

THE RAMAN SPECTRUM OF QUARTZ AND ITS INTERPRETATION

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1. INTRODUCTION

QUARTZ is the classic example of a naturally occurring transparent crystalline solid. It was the first crystal in which the existence of an observable diffusion of light as an inherent property of the substance was clearly established. It was naturally therefore also one of the first crystals in which the scattering of monochromatic light was spectroscopically investigated.

The Raman spectrum, the interpretation of which is the main theme of this paper, exhibits several distinctive characters, which have their origin in the special features of the architecture of the crystal. Firstly, the solid itself may be described as a giant molecule, the silicon and oxygen atoms in it being linked together by valence bonds stretching continuously through the crystal. Secondly, the structure of the crystal is based on a three-fold axis of screw symmetry which, as is well known, results in the crystal exhibiting optical activity and other interesting properties. Thirdly, the crystal structure is notably influenced by temperature and undergoes a transformation at 575° C. which results in a change-over of its symmetry from the trigonal class to the hexagonal class. All these circumstances make their influence felt in the Raman spectrum of the crystal and have to be considered in any attempt at its elucidation.

In seeking to interpret or explain the Raman spectra of crystals we have necessarily also to take account of their behaviour in the infra-red region of the spectrum. The absorption and reflection spectra of quartz in that region were the subject of investigations by the pioneers in the field. Several of the characteristic frequencies are however so low that they are only with difficulty accessible to study by infra-red techniques. Some progress has however been made recently in this direction and the new results which have been reported in the literature have been taken into consideration in the present paper.

A detailed experimental study of the Raman spectrum of quartz has been carried out by the author. While in the main the results confirm those reported by earlier workers, a few new features have also been noticed. However, it is in regard to the interpretation of the experimental results that the present investigation is believed to make a distinct advance.

2. THE CRYSTAL STRUCTURE OF QUARTZ

Quartz belongs to the space group D_3^4 (or D_3^6) of the enantiomorphous hemihedral class of the trigonal system. The unit cell of the quartz structure consists of three SiO_2 groups. The structure possesses the symmetry elements of a three-fold screw axis and three two-fold axes perpendicular thereto and passing through the three silicon atoms of the unit cell. The three SiO_2 groups of the unit cell are rotated with respect to each other by 120° . The three silicons are situated at levels 0, $c/3$ and $2c/3$, where c is the lattice constant along the optic axis. The oxygen atoms of each SiO_2 group are symmetrically situated on either side of the silicon above and below it, such that between two silicon planes there intervene two oxygen planes. Thus, the oxygen planes occur at levels $c/9$, $2c/9$, $4c/9$, $5c/9$, $7c/9$ and $8c/9$. We have described the unit cell here in terms of three SiO_2 groups. The prime characteristic of the structure of quartz is a continuous linking up of the silicons and oxygens so that each silicon atom is tetrahedrally surrounded by four oxygen atoms and each oxygen atom is connected to two silicon atoms. The SiO_4 group in quartz is not a regular tetrahedron, but possesses only the symmetry of a two-fold axis passing through each silicon and perpendicular to the optic axis. The three silicons in the unit cell together with the three other silicons belonging to the adjacent cells form an irregular hexagon possessing only the symmetry of a three-fold axis.

3. THE DYNAMICS OF THE QUARTZ LATTICE

The problem of the symmetry properties of the normal modes of vibration of the quartz structure was treated by Went (1935) and later in detail by Saksena (1940) on the basis of the assumption that the dynamical behaviour of the system is the same as though it belonged to point group D_3 . The point group D_3 possesses the elements of symmetry of a three-fold axis and three two-fold axes perpendicular thereto and all lying in the same plane and inclined with respect to each other at an angle of 120° . The successive operations of this simple three-fold axis thrice is equivalent to the identity operation. On the other hand, three successive operations of a three-fold axis combined with one-third the translation of the lattice each time and parallel to the optic axis result finally in a simple unit translation of the cell

along the optic axis. If it is assumed that an unit translation may be treated as equivalent to the identity operation, the point group D_3 and the space-group D_3^4 (or D_3^6) may be shown to be isomorphous with each other. It is believed that some of the so-called anomalies noticed in the Raman spectrum of quartz may have their origin in the above approximation involved in the theoretical treatment. However, we shall in the present paper try to interpret the main features observed in terms of the theoretical analysis by Saksena.

The character table for point group D_3 , the classes into which the vibrations are grouped, their number and selection rules are shown in Table I. The point group D_3 contains three irreducible representations, *viz.*, (1) A: totally symmetric, (2) B: anti-symmetric with respect to the two-fold axes and (3) E: doubly degenerate.

TABLE I
Character table and selection rules

| D_3 | E | $2C_3^z$ | $3C_2$ | Total No. of vibrations | Trans- sitions | No. of vibrations | Selection rules | |
|-------|---|----------|--------|-------------------------|-------------------|-------------------|---|-----------------------------|
| | | | | | | | Raman Effect | Infra-red |
| A | 1 | 1 | 1 | 4 | 0 | 4 | $\epsilon_{xx} = \epsilon_{yy} \neq \epsilon_{zz}; \epsilon_{ik} = 0$ | Forbidden |
| B | 1 | 1 | -1 | 5 | 1 (T_x) | 4 | Forbidden | M_x only; $M_x = M_y = 0$ |
| E | 2 | -1 | 0 | 9 | 1 (T_x, T_y) | 8 | $\epsilon_{xx} = -\epsilon_{yy} = \epsilon_{xy};$ $\epsilon_{xx} = \epsilon_{yy}; \epsilon_{zz} = 0$ | $M_x = 0$ |

4. THE PRINCIPAL FEATURES OF THE RAMAN SPECTRUM

Strongly exposed records of the Raman spectrum of quartz were obtained by the present author using the powerful λ 2536.5 resonance radiation of the mercury arc as the exciting radiation. The experimental techniques pertaining to this and other details of the set-up have been described fully in an earlier paper by the author on the Raman spectrum of calcite (1957). The spectra were recorded with the aid of two Hilger instruments, one a medium quartz spectrograph and the other a Littrow quartz spectrograph with greater dispersion and resolution. Using different specimens the spectra were recorded for three different orientations, *viz.*, (1) in which the exciting radiation was incident on a hexagonal face of the crystal and scattering was observed along the optic axis, (2) in which the optic axis was inclined at an angle to the plane of scattering and (3) in which the plane of scattering was perpendicular to the optic axis. With a slit width of 0.05 mm. exposures of the order of 100 hours were given to obtain spectrograms in

which even the faintest features are clearly recorded. From amongst the several spectra recorded we have chosen those corresponding to the first two orientations mentioned above and these are reproduced along with this paper to illustrate the numerous features that manifest themselves in the Raman spectrum of quartz. In addition, a number of microphotometer records on different scales of enlargement were obtained to reveal some of the finer features of the spectrum. Plate XV reproduces the spectra obtained with the Littrow instrument. Figure 1 in Plate XV corresponds to the orientation (1) when the scattering was observed along the optic axis, while Fig. 3 to the case (2) when the optic axis was at an angle to the plane of scattering. Figure 2 is the spectrum of the mercury arc reproduced for comparison. Plate XVI reproduces the microphotometer record (on a scale 1:4) of the spectrum shown in Fig. 3 of Plate XV. Plate XVII reproduces the spectra recorded with the medium spectrograph and Fig. 1 and Fig. 3 of this plate correspond to the same orientations of the crystal as those of Fig. 1 and Fig. 3 of Plate XV. Plate XVIII shows the microphotometer record (on a scale 1:8) of the spectrum in Fig. 3 of Plate XVII.

Fifteen frequency shifts constitute the principal features of the Raman spectrum of quartz. They are: 128 (*v.s.*), 206 (*v.s.*), 265 (*s*), 356 (*s*), 394 (*m*), 404 (*m*), 452 (*w*), 466 (*v.s.*), 696 (*m*), 795 (*m*), 806 (*m*), 1063 (*m*), 1082 (*m*), 1160 (*s*) and 1230 (*w*) cm^{-1} . The intensity of the lines, whether they are very strong, strong or moderate or weak are indicated within brackets. Of all the frequencies the 206 cm^{-1} shift may be seen (Plate XV) to be extremely broad. The most intense line of the spectrum, *viz.*, the line at 466 cm^{-1} has to its left and quite close, a rather weak line of frequency shift 452 cm^{-1} . This was first recognized by Cabannes and Bouhet (1937). It is clearly seen in Figs. 1 and 3 in Plate XV. An enlarged microphotometer record of this region of the spectrum reproduced as Fig. 1 in the text below clearly shows the line at 452 cm^{-1} to the left and on the shoulder of the line at 466 cm^{-1} .

A few other interesting features may be noticed in the spectra reproduced in Plates XV and XVII. The components of the doublet at 394–404, as well as those of the other doublet at 795–806, can be seen to exhibit striking variations in their relative intensities with different orientations of the crystal. In addition, the doublet separation of the pair of lines at 795 and 806 changes with the orientation of the crystal; *e.g.*, the separation in Fig. 3 of Plate XV may be clearly seen to be more than in Fig. 1 of the same plate. The frequency shift at 1082 cm^{-1} also exhibits a remarkable change in its intensity with different orientations of the crystal. While it appears to be almost of vanishingly small intensity in Fig. 1 (of Plates XV and XVII), it is of considerably greater intensity in Fig. 3 (of Plates XV and XVII).

Mathieu (1952) has reported the change in the intensity of the lines at 394, 404 and 1230 cm^{-1} for different orientations of the crystal, *viz.*, when the optic axis of the crystal is perpendicular to the plane of scattering and the

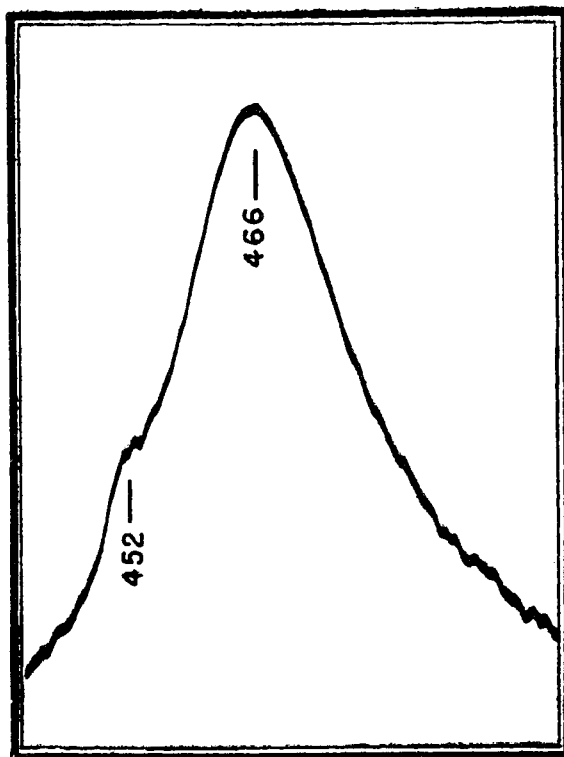


FIG. 1. Enlarged microphotometer record showing the Raman shift 466 cm^{-1} and the 452 cm^{-1} shift adjacent to it.

crystal is rotated about the optic axis to different positions. It was also noticed by him that the frequency shifts 404, 806 and 1230 cm^{-1} differ in their position for different inclinations of the optic axis with respect to the plane of scattering, the differences observed being 2 cm^{-1} for 404 cm^{-1} , 6 cm^{-1} for 806 cm^{-1} and 4 cm^{-1} for 1230 cm^{-1}

5. SUBSIDIARY FEATURES IN THE SPECTRUM

Numerous lines of low intensity appear in the Raman spectrum of quartz under prolonged exposures, as has already been noticed by Krishnan (1945). The present investigation has revealed a few new features in addition to confirming the majority of the lines already known. The present paper is mainly concerned with the necessity for a revision in the identification of the funda-

mental frequencies themselves. Naturally, these subsidiary features as well need a reinterpretation. A brief description of these features shall therefore be given.

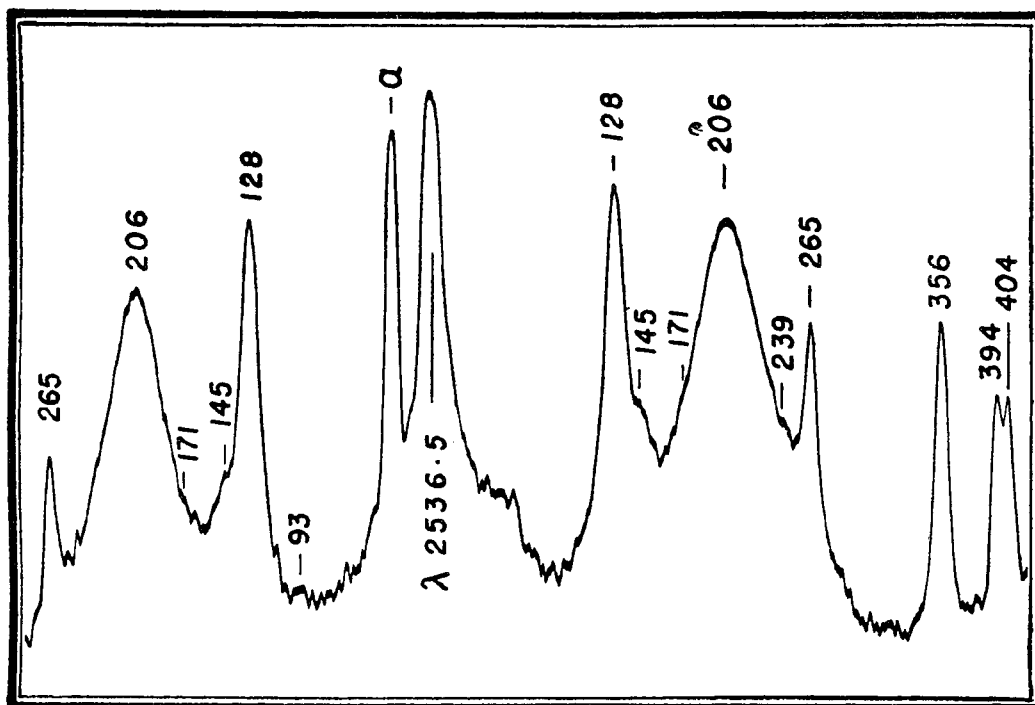


FIG. 2. Enlarged microphotometer record showing the Raman lines observed in the low frequency region.

In all, thirty-three frequency shifts at 93, 145, 171, 239, 435, 490, 509, 520, 541, 584, 728, 780, 828, 846, 867, 894, 903-908, 917, 924, 938, 947-952, 963, 978, 1046, 1269, 1291, 1361, 1381, 1420, 1435-1441, 1456, 1498 and 2129 cm^{-1} have been observed. The two low-frequencies at 26 and 39 cm^{-1} reported by Krishnan and Chandrasekharan (1945, 1950) could not be definitely confirmed by us owing to the presence in that region of the wing accompanying the $\lambda 2536.5$ radiation.

Several of these lines appear close to the stronger Raman lines, *viz.*, 128, 206, 466, 795, 806 and 1063 cm^{-1} . In particular, the line at 145 cm^{-1} appears with comparatively considerable strength close to the 128 cm^{-1} shift as can be seen from Plates XV and XVII and the microphotometer record in Plate XVI. The line at 509 cm^{-1} is quite clearly seen in Fig. 3 of Plate XVII

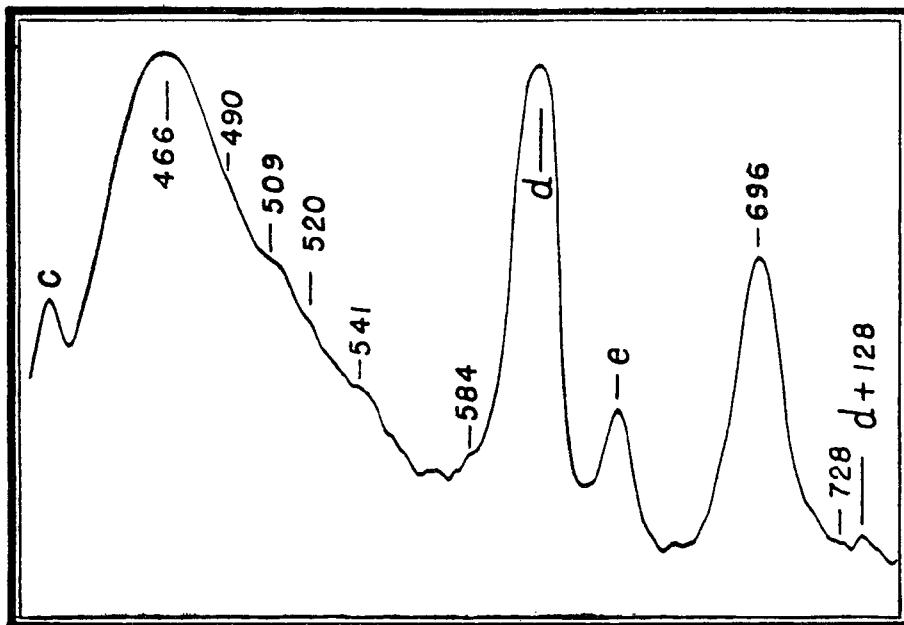


FIG. 3. Enlarged microphotometer record showing the 466 cm.^{-1} Raman line and other subsidiary features.

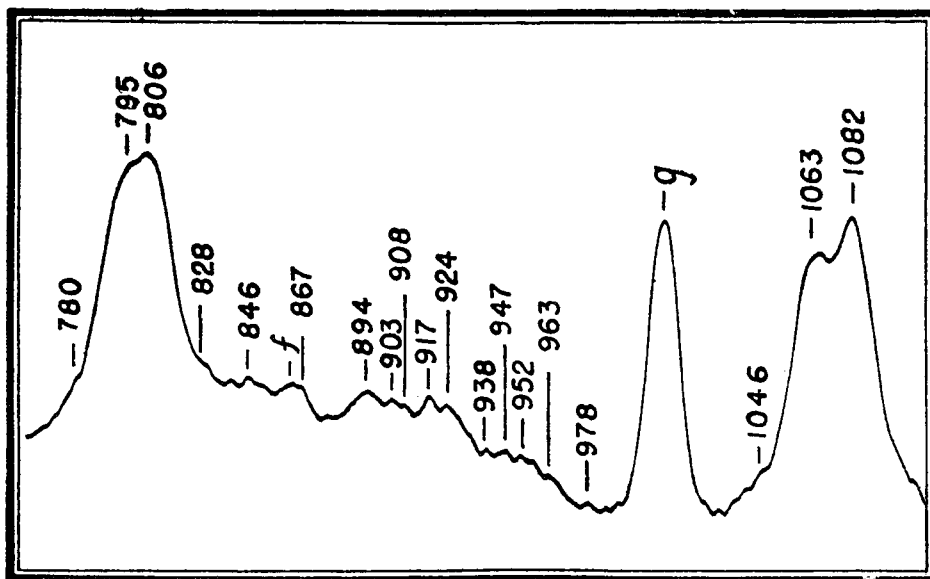


FIG. 4. Enlarged microphotometer record showing the numerous features in the region $750\text{--}1100\text{ cm.}^{-1}$

adjacent to and on the long-wavelength side of the intense Raman shift 466 cm.^{-1} . The comparatively weaker lines at 780 and 1046 cm.^{-1} close to the doublet $795\text{--}806$ and 1063 cm.^{-1} shift respectively, are indicated in the microphotometer record of Plate XVI. These and the remaining frequency shifts are clearly indicated in the enlarged microphotometer records appearing as Figs. 2, 3, 4 and 5 in the text and also in the microphotometer records of Plates XVI and XVIII.

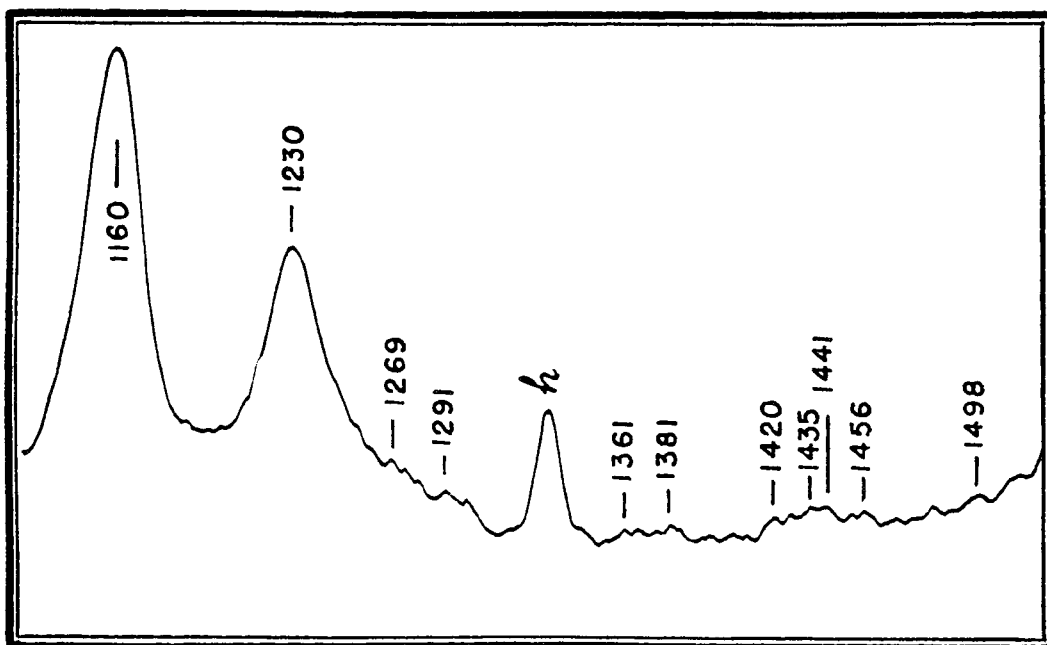


FIG. 5. Enlarged microphotometer record showing the several features observed in the range $1160\text{--}1500\text{ cm.}^{-1}$

The lines reported by Krishnan at 1596 and 1630 cm.^{-1} could not be confirmed since the anti-Stokes lines of shift 128 cm.^{-1} excited by the triplet of mercury lines at $\lambda 2652$, $\lambda 2653\cdot7$ and $\lambda 2655\cdot1$, fall in this region. The frequency shifts at 2225 and 2240 cm.^{-1} reported by Krishnan are believed to be respectively (1) the Stokes shift 466 cm.^{-1} excited by $\lambda 2655\cdot1$ of the triplet of mercury lines and (2) the anti-Stokes shift of 128 cm.^{-1} excited by the mercury line $\lambda 2698\cdot9$. The frequency shift reported by Krishnan at 2420 cm.^{-1} could not be confirmed owing to the presence in the mercury arc exactly at this point a line of wavelength $2702\cdot5\text{ A.U.}$

6. ANALYSIS OF THE RAMAN SPECTRUM

It may be seen from Table I that the 27 degrees of freedom belonging to the three SiO_2 groups in the unit cell are distributed under the three classes of vibrations A, B and E. Excluding the three translatory movements of the unit cell there are four vibrations each under the classes A and B, and eight under the doubly degenerate class E. We shall proceed straightaway to identify the frequencies appearing under each class.

(1) *Totally symmetric class A.*—The four frequencies under this class which are active only in the Raman effect should always exhibit complete polarisation owing to the vanishing of the transverse components of the polarisability tensor. The early studies of Cabannes and Bouhet (1937) and Michalke (1938) showed that the lines 206, 356 and 466 cm^{-1} exhibit almost complete polarisation. In these early studies the lines 1063 cm^{-1} and 1082 cm^{-1} , which are rather close, were unresolved. In addition, the line at 1082 cm^{-1} appears with very low intensity when the scattering is observed along the optic axis. By orientating the crystal so that the optic axis was perpendicular to the plane of scattering and using unpolarised light, Saksena (1940) found that for the 1082 cm^{-1} shift, the component parallel to the optic axis appeared strongly whereas the perpendicular component was absent. He also confirmed the findings of the earlier workers with regard to the polarisation of the lines 206, 356 and 466 cm^{-1} .

A new experimental method which made use of the optical activity of quartz to reveal the polarisation characters of the Raman lines was found by Chandrasekharan (1948). In this experiment, polarised exciting radiation was incident vertically along the optic axis of the crystal so orientated that its optic axis was parallel to the slit of the spectrograph. The scattered radiation was observed in a direction perpendicular to the optic axis. Due to the high optical rotatory power of quartz the vibration direction of the incident light vector would rotate and be parallel to the direction of observation at several points along the length of the optic axis, *i.e.*, after every 180° of rotation. The Raman lines that are completely polarised would have zero intensity at these points and hence would exhibit a characteristic banding along their length. The frequency shifts 206, 356, 466 cm^{-1} exhibit this feature. Owing to the vanishingly small intensity of the 1082 cm^{-1} shift in this orientation of the crystal, no observations could be made for this line by Chandrasekharan. Thus, it has been well established already that the four lines 206, 356, 466 and 1082 cm^{-1} belong to the totally symmetric class A.

(2) *The doubly degenerate class E.*—Contrary to the behaviour of the four frequencies under class A, the frequencies coming under the doubly

degenerate class E should appear depolarised in the Raman effect. In particular, when the incident electric vector is polarised parallel to the optic axis, the scattered light (of the E class frequency shifts) should have no component parallel to the optic axis since $\epsilon_{zz} = 0$. The detailed polarisation studies undertaken by Saksena (1940) revealed that the lines 128, 265, 394–404 (unresolved), 452, 696, 795–806 (unresolved), 1063, 1160 and 1230 cm^{-1} exhibit polarisation characters anticipated of lines coming under the doubly degenerate class. In particular, it may be mentioned that Saksena found that the weak line at 452 cm^{-1} is made much more evident by polarising the incident light or analysing the scattered light and thus diminishing the intensity of the adjacent 466 cm^{-1} shift. In agreement with the findings of Saksena, no characteristic banding was observed by Chandrasekharan (1948) in the case of the lines 128, 265, 394–404 (unresolved), 696, 795–806 (unresolved), 1063, 1160 and 1230 cm^{-1} (No banding should be exhibited by lines of the doubly degenerate class since the scattered intensity is the same irrespective of whether the incident light vector be parallel or perpendicular to the direction of observation).

We shall for the present consider in this analysis that the doublet 394–404 and 795–806 arise from single modes which have for some reason suffered a splitting. We identify the frequency shifts at 128, 265, 394–404, 452, 696, 795–806, 1063 and 1160 cm^{-1} as the eight fundamental vibrations coming under the doubly degenerate class. The polarisation characters of all the lines listed and their considerable intensity (except the 452 cm^{-1} shift) preclude any other explanation. The identification of the 452 cm^{-1} shift as a frequency coming under the class E finds additional support in the recent work of Reitzel (1955) on the infra-red reflection spectrum of quartz which reveals a very strong reflection maximum at 455 cm^{-1} in the ordinary ray. We shall presently consider the question of the explanation of the frequency shift at 1230 cm^{-1} .

These frequencies listed above under the degenerate class, being infra-red active in the ordinary ray, have been reported by different investigators. Simon and McMahon (1952) have, from a careful analysis of their data on the infra-red reflection of quartz, reported the frequencies 696, 795–802, 1065 and 1162, in close agreement with the observed Raman shifts. The frequencies 128 and 265 cm^{-1} were observed by Czerny (1929) and Barnes (1932) in the far infra-red transmission at 77μ and 38μ respectively. Liebisch and Rubens have reported a strong restrahlen band in the ordinary ray at 385 cm^{-1} in agreement with the value for the doublet at 394–404 cm^{-1} .

(3) *Anti-symmetric class B.*—According to theory (Table I), the four frequencies belonging to this class are forbidden in the Raman effect, but are infra-red active in the extraordinary ray. The important result of the present investigation is that these frequencies do appear in the Raman spectrum of quartz, though rather weakly. We identify the four frequencies at 145, 509, 780 and 1046 cm.^{-1} listed in Section 5 as the B class frequencies. The basis for this identification as well as the reasons for the appearance of these forbidden frequencies we shall now discuss. Making use of the symmetry co-ordinates derived by him for the vibrations of the A and B classes Saksena (1945) tried to calculate the frequencies under these classes using four force constants respectively due to (1) the changes in the silicon-oxygen bond lengths and (2) changes in the oxygen-oxygen distances and (3), (4) the changes in the bond angles at the oxygen and silicon atoms respectively. These were so chosen as to give a reasonable agreement with the observed frequencies of the A class. The calculated values came out as 195, 310, 508 and 1087 while the observed values are 206, 356, 466 and 1082 cm.^{-1} , a not unsatisfactory agreement. Using the same force constants the four B class frequencies were evaluated and came out as 149, 489, 809 and 1160 cm.^{-1}

A characteristic feature of the spectrum of quartz is the appearance of the stronger lines of the spectrum in groups in certain frequency ranges. For example, in the low-frequency region, there appear one A class line at 206 cm.^{-1} and two E class lines at 128 and 265 cm.^{-1} . We may therefore reasonably expect to find one B class frequency in this region. Saksena's calculated value of 149 cm.^{-1} for the lowest frequency therefore appears reasonable. Hence, the identification of the shift 145 cm.^{-1} appearing in the vicinity of the E class line 128 cm.^{-1} as a B class fundamental is justifiable. Further support for this assignment is forthcoming from the observation by Czerny (1929), Barnes (1932) and Plyler and Acquista (1955) in the infra-red transmission of quartz an absorption at $75\ \mu$ with specimens cut parallel and perpendicular to the optic axis, which is in tolerable agreement with the frequencies 128 and 145 cm.^{-1} assigned above for the E and B classes respectively. Some of the earlier investigators had chosen to regard a frequency at 364 cm.^{-1} observed in the *restrahlen* (extraordinary ray) by Liebisch and Rubens, as the lowest frequency in the B class. This may, however, be explained as arising from a combination of the 145 cm.^{-1} and 206 cm.^{-1} shifts. Such a combination would have the polarisation characters of a B class frequency and would therefore appear in the extraordinary ray.

The 509 cm^{-1} shift is another well-defined feature in the Raman spectrum of quartz noticed even by the early investigators using the less powerful $\lambda 4358$ radiation for the excitation of the Raman effect. The observation by Liebisch and Rubens in the *restrahlen* extraordinary ray a very strong maximum at 508 cm^{-1} justifies the identification of this shift at 509 cm^{-1} as a B class frequency. The observations of Liebisch and Rubens are supported by the recent studies of Reitzel (1955) who reports a strong reflection maximum in the extraordinary ray between 500 and 540 cm^{-1} .

The identification of the weak Raman lines observed at 780 and 1046 cm^{-1} respectively as the fundamental frequencies of the B class is supported by the infra-red data. A strong reflection maximum at 777 cm^{-1} in the extraordinary ray was reported by Reinkober. Recently also, Simon and McMahan (1952) from a detailed analysis of their reflection data report characteristic frequencies at 780 cm^{-1} and 1055 cm^{-1} in the extraordinary ray the accuracy claimed being $\pm 10 \text{ cm}^{-1}$.

The appearance of the frequencies of the B class in violation of the selection rules, admits of two explanations: (1) They become active in the Raman effect by reason of their contiguity to strongly active Raman frequencies and the fact of their thereby gaining dynamic characters analogous to the active Raman frequencies. (2) The selection rules have been derived assuming that all the silicon atoms are of the same mass and hence form an absolutely symmetric trigonal structure. Actually, however, the abundances of the silicon atoms are such that the silicons of atomic weight 28 form a proportion of only 92.3% of the total number, the remaining being 4.7% of Si^{29} and 3.0% of Si^{30} . A random distribution of these silicons of atomic weight 29 and 30 would in reality mean a departure from the trigonal symmetry of the crystal and hence would result in a certain amount of Raman activity for the B class vibrations.

7. COMBINATIONS AND OVERTONES

One of the principal features of the Raman spectrum of quartz that we have to explain is the 1230 cm^{-1} shift which exhibits the polarisation characters of an E class vibration. It is suggested that the frequency shift arises from the combination of the two fundamentals 780 and 452 cm^{-1} belonging respectively to the B and E classes. Such a combination would have the symmetry properties of the E class and hence would be Raman active, exhibiting the polarisation characters of that class. The intensity with which this combinational frequency shift is recorded is however rather surprising. The same frequency has been observed to be weakly active in the infra-red spectrum (Simon and McMahan, 1952).

The majority of the weak frequency shifts (referred to in Section 5) could be explained as combinations between the several fundamental frequencies. According to theory, all combinations, excepting those between the A and B class frequencies, are permitted to appear in the Raman effect. Also, all first overtones are active in the Raman effect. Table II shows the observed frequency shifts and their suggested origin.

TABLE II

| Observed Frequency Shifts in cm.^{-1} | Their Suggested Origin | Calculated Values |
|--|---|-------------------|
| 490 | 128+356 | 484 |
| 520 | 128+394-404 | 522-532 |
| 541 | 145+394-404 | 539-549 |
| 584 | 128+452 | 580 |
| 728 | 265+466 | 731 |
| 828 | 128+696 | 824 |
| 846 | 394-404+452 | 846-856 |
| 867 | 394-404+466 | 860-870 |
| 894, 903 and 908 | Overtone of 452 and its satellites and 394-404+509 | 903-913 |
| 917 | 452+466 | 918 |
| 924-938 | 128+795-806 and overtones of 466 cm.^{-1} and its satellites | 923-934 932 |
| 947-952 | 145+795-806 | 940-951 |
| 963 | 265+696; 452+509 | 961 |
| 978 | 466+509 | 975 |
| 1230 | 452+780 | 1232 |
| 1269 | 206+1063 | 1269 |
| 1291 | 509+780; 206+1082; 128+1160 | 1289, 1288 |
| 1361 | 206+1160 | 1366 |
| 1381 | ? | |
| 1420 | 265+1160 | 1425 |
| 1435-1441 | 356+1082 | 1438 |
| 1456 | 394-404+1063 | 1457-1467 |
| 1498 | 696+795-806 | 1491-1502 |
| 2129 | 2×1063 | 2126 |

It is rather surprising that the only overtone line observed is that at 2129 cm.^{-1} being the overtone of the 1063 cm.^{-1} shift. It is natural to expect that the intensely Raman active frequencies at 128, 206, 466 and 1160 cm.^{-1} and also the intensely infra-red active frequencies at 452, 509 and 1046 cm.^{-1} would manifest themselves as overtone shifts. But owing to various reasons most of them remain unobserved. The overtone of the 128 cm.^{-1} shift would

fall too close to the Raman line at 265 cm.^{-1} to be detected. Similarly, the overtone of the 206 cm.^{-1} line would be too near the Raman doublet $394\text{--}404$ to be observed.

The overtones of the frequency shifts at 466 and 452 cm.^{-1} should, however, have been clearly observed but for the fact that this region of the spectrum exhibits numerous combinational shifts. The only relevant feature with regard to these overtones is the presence in the microphotometer records of the spectrum of bands of low intensity at 894 , 903 , 908 and $924\text{--}938\text{ cm.}^{-1}$. The overtones of the Raman shifts 452 and 466 cm.^{-1} and their satellites would appear at precisely this region. The overtone of the B frequency at 509 cm.^{-1} escapes detection owing to the presence of the mercury line $\lambda 2603.2$ at about the point of its appearance. The appearance of the overtone of the frequency 1046 cm.^{-1} could not be established owing to its falling in the region where the Raman shifts of 356 and $394\text{--}404\text{ cm.}^{-1}$ excited by the triplet of mercury lines appear. The overtones of all other frequencies are presumably too weak to be observed.

In addition to the frequencies listed in Table II, there are others at 93 , 171 , 239 and 435 cm.^{-1} and those reported by Krishnan and Chandrasekharan at 26 and 39 cm.^{-1} . These cannot reasonably be explained as combinational shifts. Their appearance in the vicinity of intensely active Raman lines (excepting those at 26 and 39 cm.^{-1}) suggests that they represent the modes of vibration of the super-cell and belong to the $21 p$ class. Though these modes are theoretically forbidden to appear, their close approximation in frequency to strongly active modes and (or), their possessing similar dynamical characters would result in their becoming weakly active in the Raman effect. It is also noteworthy that two bands at 82 and 95 cm.^{-1} were observed by Barnes (1932) in the far infra-red transmission of quartz.

8. SOME GENERAL REMARKS

We shall consider in this section the probable explanation of some of the most striking features observed in the Raman spectrum of quartz.

The frequency shift 466 cm.^{-1} is by far the most intense of all, though the frequency shift 206 cm.^{-1} approximates to it closely: by reason of its diffuseness at ordinary temperatures, its intensity appears less than it would otherwise have been. Both of these frequency shifts belong to the totally symmetric class and hence their great intensity is *prima facie* not surprising. But why they should transcend so greatly in intensity the two other A class frequency shifts 356 and 1082 cm.^{-1} is not so clear. It may be suggested that both of these modes (206 and 466 cm.^{-1}) involve large changes of the silicon-

oxygen bond-lengths, but that at the same time their frequencies are rather low by reason of the atomic movements being notably inclined to the directions of these bonds. It may be remarked in this connection that in β -quartz which is the high temperature form, only one vibration of the A class survives. From the observations of Narayanaswami (1948) it would appear that it is the 466 cm.^{-1} shift of α -quartz which is carried over and appears at 453 cm.^{-1} in β -quartz. The enormous broadening of the 206 cm.^{-1} frequency shift with rise of temperature and its ultimate disappearance are clearly attributable to the progressive alteration in structure which precedes the transformation at 575° C. ; the extreme diffuseness of the line may be attributed to the anharmonicity of the vibration concerned.

A noteworthy feature of the vibration spectrum of quartz which is emphasized by the present investigation is that all the four B class frequencies appear in close proximity to four out of the eight E class frequencies. It is also noteworthy that the infra-red activities of the vibrations of contiguous frequencies which appear in the extraordinary and ordinary ray are also quite comparable. It appears reasonable to suggest that this feature is in some way connected with the approximately tetrahedral configuration of the four oxygen atoms around the silicon atom to which they are linked.

Finally, mention should be made of the doublets $394\text{--}404$ and $795\text{--}806\text{ cm.}^{-1}$ both of which belong to the E class. Various explanations have been or could be suggested for this doubling and the special features exhibited by the components of the doublet in each case. Comments on these explanations are reserved till the author has had an opportunity of making a fuller examination of the subject.

The author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in this work.

9. SUMMARY

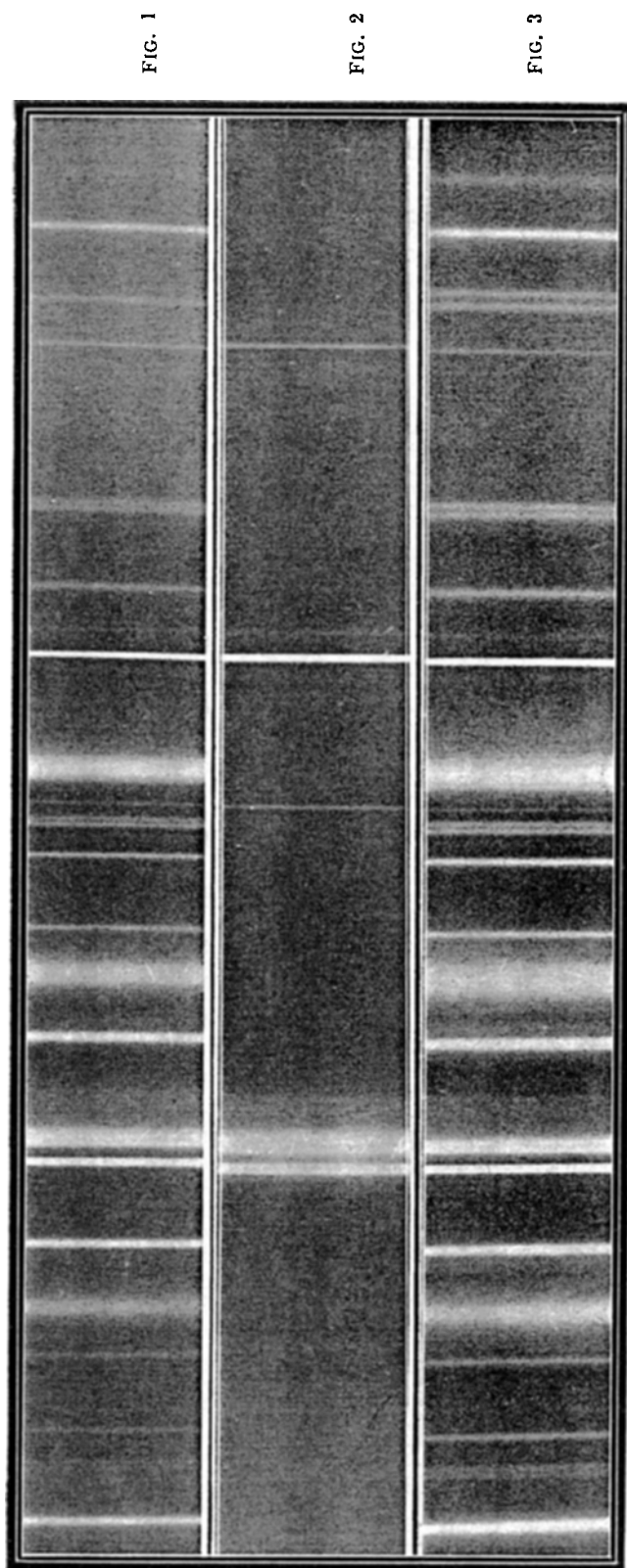
The Raman spectrum of α -quartz has been re-investigated with a view to obtain the complete spectrum and the results have been correlated with the recent infra-red data. In addition to fifteen principal frequency shifts, thirty-three other subsidiary features of low intensity are observed in heavily exposed spectrograms. These features are illustrated in the paper by microphotometer records on an enlarged scale.

The following Raman shifts are identified as the fundamental frequencies: (1) A class: $206, 356, 466$ and 1082 ; (2) B class: $145, 509, 780$ and 1046 ; (3) E class: $128, 265, 394\text{--}404, 452, 696, 795\text{--}806, 1063$ and 1160 cm.^{-1}

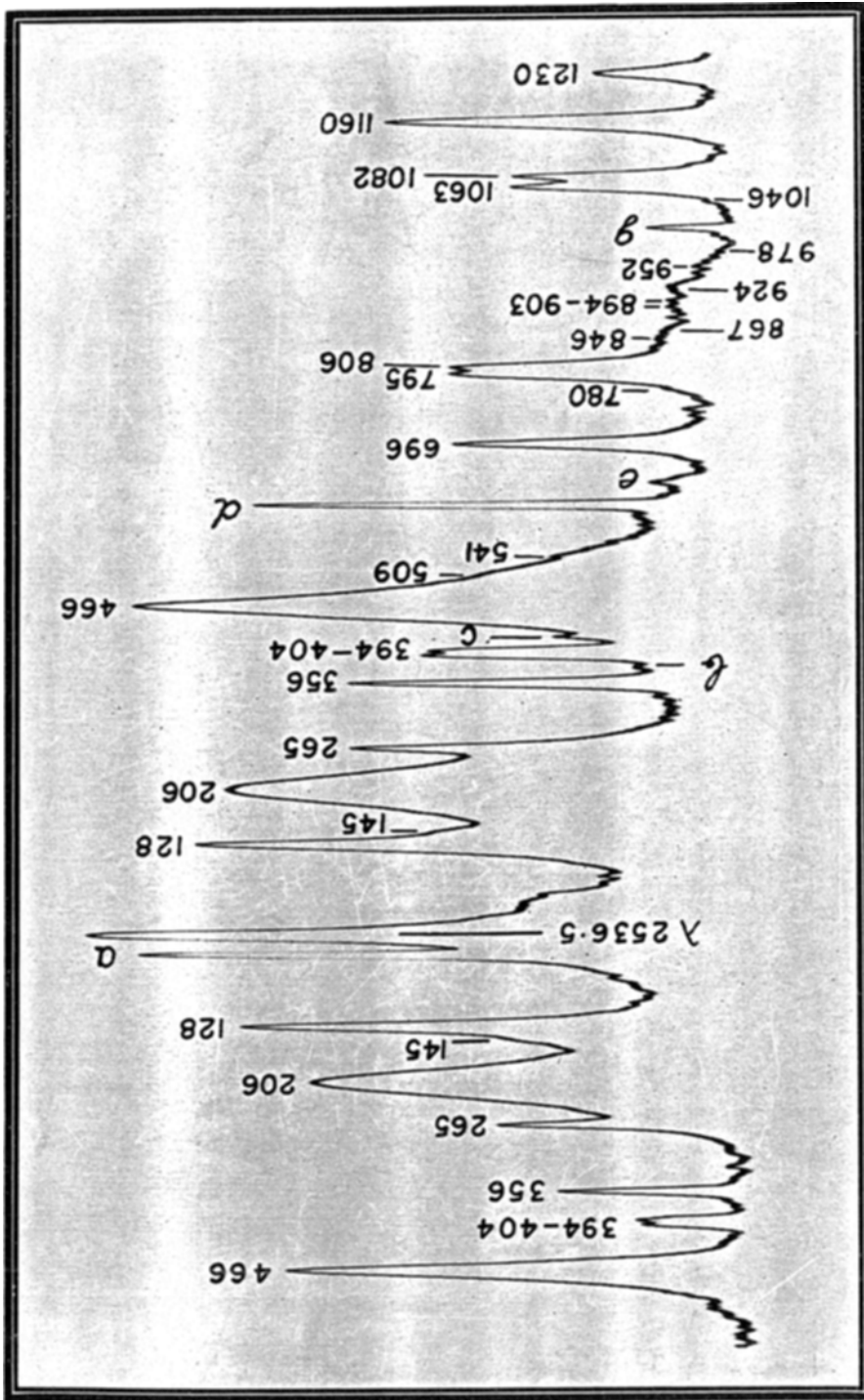
It is noteworthy that all the four B class fundamentals appear weakly in the Raman effect in violation of the selection rules. The numerous subsidiary features are explained as permissible overtones and combinations of the above fundamental frequencies.

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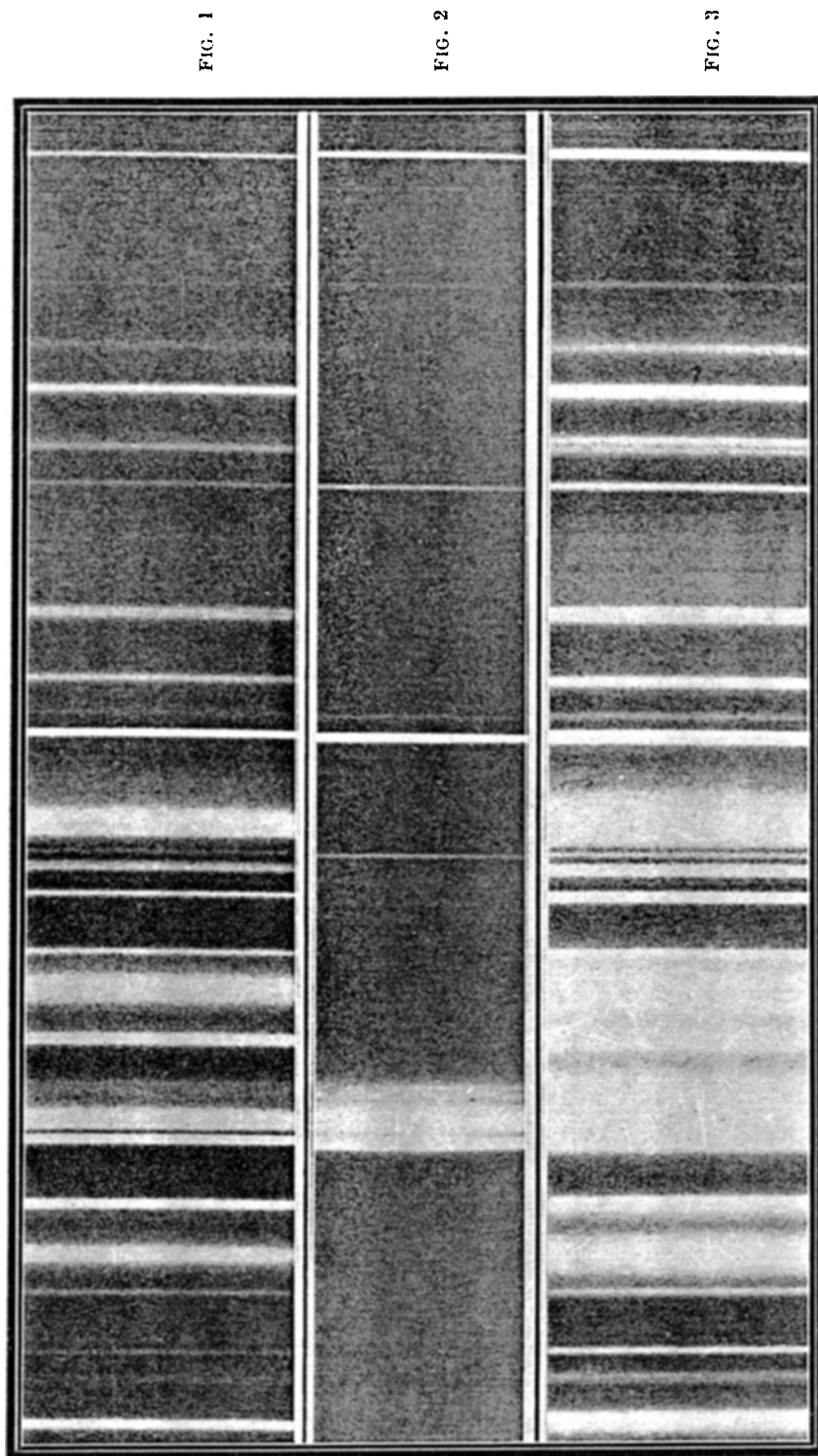
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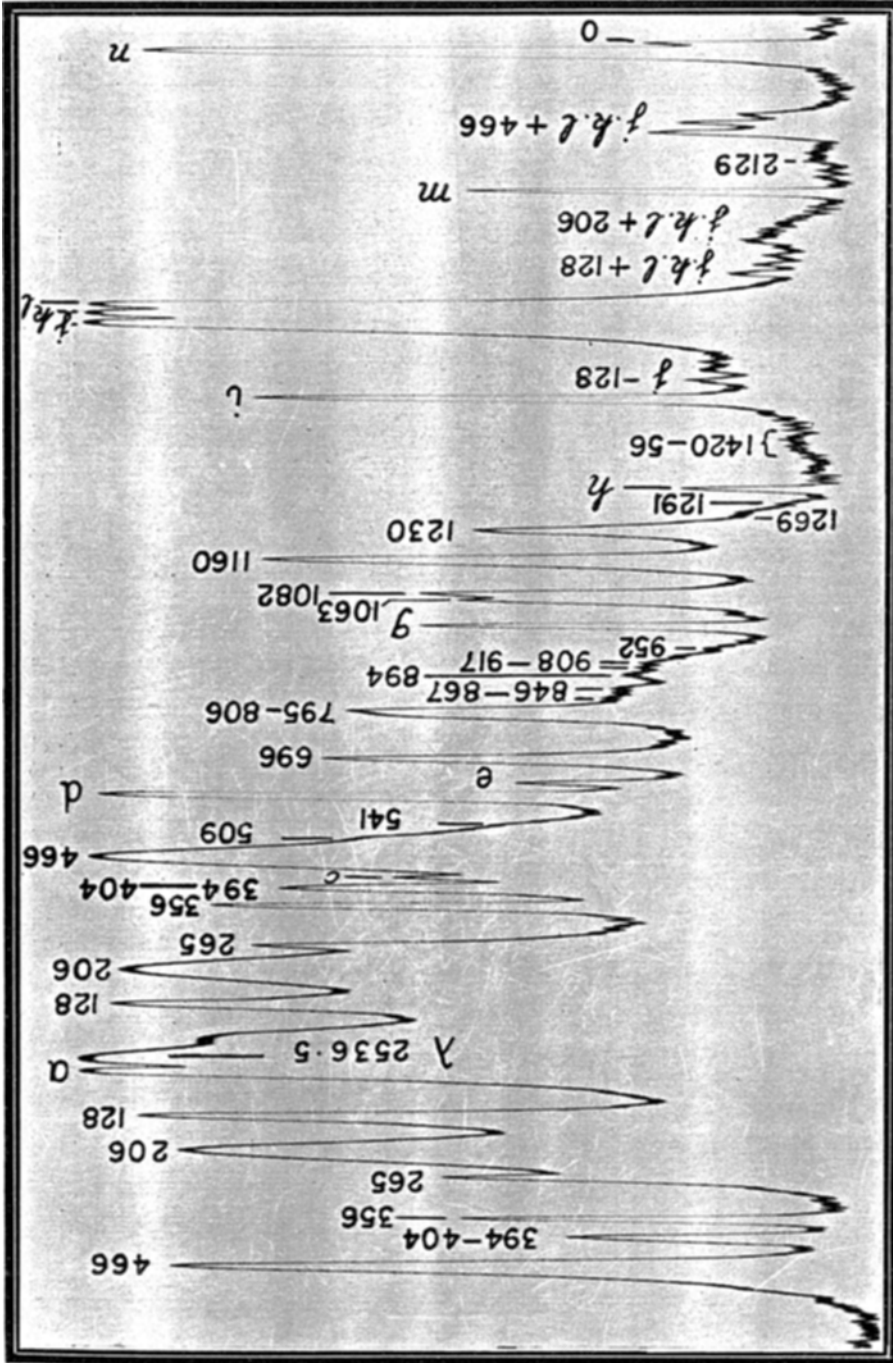
Figs. 1 and 3. The Raman spectrum of quartz recorded with Littrow spectrograph for two different orientations of the crystal.
Fig. 2. Spectrum of the mercury arc.



Microphotometer record of the Raman spectrum of quartz recorded with the Littrow spectrograph.
 Note.—The numbers denote the Raman shifts in cm^{-1} while α , β , γ , δ , ϵ , etc., refer to the mercury arc lines.



Figs. 1 and 3. The Raman spectrum of quartz recorded with the medium quartz spectrograph for two different orientations of the crystal. Fig. 2. Spectrum of the mercury arc.



Microphotometer record of the Raman spectrum of quartz recorded with the medium quartz spectrograph.