EXAMINATION OF MOLECULARLY SCATTERED LIGHT WITH A FABRY-PEROT ETALON.

Part II. Liquids: Toluene and Carbon Tetrachloride.

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In Part I the author has established, successfully for the first time using for this purpose a Fabry-Perot Etalon, the reality of the presence of the two Doppler components accompanying the Rayleigh line in the spectrum of the light scattered by a liquid, the frequency shifts being given by the formula

\[ \Delta \nu = \pm 2\nu \frac{v}{c} \sin \frac{\theta}{2} \]

where \( \nu \) = frequency of incident radiation, \( \theta \) = the angle of scattering, \( v \) and \( c \) the velocities of sound and light waves in the medium. In the same paper the dependence of the frequency shift (i) on \( \theta \) the angle of scattering, and (ii) on \( \nu \) the frequency of the incident radiation has been checked for an angle of scattering of 180° for the mercury lines \( \lambda 4047 \, \text{Å}, \lambda 4078 \, \text{Å} \) and \( \lambda 4358 \, \text{Å} \). Attention has also been drawn to the fact that the unmodified central line is always present, being distinctly brighter than the accompanying Doppler components.

In continuation of the previous work on benzene, it was thought desirable to investigate with improved experimental technique, this problem of the fine structure of the Rayleigh line, in the case of a highly anisotropic molecule like that of toluene and a very weakly anisotropic molecule like that of carbon tetrachloride, with the object of finding out the influence, if any, of the anisotropy of the scattering molecule on the structure of the Rayleigh line. This investigation was also undertaken to settle whether the alleged red shift of the centre of the Rayleigh line was real.

2. Experimental Arrangements.

The high resolving power interferometer used in this investigation was the same Fabry-Perot Etalon with invar distance pieces, specially

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made by Herr Lesche of Potsdam, Germany, and silvered by Professor Ritschl by his evaporation method.

The Wood’s tube was also of the same design as in the previous communication of the author except that this time it was slightly bigger in size so as to allow more of the scattered light to fall on the Etalon.

The illuminating source of light had to be redesigned for the following obvious reasons. The source of light used in the work described in Part I consisted of two lamps with water-cooled mercury cathodes and tungsten anodes. In the present work the two lamps were replaced by a single lamp with two vertical branches with a common water-cooled mercury cathode and two tungsten anodes. This modification was necessary to ensure continuous action of the two branches. In the previous arrangement it was not always easy to maintain the two lamps working together. Fig. 1 represents the newly designed mercury vapour lamp with the vertical cross section of the Wood’s tube in the background. The common mercury cathode C contains clean mercury up to the level indicated in figure and the discharge runs along the two vertical branches CA1 and CA2. The tungsten anode B is intended for passing a preliminary discharge from C to B by means of a small induction coil to facilitate the striking of the arc. The spherical bulb at the top is meant for the mercury vapour to condense and fall back into the cathode. The cathode was cooled by a current of cold water kept circulating in the outer tube enclosing the cathode as indicated in figure. The arc was run with a current of 4 amps, in each of the branches from a 220 D.C. supply.

The experimental arrangements regarding the alignment of the apparatus and other experimental details were the same as in the previous paper by the author on this subject.

Fig. 2 represents the distribution of the hyperfine structure satellites of the mercury lines $\lambda 4047 \, \text{Å}$, $\lambda 4078 \, \text{Å}$ and $\lambda 4358 \, \text{Å}$ in the interference pattern of the light obtained with a 5 mm. distance piece between the two quartz plates of the Etalon. The wave-numbers and the relative intensities of these satellites have been taken from the work of Schüller and Keyston. The dotted lines indicate the positions of the Doppler components due to scattering in the case of liquids toluene and carbon tetrachloride.

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In order to minimise the complications arising from the presence of these hyperfine structure satellites of the incident radiation, the following procedure was adopted. A photograph of the interference pattern of the unscattered light was taken, the exposure being so reduced that the pattern was free from any hyperfine structure satellites. Next a photograph of the interference pattern of the scattered light was taken with an exposure which showed the unmodified central component with nearly the same intensity as the corresponding main component in the pattern of the direct light. On comparison of the two it was found that the pattern of the scattered light
contained the Doppler components in the space corresponding to the blank space in the pattern of the direct light. This procedure is specially suited in cases where the hyperfine structure satellites are much fainter than the two fine structure components due to scattering.

3. Cabannes' Red Shift.

Reference has already been made to the red shift of the centre of the Rayleigh line reported by Cabannes.\(^3\) For examining this point toluene was selected as a suitable liquid since the time of exposure need not be long and any effect of an alteration in the temperature and pressure of the surrounding medium during an exposure on the pattern be minimised. A photograph was taken with the pattern of the scattered light falling on one half of the slit width of the spectrograph. Then the pattern of the direct light was arranged to fall only on the other half of the slit and a photograph taken. The result was that the two patterns were in juxtaposition facilitating comparison. An examination of the patterns reproduced in Plate XIV reveals no measurable contraction of the interference pattern of the scattered light.

Having settled this point, various experiments were conducted to examine the conditions under which a spurious red shift may be obtained. It was found that the interference pattern was influenced by long exposures to the scattered light, due to temperature and pressure variations in the surrounding atmosphere. The temperature and pressure variation of the surrounding atmosphere influences the interference pattern to such an extent that one might notice a contraction of the pattern of the incident light itself. This effect is clearly noticeable in the photographic reproduction of the interference patterns of the direct light shown in Plate XIV. The pattern (a) was taken early in the morning as soon as the mercury lamp was started and after allowing the lamp to work for about 12 hours the pattern (b) was taken after which the mercury lamp was taken off. The pattern (c) was taken the next morning when the conditions of the surrounding medium were almost the same as those in the previous morning. A comparison of these interference patterns indicates that in pattern (b) the ring system has contracted due to a change in the condition of the surrounding medium, and in (a) and (c) the patterns are almost identical. From the foregoing it is evident that one ought to take great care in avoiding all disturbing influences like variations in the temperature and pressure of the surrounding medium, before one can arrive at any conclusive evidence of a shift in the centre of the Rayleigh line.

4. Results.

Carbon Tetrachloride.—The interference pattern given by the light scattered by this liquid was characterised by a clear background enabling one to distinguish clearly the Doppler components from the hyperfine structure satellites. The photographic reproduction of the patterns of $\lambda$ 4047 Å and $\lambda$ 4358 Å in the direct and scattered light is therefore particularly striking. In the interference pattern of the direct light for $\lambda$ 4047 Å there are two satellites one of them being stronger and wider than the other, the former corresponding to the blend of the hyperfine structure satellites ($-0.743$, $+0.270$ and $+0.330$)cm.$^{-1}$ and the latter corresponding to the blend of the satellites ($-0.394$ and $+0.668$)cm.$^{-1}$. The pattern of the scattered light on the other hand contains two equally sharp and equally displaced components of the same intensity at $+0.251$ cm.$^{-1}$ and $-0.251$ cm.$^{-1}$ with the fainter of the hyperfine structure satellites ($-0.394$ and $+0.668$) cm.$^{-1}$ appearing clearly separated from the $-0.251$ cm.$^{-1}$ Doppler component. The Doppler shifts for the other mercury lines $\lambda$ 4078 Å and $\lambda$ 4358 Å were also examined for carbon tetrachloride and are to be found tabulated in Table I.

| Table I. |

**Angle of Scattering 180°.**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Radiation</th>
<th>$\bar{\nu}$ Observed</th>
<th>$\bar{\nu}$ Calculated</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride</td>
<td>4047 Å</td>
<td>0.251 cm.$^{-1}$</td>
<td>0.238 cm.$^{-1}$</td>
<td>0.013 cm.$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>4078 Å</td>
<td>0.250 ,,</td>
<td>0.236 ,,</td>
<td>0.014 ,,</td>
</tr>
<tr>
<td></td>
<td>4358 Å</td>
<td>0.230 ,,</td>
<td>0.221 ,,</td>
<td>0.009 ,,</td>
</tr>
<tr>
<td>Toluene</td>
<td>4047 Å</td>
<td>0.320 ,,</td>
<td>0.307 ,,</td>
<td>0.013 ,,</td>
</tr>
<tr>
<td></td>
<td>4078 Å</td>
<td>0.320 ,,</td>
<td>0.305 ,,</td>
<td>0.015 ,,</td>
</tr>
<tr>
<td></td>
<td>4358 Å</td>
<td>0.290 ,,</td>
<td>0.285 ,,</td>
<td>0.005 ,,</td>
</tr>
<tr>
<td></td>
<td>5461 Å</td>
<td>0.210 ,,</td>
<td>0.196 ,,</td>
<td>0.014 ,,</td>
</tr>
</tbody>
</table>

Toluene.—In the case of toluene it was found that an exposure ranging from an hour or two was sufficient to bring out the components due to scattering. This fact enabled the determination of the frequency shifts of the green radiation $\lambda$ 5461 Å of mercury, for which an exposure of 30 hours was necessary. An interesting feature that was noticed, was the appearance
of a continuous background of the interference pattern in the case of toluene even when the exposure was of the order of an hour, while in the case of carbon tetrachloride an extended exposure of about 16 hours left the interference pattern free from any appreciable continuous background. This shows that this continuous background is a characteristic feature of the anisotropy of the molecules of the liquid.

5. Theoretical Discussion.

The theory of the scattering of light in liquids has been worked out in detail by Ramanathan, Raman and Krishnan, Gans and others. According to these authors, there is, in addition to the polarised scattering due to density fluctuations, an unpolarised scattering due to local anisotropy in the medium which may be ascribed to the orientations of the molecules in the liquid. The total intensity of light scattering is the sum of the intensities of the "density" and "orientation" scattering. The "density" scattering is given by the well-known theory of fluctuations of density and the factor of multiplication to be applied to the expression given by that theory in order to include the "orientation" scattering is \( \frac{6(1+r)}{6-7r} \) where \( r \) is the observed depolarisation of transversely scattered light. The "orientation" scattering may be expected to appear partly as a radiation of unaltered wave-length (Q branch) and partly as a radiation of altered wave-length extending out as "wings" on either side of the Rayleigh line. We may tentatively assume that the whole of the "density" scattering arises from the presence of sound waves of various wave-lengths associated with the thermal energy of the medium and is therefore to be associated wholly with the two Doppler components on either side of the Rayleigh line. On this view we should expect the ratio of the intensity of the central main component to the sum of the intensities of the two outer Doppler components, to be the same as the ratio of the intensity of the Q branch of the "orientation" scattering to the "density" scattering. What this ratio is, can be estimated roughly from the known depolarisation of transversely scattered light observed with a spectrograph using a narrow slit to exclude the "wings" on either side of the Rayleigh line as completely as possible. Bhagavantam, Venkateswaran,

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* The Wood's tube used in conducting experiments with carbon tetrachloride was slightly smaller than that used later for toluene.

5 C. V. Raman and K. S. Krishnan, Phil. Mag., 1923, 5, 498.
8 S. Venkateswaran, Phil. Mag., 1932, 14, 258.
Rousset\(^9\) and others have made observations by this method. Using Venkateswaran's observations of the depolarisation of transversely scattered light with a narrow slit and a spectrograph, the intensities of "density" and "orientation" scatterings respectively have been calculated for light scattered at 180°.

The table below gives the intensities of light scattering calculated on the above hypothesis.

**TABLE II.**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>&quot;Density&quot; Scattering</th>
<th>&quot;Orientation&quot; Scattering (Q-branch)</th>
<th>&quot;Density&quot; Scattering</th>
<th>&quot;Orientation&quot; Scattering (Q-branch)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon tetrachloride..</td>
<td>0.97</td>
<td>0.93</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>1.63</td>
<td>0.96</td>
<td>0.67</td>
<td></td>
</tr>
</tbody>
</table>

Considering the figures in Table II and accepting the view stated above, it would appear in the case of carbon tetrachloride, the intensity of the central undisplaced component ought to be very weak in comparison with the intensity of the Doppler components accompanying it. The actual state of affairs is quite the contrary as can be judged from the photographs obtained with this liquid though the total intensity of scattering in carbon tetrachloride is smaller than in toluene as is clearly indicated by the exposures necessary, the central undisplaced line for carbon tetrachloride is not only very much greater in intensity than either of the outer components, but it is even stronger relatively to them than in the case of toluene. Moreover, in no case of a liquid has the central component been found to be less intense than the Doppler components. This contradiction with the facts appears definitely to indicate that the explanation of the origin of the Rayleigh line and its Doppler components indicated above is untenable.

Before discussing further the nature of the light scattered by a liquid, it would be interesting to consider the nature of the light scattered by gases and solids. In the case of light scattered by a gas, leaving aside the Raman effects due to the rotations and vibrations of the molecules, we may expect to find a Doppler broadening of the Rayleigh line, the intensity distribution being of the Maxwellian type. The broadening would also be a function of the angle of scattering being zero in the direction of the incident light and

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\(^9\) Rousset, C. R., 1933, 197, 1083,
maximum in the opposite direction.\textsuperscript{10} In the case of a solid, Brillouin\textsuperscript{11} has worked out the problem and shown that the light reflected from the sound wave trains should exhibit a Doppler effect which would take the very simple form of a doubling of the lines in the scattered light, the frequency shifts being given by the formula (1) already given. Moreover, according to this view, the central undisplaced component should be completely absent being replaced by this doublet.

It is hardly to be expected that the Brillouin equation would completely describe the Doppler effect observed in the light scattered by any actual liquid, as the theory ignores the molecular structure of the medium and is therefore an idealisation. It is only in the case of a crystal that we can expect the observed phenomena to agree most closely with Brillouin's theory. The phenomena to be expected in the light scattered by liquids should evidently be intermediate between those characteristic of a crystal and a gas. An insight into the actual state of affairs taking place in a liquid is given by the suggestion put forward by Raman\textsuperscript{12} in a communication to \textit{Nature} in which he has shown that the equation of Brillouin is only a special case of a more general treatment of the problem on quantum principles. Raman treats the medium scattering light as an assemblage of photons having energy $h\nu_l$ and momentum $\frac{h\nu_l}{c}$, material particles having translatory energy $\frac{1}{2}MV^2$ and linear momentum $MV$ and associated with the latter, quanta of sound (or 'phonons' to use the name given later by Frenkel\textsuperscript{13}), having energy $h\nu_s$ and momentum $\frac{h\nu_s}{a}$. Next he treats an individual encounter as satisfying the equations similar to the Compton type and gets two equations the first being a scalar and the second a vector equation as given below:

$$\frac{1}{2}MV^2 + h\nu_s + h\nu_l = \frac{1}{2}MV'^2 + h\nu'_s + h\nu'_l$$

If we ignore the energy and momenta of the material particles we immediately get Brillouin's result, and if we omit the energy and momenta of the sound quanta we get the classical Maxwellian broadening, these being two extreme cases. In general we have to look upon both these phenomena to be present, influencing one another in the case of a liquid.

\textsuperscript{10} C. V. Raman, \textit{Nature}, 1919, \textbf{103}, 165.
\textsuperscript{11} L. Brillouin, \textit{Ann. der Phys.}, 1922, \textbf{17}, 88.
\textsuperscript{13} J. Frenkel, \textit{Wave Mechanics--Elementary Theory}, p. 266.
From the experimental data obtained in this investigation it is very clear that the central undisplaced component is conspicuously present in all photographs of the scattered light and is found to be distinctly brighter than the outer Doppler components. The fact that with such weakly anisotropic molecules like those of carbon tetrachloride, the central component is very strong (in fact stronger than in the case of toluene), leads us to the conclusion that though the anisotropy of the molecules does contribute towards the central line (Q branch), it is not in main responsible for the appearance of the central undisplaced component.

These results lead us to postulate that the molecules in the liquid should be regarded as being divided into two sets of molecules, one set of molecules resembling those in a 'vapour' or gaseous state and the other set of molecules resembling those in a 'crystalline' or solid state; the former set giving rise to the central undisplaced component and the latter set of molecules giving rise to the two outer Doppler components. This is essentially the picture of the molecules in the liquid state put forward by Raman\textsuperscript{14} in two significant letters to Nature dealing with the theory proposed by him for the viscosity of liquids. In the same paper, an expression for the ratio of the number of molecules in the two states has been arrived at. If we call $E_1$ to be the work required to separate a pair of molecules in the 'vapour' state and $E_2$ the work required to separate a pair of molecules in the 'crystalline' state, and apply the Boltzmann distribution law, we may, as a first approximation, take the relative abundance of the molecules in the solid and the 'vapour' states to be $e^{E_2-E_1/RT}$, where $R$ is the gas constant and $T$ the absolute temperature. Here $(E_2-E_1)$ should be taken to be the latent heat of fusion of the liquid under consideration. This expression works out at room temperature 27°C. to be 2.9 and 53.0 respectively for carbon tetrachloride and toluene. It must, however, be remembered that the intensities of the central undisplaced and the outer components will not bear the same ratio as the relative abundance of the molecules in the solid and 'vapour' states, since the scattering power in a solid will be relatively very small in value. This picture of the molecules in the liquid state will not only explain the fact that the central undisplaced component is distinctly brighter than the outer Doppler components, but it will also explain the relative intensity of the central to the outer components being greater in the case of carbon tetrachloride than in the case of toluene. Thus we see that this viewpoint is in better agreement with the observed phenomena than that suggested previously.

\textsuperscript{14} C. V. Raman, Nature, 1923, 111, 532 and 600.
From the foregoing discussion it is clear that it would be of very great interest to study the modifications of the Rayleigh line when the liquid scattering light is maintained at different temperatures. We can picture to ourselves, without anticipating the results of the experiment under observation, the changes that will take place in the structure of the Rayleigh line. At very low temperatures the number of molecules in the 'vapour' state will be very few and the stratifications of optical density in the medium due to the large number of molecules in the 'crystalline' state will be very sharp, with the result that the spectrum of the scattered radiation will have a very weak central component flanked by two sharp and intense Doppler components. As the temperature is raised, the number of molecules in the 'vapour' state will begin to increase, and the stratifications of optical density become less dense and sharp; in the spectrum of the scattered radiation, the main component would brighten up and widen at the same time, while the outer components get weaker till finally at a particular temperature, they will merge into the central component. The scattering would then possess the characters observed in the light diffused by a gas. Support to the views suggested above is furnished by the experiments with Quartz by Gross\textsuperscript{15} and with vapours by Cabannes\textsuperscript{16}.

Experiments are now under progress for the study of the structure of the Rayleigh line, the scattering liquid being maintained at different temperatures; their results may be expected to lead to a clearer understanding of this aspect of the liquid state, and will form the subject-matter of a separate communication.

In conclusion I desire to express my grateful thanks to my professor Sir C. V. Raman for his kind interest and helpful guidance during the progress of this work.

Summary.

In continuation of the author's previous work on benzene, the study of the fine structure of the Rayleigh line has been extended to the cases of carbon tetrachloride and toluene with improved experimental technique. Very clear photographs of the interference pattern free from continuous background have been obtained with carbon tetrachloride and it has been found that the relative intensities of the central and the outer Doppler components is much greater in the case of carbon tetrachloride than in toluene. This fact leads us to the conclusion that, though the anisotropy of

\textsuperscript{15} E. Gross, \textit{Zeits. f. Phys.}, 1930, 63, 800.

\textsuperscript{16} J. Cabannes, loc. cit.
the molecules does contribute towards the central line ($Q$ branch), it is not in main responsible for the appearance of the central undisplaced component. It is only the wings on either side of the Rayleigh line, which become more and more prominent with increase of anisotropy of the molecules constituting the scattering medium. On account of the high scattering power of toluene, it was possible to extend the observation and test the Doppler shifts of $\lambda 5461$ Å, in agreement with equation (1). The experimental data obtained in the investigation have been examined and some relevant theoretical aspects of the problem are discussed in the last section of the paper.

The question of the reality of the red shift of the centre of the Rayleigh line observed by Cabannes has been investigated and it has been shown that there is no shift of such a nature. The conditions under which a spurious red shift might be observed have been examined and it is found that temperature and pressure variations of the surrounding atmosphere affect the interference pattern of the scattered light when exposures are of very long duration.
B. V. Raghavendra Rao.  

Carbon tetrachloride.  
\( \lambda 4047 \text{Å} \)
Direct.  Scattered.

\[ \begin{align*}
\text{cm}^{-1} \\
+0.068 \\
-0.394 \\
+0.339 \\
+0.270 \\
-0.743 \\
\end{align*} \]

\[ \begin{align*}
\text{cm}^{-1} \\
-0.099 \\
-0.154 \\
+0.836 \\
+0.240 \\
+0.556 \\
+0.508 \\
+0.836 \\
-0.555 \\
+0.106 \\
-0.251 \\
-0.960 \\
\end{align*} \]

Carbon tetrachloride.  
\( \lambda 4358 \text{Å} \)
Direct.  Scattered.

\[ \begin{align*}
\text{cm}^{-1} \\
-0.230 \\
+0.230 \\
\end{align*} \]

Toluene.  
\( \lambda 4047 \text{Å} \)

Scattered Light  
Direct Light.

Toluene.  
\( \lambda 4047 \text{Å} \)
Direct.  Scattered.

\[ \begin{align*}
\text{cm}^{-1} \\
+0.068 \\
-0.394 \\
+0.339 \\
+0.270 \\
-0.743 \\
\end{align*} \]

\[ \begin{align*}
\text{cm}^{-1} \\
-0.320 \\
-0.320 \\
\end{align*} \]

Toluene.  
\( \lambda 4358 \text{Å} \)
Direct.  Scattered.

\[ \begin{align*}
\text{cm}^{-1} \\
-0.099 \\
-0.164 \\
+0.836 \\
+0.240 \\
+0.556 \\
+0.508 \\
+0.555 \\
+0.106 \\
-0.251 \\
-0.960 \\
\end{align*} \]
This plate shows the interference patterns of the scattered and direct light taken side by side in the manner described in the body of the paper (page 476) to test the reality of the Cabannes' red shift. The centre of the interference pattern is purposely shifted so that the contraction of the rings in the scattered pattern, if any, may be noticed with greater ease. It will be noticed that the ring system is perfectly continuous without any break when we pass from the scattered to the direct pattern, showing that there is no measurable shift either to the red or to the violet region of the spectrum.

\( \lambda 4047 \text{ Å} \)

(a) Interference pattern of direct light early in the morning.
(b) ,, ,, ,, late in the noon.
(c) ,, ,, ,, early next morning.

\( \lambda 4358 \text{ Å} \)

(a) Interference pattern of scattered light early in the morning.
(b) ,, ,, ,, late in the noon.
(c) ,, ,, ,, early next morning.

In the interference pattern of \( \lambda 4358 \text{ Å} \) the centre of the pattern has changed from a bright spot surrounded by a dark ring as shown in (a) and (c) to a dark spot surrounded by a bright ring as in (b) and vice versa in the case of \( \lambda 4047 \text{ Å} \).

These pictures are intended to show how the variations of temperature and pressure of the surrounding medium influence the interference pattern of the direct light itself, giving a false shift of the centre of the main radiation.