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B.Sc., University of Madras, India

FRIDAY, SEPTEMBER 27, 1957, AT 3:00 P.M.

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THE RELATIVE INTENSITIES OF THE POLARIZED COMPONENTS OF THE SYMMETRIC RAMAN LINE OF CALCITE.

ABSTRACT

The theory of the Raman Effect in crystals has been re-examined by O. Theimer (Can. J. Phys. 1956, 34 312) in an attempt to overcome some discrepancies between experimental results and predictions of the theory. New selection rules have been derived by investigating the validity of the assumptions made in the earlier theory.

The new theory, applied to the symmetric Raman line of Calcite, predicts that, for the crystal orientated with its optic axis parallel to the illuminated surface, the "forbidden" component will be truly forbidden for forward or backward scattering, while appearing as previously reported for scattering at 90°.

The present investigation is concerned with measuring the relative intensities of the polarized components of this line for backward scattering, the measurements being made with the crystal orientated with its optic axis either parallel or perpendicular to the illuminated surface.

A method for increasing the scattering volume by joining several crystals along cleavage faces has been developed and a new mercury discharge lamp was designed which gave an appreciable increase of the illumination intensity. The relative intensities of the components of the symmetric Raman line obtained were evaluated by careful consideration of the characteristics of the photographic emulsion used to record them.

The results tend to confirm the predictions of the new theory.
"On the Construction of Large Nuclear Emulsion Block Detectors"

GRADUATE STUDIES

FIELD OF STUDY: PHYSICS

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Elementary Quantum Mechanics..................................G. Volkoff
Theory of Measurement.............................................A. M. Crooker
Nuclear Physics......................................................K. C. Mann
Electromagnetic Theory............................................J. R. H. Dempster
Molecular Spectroscopy............................................O. Theimer

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Numerical Analysis................................................F. H. C. Goodspeed
THE RELATIVE INTENSITIES OF THE POLARIZED COMPONENTS OF THE SYMMETRIC RAMAN LINE OF CALCITE.

by

GERHART BRUNO FRIEDMANN

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy in the Department of Physics

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
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Department of Physics

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Date September 27, 1957.
INTRODUCTION

The theory of the Raman effect in crystals (Placzek 1934, Born and Bradburn 1947, Smith 1948, Theimer 1951) is not confirmed by the experimental results reported for polarization studies of the spectrum of Calcite and other crystals.

In an attempt to reconcile the conflicting data, Theimer (1956) has analysed the assumptions made in arriving at the theoretical predictions. By removing some of the limitations these assumptions involve, a new approach can be made to the selection rules governing the Raman effect in crystals.

One prediction of the new theory is that the depolarization $p$, defined as the ratio of the intensity of component polarized in a vertical plane, to that of the component polarized in a horizontal plane, will be different from unity for forward or backward scattering from Calcite orientated with its optic axis perpendicular to the incident beam. Only when the scattering is from a crystal with its optic axis parallel to the beam will the depolarization $p$ be unity; this latter being the general condition for the earlier theories.

The present investigation is concerned with measuring the relative intensities of the polarized components of the symmetric Raman line in Calcite for backward scattering, the crystal being provided with faces parallel, perpendicular and at $45^\circ$ to the optic axis respectively. A lamp developed for the particular conditions of the experiment is described, as is a comparator built after the description of Tomkins and Fred (1951) and Dieke et al (1956), which was used in evaluating the results.

For the several orientations reported on, and within the limits of accuracy of the experiment, $p$ is unity. A value of $p = 3/2$ could certainly have been detected.
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CHAPTER I.
THE THEORY OF THE RAMAN EFFECT IN CRYSTALS

Since its experimental discovery in 1928 (Raman 1928, Landsberg and Mandelstam 1928), the Raman effect has become an important tool in many branches of physical research. The major part of the work in this field has been devoted to liquids, but several hundred papers dealing with solids have been published (Menzies, 1953). On the experimental side important advances were made with the introduction of the powder technique which allowed Raman spectra to be obtained from other than large single crystals (Baer 1929b, Menzies 1929); and by the use of complementary filters (Gerlach 1930, Anantakrishnan 1937) to select and eliminate the monochromatic illumination as desired within certain regions of the spectrum. Menzies (1953) however, stresses that for polarization determinations in Raman spectroscopy, only single crystals can be used. This requirement has sharply limited the study of polarisation to such crystals as can be obtained in sufficiently large blocks. The two structures most commonly studied are Quartz and Calcite. Indeed, the original communication of Landsberg and Mandelstam (1928) is based on studies with Quartz.

In a general way a Raman line may be regarded as the result of an impinging quantum of frequency $v$ exchanging energy with a molecule in accordance with the scheme (Bhagavantam 1940 b, Ch XI):

$$\text{Molecule } + \ h\nu \rightarrow \text{Molecule } + \ h\nu'$$

causing a quantum of frequency $v'$ to be emitted. The exchange of energy may go either way - thus causing Stokes Raman lines ($v' < v$) or anti-Stokes Raman lines ($v' > v$); only discrete energy values can be exchanged, characteristic of the molecular eigenstates.

Mathematically, this general consideration can be most simply expressed by assuming an incident electric field $E \sin 2\pi \nu t$ inducing an oscillatory electric field $aE \sin 2\pi \nu t$ in the molecule. If now some mechanism intrinsic in the
molecule periodically alters the emitted wave with a frequency \( v'' \), the electric moment of the oscillator at any instant can be written as

\[
aE \sin(2\pi vt) \cos(2\pi vt + \epsilon) \cdot \frac{1}{2} aE \left[ \sin\left\{ 2\pi (v + v') t + \epsilon \right\} + \sin\left\{ 2\pi (v - v') t - \epsilon \right\} \right]
\]

and there results the three possible frequencies \( v - v' \), \( v \) and \( v + v' \) in the emitted light.

The earliest theory applying these general ideas to crystals was developed by Mandelstam and co-workers (Mandelstam, Landsberg and Leontowitz, 1930a, 1930b). Their calculations are based on changes occurring in the dielectric tensor for the crystal. It was possible to derive a symmetric tensor from the eigenvectors of the oscillations induced in the lattice, and thence predict the intensities of Raman lines as well as their polarizations. For the totally symmetric line 1087 cm\(^{-1}\) in Calcite, the theory predicted

\[
P_x = P_y = P_z = 0
\]

where \( p_i \) is the depolarization obtained when the optic axis of the crystal lies along the \( i \) axis (\( i = x, y, z \)), and the scattered light is viewed at 90\(^\circ\) to the incident beam.

A more general theory of the Raman effect has been developed by Placzek (1934). On this theory, scattering is due to electronic movements. Because of the large mass difference between nuclei and electrons, any vibrations are not likely to affect the position of the nuclei. However, (Placzek 1931) the Raman shifts are ascribed to nuclear transitions.

The Placzek theory assumes that the polarizability \( a \) is characteristic of the influence of electrons on the nucleus. \( a \) will then be affected by nuclear vibrations. Furthermore, nuclear motion is slow compared to electronic motion, and compared to the frequency of light. It follows that only
the nuclear coordinates will be factors in changes of $a$.

If the polarizability, expressed as a function of normal coordinates $Q_i$, is expanded about the equilibrium value

$$a(Q_1 \ldots Q_n) = a_0 + \sum (\frac{da}{dQ_i})_0 Q_i + \sum (\frac{da^2}{dQ_i^2})_0 Q_i^2$$

and the nucleus allowed to vibrate thus making the $Q_i$ time dependant, it is shown that, for an incident electric wave $E e^{2\pi i vt} \cdot E$, the induced moment $M = aE$ can be obtained:

$$M = E a_0 e^{2\pi i vt} + \sum (\frac{da}{dQ_i})_0 \sqrt{C_i} \left\{ n_i - 1 \exp [2\pi i (v-v_i)t - \phi_i^{v+1}v] \\
+ \sqrt{n_i} \exp [2\pi i (v+v_i)t + \phi_i^{v-1}v] \right\}$$

where $C_i = \hbar/4m_i v_i$, $n_i$ are quantum numbers, $m_i$ reduced masses of the nuclei, and $\phi$ are phase terms.

The Raman terms arise due to changes $d_n$, following certain selection rules.

The polarizability is most generally a tensor. The $\frac{da}{dQ_i}$ of equation (1) form a symmetric tensor; this tensor contains information about the intensity and polarization of Raman scattering. The selection rules derived by Placzek are determined by the symmetry of the molecule, and the eigenfrequencies derived from it.

In particular, Michalke (1938) quotes the results of applying the theory to Calcite, illuminated with natural light along direction $x$ and observed along the perpendicular direction $y$. In this case the components of the light are $E_x = 0$, $E_y = E_z$. Assuming the axes fixed in space, and the value of $M$ to give the intensities, it is then shown that
(3) \( I_x = \text{Const} \left[ da^2_{yx} E^2_y + da^2_{zx} E^2_z \right] \)

(4) \( I_z = \text{Const} \left[ da^2_{yz} E^2_y + da^2_{zz} E^2_z \right] \)

thus, the depolarization \( p = I_x/I_z \). Introducing a set of axes \((1,2,3)\) fixed in the crystal as indicated in diagram \( F \), page 9, and letting the axis 3 (the optic axis) successively coincide with \( x, y, \) and \( z \), then:

(5) \[
\begin{align*}
P_x &= \frac{C_{13}^2 + C_{23}^2}{C_{12}^2 + C_{22}^2} \\
P_y &= \frac{C_{32}^2 + C_{12}^2}{C_{31}^2 + C_{11}^2} \\
P_z &= \frac{C_{21}^2 + C_{31}^2}{C_{23}^2 + C_{33}^2}
\end{align*}
\]

\((x = 3, y = 1, z = 2)\)

where the \( C_{ik} \) refer to the tensor components \( da \) in \((1,2,3)\).

The selection rules of Placzek, when applied to the \( C_{ik} \), will then predict the values of \( p_i \). For the vibration 1087 cm\(^{-1}\) in Calcite, #

(6) \[
\begin{align*}
C_{ik} &= 0, \quad C_{11} = C_{22} + C_{33}, \\
P_x &= P_y = P_z = 0
\end{align*}
\]

Though this agrees with the earlier theory, the result contradicts the experimental values (Table 2:II page 12).

The Placzek theory has been elaborated for the special case of crystals by Born and his co-workers (Born and Bradburn 1947, Smith 1948, Theimer 1951, 1955, and 1956). In an analysis of this application of the theory, Theimer (1956) has drawn attention to the assumptions on which it is based, in an effort to find a solution to the discrepancy between the experimental and theoretical results.

# In Chapter 2 the structure of Calcite and assignment of Raman frequencies is dealt with.
The selection rules of the theory, as we have seen, yield information concerning the polarization. It becomes apparent that for Calcite, and similar crystals, these break down. Some of the tensor components \( a_{ik} \) that should vanish have, in fact, finite values, such that the polarized components forbidden by the above theory is of the same order as the allowed one.

The extended Placzek theory takes no account of the directions of the incident and scattered light in the crystal. All properties result from the transformations of the \( a_{ik} \).

By dropping the simplifying assumptions of the theory: that \( M \) and \( a \) are considered to be the sum of the contributions of the individual atoms; and that \( a \) is a characteristic property of the electronic ground state of the scattering crystal, depending on the incident light only through a resonance denominator; a new set of selection rules can be developed.

The forbidden polarized component is now no longer due to anharmonicities in the crystal structure (Born and Bradburn 1947). The polarizability must take account of the forces between the atoms themselves as well as the forces between the "free" electrons in the crystals. In other words, the electrons in non-localized orbitals are taken to account for the forbidden component. It turns out that the selection rules for these electrons, as opposed to the selection rules for localized orbitals, show strong dependence on the orientation of the crystal with respect to the incident light.

Applied to Calcite, the theory shows, for scattering at 90°,

\[
\begin{align*}
P_x &= \frac{C_{13}^2 + C_{23}^2}{C_{12}^2 + C_{22}^2} \\
P_y &= \frac{C_{12}^2 + C_{31}^2}{C_{22}^2 + C_{23}^2} \\
P_z &= \frac{C_{12}^2 + C_{31}^2}{C_{23}^2 + C_{33}^2}
\end{align*}
\]

The \( C_{ik} \) computed from equation (7) and Table 2:II (page 12) are
(8) \[ C_{23}^2 = C_{31}^2 = 0 \quad C_{12}^2 = .4 \quad C_{22}^2 = 1 \] (3 parallel to x or y)

\[ C_{23}^2 = C_{31}^2 = 0 \quad C_{12}^2 = .048 \quad C_{33}^2 = .25 \] (3 parallel to z)

It was suggested that a measurement be made for the polarized components of the Calcite line 1087 cm\(^{-1}\) for scattering at 0 or 180°. For such an experiment, the new theory predicts, in agreement with the earlier theory, that the depolarisation \( p = 1 \) when the light is scattered along the optic axis (Diagram A, page 7). However, for the case of scattering perpendicular to the optic axis (Diagram B, page 7), the new theory predicts a depolarisation \( p \neq 1 \), whereas the older theory predicts \( p = 1 \). Finally, for the case shown in Diagram C (page 7), the new theory, as opposed to the earlier one, again predicts \( p \neq 1 \).

The experimental arrangement for a scattering experiment at 180° is more advantageous as compared with an arrangement at 0°, mainly because, as will be described later, this method of attack permits the light source providing the incident beam to be shielded from the recording spectrograph. Accordingly, the present investigation was pursued in an attempt to measure the polarizations of the components of the totally symmetric \( ^{\text{2}} \text{aman} \) line of Calcite.
Diagram A: Schematic: Crystal with optic axis parallel to y.

Diagram B: Schematic: Crystal with optic axis at 45° to y.

Diagram C: Schematic: Crystal with optic axis perpendicular to x.
The structure of Calcite

Two broad types of crystal structure are recognized (Born and Goeppert Mayer 1933): 1) those whose structure can be determined solely through a knowledge of the unit cell volume and the symmetry conditions satisfied by the cell; and 2) those that require additional parameters. To this latter, non regular, lattice type belong many two metal carbonates, and also Calcite.

For non-linear molecules it is convenient to consider the dimensions separately from the symmetry properties; the two together provide the basis for the theory of non-linear molecular structure (Herzfeld 1933).

The rhombic unit cell of Calcite, CaCO$_3$ is obtained from a regular cubic cell through an elongation of the axis (Born and Goeppert Mayer 1933) caused by the carbonate ion. The CO$_3$ ion itself, which forms a compact group in the Calcite lattice, is assumed to be in the form of a plane equilateral triangle, the three oxygen atoms being at the vertices and the carbon atom at the centre. Two such ions lie on the axis of the rhomb formed by calcium atoms at its corners. To specify the rhomb, the additional parameter $\alpha$, the angle between a carbon atom and its nearest two calcium atoms is required. (See Diagram 0, page 9). On the assumption that the carbon is C$^{+++}$, the oxygen O$^{--}$ and the calcium Ca$^{++}$, Bragg and co-workers (Bragg et al 1924, Chapman et al 1926), using X ray scattering data, have calculated this parameter for Calcite: $\alpha$: 120°4' from the C-O distance of 1.25 Å and an assumed charge separation of C$^{+++}$-O$^{--}$ = 0.92Å. The observed value is $\alpha_{obs}$=101°55'.

Brester (1923) has dealt with the plane carbonate ion. It
Diagram 0: Unit cell and Rhomb of CaCO₃

Diagram E: Atoms on Rhomb of CaCO₃

Diagram F: Planes normal to optic axis in Rhomb of CaCO₃ above.
belongs to the point group $D_{3h}$, that is (Herzberg 1945, page 8) the ion has a three-fold axis of symmetry ($C_3$), three vertical planes of symmetry ($3C_v$) at $60^\circ$ to each other through it, and one horizontal plane of symmetry ($C_h$) perpendicular to the $C_3$ axis. There are also three two-fold axes ($3C_2$) which follow from these symmetry elements. Of the six vibrations (Herzberg 1945 Chapter 2) that may arise, only the infra-red inactive vibration will appear in the Raman effect (Herzfeld 1933).

The Calcite lattice is rhombohedric and belongs to the point group $D_{3d}$. The symmetry elements in this case are (Herzberg 1945, page 8) one $C_3$, $3C_2$, $3C_v$ bisecting the angles between successive two-fold axes and going through the three-fold axis; and as a consequence to these elements, there are also two 6 fold rotation reflection axes ($2S_6$) coinciding with $C_3$, and a centre of symmetry (i). Thus, there are 12 symmetry elements. To these elements correspond six oscillations (see Appendix 1), of which four are internal, the remaining two being external vibrations.

The unit cell of Calcite is related to the cleavage rhomb as indicated in Diagram D (page 9), the atoms being situated as shown in Diagrams E and F (page 9).

Experimental

The experimental material on Calcite may be easily summarised: Studies on infra-red absorption have revealed bands at 7, 11 and 14 $\mu$. Polarization measurements have shown (Nywater 1909, Schaeffer and Schubert 1916) that only the band at 11 $\mu$ vibrates perpendicular to the plane of the CO$_3^{--}$ ion, the other two bands vibrating in the plane.

The bands at 7 and 14 $\mu$ are not single (Brester 1924, Schaeffer 1929). The reasons for their structure have not been finally explained though it may perhaps be assumed that the CO$_3^{--}$ ion is in actuality not completely plane (Herzfeld 1933).
In the Raman spectrum, six lines have been identified and related to the infra red absorption lines (Daure 1929, Cabannes 1929, Schaeffer 1930, Matossi 1944). They are divided into internal and external lines; the internal ones being found in all carbonates as the manifestation of oscillations of the carbonate ion.

The internal lines are accordingly identified as in Table 2:I

<table>
<thead>
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<td>INTERNAL EIGEN-FREQUENCIES OF CALCITE</td>
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| Raman       | 714 cm\(^{-1}\) | 1087 cm\(^{-1}\) | 1438 cm\(^{-1}\) | 1741 cm\(^{-1}\) |
| Infra-red   | 13.99 \(\mu\)   | 11.38 \(\mu\)   | 6.96 \(\mu\)     |
| \(W_3\)     | \(W_1\)         | \(W_4\)         | \(W_2\)          | \(W_4 + W_3\) |

The assignment of \(W_4\): 1087 cm\(^{-1}\): 9.19 \(\mu\), the strongest Raman line in Calcite, as well as the assignment of \(W_4 + W_3\): 1741 cm\(^{-1}\): 5.75 \(\mu\) was arrived at before the spectrum was obtained, on theoretical grounds (Schaeffer et al 1926); the absence of \(W_1\): 870 cm\(^{-1}\): 11.38 \(\mu\) in the Raman spectrum is due to symmetry conditions.

Polarization Experiments

As will be evident from the arguments in Chapter 1, study of the polarization of Raman lines in crystals, together with the considerations above, yields information about the crystal structure, while also permitting some of the conclusions reached in the theoretical formulation of the basis of the Raman effect to be checked.

The experimental data reported in several publications (Cabannes 1929, 1931, Schaeffer et al 1930, Matossi 1936, Osborne 1933, Michalke 1938, Bhagavantam 1940a) is summarized in Table 2:II (Matossi 1944, Ebert 1951). All the measurements are for scattering at 90° to the incident beam. There are serious discrepancies, especially for the totally symmetric vibration 1087 cm\(^{-1}\).
# TABLE 2:11

## POLARIZATION MEASUREMENTS FOR CALCITE

<table>
<thead>
<tr>
<th>Raman Line cm(^{-1})</th>
<th>Natural Incident light</th>
<th>Observer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(P_x)</td>
<td>(P_y)</td>
</tr>
<tr>
<td>156 (Eg)</td>
<td>4.5</td>
<td>1</td>
</tr>
<tr>
<td>283 (Eg)</td>
<td>4.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
<td>1</td>
</tr>
<tr>
<td>714 (Eg)</td>
<td>0.4</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>1087 (Aig)</td>
<td>0.04</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>1437 (Eg)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1749 (Aig)</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Note** \(P_i = I_x/I_z\) and \(i\) indicates the direction of the optic axis.

\(I_j\) is the intensity along \(j = x, z\).
A careful analysis of the data was made by Matossi (1937) and again by Michalke (1938), in an attempt to find the cause for these discrepancies and for the contradictions between the results in general and the theoretical predictions. More recent experiments (Couture 1947, Giulotte and Olivetti 1948, Agnard 1952) have not resolved the difficulty.

As can be seen from the table, agreement in the case of the 1087 cm\(^{-1}\) line occurs only for the case of \(P_x\): the optic axis of the crystal parallel to the x axis, light scattered along the y axis. In the case of \(P_y\) and \(P_z\), the values quoted by Schaeffer have been revised (Michalke 1938) by considering faults in the apparatus used for the measurements: the revised values are then in agreement with those of Michalke; but they conflict with the earlier values of Cabannes. The values found by Couture (1947) agree with those of Michalke. However, all results conflict with the requirements of the Placzek theory,

\[
P_x : P_y : P_z : 0.
\]

Michalke is quite definite on the point that the results cannot be due to errors in experiments or measurements. He sees the discrepancy as due to the approximate nature of the theory as applied to crystals at that time.
CHAPTER 3
THE APPARATUS

The Spectrograph

A glass spectrograph of f/10 was available in the Department. The details of this instrument are as follows (MacDonald 1948):

60° Prism of EDF 649338 flint glass, 11 cm face height. Collimator 11.5 cm aperture flint crown achromat by Carl Zeiss, Jena, of focal length 167.5 cm. Camera: Telestigmat lens of 100 cm focal length, 11 cm aperture and f/7 by Bausch & Lomb, Rochester. Slit 0.7 mm maximum in steps of 0.02 mm.

The prism of this instrument was at the minimum deviation for mercury 4358 Å and the optimum slit width (Baly 1929) $s = 2f \frac{\lambda}{A} = 0.02$ mm, $A$ being the effective aperture and $f$ the focal length of the collimator lens.

With the data on the prism (collected in Table 3:I page15) the dispersion at 4358 Å was calculated to be 19.5 Å/mm, using the Hartmann formula $n = n_o - c/(\lambda - \lambda_o)$, where $\lambda_o = 2193.4$ Å and $c = 131.49$ Å; and 22.7 Å/mm using the Cauchy formula $n = A - B/\lambda^2$, with $A = 1.620, B = 1.00 \times 10^6 \lambda^2$.

The dispersion was measured over two ranges and the results are collected in Table 3:II (page 15). The Raman line $1087$ cm$^{-1}$ occurs at $4575$ Å when excited by Hg 4358 Å.

Though this spectrograph is a very fast one, it was found necessary to enhance the feeble Raman scattering that would be obtained. An auxiliary cylindrical lens was therefore used at the camera end in the final exposures.

A lens of 12.7 mm radius, 7 mm thick and 19 mm high was made from a piece of 1648 glass, 3.5 mm long ##. The lens

# See Appendix 2  ## See Appendix 3
TABLE 3: I
REFRACTIVE INDICES FOR PRISM OF SPECTROGRAPH

<table>
<thead>
<tr>
<th>Wave Length (Å)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>6563 (Hc)</td>
<td>1.64355</td>
</tr>
<tr>
<td>5893 (NaD)</td>
<td>1.64900</td>
</tr>
<tr>
<td>4861 (Hg)</td>
<td>1.66275</td>
</tr>
<tr>
<td>4359 (Hg_e)</td>
<td>1.67408</td>
</tr>
<tr>
<td>4359 (Hg_g)</td>
<td>1.67458</td>
</tr>
<tr>
<td>4047 (Hg_h)</td>
<td>1.68397</td>
</tr>
</tbody>
</table>

TABLE 3: II
DISPERSION OF SPECTROGRAPH

<table>
<thead>
<tr>
<th>Wave Length Region</th>
<th>Mean Separation</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>4078 - 4047 Å</td>
<td>1.849 mm</td>
<td></td>
</tr>
<tr>
<td>4339 - 4078</td>
<td>13.113</td>
<td>4047 - 4358 - \frac{311}{15.78} - 19.7 Å/mm</td>
</tr>
<tr>
<td>4347 - 4339</td>
<td>0.350</td>
<td></td>
</tr>
<tr>
<td>4358 - 4347</td>
<td>0.471</td>
<td>4347 - 4358 - \frac{11}{0.47} - 23.9 Å/mm</td>
</tr>
<tr>
<td>5460 - 4358</td>
<td>30.523</td>
<td></td>
</tr>
</tbody>
</table>
just fitted into the slot of the camera plate holder, some 5 mm from the plane of the emulsion. It remained snugly in place after the refocusing of the spectrograph was completed.

The refocusing was done with the aid of an iron arc at the slit of the instrument. After the camera lens had been shifted by the calculated amount, a series of exposures was made for various positions of the slit. The position that gave the sharpest lines in the region 4350 - 4600 Å was used. Final adjustments were then made by slight changes in the tilt of the plate holder. The best definition that could be obtained nevertheless produced broadened lines (Figure 3:1, page 40). This was in part due to the large curvature of the emulsion, in part due to slight imperfections in the lens. The Raman line 1087 cm⁻¹ was therefore not as sharp as it would normally be. It remained sufficiently well defined for measurements.

The Light Source

The main problem was to obtain as large an incident intensity as possible. Several lamps were tried. In particular, a large helical type mercury lamp with water cooled electrodes was found to yield large intensities; the half angle of the emitted beam was, however, correspondingly large. This lamp had a discharge length of 250 cm and could carry a current of 14 amp. at about 100 V. the power was thus 5.6 W/cm. Only a small length of the lamp could be used.

The requirement of a parallel beam of incident light cannot be reconciled with high intensity. Hence it was attempted to approach the limit of a parallel beam by interposing circular apertures between the lamp and the crystal. Three half angles were thus defined on the assumption that the half angle depended only on the size of the circular aperture. The calculations were as follows:
Length of source 16 cm
Height of source 10 cm
Distance from centre of coil to crystal 26.5 cm
Half angle of beam = \( \tan^{-1} \frac{16}{2 \times 26.5} = \tan^{-1} 0.302 \approx 17^\circ \)

Assuming the lamp equivalent to a circle of radius 8 cm, a circular aperture of 6.25 cm \((\approx 4.5")\) would give a half angle of \(\approx 13^\circ\) and one of radius 5.65 cm \((\approx 4.0")\) a half angle of \(\approx 12.5^\circ\).

Two apertures of each size were accordingly interposed (Michalke 1938), one near the lamp, the other near the crystal. Good Raman spectra were obtained in this way for scattering perpendicular to the optic axis of Calcite. These spectra were not sufficient to indicate the intensities that would result from a perfectly parallel beam. According to Michalke however, an angle of some 5° allows reduction to a perfectly parallel beam without serious error. It was therefore felt that a new lamp should be constructed to allow such a small half angle for a reasonable exposure.

A survey of the literature suggested several points which had to be borne in mind (Harrison and Forbes 1925, Stockbarger 1927). The intensity of the mercury lamp as a whole shows no reciprocity between current and voltage applied. The voltage, as well as the ratio of current to voltage are of importance in considering the intensity produced. In any mercury arc, the 4358 Å line is far from the most intense, though it is one of the most useful for Raman scattering since there is no strong mercury line on the long wavelength side of it. On the other hand, a continuum attributed to the mercury pressure in the discharge being too high (Rank and MacCartney 1948) is often a troublesome factor.

In recent years several water cooled high intensity lamps have been described: these reduce the background continuum, while at the same time permitting a larger power rating of the lamp. Welsh and co-workers (Welsh et al. 1952, 1955)
describe a fully water cooled lamp and note that the intensity decreases as the lamp is cooled: a 40 - 50°C external cooling bath gives the best compromise. Both Welsh and co-workers (1952) and Shull (1955) however, note that pyrex lamps "blacken" after several hours of operation, causing severe loss in intensity. The "blackening" becomes larger, the larger the current, which in the Welsh lamp was taken up to 50 amp.

An improved version of the water cooled lamp is described by Stoicheff (1954). In order to avoid, or at least lessen the "blackening", Corning glass 1710 is recommended for the straight central discharge section. The discharge length is some 100 cm, and the lamp can be run up to about 25 amp. This lamp is claimed to be a strong source for the blue mercury region.

The principle of the Welsh and Stoicheff lamps was applied in designing a new discharge lamp, capable of high intensity over a short length. Figure 3:2 (page 20) is a photograph of the lamp in its final form, while Figure 3:3 (page 25) shows a sectional view.

The lamp consisted of an inverted U tube of 2.25 cm bore pyrex tubing with water cooled electrodes. The cooling water entered and left through long vertical extensions A,B of the entrance and exit tubes C,D at the base of the electrodes, and power was supplied through a sealed in Tungsten wire W one end projecting into the electrode, the other into long vertical tubes P partly filled with mercury. In this way it was possible to immerse the whole lamp in a lucite tank T in which cold water entered at the bottom through a shaped glass syphon S. The flow through the tank was kept low, a mechanical stirrer allowing for rapid water circulation in the tank. Over the surface of the discharge tube, the water heated very Buttolph (1930) requires specifications of diameter, length of arc and power rating. These are included above.
rapidly, but the equilibrium temperature of the cooling bath was around 37 - 40°C. The discharge length was 30 cm and a current of 26 amp at 43 V was used. This gave a power dissipation of 37 W/cm. To keep the mercury pressure low, the lamp was continually pumped through an oil diffusion pump. It was essential to keep the background as low as possible, since the auxiliary lens concentrated both the "signal" and the "noise" equally.

The lamp started without difficulty when tickled with a tesla coil. However, on several occasions, after the lamp had been in use for considerable lengths of time, cracks developed. These appeared to be internal and may have been caused by too large a temperature gradient across the glass walls. At times the cracks passed right through the wall, allowing water to be sucked into the lamp. This water concentrated in the low temperature trap before the diffusion pump, and it was difficult to start a repaired lamp unless the trap was emptied. With care, the cracks could be retained as internal ones, and the lamp restarted several times.

The pyrex "blackened" after some 100 hours of operation. Corning glass 1710 was never used, partly because of difficulty in working it (a fact not recorded by Stoicheff (1954), where only a straight piece of tubing was used), and partly because the lamp could easily be cleaned with nitric or hydrofluric acid as the need arose. A fresh clean lamp required a few hours pumping before the mercury pools were sufficiently degassed to carry a discharge. The boiling of the mercury surface during the discharge thereafter rapidly "cleaned" the lamp.

In use, the negative electrode flicker (Harrison and Forbes 1925) was masked by painting the sides of the tank black. The positive column, 13 cm high, was used to illuminate the crystal placed behind it. The distance between lamp and crystal was 18 cm, so that the maximum half angle of incident light was $\tan^{-1} \frac{6.5}{18} \approx 20^0$. 
To reduce the angle a square hole was cut out of a thick block of wood. This hole could be made 4 x 3 or 3x3 cm at will. It was placed 4 cm from the crystal and allowed half angles of ± 10° and ± 5° to be obtained. The choice of the shape of the baffle was dictated by the fact that the discharge column was in this case vertical.

The Crystal

Calcite occurs mainly in small crystals. The scattering is, therefore relatively feeble. A larger volume would be desirable to enhance the scattering. Furthermore, a successful polarisation measurement with a built up aggregate would greatly enhance the possibilities for crystal Raman spectroscopy.

An attempt was made to obtain a compound structure. Several good cleavage crystals were selected, their faces polished, and the several face angles measured to assure true cleavage planes. The appropriate corners of two of the crystals were ground and polished to obtain plane faces respectively perpendicular and at 45° to the optic axis.

Of several methods tried to assemble the compound structure, small blobs of Plyobond cement, placed only near the outer edges of the assembly proved most satisfactory. The interfaces remained completely free and clean, and were filled with glycerine (refractive index = 1.47; refractive index for Calcite, n_{av} = 1.5). The unwanted faces were painted black, and the whole complex immersed in a cylindrical vessel filled with glycerine. The appropriate crystal face could be presented to the light source by retaining the complex in position with strips of suitably bent copper.

It was hoped in this way to double the effective scattering volume, while reducing reflections at the
interfaces. The results are discussed chapter 5.; they were disappointing. The measurements which serve as the basis of this thesis were therefore obtained by using the largest available single crystals. These were in each case as free of internal defects as possible.

Three such crystals had faces cut and polished respectively parallel, perpendicular and at 45° to the optic axis. These faces could be presented to the light source in any relative orientation by means of plaster of paris supports.

**Emulsion**

At the beginning of this project, only Ilford HP3 and Kodak F II emulsions were available. These proved too slow to record faint images during long exposures.

According to the recommendations of Eastman Kodak (Kodak 1949), the best emulsion for such a purpose is 103. Several sensitizations were accordingly tested to determine the most sensitive one for the region 4300 - 4600 Å. The results are summarized in Table 3:III.

**TABLE 3:III**

<table>
<thead>
<tr>
<th>Emulsion</th>
<th>Limit of max. Exposure</th>
<th>Development</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>103a0</td>
<td>approx. 4850 Å</td>
<td>60 min.</td>
<td>3½ m at 20°C</td>
</tr>
<tr>
<td>IIa0</td>
<td>4850</td>
<td>60 min.</td>
<td>&quot;</td>
</tr>
<tr>
<td>103aC</td>
<td>1300</td>
<td>30 min</td>
<td>&quot;</td>
</tr>
<tr>
<td>103 aF</td>
<td>6300</td>
<td>30 min.</td>
<td>&quot;</td>
</tr>
<tr>
<td>103 aE</td>
<td>6400</td>
<td>30 min.</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

# All exposures made for scattered light at 90°.
The final choice was 103a0, an unsensitized spectroscopic emulsion sensitive to a maximum wavelength of approximately 5000 Å°. This emulsion is recommended especially for astronomical photography. One drawback of this emulsion is its granularity. For the present purpose, the primary consideration being speed, the granularity had to be accepted as a necessary evil. The emulsion is also claimed to have a large linear characteristic for densities ranging from about 1 to 3. It turned out however, that the Raman lines fell below this region. The characteristic curve had, therefore, to be obtained in the region where the emulsion showed its inertia.

Attempts made to overcome the inertia by pre-exposures to a continuum were not satisfactory.

The recommended development for Kodak spectroscopic film is developer D 19 for 4 minutes at 20°C in a tray. It was found after some experimentation that 4 minutes at 19°C gave good results. Like all emulsions, 103a0 deteriorates over long periods of time: one roll of film, stored in the darkroom at some 25°C over 18 months developed extreme background fog when fully developed. To remedy this, some development tests were made with Kodak developer D 76 and with Promicrol. More contrasty plates resulted, and it was hoped that the Raman line image might be improved in this way.

All the later results were accordingly recorded on new 103a0 film and developed in D 76 for 10 minutes at 19°C. Fixing was done in Edwal Industrafix. It was hoped that small errors in development time would in this way produce less serious changes between the various plates than would equivalent errors in the 4 minute development time for D 19.

The Comparator

Tomkins and Fred (1951) and Dieke et al (1956) have described a semi-automatic spectral comparator. A similar
instrument was built in this department and has been used in evaluating the later results. A photograph of the instrument is reproduced in Figure 3:4, page 26, while the circuit design is given in Figure 3:5, page 32.

In this instrument, the light which has passed the emulsion falls on a beam splitter: part of the light going into a high power eyepiece to permit visual inspection of the region to be scanned (Dieke et al 1956) and the remainder falling on a rotating prism. Behind the prism is placed the slit (with provision for changing its length as desired) and a type 6064 photo-multiplier tube. The voltage produced in the photo-multiplier is fed into the vertical input of a D C oscilloscope. The horizontal sweep is provided by a type 930 photo tube activated by a light beam from a straight tungsten filament bulb (Type 9A/TIOP/6V oscillograph is convenient). This beam, projected onto a circular lucite sheet attached through its centre to the shaft of the synchronous motor rotating the prism, was cut off by a mask painted on the lucite.

The plate voltage for the photo-multiplier was obtained from a stabilised power supply. No attempt was made to stabilize the voltage for the illuminator or tungsten filament lamps, both being fed from the 110 volt mains. The trace on the oscilloscope screen showed some vertical oscillations. These did not affect the reproducability of the readings obtained with standard marks.

Initially, an octagonal prism, with alternating faces blackened out, was used to display the trace. It was found, however, that the masking on the lucite sheet (in the form of two opposite quarter segments) could not be made sufficiently accurate to completely superpose the halves of the trace. A slight non-parallelity of the prism faces may have contributed to this effect as well. A square prism
FIG. 3.3

THE LAMP, SECTIONAL VIEW
was finally used, and care was taken to mask its corners from stray reflections (Tomkins and Fred 1951). The mask on the lucite was now a half segment, and the half traces could be superposed.

The oscilloscope used was a Dumont Model 401. It was necessary to replace the vertical amplification knob with a pointer moving over a scale: accurate setting for any desired trace height was thus assured.

The eyepiece carried two horizontal and one vertical cross hair. The vertical hair was adjusted to the position where a line, projected on the slit, lay just below it. The region of the line passed by the length of slit selected was then indicated by lying between the two horizontal hairs. The slit and the vertical cross hair were parallel. The eyepiece field of view had straight edges, and the horizontal cross hairs were parallel to these, as well as perpendicular to the third hair.

The film was carried on a metal holder under a piece of plate glass. The holder rested on a stage constructed by Professor H.D. Smith to Dominion Astrophysical Observatory specifications. The stage could be moved in two perpendicular directions, the x axis movement being provided by a uniform screw coupled to a drum calibrated in steps of one micron. Provision was also made for angular movement about the x axis. In practice it was found most convenient to align each plate by hand, using the strong mercury lines for reference against the straight edge of the eyepiece field of view. The x movement was parallel to the horizontal eyepiece cross hairs.
The Optical System

The optical arrangement is shown schematically in Figure 4:1 (page 47). To record the Raman scattering at 180°, a small plane galvanometer mirror, M, 1.5mm in diameter, was suspended at 45° to the spectroscope axis, just off the face of the scattering volume C (Baer 1929a, Baer 1929c, Hanle 1931). Light which passed through the scattering volume fell into a large black box B in order to minimize stray light. All surfaces not contributing to the Raman scattering were painted black.

The scattered light next passed through a condensing lens L close to a Wollaston prism ,W, before being focused on the slit of the spectrograph, S.

Alignment was done as follows:

An incandescent 40 Watt lamp was placed at the camera end of the spectrograph. The Wollaston and lens produced a double image of the slit on a pinhole screen suitably placed on the spectroscopic axis. This image was made to fall on the pinhole such that the doubling produced by the Wollaston occurred in a vertical direction. A high pressure mercury lamp H1000A was then used behind the screen to produce two images of the pin hole on the slit. Pin hole and Wollaston were then so adjusted that each image covered one half of the slit fully. The H1000A lamp was then removed. This method of adjustment insured that the full opening of the spectroscope would be utilised.

The mirror could now be placed in position. To minimize spurious light (McLennan et al 1929), it was desirable to have the slit image in focus at, or just within, the scattering volume. The mirror was accordingly placed such
that the distance from it to the screen would be equal to the distance from the mirror to the crystal (PM = MC in Figure 4:1. In this position no light reached the pin hole screen from the slit, while the focal plane was shifted from P to C.

The mirror was cemented to the centre of a length of steel wire clamped at its lower end in a D shaped holder. The upper end of the wire was joined to a calibrated knob which could be rotated or clamped at will. By turning the knob, that position was found for which the mirror reflected back to the slit all the light gathered by it. Rotation of the knob by 90° then turned the mirror by 45° in the desired direction.

The crystal was then placed at the appropriate position behind the mirror and the mercury lamp used for the particular exposure placed in line with both. In this way, the crystal received the best illumination for the axis maximum scattering.

The images formed by the mirror on the slit were of the same size; the centre of the slit was covered with a narrow mask so as to separate them on the emulsion. In trial exposures with the H1000A lamp replacing the crystal, two distinct mercury spectra were actually observed. When the crystal scattering was photographed, however, the auxiliary lens produced some overlap along the midline. In the subsequent evaluation of the spectra no difficulty was encountered in selecting appropriate sections of the two polarized components.

To place the crystal in the best position for collecting the scattered light in the mirror, the light source was viewed through the crystal. There was always one position which transmitted most light at the height of the mirror. This position also provided the best alignment for scattering. The crystal was carried on an adjustable table to permit the correct height to be obtained in each case.
Raman Exposures

At the beginning of this project it was thought that the use of complementary filters might be useful in enhancing the Raman spectrum since they would eliminate a large part of the stray light in the spectrograph, apart from suppressing the strong mercury lines in the blue region of the spectrum. Of the several filters that have been tried for this purpose (Bayley 1937, Wright 1919, Crymble 1914, Wood, 1931, Baly and Rice 1913 and Hollaender and Williams 1931) only three possibilities emerged: Kodak Wratten Filter 2A or an aqueous solution of sodium nitrite to remove the mercury lines 4047/78 Å (Bayley 1937) and iodine in carbon tetrachloride to suppress mercury 4358 Å (Wood 1931). Of these, Kodak Wratten Filter 2A was no longer available.

A series of tests were made with the two solutions mentioned using a Beckman photometer to measure the relative transmissions at different wavelengths in the region 4300 - 4600 Å. It was found possible to suppress the 4047/78 Å to some 6% and the 4358 Å to some 9% by suitable choice of concentrations of the solutions. At the same time, however, the region around 4575 Å, where the symmetric Raman line excited by 4358 Å would appear, was also reduced by at least 20%. This could not be tolerated, in view of the low intensities expected for this line.

There remained the possibility of finding a new filter. Reference to the absorption bands of the rare earth salts seemed to indicate that some Praseodymium salts have a sharp absorption band in the desired region. The several workers (Jones and Anderson 1909, Jones and Strong 1911, Jones and Guy 1913) differ in their values for the width of this band, though it always was stated to lie around 4358 Å.
Various concentrations of an aqueous solution of Praseodymium chloride were accordingly examined. It was found that the absorption band depends strongly on the concentration of the solution: no satisfactory stability could be obtained over a period of several days. By this time, the arrangement described above was being pursued; it proved satisfactory and no further experiments with rare earth salts were undertaken.

A faint Raman spectrum was observed after some 4 hours exposure with the optical arrangement described, using the maximum beam angle available. A set of exposures was made with the original helical lamp for the crystal orientated with its optic axis at 45° to the illuminated face. It was immediately apparent that the incident beam was too wide, and the new mercury lamp was accordingly built.

With this lamp the exposures listed in Table 4:1 were made. The last column in the Table gives the age of the lamp at the start of an exposure. This data gives an idea of the compensation needed to overcome lamp "blackening". Serious reduction in intensity became apparent after about 100 hours of operation. There seemed to be some indication that a small amount of blackening reduced the intensity of the continuum considerably, but this point was not pursued quantitatively.

Some idea of the Raman lines obtained may be gained from the reproductions in Figures 4:2 and 4:3 on page 40.

Calibration of the Emulsion

Of the several methods described (Sawyer 1951, Dorgelo 1925), those using simultaneous recording of a series of intensity marks on the film are the most convenient. In the first few exposures made with the helical lamp, intensity marks were impressed on each film with a rotating sector (Bedford 1953). This was subsequently replaced by a Hilger density wedge which was more adaptable in use.
## TABLE 4: I

### RAMAN EXPOSURES

<table>
<thead>
<tr>
<th>Plate Scattering</th>
<th>Volume Orientation</th>
<th>Opening angle</th>
<th>Time of exposure</th>
<th>Age of Lamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 1</td>
<td>Crystal Complex</td>
<td>1/(y), 2/(z), 3/(x)</td>
<td>20°</td>
<td>6 hrs</td>
</tr>
<tr>
<td>I 2</td>
<td></td>
<td></td>
<td>20°</td>
<td>8</td>
</tr>
<tr>
<td>II 1</td>
<td></td>
<td></td>
<td>10°</td>
<td>24</td>
</tr>
<tr>
<td>II 2</td>
<td></td>
<td></td>
<td>10°</td>
<td>40</td>
</tr>
<tr>
<td>III a</td>
<td>Single Crystal</td>
<td></td>
<td>5°</td>
<td>48</td>
</tr>
<tr>
<td>III a'</td>
<td></td>
<td></td>
<td>5°</td>
<td>34</td>
</tr>
<tr>
<td>III c</td>
<td></td>
<td></td>
<td>5°</td>
<td>34</td>
</tr>
<tr>
<td>III d</td>
<td></td>
<td></td>
<td>5°</td>
<td>34</td>
</tr>
<tr>
<td>IV</td>
<td>Crystal Complex</td>
<td></td>
<td>20°</td>
<td>12</td>
</tr>
<tr>
<td>V</td>
<td></td>
<td></td>
<td>10°</td>
<td>36</td>
</tr>
<tr>
<td>VI a</td>
<td>Single Crystal</td>
<td></td>
<td>5°</td>
<td>84</td>
</tr>
<tr>
<td>VI a'</td>
<td></td>
<td></td>
<td>5°</td>
<td>48</td>
</tr>
<tr>
<td>VI b</td>
<td></td>
<td></td>
<td>rotated by 45°</td>
<td>5</td>
</tr>
<tr>
<td>VII a</td>
<td></td>
<td></td>
<td>5°</td>
<td>48</td>
</tr>
<tr>
<td>VII c</td>
<td></td>
<td></td>
<td>5°</td>
<td>40</td>
</tr>
</tbody>
</table>
It was also felt desirable to reduce the total exposure time for any one set of Raman spectra. To this end, each film carried two reference intensity marks (Sawyer 1951) which could later be referred to a calibration curve. These marks were obtained with the (non spectral) scale lamp of a Hilger medium quartz spectrograph. By controlling the current through the lamp, the scale was photographed for times of 20 seconds and 120 seconds above and below the Raman spectrum respectively.

In the evaluation of the plates, the scale line 45 was arbitrarily chosen as the reference mark. It was found that the several marks showed small variations amongst themselves: this was presumably due to small variations in the exposure times, variations in the current through the lamp and in the line voltage. However, as will be clear from the analysis in Chapter 5, corrections could be applied to overcome these defects.

To determine the characteristic curve for the emulsion, a series of photographs were obtained with the Hilger wedge before the slit of the medium quartz spectrograph. The source for all these exposures was a 40 watt incandescent lamp. It was enclosed in a black box with a circular opening slightly smaller than the diameter of the bulb. Over this opening aluminium discs of 6.5 cm diameter could be placed. these discs had appropriate holes drilled at their centre, which allowed the illuminating intensity to be varied.

To calculate the ratios of exposures, it was assumed that the intensity falling on the spectrograph slit was proportional to the time of exposure, the area of the lamp house opening and inversely as the square of the distance from lamp to slit:

\[ I = k \frac{tA}{d^2} = K \frac{tr^2}{d^2} \]  
\[ (r = \text{radius of opening}) \]
A diffusing screen was at all times interposed between the lamp and the slit to ensure a uniform illumination (Sawyer 1951). The current through the lamp was controlled by an ammeter and variac; this allowed somewhat better control than a measurement of the voltage.

Photographs were made for exposures of 20 seconds and 120 seconds to give a range of relative blackening, I_{cl}/I, of from 1.5 to 200 on the film (I_{cl} - clear plate reading, I - step reading). On each film the reference scale marks were also recorded. Two sets of wedge blackening marks could be carried on any one film.

A series of exposures was also made for the time of 8 hours, the time used for the shortest Raman Exposure. The relative blackening for these ran from 1 to 50.

The details of these several films are contained in Table 4:I. Short and long exposures were developed together to enable a relative blackening comparison. The last set of films was obtained subsequently for the express purpose of recording small values of the blackening. It was hoped in this way to determine the reciprocity failure of the emulsion for a factor 6 in exposure times, this being the ratio of the Raman exposure times (Table 4:I, page 33).

The dispersion of the medium quartz spectrograph at 4358 Å was only 37 Å/mm. No serious error was therefore expected if the films were scanned across the blackening steps in the region of the scale mark 45. Care was taken to use the same region for all the calibration films.

The relative blackening was accordingly determined for each step. Clear plate readings were taken near the scale marks (Sawyer 1951), and a mean of several readings used to relate the calculations. Measurement errors were based
### TABLE 4:II

**CALIBRATION EXPOSURES**

<table>
<thead>
<tr>
<th>Plate</th>
<th>Exposure</th>
<th>Distance of lamp from slit</th>
<th>Lamp opening diameter</th>
<th>Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>8 hours</td>
<td>260 cm</td>
<td>.5 cm</td>
<td></td>
</tr>
<tr>
<td>B₁</td>
<td>20 sec</td>
<td>16 cm</td>
<td>1.2 cm</td>
<td>Together at 19°C</td>
</tr>
<tr>
<td></td>
<td>120 sec</td>
<td>16 cm</td>
<td>.5 cm</td>
<td></td>
</tr>
<tr>
<td>A₂</td>
<td>8 hours</td>
<td>260 cm</td>
<td>.3 cm</td>
<td></td>
</tr>
<tr>
<td>B₂</td>
<td>20 sec</td>
<td>16 cm</td>
<td>1.2 cm</td>
<td>Together at 19°C</td>
</tr>
<tr>
<td></td>
<td>120 sec</td>
<td>16 cm</td>
<td>.5 cm</td>
<td></td>
</tr>
<tr>
<td>A₃</td>
<td>8 hours</td>
<td>260 cm</td>
<td>.3 cm</td>
<td>Together at 19°C</td>
</tr>
<tr>
<td>A₃a</td>
<td>8 hours</td>
<td>260 cm</td>
<td>.2 cm</td>
<td></td>
</tr>
<tr>
<td>B₃</td>
<td>20 sec</td>
<td>16 cm</td>
<td>1.2 cm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120 sec</td>
<td>16 cm</td>
<td>.5 cm</td>
<td></td>
</tr>
<tr>
<td>B₃a</td>
<td>20 sec</td>
<td>30 cm</td>
<td>1.2 cm</td>
<td>Together at 19°C</td>
</tr>
<tr>
<td></td>
<td>120 sec</td>
<td>30 cm</td>
<td>.5 cm</td>
<td></td>
</tr>
</tbody>
</table>
on the maximum error that could be estimated for any one reading. The wedge calibration supplied by the manufacturers, measured at 4500 Å (and included in Table 4:III, page 41) was used to relate the measured blackening to relative exposure on a log log plot (Sawyer 1951). The curves for the several exposure times were then superposed to give the composite calibration curve. This, according to Sawyer (1951) is a good check on the consistency of the measurements.

The curves are reproduced on a reduced scale in Figure 4:4, page 42. It will be seen that reciprocity failure for a factor 6 in exposure time is negligible, within the accuracy of the measurements, for relative blackening produced by the reference scale marks. No correction had therefore to be applied to the measurements on these marks on this account.

Reciprocity failure showed for the smaller relative blackening, the region corresponding to the Raman line intensities.

The Kodak data (Kodak 1949) indicates that 103a0 emulsion shows negligible reciprocity failure over a considerable range of exposure times, provided the intensity is greater than about 0.1 Meter Candles. A rough estimate of the intensity of the calibrating lamp was obtained with a Weston photometer. With the diffusing screen close to the lamp house opening, an intensity of near 2 Meter Candles was emitted through the 1.2 cm opening. At a distance of 16 cm, this would reduce to about 0.1 Meter Candles and at 30 cm to some 0.04 Meter Candles. For the 0.5 cm opening, the values would be (2x0.5^2)/1.2^2 ≈ 0.04 Meter Candles at the lamp, or 0.007 Meter Candles at 16 cm and 0.0004 Meter Candles at 30 cm.

From the graphs published by Kodak and reproduced on a larger scale by Sawyer (1951), the intensity failure was estimated at some 20% at the low density end of the calibration.
In Figure 4.4, curve III is the composite calibration for all 8 hour exposures. To this curve the low intensity values for the 20 and 120 second exposures (plate B 3a of Table 4.11) were normalised at their upper end. In this region the curves are strictly parallel. This may imply that the only failure at the lower intensity of the three curves is due to intensity failure, but not due to any reciprocity failure with time; this would also follow from the Kodak data.

Use of the Comparator.

Before the instrument could be used, it was necessary to allow the power supply and amplifier to warm up for at least one hour. After that time, the oscilloscope trace showed no appreciable drift.

As a first step, the vertical gain control was calibrated. It showed linearity over a large region of positions in the range most useful for the measurements required. The calibration is shown in Figure 4.5 (page 47). For the reference scale marks, the setting was around 170°; for the Raman lines always at 320°. In all the measurements, the height of the trace, I₀, produced by the illuminator lamp without any emulsion interposed, was kept constant. This involved only very slight changes in the setting for the several runs done at various times.

The reproducability of the instrument in its final state of adjustment was tested with the steps of the Hilger wedge. Readings were taken over an interval of two days, and the results are collected in Table 4.111 (page 41). Within the errors of measurement, the readings agree satisfactorily.

#The curves are discussed fully in Chapter 5.
To measure the Raman lines, it was necessary to choose a suitable slit length and width to allow maximum response in the photomultiplier. The height of the spectral lines on the film was 1.8 mm; this allowed for at most 0.9 mm for either polarised component. Since there was an overlap between the components, no more than 0.5 mm could reasonably be used.

The image on the film was projected onto the slit with a magnification of 5 x. It was found that a slit of 1.5 mm length and 40 microns width gave reasonable traces without overloading the photomultiplier. Slight variations in slit size produced variations in the trace, so that it was possible to photometer different lengths of line. This length was never more than 1.5/5 = 0.3 mm. Hence the region of the line used could be chosen far from any disturbance due to the central overlap.

For the alignment of each plate, the mercury lines 4358, 4339 and 4916 Å were used, as described in Chapter 3, page 27. The region 4350 - 4950 Å was covered by the auxiliary lens in the spectrograph, thus allowing the alignment of the strong lines to be used as alignment for the weak Raman line at 4575 Å.

For the microphotometry, the section of the line desired was chosen on the sharp mercury line 4916 Å, and the plate then moved till the Raman line was being scanned. In each case, readings of corresponding points on the two components were taken.

For all measurements made with the comparator, clear plate readings were recorded. For calibration steps, the trace height for each step was obtained, several scans being made over each film. For the Raman lines, three alternate readings for each component peak were recorded, as well as the background on either side of the line. The
Fig. 3:1  IRON ARC SPECTRUM THROUGH AUXILIARY LENS (NON-VERTICAL SLIT; 4575 Å ON RIGHT)

Fig. 4:2  TYPICAL RAMAN LINE

Fig. 4:3  TYPICAL RAMAN LINE
TABLE 4:III
WEDGE STEP DATA

<table>
<thead>
<tr>
<th>Step</th>
<th>Arbitrary position</th>
<th>Reversed</th>
<th>Arbitrary position</th>
<th>Mean $\frac{I}{I}$</th>
<th>Relative Intensity of wedge steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>26.0</td>
<td>26.0</td>
<td>26.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>24.2</td>
<td>24.2</td>
<td>24.4</td>
<td>1.07±0.01</td>
<td>.202</td>
</tr>
<tr>
<td>2</td>
<td>16.8</td>
<td>17.0</td>
<td>17.3</td>
<td>1.55±0.01</td>
<td>.402</td>
</tr>
<tr>
<td>3</td>
<td>10.3</td>
<td>10.4</td>
<td>10.7</td>
<td>2.52±0.03</td>
<td>.595</td>
</tr>
<tr>
<td>4</td>
<td>5.5</td>
<td>5.6</td>
<td>5.8</td>
<td>4.72±1.0</td>
<td>.810</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>3.1</td>
<td>3.2</td>
<td>8.67±.29</td>
<td>1.015</td>
</tr>
<tr>
<td>6</td>
<td>1.6</td>
<td>1.5</td>
<td>1.6</td>
<td>16.65±1.07</td>
<td>2.222</td>
</tr>
</tbody>
</table>
Fig. 4.4 Calibration Curves for the Emulsion
reference scale marks were measured in the same way after all the Raman lines had been done. Thus, for any series of measurements, only one change in the gain control setting was required. In all cases, the trace height for the Raman measurements, $I_0$, was chosen to be 37 scale divisions above zero (this being the maximum available), while all other readings were taken with an $I_0 = 26$ scale divisions.

The readings obtained in this way were then converted to density values by dividing the values into the clear plate readings (Sawyer 1951):

$$D = \log_{10} \frac{I_{cl}}{I}$$

The corresponding intensities were obtained from the characteristic curve of the emulsion, as discussed in the next Chapter.
Before the measured blackening could be converted to intensities, a means had to be found to use the experimentally determined characteristics curves of the emulsion. In practice, no curve could be obtained for an exposure time in excess of 8 hours – this limit being set by the need to reduce the intensity sufficiently for a suitable photographic plate to result over the long time period (the small incident intensity required for the 8 hour curve is indicated on page 37).

**Determination of Relative Intensities**

The curves of figure 4:4 (page 42) make it apparent that failure of the emulsion for the spread of time involved in the several Raman exposures cannot be considerable. A factor of 6 in time displaces curve I to the position of curve II for low intensities; and a further factor of 240 in time moves the curve to the position III. The time spread between the several Raman exposures (Table 4:1 page 33 and Table 5:3 page 49) on the other hand, is always less than a factor 10, and most generally is around a factor 5. It may therefore, be a reasonable assumption to expect no measurable shift for curve III under these conditions. Provided that it can be shown that any shift is within experimental error, it will then be justified to use the 8 hour curve throughout for the conversion of blackening to relative intensity.

It is always possible to fit any three points to a suitable curve. By choosing curves of maximum and minimum slope in the region of interest, it then becomes possible.
to estimate the variation within the interval.

The curves chosen in the present instance, to fit the three points, obtained for any constant value of \( \frac{I_0}{I} \), of relative intensity \( I \) were

1) \[ T = AI^2 + BI + C \]

2) \[ \log T = DI^2 + EI + F \]

The several constants and calculated values of \( T \) for specific values of \( I \) are contained in Table 5:1, while the fitted curves are reproduced in Figure 5:1 (page 52).

For equation (1), the slope

\[ \frac{dI}{dT} = \frac{1}{2(T - C) - B} \]

As \( T \) tends to infinity, \( I \) tends to infinity in equation (1), hence

\[ \lim_{T \to \infty} \left( \frac{dI}{dT} \right) = \frac{1}{B} \]

The value of \( B \) is sufficiently large to make this slope very nearly zero.

For equation (2), on the other hand,

\[ \frac{dI}{dT} = \frac{1}{2T \log T - F - E} \]

and again, since as \( T \) tends to infinity \( I \) tends to infinity,

\[ \lim_{T \to \infty} \left( \frac{dI}{dT} \right) = -\frac{1}{E} \]

\( E \) being of the order of 30, the limit of the slope will be of the order of 0.03 - 0.04. Near the limit, extrapolation of \( T \) causes a change \( \Delta I = T \frac{dI}{dT} \); for the two curves considered, this lies between 0 and 0.2 for an extrapolation of \( T \) by a factor of 6. This then would be the maximum probable change in \( \Delta I \).
TABLE 5: I

A) Equation \( T = AI^2 + BI + C \)

For \( I_0/I = 1.5 \):

<table>
<thead>
<tr>
<th>I</th>
<th>0.14 #</th>
<th>0.528 #</th>
<th>0.53</th>
<th>0.6</th>
<th>0.687 #</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>20</td>
<td>120</td>
<td>192</td>
<td>8874</td>
<td>28800</td>
<td>32924</td>
<td>70565</td>
<td>121798</td>
<td>186619</td>
</tr>
</tbody>
</table>

For \( I_0/I = 2.0 \):

<table>
<thead>
<tr>
<th>I</th>
<th>0.631 ##</th>
<th>0.705 ##</th>
<th>0.77</th>
<th>0.8</th>
<th>0.848 ##</th>
<th>1.0</th>
<th>1.1</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>20</td>
<td>120</td>
<td>8519</td>
<td>14870</td>
<td>28800</td>
<td>100108</td>
<td>169305</td>
<td>258888</td>
</tr>
</tbody>
</table>

B) Equation \( \log T = DI^2 + EI + F \)

For \( I_0/I = 1.5 \):

<table>
<thead>
<tr>
<th>I</th>
<th>0.4</th>
<th>0.414 #</th>
<th>0.5</th>
<th>0.528 #</th>
<th>0.6</th>
<th>0.687 #</th>
<th>0.7</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>18.8</td>
<td>20</td>
<td>65</td>
<td>120</td>
<td>923</td>
<td>28800</td>
<td>54200</td>
<td>16220000</td>
</tr>
</tbody>
</table>

For \( I_0/I = 2.0 \):

<table>
<thead>
<tr>
<th>I</th>
<th>0.5</th>
<th>0.6</th>
<th>0.631 ##</th>
<th>0.7</th>
<th>0.705 ##</th>
<th>0.8</th>
<th>0.848 ##</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>5</td>
<td>12</td>
<td>20</td>
<td>161</td>
<td>120</td>
<td>3373</td>
<td>28800</td>
<td>411100</td>
</tr>
</tbody>
</table>

# Fitted points for \( I_0/I = 1.5 \). ## Fitted points for \( I_0/I = 2.0 \)
Fig. 4:1 THE OPTIC SYSTEM, SCHEMATIC

Fig. 4:5 CALIBRATION FOR OSCILLOSCOPE GAIN CONTROL
<table>
<thead>
<tr>
<th>Plate</th>
<th>Vert. Comp.</th>
<th>Horiz. Comp.</th>
<th>Ratio $I_y/I_z$</th>
<th>Ratio of ref. marks</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_1$</td>
<td>0.096</td>
<td>0.075</td>
<td>1.28</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>0.11</td>
<td>0.093</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>$I_2$</td>
<td>0.094</td>
<td>0.10</td>
<td>0.94</td>
<td>1.55</td>
</tr>
<tr>
<td>$II_1$</td>
<td>0.077</td>
<td>0.09</td>
<td>0.85</td>
<td>1.47</td>
</tr>
<tr>
<td>$II_2$</td>
<td>0.055</td>
<td>0.065</td>
<td>0.85</td>
<td>1.50</td>
</tr>
<tr>
<td>$III_a$</td>
<td>0.035</td>
<td>0.067</td>
<td>1.90</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>0.040</td>
<td>0.040</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>0.05</td>
<td>0.035</td>
<td>0.70</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>0.085</td>
<td>0.055</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.025</td>
<td>0.029</td>
<td>1.16</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>0.075</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>0.015</td>
<td>0.16</td>
<td>10.0</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>0.013</td>
<td>0.14</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 5: III

RELATIVE INTENSITIES USING SINGLE CRYSTALS
(UNCORRECTED)

<table>
<thead>
<tr>
<th>Plate</th>
<th>Vert. Comp. $I_z$</th>
<th>Horiz. Comp. $I_y$</th>
<th>Ratio $I_z/I_y$</th>
<th>Ratio of ref. marks</th>
<th>Exposure time</th>
</tr>
</thead>
<tbody>
<tr>
<td>III$^{a}$</td>
<td>0.203</td>
<td>0.17</td>
<td>1.2</td>
<td>1.93</td>
<td>34 hrs.</td>
</tr>
<tr>
<td>III$^{c}$</td>
<td>0.193</td>
<td>0.10</td>
<td>1.9</td>
<td>1.90</td>
<td>34</td>
</tr>
<tr>
<td>III$^{d}$</td>
<td>0.12</td>
<td>0.07</td>
<td>1.7</td>
<td>1.56</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.10</td>
<td>1.4</td>
<td>1.68</td>
<td>34</td>
</tr>
<tr>
<td>VI$^{a}$</td>
<td>0.19</td>
<td>0.13</td>
<td>1.5</td>
<td>1.49</td>
<td>48</td>
</tr>
<tr>
<td>VI$^{b}$</td>
<td>0.11</td>
<td>0.095</td>
<td>1.2</td>
<td>1.69</td>
<td>40</td>
</tr>
<tr>
<td>VII$^{a}$</td>
<td>0.15</td>
<td>0.089</td>
<td>1.6</td>
<td>1.70</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>0.10</td>
<td>1.4</td>
<td>1.90</td>
<td>40</td>
</tr>
<tr>
<td>VII$^{c}$</td>
<td>0.16</td>
<td>0.13</td>
<td>1.2</td>
<td>1.77</td>
<td>40</td>
</tr>
</tbody>
</table>
However, in the present case, the limit was not approached. Using the curves of Figure 5:1, the agreement is found to be worst at the lowest intensities, as is to be expected; but not in excess of some 30%. This means that the error made in taking the 8 hour curve as the curve for all the longer exposures is less than 17%.

The calibration curves are good to at least 10% (probably better) in the region where they are determined experimentally. This accuracy takes into account the errors involved in measurements with the comparator and errors involved in the development of the several calibration films. Each measurement on a Raman line was also accurate to 10%. Thus any one measurement of intensity was accurate to some 14%. Under these conditions then, no serious increase in the error will be made by using only the 8 hour curve. This curve was extended to as low values of relative intensity as possible; all Raman lines falling within the region where the analysis for equations (1) and (2) gave a departure of 12% between the two curves.

The measured data, obtained with the crystal complex is collected in Table 5:2; that for single crystals in Table 5:3 (pages 48 and 49). In each case, the intensity corresponding to the background was determined separately from the intensity corresponding to the line peak. The true line peak intensity was then obtained by subtracting one from the other (Sawyer 1951).

Corrections

(1) The use of a prism spectrograph involves an instrumental polarization that has to be allowed for in any measurement of polarization. Introducing in addition a metallic reflecting surface, a Wollaston prism and a condensing lens will make the instrumental polarization more complex of
analysis. The magnitude of the overall effect can, however, be determined by using a short exposure with the crystal face acting as a reflecting surface behind the mirror.

The incident mercury light is itself unpolarized. The two weak components of the $4358\ \text{Å}$ triplet allow the ratio of the polarized components $I_y/I_z$ to be measured for this arrangement - one which duplicates the arrangement used for the scattering experiments - using the characteristic curve already determined.

A mean of several measurements gave the ratio

$$\frac{I_y}{I_z} = 1.04$$

As a matter of interest, a series of exposures was made by rotating a nicol prism between a mercury source and the spectrograph slit. These measurements showed a ratio

$$\frac{I_y}{I_z} = 1.65$$

for the spectrograph alone. Combined with the previous ratio, this seems to indicate that the auxiliary reflecting and refracting surfaces cause the polarization of the spectrograph to be very nearly removed (Jenkins and White, 1950).

(2) The auxiliary lens was not perfect (See page 16): this gave rise to a distortion in line shape between the two components. Since a true measure of line intensity is not the peak height but the integrated intensity under the peak, it becomes necessary, with distorted lines, to determine the ratio of the integrated intensities under the two peaks. This ratio can then be related to the ratio of the peak heights, which were used during the measurements of the several Raman exposures.

The best exposures were selected, and a trace of the
Fitted $T$ vs. $I$ Curves
line, as displayed on the flat oscilloscope screen of the comparator was obtained. The ratio of the areas above background was determined and compared to the ratio of peak heights. Three sets of measurements were made, and gave a correction factor of 0.93.

(3) Correction for reference marks:
The unequal ratios measured for the reference marks were corrected for in the following manner:

For $R_{ij}$ as the reference mark $i$ on plate $j$, $S_{ij}$ as the line component $i$ on plate $j$,

$$\frac{R_{11}}{R_{21}} = g \frac{R_{12}}{R_{22}} ;$$

then it is necessary to find some $K$, such that

$$\frac{S_{11}}{S_{21}} = K \frac{S_{12}}{S_{22}} .$$

Assuming some true $R_{1x}$ to exist – for standard development, $R_{2x}$

exposure and signal strength,

then,

$$\frac{R_{11}}{R_{21}} = a \frac{R_{1x}}{R_{2x}} \text{ and }$$

$$\frac{R_{12}}{R_{21}} = b \frac{R_{1x}}{R_{2x}} ;$$

$$g = \frac{a}{b} .$$

Also,

$$\frac{R_{11}}{R_{21}} = A \frac{S_{11}}{S_{21}} ;$$

$$\frac{R_{12}}{R_{22}} = B \frac{S_{12}}{S_{22}} ;$$

Hence,
\[
A \frac{S_{11}}{S_{21}} \quad \text{or} \quad B \frac{S_{12}}{S_{22}}
\]

Within narrow limits, the implied assumption of linearity will hold. The actual ratios for each series of exposures are nearly equal, thus allowing a correction of this nature to be applied (curve V in Figure 4:4, page 42).

Applying all the corrections, the mean values for the relative intensities are listed in Table 5:4.

**Estimation of overall error**

It was already stated (see page 50) that the characteristic curves are accurate to 10% and that the individual peak readings of the Raman lines are also accurate to 10%. The limit of this accuracy was set by the fact that the Raman lines themselves were weak. This involved working with high gain on the comparator. On the oscilloscope screen, the reading accuracy was then limited by the noise. Similarly, the weaker step calibrations could only be read over an equivalent amount of noise. Thus, the scale on the oscilloscope screen could be read at best to one tenth scale division.

However, the several readings made on any one line, area or calibration step showed a spread of some 6% amongst themselves. Thus, the maximum error from these causes is near 18%. If furthermore the inaccuracy in the several corrections is allowed for, a liberal estimate of the overall error would be 20%. This error is quoted in Table 5:4.
TABLE 5: IV

CORRECTED RELATIVE INTENSITIES #
(Single Crystals)

<table>
<thead>
<tr>
<th>Plate</th>
<th>Orientation</th>
<th>Mean Relative Intensity $I_z/I_y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>III$'_a$</td>
<td>1/¿, 2/¿, 3/¿</td>
<td>0.86 ± 0.2</td>
</tr>
<tr>
<td>III$'_c$</td>
<td>1/¿, 2/¿, 3/¿</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>III$'_d$</td>
<td>1 45¿, 2 45¿, 3 45x</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>VI$'_a$</td>
<td>1 45¿, 2 45¿, 3 45x</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>VI$'_c$</td>
<td>Rotated by 45°</td>
<td>0.92 ± 0.2</td>
</tr>
<tr>
<td>VII$'_a$</td>
<td>1/¿, 2/¿, 3/¿</td>
<td>1.2 ± 0.3</td>
</tr>
<tr>
<td>VII$'_c$</td>
<td>1/¿, 2/¿, 3/¿</td>
<td>0.90 ± 0.2</td>
</tr>
</tbody>
</table>

# Corrections applied for instrument polarization, line shape and development conditions.
Discussion

Table 5:2 lists the results obtained with a crystal complex used as scattering volume; Table 5:3 the comparable values obtained with single crystals. It is obvious that the complex gives spurious results. The reasons for this must be sought in the behaviour of the incident and scattered beams at the interfaces of the component crystals, since these interfaces could not be wholly suppressed. The critical angle for a calcite glycerine surface, or for a glycerine calcite surface, is sufficiently near the actual cleavage angle of the crystal that undue distortion of the polarized components must be expected. It may be possible to build up a suitable complex using only oblong crystal units, since in this case all incident angles would be normal; whereas a detailed trace of possible reflections out of the complex for the scattered light would permit the elimination of spurious light. Such a complex, however, would not be any more useful than large single crystals, where these are available.

The only results of value, therefore are those of Table 5:3, corrected and presented in Table 5:4. These results were obtained for an equilibrium temperature of 25 ± 2°C. The temperature was measured during exposures with a thermocouple in contact with the crystal face.

Michalke (1938) has concluded that the theory of Raman scattering as developed for a perfectly parallel incident beam may be investigated, within the limits of accuracy of his experiment, with incident beam angles near 50°. For the most intense lines, this error is there quoted as 25%. Thus, in the present case, the values obtained for the smallest beam angle may also be considered to give values
for a parallel beam. In fact, the values of Table 5:4 refer only to this beam angle. The trend shown by the values for the complex (Table 5:2, page 48) indicates that only the smallest baffle approached the narrow incident beam angle needed to justify the Michalke assumption.

The theory advanced by Theimer (1956), as pointed out earlier (page 6) predicts a polarization $p \neq 1$ for scattering other than along the optic axis. Such a conclusion cannot be drawn from the results presented here. In particular, a ratio of intensities of 3:2 in the components would have shown up strongly, if present, when the crystal was rotated through $90^\circ$ about the incident light beam as axis. Furthermore, there are no large systematic errors in the present method of measurement, since the measured values of the ratio of polarizations fall below unity thrice and above unity four times amongst a total of seven orientations reported. Again, the values greater than unity differ by about as much from unity as do the others. Hence, it can be concluded that, unless the errors are read to their extreme limit, no difference from unity of the polarization $p$ can be demonstrated.

The final estimation of the present investigation must be, therefore, that within its scope, there is no experimental evidence that polarisations of the two components of the symmetric Raman line of Calcite are widely different. Further experimental and theoretical investigation is desirable to try to settle the behaviour of this Raman line. An alternative approach, suggested by Theimer (1956), would be to investigate the temperature dependance of the line. In the new theory, terms of higher order, previously neglected, are considered as giving rise to some off the experimental results previously reported. This assumption could thus be tested.
The considerable importance attached to satisfactorily explaining the experimental results of the Raman effect, especially in solids, justifies further work in this field.
APPENDIX 1.

CRYSTAL STRUCTURE AND NORMAL VIBRATIONS OF CALCITE

Group Theoretical Basis (Bhagavantam & Venkatarayulu 1939, Bhagvantam 1940b, Matossi 1944 p60 f, Placzek 1934, Herzberg 1945, Wilson et al 1955 pl5 et seq.).

Normal modes of oscillation

For n atoms of one set of non equivalent points, there will be 3n cartesian coordinates. For oscillations of small amplitude, the kinetic and potential energies may be simultaneously reduced to the canonical form

\[ 2V = \sum \lambda_i Q_i^2 \quad ; \quad 2T = \sum \dot{Q}_i^2 \]

the \( Q_i \) being normal coordinates obtained by suitable linear transformations, and the \( \lambda_i \) being related to the corresponding normal frequencies by

\[ \lambda_i = 4\pi^2 \omega_i^2 \]

The normal coordinates give the normal modes of oscillation:

\[ Q_k = \sum a_{kl} x_l + \sum b_{km} \nu_m + \sum c_{kn} z_n \]

in terms of the 3n cartesian coordinates, the amplitude of oscillation of the l th atom in the x direction is given by \( a_{kl} \).

If now \( Q_k \) represent the configuration of the lattice, \( RQ_k \) represents a new configuration after the symmetry operation \( R \). The new configuration has a new mode of oscillation.

Thus if \( R \) runs through all symmetry operations, one gets all the possible modes of oscillation. It then follows that
a set of normal coordinates of a definite frequency defines
an irreducible representation; such a representation being
defined as

If for a group of homogeneous linear transformations
it is not possible to find a set of linear functions
of the variables \((x_i)\) less in number than the variables,
such that they transform amongst themselves by every
operation of the group; such group is said to be
irreducible. Otherwise, it is reducible.

Symmetry of normal vibrations

A normal vibration is one in which the frequency and
phase of motion, but not the amplitude, is the same for each
coordinate, as follows from egn (3).

The various normal modes of oscillation may be
classified into pure translations (rotations), lattice
oscillations or internal vibrations. Pure rotations need
not be considered further here.

The set of lattice and internal vibrations may be
further divided into degenerate and non-degenerate vibrations;
degeneracy means that two vibrations have the same frequency.
Degeneracy may be accidental or a consequence of symmetry
conditions; in the former case, no further information may
be gained.

With respect to a given symmetry operation, a normal
vibration may remain unchanged (be symmetric), change its
sign (be antisymmetric), or change by more than its sign
(be degenerate) (Herzberg 1945, Ch. II) A non degenerate vibration can only be symmetric or antisymmetric to the symmetry operation; while a degenerate vibration may be symmetric or antisymmetric to only certain symmetry operations.

For a molecule with a three fold axis $C_3$ it can readily be shown that there can be only one type of (plane doubly) degenerate vibration, $E$: the one in which the displaced vectors in a plane perpendicular to the symmetry axis rotate by $120^\circ$ for a clockwise rotation of the molecule by $120^\circ$. Furthermore, two mutually degenerate vibrations are either both symmetric or both antisymmetric with respect to a centre of symmetry $i$ and a two fold axis $C_2$ coinciding with the $C_3$ with respect to which the vibrations are degenerate, if such symmetry elements are present. Finally, with respect to planes through the $C_3$ or $C_2$ perpendicular to it, degenerate vibrations may or may not be symmetric or antisymmetric. It is then always possible to find two linear combinations of the mutually degenerate vibrations that are symmetric and antisymmetric respectively with respect to the particular plane or $C_2$.

Conversely then, a molecule which has a $C_3$ axis necessarily has a degenerate vibration.


The set of normal coordinates $Q_k$ form a system of linear homogeneous equations in $x_i$. Solutions of these
equations for the normal vibrations $\lambda_i$ are obtained most simply by solving the determinant of co-efficients. For such a system, the sum of diagonal elements $d_{ii}$ remains invariant under transformations. This sum is called the trace or character of the representation (Weyl, 1946). In particular, equivalent representations have the same character.

In general then it follows that in the reducible representation defined by cartesian coordinates, the character of any operation $R$, $X^R = n_R \left( \pm 1 - 2 \cos \phi_R \right)$, $n_R$ being the number of invariant atoms under $R$.

The character for the reducible representation $X^R$ is equal to the sum of the characters of the irreducible representation $X^1_R$.

For the case of symmetric and antisymmetric non degenerate vibrations (no $C_3$ or higher symmetry element), the characters $X^1_R$ are $1$ or $-1$ respectively. For symmetry arising out of $C_3$ or higher elements, it can be shown (Herzberg 1945 Ch. II) that it is sufficient to form the sum $X^1_R = d_{kk}$ where $d_{kk}$ are the coefficients (with equal subscripts) for the normal coordinates characterizing degenerate vibrations. In particular, for doubly degenerate vibrations,

$$X^1_R = d_{aa} + d_{bb}$$

Hence,

$$X^1 = \pm 2; \quad X_{2^1}^1 = 2 \cos \left( \frac{2\pi}{p} \right), n = 1, 2, \ldots, p-1; \quad X_{\rho}^1 = 0.$$
It is now possible to find the number of times ($N_j$) a particular irreducible representation $B$ is contained in the reducible representation $A$:

$$N_j = \frac{1}{h} \sum_j X_R^i X_R^r$$

where $h$ is the order (number of operations) of the group, and the sum is over all classes of the group, since any operation $R$ can be divided into classes whose members have the same character. Thus, the number of characters required to specify a representation is reduced to the number of classes.

**Application to Calcite** (Herzberg 1945 Ch.II)

a) Point group $D_3$

1) degenerate vibrations: for a $C_3$ axis there is only one type of degenerate vibration $E$.

2) Since there is a $C_3$, the other vibrations cannot be antisymmetric with respect to it; hence there can be only two species of non degenerate vibrations, both symmetric to the $C_3$: one symmetric with respect to the planes $3\sigma_v$, or the $3 C_2$; the other antisymmetric. These may be called $A_1$ and $A_2$.

3) There can be no vibration symmetric to one and antisymmetric to another of the $\sigma_v$ or $C_2$.

b) Point Group $D_{3d}$

The addition of $3\sigma_v$ and the consequent $S_6$ and $i$ to the group $D_3$ has as effect:
1) The degenerate vibration may now be of two types: \(E_g\) and \(E_u\), symmetric and antisymmetric to \(i\) respectively.

2) Each of the vibrations \(A\) may now be symmetric or antisymmetric to \(i\). Thus, there are \(A_{1g}, A_{2g}\) and \(A_{1u}, A_{2u}\).

c) The values \(n_R\) and \(X_R^r\) can be obtained from the symmetry elements. They are included in Table A:1.

d) The values of \(X_R^i\) follow from formula (4) and the known symmetry conditions. They make up the bulk of Table A:1.

**Determination of Normal Vibrations**

For a non-linear molecule of \(N\) atoms, there will be \((3N-6)\) normal modes of vibration arising out of the \(3N\) degrees of freedom. The six modes subtracted refer to the non-genuine vibrations (rotations and translations).

Each molecule may be divided into sets of equivalent nuclei that can be transformed into one another by the symmetry operations permitted by the molecule. For non-degenerate vibrations, the displacements of all nuclei of a set are fixed by the displacement of one of them. Hence, the nuclei of a set can at most contribute three degrees of freedom to each such symmetry type. For degenerate vibrations, the number of degrees of freedom is larger: there are now more than just one displacement for the nuclei of a set.

A nucleus in a general position on a lattice contributes 12 degrees of freedom of the degenerate species.
<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>2C₃</th>
<th>3C₂</th>
<th>i</th>
<th>2S₆</th>
<th>36v</th>
</tr>
</thead>
<tbody>
<tr>
<td>A¹ₐₑ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A¹ₑₑ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>A²ₐₑ</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>A²ₑₑ</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>E⁶ₐₑ</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>E⁶ₑₑ</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>nₐₑ</td>
<td>10</td>
<td>4</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>xₐₑ</td>
<td>3</td>
<td>0</td>
<td>-3</td>
<td>-3</td>
<td>-0</td>
<td>3</td>
</tr>
</tbody>
</table>
A nucleus on the axis of symmetry will contribute only two degrees of freedom (Herzberg 1945).

It becomes possible in each case to determine the number of degrees of freedom for any species. The number of normal vibrations is then calculated from eqn (3 and 5).

In Calcite (Bhagavantam & Venkatarayulu 1939), there will be one vibration of the type $\text{A}_{1g}$. This is the line 1087 cm$^{-1} = W_4$, and appears only in the Raman effect. Similarly, there is only one vibration $\text{A}_{2u}$ active in infrared absorption only (879 cm$^{-1} = W_1$). Finally, there are two modes each for $\text{E}_u$ and $\text{E}_g$ amongst the internal vibrations; the crystals split up the degeneracy to yield 714 cm$^{-1} = W_3$, 1438 cm$^{-1} = W_2 (\text{E}_g)$ in Raman effect, and 706 cm$^{-1} = W_3$ and 1429/92 = $W_2 (\text{E}_u)$ in infrared. The Raman line 1749 cm$^{-1}$ must then be assigned as an overtone ($W_4 + W_3$).
A. The Cauchy Formula: \( n = A - \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \)

To the second term, \( n_D = A - \frac{B}{5983^2} \)

\( n_T = A - \frac{B}{4861^2} \)

\( n_C = A - \frac{B}{6563^2} \)

Hence \( n_T - n_C \) = \( B(\frac{1}{4861^2} - \frac{1}{6563^2}) \)

or \( B = 1.0052 \)

\( n_D - n_C \) = \( B(\frac{1}{5893^2} - \frac{1}{6563^2}) \)

Set \( B = 1.000 \times 10^6 \)

Then \( A_{nD} = 1.62021 \)

\( A_{nE} = 1.62043 \)

\( A_{nC} = 1.62033 \)

Set \( A = 1.620 \)

B. The Hartmann Formula: \( n = n_0 - \frac{c}{\lambda - \lambda_0} \)

Hence \( n_T - n_D = \frac{c}{\lambda_T - \lambda_0} - \frac{c}{\lambda - \lambda_0} \)

\( n_T - n_C = \frac{c}{\lambda_T - \lambda_0} - \frac{c}{\lambda_C - \lambda_0} \)

\( n_D - n_C = \frac{c}{\lambda_D - \lambda_0} - \frac{c}{\lambda_C - \lambda_0} \)
Subtracting and dividing yields
\[
\lambda_0 = \frac{a\lambda_D - b\lambda_F}{a-b} = \frac{c\lambda_C - d\lambda_F}{c-d}
\]
where
\[
a = \frac{n_F - n_D}{n_F - n_C}, \quad b = \frac{\lambda_D - \lambda_F}{\lambda_C - \lambda_D}, \quad c = \frac{n_F - n_D}{n_D - n_C}
\]
\[
d = \frac{\lambda_D - \lambda_F}{\lambda_C - \lambda_D}
\]
= 2193.36 and
= 2193.43
Set = 2193.4 A°

Thence
\[
c = \frac{(n_F - n_D)(\lambda_F - \lambda_0)(\lambda_D - \lambda_0)}{\lambda_D - \lambda_F} = \frac{(n_F - n_C)(\lambda_F - \lambda_0)(\lambda_C - \lambda_0)}{\lambda_C - \lambda_D} = \frac{(n_D - n_C)(\lambda_D - \lambda_0)(\lambda_C - \lambda_0)}{\lambda_C - \lambda_D} = 131.49 \text{ A°}
\]

C. Dispersion
\[
\frac{d\lambda}{ds} = \frac{d\lambda}{dn} \frac{dn}{de} \frac{de}{ds}, \text{ where}
\]
\[
\frac{d\lambda}{ds} = \frac{\lambda^3}{2B} \text{ for the Cauchy formula, and}
\]
\[
= \frac{(\lambda - \lambda_0)^2}{c} \text{ for the Hartmann formula;}
\]
\[
\frac{dn}{de} = \sqrt{1 - \frac{n^2}{4}} \text{ at minimum deviation for a 60° prism}
\]
\[
\frac{de}{ds} = \cos \varnothing \quad \varnothing = \text{tilt of plate},
\]
\[
\frac{ds}{F} \quad F = \text{focal length of camera lens}
\]
\[
\varnothing = 0 \text{ at } 4358 \text{ A}°
\]
APPENDIX 3
RAY TRACING FOR AUXILIARY LENS

(1) Paraxial. If $N$, $N'$ are the refractive indices of air and lens respectively, and if $l$ is the distance behind the lens where the image would fall without this lens, $l'$ the focal length of the lens and $u$, $u'$ the angles subtended in the lens at the distances $l$, $l'$, then, for a lens of radius of curvature $r$, and an image $y$ above the axis, the Abbe Invariant (1) $N \left( \frac{1}{l} - \frac{1}{l'} \right) = N' \left( \frac{1}{l'} - \frac{1}{r} \right)$

and the condition (2) $lu = y = l'u'$

permit the calculation of the focal length $l'$ of the lens:

(3) $N'u' = Nu + \frac{(N' - N)}{r} y$

(4) $y_2 = y - \frac{d}{N} Nu$

d being the thickness of the lens.

The lens produces a reduction of image size. The reduction factor follows from the Lagrange invariant

(5) $hUN - h'U'N'$ (where $h, h'$ are the image heights)

(2) Axial. The position of the focal plane is determined geometrically using the values resulting from the paraxial trace for $r$, $u$ and $y$.

Finally, the camera lens needs to be shifted so as to keep the image produced by the lens at the plane of the emulsion. This shift is given by

(6) $L = y/u$
Applications of the foregoing theory to a cylindrical lens of radius of curvature $r = 12.7$ mm (it being necessary to select a radius that could be readily manufactured) of thickness $7$ mm gave a reduction factor of $6$ in eqn (5), and the positions of the axial and paraxial focii at $11.62$ and $11.97$ behind the lens. The difference between the focii would broaden the line, but a compromise setting between them reduces this broadening to a minimum. The lens being $7$ mm thick, a position some $5$ mm from the plane of emulsion allowed the best position to be obtained.

The choice of $r = 12.7$ mm was arrived at by cutting several lucite rods to give lenses of various radii. Trial exposures indicated that a radius of curvature of $\frac{1}{2}$" would be the best choice.
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