DEPOLARISATION OF UNMODIFIED LIGHT-SCATTERING IN LIQUIDS.

By Bishambhar Dayal Saxena.

1. Introduction.

Experimental.—One of the most easily observable facts concerning the diffusion of light in dust-free liquids is the partial polarisation of the transversely scattered light. This can be seen at once on viewing the path of a beam of light through a liquid with a double-image prism, and requires neither a monochromatic source nor a spectroscope. The defect of polarisation depends on the chemical nature of the liquid and on the temperature of observation, and quantitative measurements of it for a variety of substances are recorded in the earlier literature on light-scattering and especially in the careful and extensive investigations of K. S. Krishnan (1925). In the classical theory of light-scattering, the depolarisation is ascribed to the optical anisotropy of the molecules and their random orientation in the liquid. As the result of the discovery of the Raman effect in 1928, the subject has however assumed an entirely new complexion. When it is realised that the light scattered by a liquid includes a whole range of frequencies different from that of the incident light, it might seem at first sight that measurements of depolarisation made without a spectroscope have no significance. That this is not really the case and that the earlier measurements of depolarisation have an important bearing on the effects observed with the spectroscope was shown by Raman and Bhagavantam (1931) with the aid of a new technique devised by them, namely, the spectroscopic measurement of depolarisation with a slit of variable width. They showed that if the incident light is monochromatic and the polarisation of the transversely-scattered light is measured with the slit of the spectrograph wide open, the value of the depolarisation observed is sensibly the same as that obtained in the earlier (non-spectroscopic) observations. When, however, the slit is narrowed down, the depolarisation falls off, until finally with a very fine slit, it may reach a considerably lower value. This conclusion has been fully substantiated by the work of later observers, namely Venkateswaran (1932), Ranganadhram (1932 and 1933) and Rousset (1935). The explanation of the results stated depends on a fact first noticed by Sir C. V. Raman (1928) namely that the spectrum of monochromatic light scattered by a liquid includes not only discrete lines, but in many cases also a continuous spectrum with a marked defect of polarisation. This continuous spectrum appears overlying the discrete lines in the spectrum and is especially
intense in their immediate neighbourhood. As the undisplaced lines are by far the strongest in the scattered light, the nebulosity which appears superposed on them is of correspondingly great intensity, and as it is depolarised to the maximum extent (6/7), its presence notably influences the defect of polarisation of the total scattered light. With the slit wide open, the image of an incident line as recorded on the photographic plate becomes broad enough to include within itself the whole region of sensible intensity in the continuous spectrum in its neighbourhood, and the observed depolarisation reaches a value practically the same as that obtained without the use of monochromatic light or a spectroscope. By reducing the slit-width progressively, the continuous spectrum is excluded from the recorded image of the incident line to a corresponding extent, until finally when the slit is narrow enough to give the full resolving power of the instrument, only those scattered radiations are recorded in the position of the line due to the incident radiation which are inseparable from the latter by the spectroscope used. The depolarisation as measured in this limiting case may clearly be regarded as a physical constant for the liquid studied, provided the spectroscope used is powerful enough to make the separation of the discrete incident line from the continuous spectrum overlying it effectively complete.

Theoretical.—Very early in the history of the subject, it was suggested by Raman and Krishnan (1928) that the continuous band which appears overlying the undisplaced lines in the spectrum of the scattered light owes its origin to the rotation of the molecules in the liquid. This view receives support from various considerations and especially from the fact that the band is most conspicuous with molecules which have a high degree of optical anisotropy, e.g., benzene or carbon disulphide. In view of the dense packing of the molecules in a liquid, the band could scarcely be expected to exhibit a discrete rotational structure or even the same general distribution of intensity as in the corresponding phenomenon observed with gases. This theory of the origin of the continuous band finds support in the observation by McLennan (1930) that liquid hydrogen exhibits discrete rotational lines instead of a continuous band. It is also substantiated by the investigations of Bhagavantam (1931), Trumey (1933), Bhagavantam and Rao (1933) and of Weiler (1935), who have shown that in the rotational Raman spectrum of compressed gases, the discrete lines tend to be replaced by a continuous band with increasing pressures, and that the intensity-distribution in the same tends to approach that in a liquid. The most essential consequence of the Raman-Krishnan theory is however that the undisplaced lines in the spectrum should exhibit a depolarisation which is smaller than the depolarisation of the total scattering. If it be assumed
that the part of the scattering due to the anisotropy of the molecules is-parti-
tioned between the undisplaced line (Q-branch) and the continuous band
(P and R branches) in some known proportion, e.g., the proportion indicated
by theory for the scattering by the same substance in the gaseous state, the
depolarisation factor for the total scattering can be very simply calculated
from the depolarisation factor for the undisplaced line, or vice-versa. If we
assume, on the other hand, that the molecules in a liquid instead of being
more or less free to rotate, are held rigidly in fixed but arbitrary orientations
(which is not an unreasonable supposition for a highly viscous liquid or
glass), the P and R branches of the scattering would disappear, and the entire
scattered light would appear in the Q-branch. The depolarisation factor
of the undisplaced line would then be considerably greater than on the
assumption of freedom of rotation, and we have the further consequence
that the depolarisation factor as determined spectrographically with a wide
and a narrow slit respectively would not be sensibly different.

It will be clear from the foregoing review that studies of the state of
polarisation of the scattered light by the Raman-Bhagavantam technique
have an important bearing on the problem of the structure of liquids. It is
the purpose of this paper critically to examine the earlier investigations
in this field and to describe some observations and measurements showing
that the "depolarisation of unmodified scattering" in a liquid is a definite
physical constant depending on the chemical nature of the substance and its
temperature.

2. Definition of "Unmodified Scattering".

It will be understood that when we refer to the undisplaced lines in the
spectrum of the scattered light, we are ignoring the changes of frequency
which are in the nature of Doppler displacements; these are so small that
they would not be readily detectable with a prismatic spectroscope. It is
known that when the incident light is so highly monochromatic as to be
represented by a single sharp line in an interferometer pattern, the radiation
after being transversely scattered in a liquid, e.g., benzene, is modified by
the thermal agitation into a band in which there are usually three recognis-
able components. In this triplet, the central component is in the undis-
placed position of the incident radiation, while the two outer components
are displaced by about 0.2 wave-number on either side. A prismatic spectro-
graph having a resolving power of as much as 100000 in the 4000 Å region
of the spectrum would fail to resolve the triplet into its components and would
thus present them together as a single line on the plate; at the same time, it
would effectively exclude all the continuous radiations in the scattered light
from the recorded image of this line, except such of it as actually falls within
the region of the triplet. A spectrograph of this resolving power would therefore enable the depolarisation of the aggregate radiation comprised within the triplet to be measured without sensible error. We may define the depolarisation as measured under these conditions as the "depolarisation of unmodified scattering" by the liquid. Instruments of a smaller resolving power, e.g., 50000, would naturally allow part of the continuous spectrum lying outside the triplet to be superposed upon the image of the latter. The error in the measurement of depolarisation thus resulting would depend on the relative intensity of the radiations composing the triplet and of the continuous spectrum outside it, and also on the actual value of the depolarisation itself. So long as the latter is not too small and provided the continuous spectrum is of sufficiently low intensity, the error involved in the use of an instrument of inadequate resolving power would not be serious. The effect of opening the slit of a spectrograph beyond a certain permissible limit is to reduce its resolving power. It should therefore be possible by extrapolation to make at least a rough estimate of the error involved in using an instrument of inadequate power for the measurement of depolarisation in any particular case by the method of variable slit-width.


The depolarisation of unmodified scattering was measured for a series of liquids at the suggestion of Sir C. V. Raman by S. P. Ranganadham (1932, 1933). In his first set of experiments, Ranganadham (1932) used a small instrument (a wave-length spectrometer by Hilger) with a resolving power of about 5000, and the results obtained with its aid showed only a moderate difference between the wide and the narrow slit depolarisation values. A little later, Ranganadham (1933) repeated the work, using an improved photometric technique and with a larger instrument (a Fuess glass spectrograph) with a resolving power about 25,000; he also used the finest possible slits for determining the depolarisation of the unmodified scattering. In this work, much greater differences were observed between the wide and narrow slit values for the depolarisation. He found also that when the "narrow" slits used with the Fuess instrument were not set sufficiently fine, the values obtained with the instrument of less resolving power could be reproduced. The importance of using an instrument of adequate power was very clearly realised and set out in Ranganadham's M.Sc. thesis of 1933 which is deposited in the Madras University Library, but has remained unpublished. It appears therefore desirable to reproduce below the following data extracted from this thesis. The figures shown in all the columns indicate the depolarisation factor of the transversely scattered light, the incident light being unpolarised.
TABLE I.

Depolarisation with Narrow and Broad Slits.

(Determined by S. P. Ranganadham in 1933.)

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Hilger Spectrograph Resolving power ~ 5000</th>
<th>Fueß Spectrograph Resolving power ~ 25000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Narrow slit</td>
<td>Broad slit</td>
</tr>
<tr>
<td>1. Benzene</td>
<td>0.34</td>
<td>0.425</td>
</tr>
<tr>
<td>2. Carbon disulphide</td>
<td>0.50</td>
<td>0.65</td>
</tr>
<tr>
<td>3. Carbon tetrachloride</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>4. Toluene</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>5. Acetone</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td>6. Diethyl ether</td>
<td>0.055</td>
<td>0.08</td>
</tr>
<tr>
<td>7. Ethyl alcohol</td>
<td>0.03</td>
<td>0.055</td>
</tr>
<tr>
<td>8. N. Propyl alcohol</td>
<td>0.04</td>
<td>0.065</td>
</tr>
<tr>
<td>9. Isopropyl alcohol</td>
<td>..</td>
<td>0.03</td>
</tr>
<tr>
<td>10. Butyl alcohol</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>11. Isobutyl alcohol</td>
<td>0.055</td>
<td>0.075</td>
</tr>
<tr>
<td>12. Amyl alcohol</td>
<td>0.065</td>
<td>0.080</td>
</tr>
<tr>
<td>13. Propyl acetate</td>
<td>0.160</td>
<td>0.20</td>
</tr>
<tr>
<td>14. Chloroform</td>
<td>0.145</td>
<td>0.21</td>
</tr>
<tr>
<td>15. Formic acid</td>
<td>0.49</td>
<td>0.52</td>
</tr>
<tr>
<td>16. Acetic acid</td>
<td>0.385</td>
<td>0.40</td>
</tr>
<tr>
<td>17. Butyric acid</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>18. Salol</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>
It will be noticed from the figures in the table that in the case of many common liquids such as benzene, toluene, acetone and carbon disulphide, the depolarisation of the unmodified scattering as determined with the Fuess spectrograph is strikingly less than that of total scattering. In the case of highly associated liquids such as the fatty acids, on the other hand, the difference is much less striking, and in the case of a very viscous liquid such as salol, there is no noticeable difference between the two values.

The depolarisation values for four liquids (benzene, carbon disulphide, acetic acid and sulphur dioxide) determined with a series of slit-widths ranging from 2500 µ to 25 µ are recorded by Rousset in his doctorate thesis (Paris, 1935). The instrument used in this work was a two-prism glass spectrograph having a dispersion of 20 Å per millimeter in the region of 4358 Å and a theoretical resolving power of about 50,000. The focal length of the collimator was 67 cm. and that of the camera, 47 cm. An extract from Table VIII of Rousset's thesis giving his data for the four liquids is reproduced below as Table II. In Fig. 5 of his thesis, Rousset has given graphs of his depolarisation data as a function of slit-width from which it would appear that the form of the curves for these four liquids is rather varied. The graphs for acetic acid and sulphur dioxide show points of inflexion as they approach the axis of zero slit-widths, while the curves for benzene and carbon disulphide go steeply downwards in such manner as to suggest that the depolarisation of the unmodified scattering is very small if not actually zero.

**Table II.**

*Depolarisation with Varying Slit-Width.*

Rousset (1935).

*Resolving Power of Spectrograph ~ 50000.*

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Slit Width in µ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2500</td>
</tr>
<tr>
<td>Benzene</td>
<td>...</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>...</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>...</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>...</td>
</tr>
</tbody>
</table>
Rousset's graphs are however on a small scale and the actual measured values are not plotted therein. The reader of the thesis is unable therefore to judge for himself to what extent the graphs are a representation of the actual observations and to what extent they represent conjectural extrapolations. Accordingly, the present author has plotted out all the observations of Rousset for the four liquids on a large scale, and the same is reproduced as Fig. 1 below in which for convenience of reproduction, the portion of the graph for slit-widths greater than 1000 $\mu$ has been omitted. Rousset remarks in his paper "Les valeurs de $p$ pour les fentes de 25 $\mu$ sont obtenues apr\'es une comparaison grossi\'ee des densit\'es au microscope", and indicates in his Table VIII that they are not to be given the same weight as the observations with wider slits. It will be seen that all the measurements with acetic acid fall on a smooth curve which becomes a horizontal straight line for large slit-widths, and bends round and cuts the vertical axis of the graph sharply at an angle. The observed values for sulphur dioxide also fit tolerably well into a smooth graph of the same general form. All the observations for carbon disulphide fit perfectly into a curve of the same general form (though naturally higher and steeper) except the doubtful observation for 25 $\mu$ which falls a little out of the graph. The observations for benzene, though most numerous, are curiously enough, the least regular. A graph of the same general form as for the three other liquids, can, however, be drawn which
passes pretty evenly through the observed points, except however the
doubtful observation for 25 μ which falls out of the graph. The curve for
benzene is less steep than for carbon disulphide but steeper than for the
other two liquids.

A re-examination of Rousset's own data thus makes it highly probable
that the graphs for all the four liquids studied by him are of the same general
form though of different height and steepness, meeting the vertical axis
sharply at an angle and giving finite values for the depolarisation with the
narrowest slits as shown below:

Benzene, ρ₀ = 0.16, carbon disulphide, ρ₀ = 0.30
Acetic acid, ρ = 0.28, sulphur dioxide, ρ = 0.15.

If we exclude the observations with the 25 μ slit which according to Rousset
himself are not entitled to the same weight as the values with wider slits,
his data clearly offer no basis for the suggestion that the depolarisation of the
unmodified scattering in benzene and carbon disulphide is very small or zero.
If his values for the 25 μ slit had been 0.185 instead of 0.13 for benzene,
and 0.36 instead of 0.33 for carbon disulphide, they would have fitted per-
factly into our present graph. To assume that errors of the magnitude
indicated were not possible in what was admittedly "une comparison
grossière" and to base upon them an extrapolation having no observational
support does not seem to be a justifiable procedure. A conclusion of such
fundamental importance as that suggested by Rousset could only be
accepted on the clearest experimental evidence, and that its truth is highly
improbable is indicated by his own data. As we shall see later, it is definitely
contradicted by the experimental evidence offered in the present paper.


The relative intensity with which monochromatic light and a continuous
spectrum superposed upon it are recorded by a spectrograph depends on the
resolving power of the instrument and, in fact increases pari passu with the
"purity" of the spectrum given by the instrument. With an instrument
of low power, the continuous spectrum appears relatively brighter, and
when, as in the present case, its maximum intensity coincides with the mono-
chromatic line itself, the line and continuous spectrum tend to fuse into each
other on the photographic plate and to convey the impression that the line
has suffered an "élargissement" or widening. This effect would naturally
be aggravated by the photographic broadening due to over-exposure of the
intense image of the monochromatic radiation, and the net result would be to
convey an incorrect impression of the real nature of the phenomenon encoun-
tered in the scattering of monochromatic light by liquids. Actually, there is no
“elargissement” or widening of the incident radiation; when a spectrograph of sufficient power is used, it is observed that the undisplaced line in the scattered light has precisely the same degree of sharpness as in the incident light. This is most evident with an instrument in which a large linear dispersion is combined with a great resolving power, as the effect of photographic broadening is then minimised. If a photograph is taken of the spectrum of scattered light with such an instrument, and the negative is examined against a strong light, it will be seen that the undisplaced lines appear with undiminished sharpness superposed on a continuous spectrum which has its maximum intensity at the line itself. Fig. 1 (Plate) represents the 4358 group of lines of the mercury arc in the transverse scattering by benzene, recorded with a three-meter-focus glass spectrograph constructed by Dr. C. S. Venkateswaran with optical parts by Hilger. In the reproduction of this picture which was taken as a test of the instrument by Dr. Venkateswaran with an exposure of 48 hours and without any special precautions for maintaining constancy of temperature, the weaker lines which have not suffered from over-exposure appear defined with hair-like sharpness.

If the depolarisation of the undisplaced line in the transverse scattering by benzene were very small or zero as suggested by Rousset, then the incident lines should completely disappear and be lost in the continuous background if the scattered light were analysed with a double-image prism and the horizontal component alone were recorded. The experiment is readily tried and it is found that the facts afford no support to Rousset’s conclusion. Actually, the lines are seen in the vertical and horizontal components (Fig. 2 in the plate) with entirely comparable clearness and definition. Though the lines in the horizontal component are weaker, their intensity is far from being negligible, and in fact, is a very considerable fraction of the intensity in the vertical component. The visibility of the lines in the horizontal component against the continuous background is not notably inferior to the visibility of the lines in the vertical component. The greater relative intensity of the continuous background in the horizontal components however affects the appearance of the lines as recorded on a photograph and seen under a microscope or in a microphotometer record. The reason for this will be clear from Fig. 2 (a), (b) and (c) below; in (a) we have the vertical component alone, in (b) the horizontal component alone and in (c), the two together. As the result of photographic spreading, the vertical component in (a) will, when reduced to the same intensity as the horizontal component in (b) by a suitable device e.g., by a nicol following the double-image prism, will appear sharper than the latter. The magnitude of this effect will depend on the degree of depolarisation of the undisplaced line and its intensity relatively to the continuous
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Intensities of modified and unmodified radiations.

Microphotometric records of the undisplaced line in the horizontal and vertical components taken with a Hilger E 349 spectrograph and slit only 10 μ wide are reproduced in Fig. 3 and Fig. 4 in the plate. Fig. 3 refers to phenol and it will be seen that the horizontal and vertical components are of equal sharpness. Fig. 4 refers to benzene, and the vertical component appears somewhat sharper than the horizontal one, for the reason already explained.
Variation of depolarisation (wide and narrow slits) in phenol with temperature.


To remove all possible doubt on the issues now under discussion, it is clearly necessary that the measurements of depolarisation should be made with a spectrograph of the largest possible resolving power and dispersion, and that observations should be secured covering a range of slit-widths up to the very finest possible, thus enabling the whole course of the curve to be traced from actual observations and not by extrapolation. Both Ranganadham and Rousset used the methods of photographic photometry for making their determinations. In Ranganadham's first series of measurements and in Rousset's work, Schwarzschild's formula connecting the depth of blackening and the time of exposure was used to determine the ratio of the intensity of the vertical and horizontal components. In Ranganadham's second series of measurements, the comparison was based on the method of intensity marks. When the images under comparison are extremely fine lines on the plate of width comparable with that of the grains of the emulsion,
a method of measurement independent of the laws of photographic action and which merely uses the plate as a detector seems preferable.

In the present investigation, the spectrograph used was a large Littrow glass spectrograph by Hilger (E 349) of aperture F/7, the diameter of the camera objective being 127 mm. The prism system of dense flint glass is equivalent to three 60° prisms of 15.2 cms. face and 11.7 cm. high. The dispersion is 11 Å per mm. in the 4358 region of the spectrum. A mercury arc lamp was the source and the lens which condensed the light from it was screened off by an aperture 3 cm. square. The lens itself was 8 cm. in diameter and 24 cm. distant from the tube. The liquid under study was contained in a cylindrical glass tube with a fused-on flat end, and the scattered light was taken from an aperture 0.2 cm. wide at the centre of the latter. This light was condensed on the spectrographic slit by a convex lens of diameter 3.5 cm. (focal length 11 cm.) which was 26 cm. distant from the slit and 18 cm. from the tube. A double-image prism of quartz was mounted on the same stand as the lens and faced the slit of the spectrograph. The method adopted for measuring $p$ was different from that of previous workers. A nicol was interposed in the path of the scattered beam after it had traversed the double-image prism and before it entered the slit of the spectrograph. Successive exposures were given with the nicol turned round $1°$ at a time, until the relative intensity of the two images recorded showed a reversal, that is, till the weaker image became the stronger and vice versa. If $a$ be the orientation of the nicol, the depolarisation factor is given by the usual formula $p = \tan^2 a$. The method, though tedious, has the merit of being entirely reliable and applicable to the finest slit-widths.

6. Results.

_Hilger E 349 Glass Spectrograph, Resolving Power ~ 75000_

_A. Variation of Depolarisation with Slit-width in benzene._

<table>
<thead>
<tr>
<th>Slit-width in $\mu$</th>
<th>1500</th>
<th>1000</th>
<th>750</th>
<th>500</th>
<th>300</th>
<th>200</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depolarisation factor</td>
<td>0.44</td>
<td>0.41</td>
<td>0.39</td>
<td>0.38</td>
<td>0.37</td>
<td>0.32</td>
<td>0.27</td>
</tr>
<tr>
<td>Slit-width in $\mu$</td>
<td>50</td>
<td>25</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Depolarisation factor</td>
<td>0.20</td>
<td>0.17</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
B. Depolarisation with wide and narrow slits in different liquids at room temperature, 20 °C.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Wide slit</th>
<th>Narrow slit (10 μ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.44</td>
<td>0.16</td>
</tr>
<tr>
<td>Phenol</td>
<td>0.70</td>
<td>0.53</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>0.75</td>
<td>0.66</td>
</tr>
<tr>
<td>Glycerine</td>
<td>0.33</td>
<td>0.30</td>
</tr>
</tbody>
</table>

C. Variation of ρ with temperature in Phenol.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>175 °C.</th>
<th>134 °C.</th>
<th>100 °C.</th>
<th>84 °C.</th>
<th>65 °C.</th>
<th>45 °C.</th>
<th>23 °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slit-width 1000 μ</td>
<td>0.49</td>
<td>0.55</td>
<td>0.59</td>
<td>0.64</td>
<td>0.60</td>
<td>0.66</td>
<td>0.70</td>
</tr>
<tr>
<td>Slit-width 10 μ</td>
<td>0.29</td>
<td>0.32</td>
<td>0.36</td>
<td>0.40</td>
<td>0.43</td>
<td>0.46</td>
<td>0.53</td>
</tr>
</tbody>
</table>

7. Interpretation of the Results.

The experimental results for benzene given above have been represented graphically in Fig. 3. The ordinates are the observed depolarisation factors, and the abscissae are the half-width of the image of the slit as it appears on the photographic plate expressed in wave-numbers, in other words, the actual range of the continuous spectrum on either side which appears superposed on the central undisplaced line. The graph also shows the values calculated from the empirical formula

$$\rho = \frac{7.7 - 6e^{-Kv}}{17.4 - 7e^{-Kv}}$$

(Benzene)

where ν is the half-width of the slit expressed in wave-numbers and K = 0.10. For ν = 0, that is, for a very fine slit, ρ becomes 0.16, while for large values of ν, ρ becomes 0.44. This empirical formula can be derived theoretically, if the distribution of intensity in the continuous spectrum is assumed to be proportional to $e^{-Kv}$, in other words, that it has a finite maximum intensity at the position of the undisplaced line and falls off exponentially with increasing wave-number shift from it. The asymmetry in the intensity of the continuous spectrum on the two sides of the undisplaced line which
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develops with increasing \( \nu \) is rather small compared with the rapid fall in the intensity of the continuous spectrum which occurs simultaneously; it is therefore neglected in the derivation of the formula for the sake of simplicity, though it is easily possible to take account of it as well. The depolarisation factor of the continuous spectrum is taken as 6/7, and these integers, it will be seen, appear respectively in the numerator and denominator of the formula.
The agreement between the observed values of \( \rho \) and those given by the empirical formula though fair, is not all that could be desired. A formula of the general type

\[
\rho = \frac{x - 6 \cdot e^{-K\nu}}{y - 7 \cdot e^{-K\nu}}
\]

has been tested out and is found to fit Rousset's data (Fig. 1 above) tolerably well. The constants found are:

- Benzene: \( x = 7.7 \), \( y = 17.4 \), \( K = 0.09 \)
- Carbon disulphide: \( x = 7.6 \), \( y = 12.2 \), \( K = 0.12 \)
- Acetic acid: \( x = 14.3 \), \( y = 36.7 \), \( K = 0.10 \)
- Sulphur dioxide: \( x = 10.3 \), \( y = 35.4 \), \( K = 0.13 \)

The observations recorded above for the viscous liquids benzophenone and glycerine show very clearly that the intensity of the continuous spectrum relatively to that of the undisplaced line is very small with these liquids, and also that the depolarisation of unmodified scattering is correspondingly high in these cases. These facts fit in very well with the theoretical considerations referred to in the introductory part of the paper. The case of phenol is particularly interesting, as it evidently stands midway between the class of liquids including benzene and carbon disulphide in which the depolarisations of the total scattering and of the unmodified scattering differ widely, and the class of viscous liquids including benzophenone and glycerine in which they differ very little. It might reasonably be anticipated that with rise of temperature, phenol would tend to behave more like the liquids in the former class. The relation between \( \rho \) and the temperature for the largest and the smallest slit widths respectively for phenol has been plotted in Fig. 4, and it will be seen that this anticipation is at least partially fulfilled. The experiment clearly indicates that we may expect the depolarisation of unmodified scattering to be markedly a function of temperature in all liquids, and that it would differ markedly from the depolarisation of total scattering at higher temperatures, even with those liquids for which the difference is ordinarily small.
8. Summary.

The investigations of Ranganadham and of Rousset have been critically examined, and it has been shown that, contrary to the latter’s conclusion, normal liquids such as benzene and carbon disulphide show a definite depolarisation of the unmodified scattering which is notably smaller than the depolarisation of the total scattering. From Rousset’s data for the four liquids studied by him, the following results have been derived:

<table>
<thead>
<tr>
<th></th>
<th>Unmodified</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.16</td>
<td>0.44</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>0.30</td>
<td>0.62</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.28</td>
<td>0.39</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>0.15</td>
<td>0.29</td>
</tr>
</tbody>
</table>

The value for benzene deduced above is confirmed by a thorough re-investigation with a spectrograph of adequate power and an exact experimental technique. Viscous liquids such as phenol, benzophenone and glycerine give relatively smaller differences between the depolarisations of unmodified scattering and of total scattering at room temperatures as shown below:

<table>
<thead>
<tr>
<th></th>
<th>Unmodified</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>0.53</td>
<td>0.70</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>0.66</td>
<td>0.75</td>
</tr>
<tr>
<td>Glycerine</td>
<td>0.30</td>
<td>0.33</td>
</tr>
</tbody>
</table>

The depolarisation of unmodified scattering diminishes with rising temperature, and the investigation with phenol at temperatures ranging from 23°C to 175°C. shows that it tends to differ more markedly from the depolarisation of total scattering at the higher temperatures than at the lower.

In conclusion, the author wishes to express his grateful thanks to Sir C. V. Raman at whose suggestion this investigation was undertaken for his sustained interest in its progress.
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Weiler .... Z. Phys., 1933, 84, 282.
Fig. 1. Wing in Benzene.

Fig. 2. Transverse Scattering in Benzene.

Fig. 3. Phenol.

Fig. 4. Benzene.