# THE SCATTERING OF LIGHT IN FUSED QUARTZ AND ITS RAMAN SPECTRUM

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## 1. Introduction

Although quartz in the crystalline form has been the subject of numerous investigations, very little work appears to have been done on the scattering of light in fused quartz. This is mainly due to the fact that till recently it was not possible to obtain fairly large specimens of fused quartz of good optical quality. Most of the specimens prepared in the early days had inclusions of air bubbles, the presence of which made accurate measurements on the scattering of light very difficult. The Thermal Syndicate Ltd., recently supplied to the Department a rectangular block ($1'' \times 1'' \times 2''$) with polished faces of fused quartz of optical A quality. This specimen was completely free of any inclusions and exhibited a perfectly bluish track when a beam of light was passed through the same. The acquisition of such a specimen has enabled the author to make a detailed study of the scattering of light and the Raman effect in fused quartz.

## 2. Some Preliminary Observations

Ever since 1935, the Department of Physics at this Institute has been getting fused quartz materials (such as discs, plates, tubes, rods, etc.) from the Thermal Syndicate Ltd., England. It was found that transparent specimens of fused quartz when exposed to the radiation from a water-cooled, magnet-controlled quartz mercury arc developed a pale violet colouration. Similar colouration is also exhibited by the walls of an ordinary quartz mercury arc after it is run for several hours. Usually, when a plate is exposed to the ultraviolet radiation it develops uniform violet colouration. But a rod of fused quartz (AA quality) of dimension (2 cm. in diameter and 6 cm. long) purchased from the Thermal Syndicate Ltd., in 1939, exhibited a very peculiar behaviour. In order to take the Raman spectrum of the specimen using the $\lambda$ 2536 excitation, it was covered with black paper at the two ends and also on the sides excepting for two long apertures along the side for illumination. The uncovered portion of the rod was exposed to the strong ultraviolet radiation from a water-cooled magnet-controlled quartz mercury arc. After an hours' exposure, a fairly large number of

violet coloured streaks developed inside the specimen. These streaks coiled round the axis of the rod. Further exposure did not increase the number of streaks. A photograph exhibiting the streaks is reproduced in Fig. 2 *a* on Plate XVII. An end-on view of the streaks is reproduced in Fig. 2 *b* on Plate XVII. The direction of illumination is indicated by the arrow. It is surprising to note that the streaks appeared not only in the direction of illumination but were concentrated in the outer regions, the central portion near the axis of the rod being comparatively free from streaks. This will be evident from a careful examination of the photograph reproduced in Fig. 2 *b*.

When specimens of fused quartz acquired a violet colour on exposure to the far ultraviolet radiations, they were found to be less transparent to $\lambda$ 2536 radiation than the colourless ones. The spectrum of the light scattered by such coloured specimens under $\lambda$ 2536 excitation exhibited a weak fluorescence extending from $\lambda$ 2536 to the visible region. No attempt was, however, made to examine the fluorescence of such specimens in the visible region. Because of the colouration and consequent diminution of transparency to $\lambda$ 2536 radiation, it was not possible till recently to take satisfactory photographs of the Raman spectrum of fused quartz using $\lambda$ 2536 excitation.

The violet colour as well as the fluorescence exhibited by fused quartz disappeared completely when the specimens were heated above 250° C. The streaks developed in the fused quartz rod and shown in Figs. 2 *a* and 2 *b* also disappeared on heating. When a specimen which had its colour removed by single heating was exposed to the far ultraviolet radiations it again acquired slight violet colour but not to the same extent. It was noticed that after repeated and prolonged heating and cooling, certain specimens did not acquire the violet colour under ultraviolet excitation.

The rectangular block of fused quartz of optical A quality was, however, found to be free from the troubles mentioned above. As such it was possible to study not only the Rayleigh scattering but also the Raman effect in fused quartz using this specimen and the $\lambda$ 2536 excitation.

## 3. THE SCATTERING OF LIGHT

The rectangular block of optical fused quartz was first tested for any residual strain. Careful examination of the specimen under crossed polaroids and also using a polariser and a Babinet compensator indicated that it was free from any strain. The interior of specimen was then scanned for any inclusions by sending a powerful condensed beam of sunlight through

it and observing the track inside in the forward direction. It was found to be perfectly free from inclusions of any kind. The depolarisation factors $\rho_u$, $\rho_v$ and $\rho_h$ were then measured visually employing the Cornu method. The source of illumination was a 40 ampere projection lantern (Magnarc). The convergence of the incident beam was reduced to a minimum. The measured values of $\rho_u$, $\rho_v$ and $\rho_h$ for ordinary light are 11·5%, 5% and 80% respectively. When the incident beam was polarised with vibrations horizontal, the two tracks of the transversely scattered beam as observed through a Wollaston double-image prism were found to be slightly different in colour at the matching position. In view of this fact and in view of the feebleness of the scattering for this case, $\rho_h$ could not be measured with the same accuracy as $\rho_u$ and $\rho_v$. In any case, it has been definitely established that $\rho_h$ is less than 100% and that the scattering in fused quartz is multipolar in character. In this respect fused quartz behaves in the same way as ordinary glass (Krishnan, 1936).

The intensity of scattering in fused quartz was measured as follows:— A glass cell with flat windows nearly of the same dimensions as the fused quartz specimen was made as the container for dust-free ether. Using two photo-multiplier tubes and a " ratio circuit ", the intensity of the transversely scattered light in pure ether was compared with that in fused quartz. White light with blue filter was used as the source of radiation. It was found that the scattering in fused quartz was only 1/3·5 of that of pure ether. In ordinary silicate glasses, on the other hand, the intensity of scattering is nearly of the same order or greater than that in ether (Krishnan, 1936).

The absolute intensity of thermal scattering per unit volume of fused quartz could be calculated using the well-known relation

$$I = \frac{\pi^2 k T n^8}{2\lambda^4} \left[ \frac{p_{12}^2 + p_{44}^2}{C_{11}} + \frac{p_{44}^2}{C_{44}} \right], \qquad (1)$$

where I represents the intensity of light scattered by a unit volume of the isotropic substance, when the incident light is of unit intensity. The values of the elastic constants $C_{11}$ and $C_{44}$ and the photo-elastic constants $p_{12}$ and $p_{44}$ for fused quartz were taken from the measurements of K. Vedam (1950). The value of I comes to about $1{\cdot}63 \times 10^{-7}$ for $\lambda$ 4358. Taking the absolute intensity of the transversely scattered light for benzene as $49{\cdot}5 \times 10^{-6}$ for $\lambda$ 4358 (Carr and Zimm, 1950), and the ratio of intensities of scattering in benzene and ether as 3·06, the observed intensity of scattering in the specimen of fused quartz can be expressed in absolute values as equal to $4{\cdot}84 \times 10^{-6}$. The data for light scattering in fused quartz are summarised below:—

TABLE I. *Fused Quartz*

| $\rho_u$ | $\rho_v$ | $\rho_h$ | Intensity of Rayleigh scattering, observed $I_0$ | Intensity of thermal scattering, theoretical $I_t$ | $\frac{I_0}{I_t}$ |
|---|---|---|---|---|---|
| 11·5% | 5% | 80% | $4{\cdot}84\times10^{-6}$ | $1{\cdot}63\times10^{-7}$ | 29·7 |

It is evident from a perusal of the figures given in Table I that the observed intensity of scattering in fused quartz is about 30 times greater than the value calculated on the basis of equation (1). This fact supports the view that in fused quartz also there is molecular aggregation as in the case of ordinary glass. The value of the ratio $I_0/I_t$ is of the order of 80 and above in the case of the ordinary silicate glasses.

## 4. THE DOPPLER-SHIFTED COMPONENTS

To a first approximation, one can assume that the intensity of scattering given by equation (1) above represents the total intensity of the Doppler-shifted components arising from the scattering of thermal elastic waves in the medium. The intensity of these components in fused quartz is therefore only one-thirtieth of that of the observed intensity of Rayeligh scattering (see Table I). As such, in order to record the Doppler-shifted components, it is necessary to employ the best experimental conditions. These are provided by the use of the ultraviolet technique of excitation. Using the $\lambda$ 2536 radiation as exciter and a mercury vapour filter in the path of the scattered light, the author successfully recorded the Doppler-shifted components in the fused quartz rod mentioned in the Introduction at two different temperatures. A preliminary report of the results was published in *Nature* (Krishnan, 1950). The experiment has now been repeated with the rectangular specimen of fused quartz of optical quality. The photographs of the Doppler-shifted components for transverse scattering and backward scattering taken with a Hilger three-metre quartz spectrograph are reproduced in Figs. 3 *a* and 3 *b* on Plate XVII respectively.

It may be remarked that the components appear broader for the transverse scattering (Fig. 3 *a*) than for the backward scattering (Fig. 3 *b*). This is due to the fact that the angle of scattering in the former case was less well defined than that in the latter case. In the case of transverse scattering, although the arc was kept close, the angle of convergence was limited

to about 15° by the use of opaque parallel vanes. In both cases only the Brillouin components due to the longitudinal sound waves are observed.

The unmodified line has been completely cut off by the mercury vapour filter. It will be observed that the component on the longer wavelength side is less intense than the one on the shorter wavelength side. This asymmetry in intensity is more prominent for the transverse scattering than for the backward scattering. This is due to the fact that the absorption of mercury vapour is not confined to λ 2536·5, but extends though feebly but asymmetrically on either side, the absorption being greater on the longer wavelength side (Mitchell and Zemansky, 1934). Due to this effect the Brillouin components are also reduced in intensity, and this reduction in intensity is more for a component which is nearer to the exciting line than for one on the same side but farther away. The measured separation of the Brillouin components for the two cases are given in Table II.

TABLE II

| $\Delta\nu$ | Transverse scattering cm.$^{-1}$ | Backward scattering cm.$^{-1}$ |
|---|---|---|
| Observed .. | 1·83 | 2·22 |
| Calculated .. | 1·68 | 2·36 |

The values of the Doppler shifts calculated from the known value of the elastic constant of fused quartz on the basis of the Brillouin formula are given in Table II. The agreement between the theoretical and experimental values of the shifts is fairly satisfactory.

## 5. THE RAMAN SPECTRUM

The Raman spectrum of fused quartz was recorded by Gross and Romanova (1929), Kujumzelis (1935) and Langenberg (1937). They used the λ 4358 radiation of the mercury arc for excitation. Using the λ 2536 resonance radiation of mercury as exciter and optical A quality of fused quartz specimen, the Raman spectrum has been photographed. The photograph taken with a Hilger medium quartz spectrograph and with an exposure of eight hours is reproduced in Fig. 1 *a* on Plate XVII. The corresponding microphotometer record is reproduced in Fig. 1 *b*.

The recorded spectrum exhibits only one intense fairly sharp line with a frequency shift of 495 cm.$^{-1}$ Besides this, the spectrum consists of five

broad lines and six bands of varying intensities and widths. The frequency shifts of these are entered in Table III. They are also indicated in the figure. The values of the frequency shifts reported by Gross and Romanova and Kujumzelis are also given in the same table. The most important new result is the appearance of a broad and intense band at $30 \rightarrow 120$ cm.$^{-1}$ which has not been recorded before. This band has its maximum intensity at the low frequency end and the intensity falls off continuously as one moves away from the exciting line. There is a weak continuum extending from 30 cm.$^{-1}$ to about 500 cm.$^{-1}$ and showing fairly well-defined limits at the two ends. This continuum masks the discrete nature of the three broad lines at 285, 370 and 430 cm.$^{-1}$ The lines at 635 and 660 cm.$^{-1}$ are very faint. The bands at $775 \rightarrow 805$ cm.$^{-1}$ and at $810 \rightarrow 845$ cm.$^{-1}$ lie close to each other thereby giving the appearance of a single band.

TABLE III

*Raman Spectrum of Quartz*

*Frequency Shifts in Wavenumbers*

| Crystalline quartz | Fused Quartz | | |
|---|---|---|---|
| | Author | Gross and Romanova | Kujumzelis |
| 128 | 30 → 120 v.s. | | |
| 207 | | | |
| 266 | 285 b, s. | 265, 325 | 230 → 450 |
| 356 | 370 b, v.s. | 365 | |
| 394, 403 | 430 b, v.s. | 450 | |
| 466 | 495 v.s. | 500 | 500 |
| | 635 v.w. | 625 | 607 |
| 695 | 660 v.w. | 660 | |
| 796 | 775 → 805 s. | 790 → 830 | 780 → 840 |
| 809 | 810 → 845 f.s. | | |
| | 885 → 940 v.w. | | |
| 1063, 1082 | 1022 → 1098 f.s. | 1020 → 1070 | 1030 → 1090 |
| 1160, 1227 | 1140 → 1245 w. | 1180 → 1230 | 1160 → 1230 |

*v.s.* = very strong; *s* = strong; *b* = broad; *v.w.* = very weak; *w* = weak; *f.s.* = fairly strong

The band at $885 \rightarrow 940$ cm.$^{-1}$ is extremely faint and can be observed in the photograph only with some difficulty. It can be seen more clearly in the microphotometer record. Both Kujumzelis and Langenberg reported the existence of a line at about 607 cm.$^{-1}$ This line even if present in the

spectrum taken by the author would have fallen on the mercury line λ 2576 which has a separation of 609 cm.$^{-1}$ from λ 2536.

The frequency shifts of the principal Raman lines observed in the spectrum of crystalline quartz are given in column 1 of Table III. The most intense line of crystalline quartz, 466 cm.$^{-1}$, appears shifted to 495 cm.$^{-1}$ in fused quartz. As is to be expected, the Raman bands observed in the case of fused quartz correspond roughly to the lines of crystalline quartz. It will be interesting to study the Raman spectrum of fused quartz at liquid-air temperatures.

I wish to express my appreciation of the valuable assistance rendered by Dr. P. S. Narayanan who took some of the spectrograms illustrating this paper.

## 6. Summary

A detailed study of the scattering of light in fused quartz and its Raman spectrum has been made. A rectangular specimen of fused quartz of optical A quality has been used. The depolarisation factors $\rho_u$, $\rho_v$ and $\rho_h$ have been measured. They are respectively 11·5%, 5% and 80%. The intensity of scattering in fused quartz is found to be 1/3·5 of that in pure dust-free ether. The Doppler-shifted components in the light scattered by fused quartz have been recorded using λ 2536 excitation both for the case of transverse scattering and backward scattering. The observed frequency shifts are in general agreement with those calculated from the known elastic constants of fused quartz.

The Raman spectrum of fused quartz has been recorded with λ 2536 excitation. The recorded spectrum exhibits six lines and six bands of varying width and intensity. The frequency shifts are 285, 370, 430, 495, 635, 660, 30 → 120, 775 → 805, 810 → 845, 885 → 940, 1022 → 1098 and 1140 → 1245 cm.$^{-1}$ Besides, there is a weak continuum extending from 30 cm.$^{-1}$ to 500 cm.$^{-1}$ with well-defined edges.

## References

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## DESCRIPTION OF PLATE

FIG. 1 *a*. The Raman spectrum of fused quartz taken with a Hilger medium quartz spectrograph using λ 2536 as exciter.

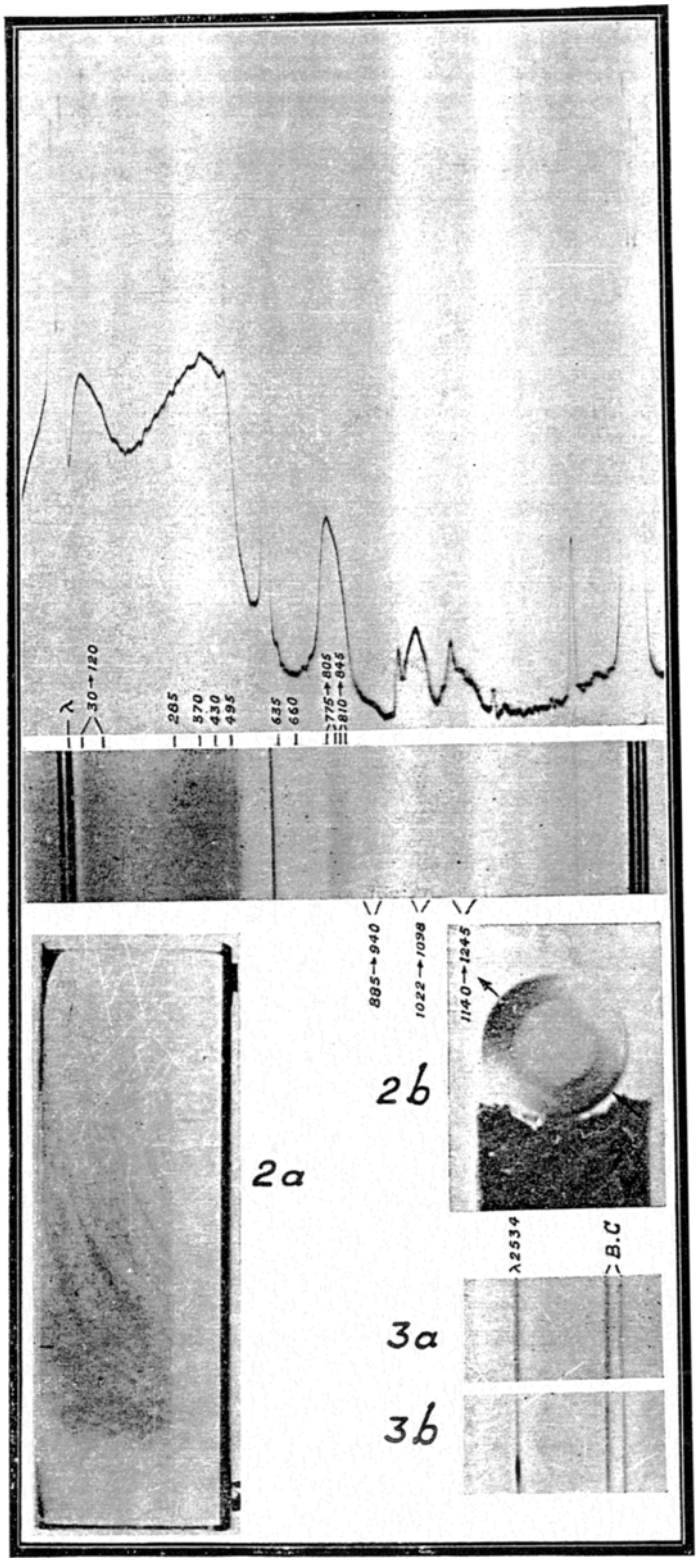
FIG. 1 *b*. Its microphotometer record.

FIG. 2 *a*. The streaks developed in a specimen of fused quartz under far ultraviolet irradiation.

FIG. 2 *b*. End-on view of the same.

FIG. 3 *a*. An enlarged photograph showing the Brillouin components in the light scattered transversely by fused quartz taken with a Hilger three-metre quartz spectrograph and λ 2536 as exciter.

FIG. 3 *b*. Same for backward scattering.




1b

1a

2b

2a

3a

3b