. This result has also been verified (no photograph is reproduced).

In the previous paper, it was reported that the sphere of quartz used was a left-handed one. Between crossed polaroids, the observation recorded that the rings of any particular colour appear to expand indicates actually that the sphere is a right-handed one (Cady, 1946).

In conclusion, the author wishes to thank Prof. Sir C. V. Raman and Prof. R. S. Krishnan for their keen interest in the work and for the useful discussions he had with them.

5. Summary

A vertical plane-polarised beam of intense λ 2537 mercury radiation travels along the optic axis of a crystal of quartz and the light vector is alternately parallel and perpendicular to the direction of observation transverse to the beam. A spectral analysis of the scattered light, using a mercury vapour filter to absorb the λ 2537 line, yields bands of fluctuating intensity along the length of the slit for the Brillouin components and for the two symmetric 207 and 466 cm.$^{-1}$ Raman lines. On the other hand, the degenerate lines 128,800 (doublet) and 1159 cm.$^{-1}$ lines belonging to the different

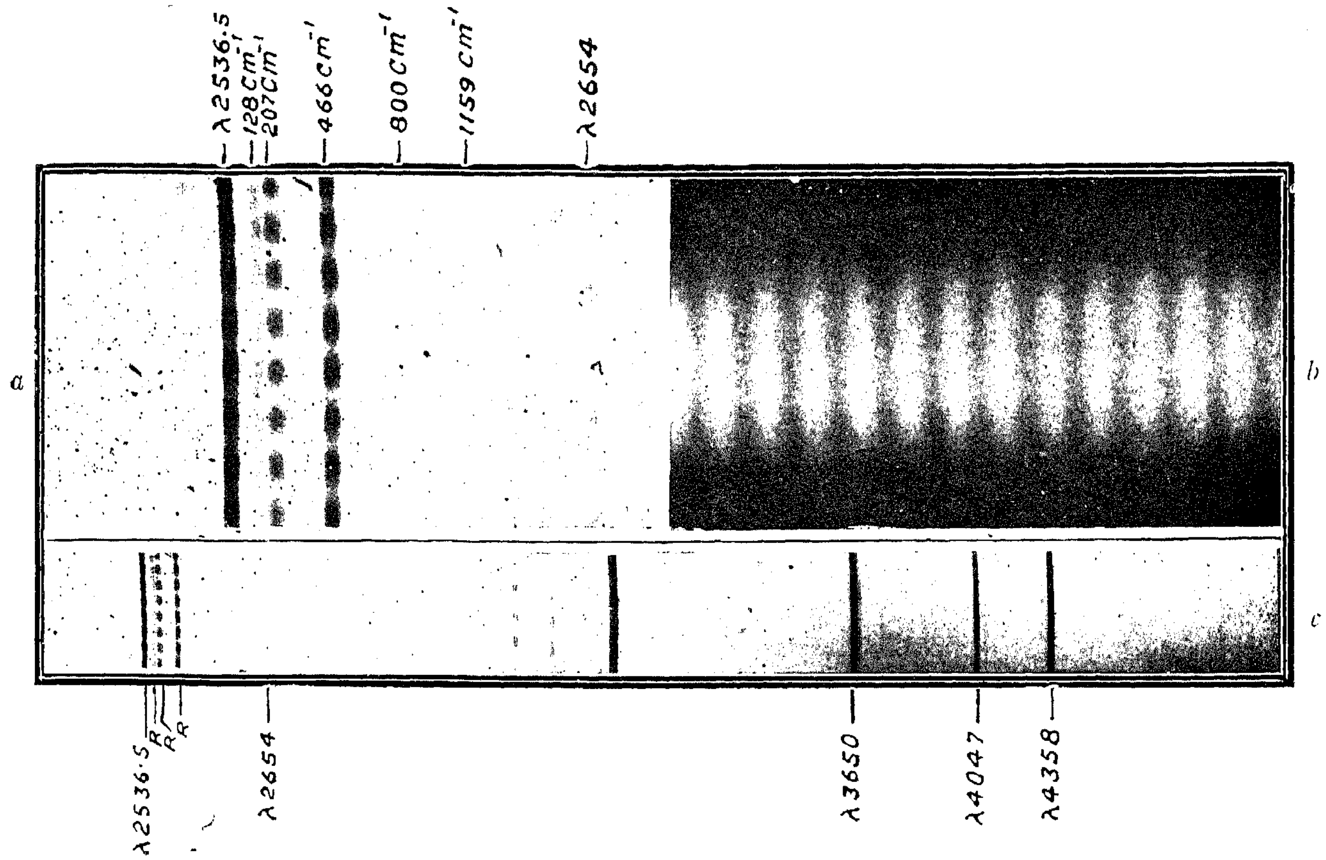

λ2536.5
128 cm⁻¹
207 cm⁻¹
466 cm⁻¹
800 cm⁻¹
1159 cm⁻¹
λ2654
a
b
c
λ2536·5
R
R
R
λ2654
λ3650
λ4047
λ4358

FIG. 1

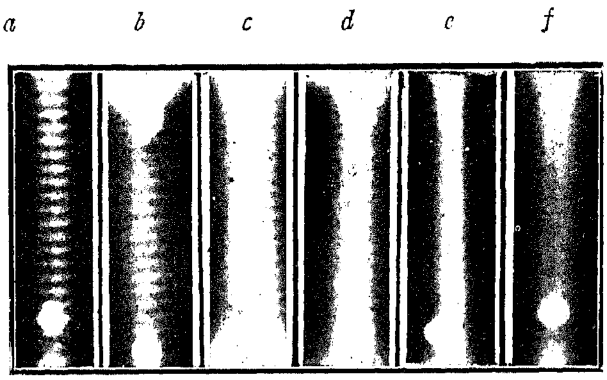
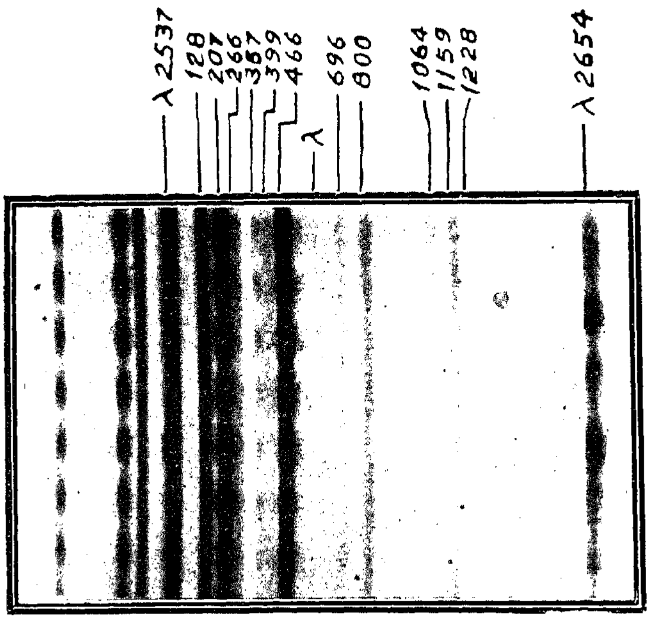

a
b
c
d
e
f

FIG. 2


λ2537
128
207
266
387
399
466
λ
696
800
1064
1159
1228
λ2654

subgroups are of uniform intensity irrespective of their depolarisation values. This result, which is in complete conformity with theory, verifies for the first time the selection rules for polarised light travelling along the optic axis of quartz—the optical activity itself, usually a disturbing factor, being made use of for the purpose. That the band widths of the Raman lines and that of the exciting line are identical is interesting. The variation in band width of some intense mercury lines, recorded due to inclusions present in the crystal used, shows clearly the rapid increase in the rotatory power of quartz in the ultraviolet.

The obliteration of the banding when the incident light travels at small angles to the optic axis of a clear and transparent sphere of quartz is recorded and a theoretical explanation is given.

Note added in Proof.—Since sending the paper for publication, the author has obtained an intense spectrogram of the scattering in quartz, giving an exposure of the order of 7 days and using a slit width of 0·08 mm. An enlargement of the same is reproduced in Fig. 3, Plate VII. It shows clearly all the principal Raman lines of quartz except 1082 cm.$^{-1}$ line. Of these, three lines (207, 357 and 460 cm.$^{-1}$) belonging to Class A exhibit the banding, while the rest—128, 266, 399, 696, 800, 1063, 1159 and 1228 cm.$^{-1}$ lines—are of uniform intensity. The 266 cm.$^{-1}$ line appears to have a trace of banding, but it is due only to the halation produced by the bands of the intense adjacent 207 cm.$^{-1}$ line. The 1082 cm.$^{-1}$ Raman line, coming under the symmetric Class A, has zero intensity for the particular direction of excitation used in the present investigation (Saxena, 1940) and hence, is not recorded.

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Description of Plate

FIG. 1 *b*. Scattering of a clear sphere of quartz traversed by plane-polarised λ 2537 along optic axis.

FIG. 1 *c*. Spectrum of scattering of quartz traversed by plane polarised light along the optic axis.

FIG. 1 *a*. Enlargement of Fig. 1 *c* showing the portion between λ 2537 and λ 2654.

FIG. 2 *a*. Same as 1 *b*.

FIG. 2 *b*. Incident light inclined at 4° to the optic axis.

„ 2 *c*,*d*,*e* Incident light inclined at 8° to the optic axis for three different angles of convergence of the beam.

FIG. 2 *f*. Incident light inclined at 10° to optic axis. Fairly wide beam.

FIG. 3. Same as Fig. 1 *a*. Intense picture.