

The Dispersion of Polarisation of Light-Scattering

BY

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(Plate VI)

1. Introduction.

As is well-known, the birefringence of crystals shows a remarkable dependence on wave-length, increasing in general rapidly as we proceed towards the ultra-violet. For example in the case of calcite the value of $n_o - n_e$ which is only 0.172 for the D-lines of sodium (589 $m\mu$) rises to 0.207 at 300 $m\mu$ and to 0.327 at 200 $m\mu$, the last value being almost double the first. We should expect a similar dependence on wave-length also for the optical anisotropy of individual molecules, because according to the theory of Silberstein,¹ developed by Bragg,² Ramanathan³ and others, the optical anisotropy of molecules arises from essentially the same causes as are responsible for the birefringence of crystals, *viz.*, the mutual interaction of the optical doublets induced in the component atoms by the incident light-wave. Since the depolarisation of the light transversely scattered by the molecules in the fluid state is a measure of their optical anisotropy, the depolarisation should then exhibit a large dispersion.

¹ L. Silberstein, *Phil. Mag.*, Vol. 33, p. 521 (1917).

² W. L. Bragg, *Proc. Roy. Soc. A*, Vol. 105, p. 320 (1924).

³ K. R. Ramanathan, *Proc. Roy. Soc. A*, Vol. 107, p. 684 (1925).

2. Discussion of Earlier Measurements.

Some early investigations carried out by one of us on a large number of liquids, using sun-light filtered through suitable coloured glasses, did not show any large dependence on wave-length.⁴ These measurements, however, so far as the dependence on wave-length is concerned, must necessarily be taken as only preliminary, since in the first place the incident light was not *monochromatic*, the filters used transmitting fairly large regions of the spectrum, and secondly, no attempt was made to isolate the classical scattering from the Raman radiations which, as we now know, always accompany them; however, the general result is not likely to be affected by either of these considerations. Taking the latter effect first, the Raman scattering is very much feebler than the classical scattering, being according to recent estimates⁵ only a small fraction of the latter (about one or two per cent.). Since the Raman scattering is in general also polarised in the same direction as the classical scattering, the value of the depolarisation of the latter is not likely to be affected much by its admixture. When we consider the *variation* of this value with the wave-length, the influence of the Raman scattering will be even smaller, since it increases with practically the same rapidity as the classical scattering with the diminution of the exciting wave-length.⁶

The want of perfect monochromatism of the incident light used in these experiments does not also seriously affect the result when it is negative, as it happens to be; all that is necessary for establishing the independence on wave-length being that the spectral regions transmitted by the different filters should widely differ from one another—which was actually the case.

⁴ K. S. Krishnan, *Phil. Mag.*, Vol. 50, p. 697 (1925).

⁵ S. C. Sirkar, *Ind. Journ. Phys.*, Vol. 5, p. 159 (1930).

⁶ See C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc. A*, Vol. 123, p. 23 (1929); Ornstein and Rekveld, *Zeits. für Physik*, Vol. 61, p. 593 (1930); S. C. Sirkar, *loc. cit.*

Mr. P. V. Krishnamurthy⁷ has repeated the investigation by a method which in principle is an improvement on the previous method. He uses light from a mercury arc as source and investigates the polarisation of the different mercury lines scattered by the liquid with the help of a nicol and a quartz spectrograph. The method besides enabling the depolarisation to be determined for any particular wave-length, also automatically eliminates the effect, if any, of the Raman radiations. Mr. Krishnamurthy has studied by this method five or six liquids and gets in all cases a considerable change of the depolarisation with wave-length, in striking contrast with our results mentioned. As he proceeds from the yellow towards shorter wave-lengths, the depolarisation at first diminishes to a minimum and rises rapidly as we proceed further, the value for the 3,650 group of lines of mercury being about one and a half times (or even more in some cases) the value for the visible regions. What is more remarkable, the region of minimum value for the depolarisation factor is practically the same for all the liquids studied by him, *viz.*, in the violet. That the optical anisotropy of the molecules should depend on the wave-length is understandable or probably even to be expected as we have already mentioned in the introduction, but that it should reach a minimum value in the violet for all the molecules and again rise as we proceed towards the ultra-violet, is rather surprising. Also his absolute values for the depolarisation factor for the visible region differ considerably from those obtained by other investigators.

More recently Szivessy and Dierkesmann⁸ have investigated the dispersion of the electric double-refraction (Kerr-effect) of some liquids. As is well-known, the magnitude of this effect depends on the optical as well as the electrical

⁷ Quoted by A. S. Ganesan and S. Venkateswaran, *Ind. Journ. Phys.*, Vol. 4, p. 359 (1929).

⁸ G. Szivessy and A. Dierkesmann, *Ann. der Physik*, Vol. 8, p. 507 (1929).

anisotropy of the molecules, as also on the refractive index of the medium.⁹ Szivessy's results in all cases show a slight increase of the effect as we go to the ultra-violet which is *wholly* explicable as being due to the increased refractive indices of the liquids without any change in the optical or electrical anisotropy of the molecules in the liquid, thus supporting the results of our measurements as against Mr. Krishnamurthy's.

In view of the conflicting nature of the results given above and the theoretical importance of an accurate determination of the dispersion, it was thought that a thorough investigation of one typical substance like benzene, over a wide range of wave-lengths would be desirable. The present paper describes the results of such an investigation.

3. *Use of Spectrograph in Polarisation Measurements.*

The general principle involved in the usual method of determination of the polarisation of the scattered light for different wave-lengths with the help of the spectroscope is as follows. A narrow parallel beam of light traverses the liquid, say, in a horizontal direction. The spectrograph is adjusted so as to have the axis of its collimator horizontal and normal to the track in the liquid; in this position the light that gets into the spectrograph would be the one transversely scattered by the liquid. As we know, this is partially polarised, the direction of vibration of the polarised part being vertical. If now a nicol is introduced in front of the slit of the spectrograph in the path of the scattered light, by having its transmission axis vertical and horizontal respectively, either of the two components in the scattered light can be separately transmitted into the spectrograph. By photographing the two polarised spectra in juxtaposition, as can be easily done by using a suitable Hartmann diaphragm for the slit of the

⁹ See C. V. Raman and K. S. Krishnan, *Phil. Mag.*, Vol. 3, pp. 713 and 724 (1927).

spectrograph, the two intensities can be compared. Indeed by using a steady source of illumination and by suitably adjusting their relative times of exposure so as to obtain equality of density on the photographic plate for any given wave-length, their relative intensities for this wave-length can be calculated.

Evidently any part of the spectrograph which is likely to affect the intensities of the two principal vibrations *differently* has to be carefully studied and if its behaviour is uniform the instrument has to be calibrated for the polarisation induced by these parts.

The present measurements were made with a Hilger quartz spectrograph (their new 'All-Metal' instrument). For the purpose of calibrating it for polarisation, a 'pointolite' lamp fed from a storage battery of constant voltage, with a ground glass plate in front of it, was used as the source of light. When the lamp has been burning for some time, its intensity may be taken to be practically constant. On viewing it through a Savart plate backed by a suitably oriented nicol, no fringes were visible, showing that the source of light was perfectly unpolarised. It was mounted on the line of axis of the collimator of the spectrograph and at a large distance from it so as to illuminate the slit quite uniformly. A square ended nicol of large aperture served to polarise the light falling on the slit. That the slit was uniformly illuminated and that the source of light was also quite steady were tested by taking two spectrograms in juxtaposition, using the Hartmann diaphragm, under the same exposure, the orientation of the nicol being the same in both cases. It was hardly possible to distinguish the two halves.

Next, two spectrograms were taken also in juxtaposition but one of them with the nicol so oriented as to transmit only vertical vibrations and the other with the nicol transmitting horizontal vibrations. They are reproduced in Fig. 1

(Plate VI) where the upper half of the picture corresponds to vertical vibrations and the lower half to the horizontal. The intensities of the two halves are no more equal, thus pointing to an appreciable difference in transmission by the spectrograph of the two vibrations. What is curious, their relative intensities show an alternating fluctuation as we move along the spectrum. For the region at about 5500 A.U.—the extreme right of the picture—the horizontal vibration is much stronger than the vertical, and it tends to approach the latter as we go towards the violet, the two becoming equal at about 4400 A.U. Further beyond, the horizontal component again increases, the whole region up to about 3900 A.U. showing distinctly a larger intensity for the horizontal. Beyond this wave-length the intensities are reversed, the vertical being now stronger. The two again approach at about 3300 A.U., and for shorter wave-lengths the vertical is always the stronger. Their relative values are roughly represented by the curve in Fig. 3.

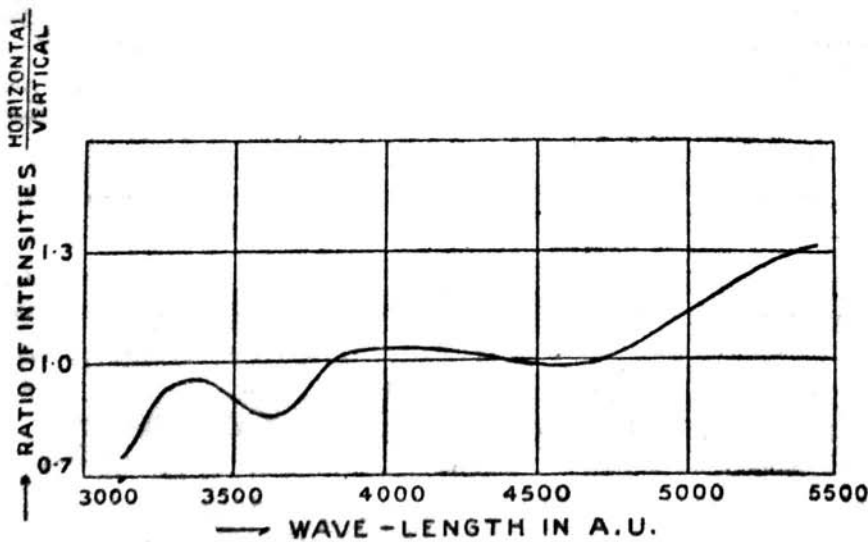


FIG. 3.

It would be of interest to locate the origin of the polarisation in the spectrograph. It is well-known that light on passage through narrow metallic slits are considerably polarised; but in the above experiment the slit was kept fairly wide, so that the polarisation due to the slit is eliminated. The only other obvious (at first sight) source of polarisation in the spectrograph would be the unequal reflection of the two components from the two faces of the prism. The vertical vibration would be more copiously reflected and would therefore be correspondingly feebler in transmission. But by itself this cannot account for the alternation in intensity actually observed, which suggests in addition some kind of rotation of the plane of polarisation of the light while traversing the spectrograph. That actually such a rotation takes place is shown by allowing plane polarised light to fall on the slit and analysing the light transmitted at the camera end. The latter is found to be elliptically polarised, its weaker principal component being however so much feebler than the stronger that it can be practically regarded as plane polarised. Its plane of polarisation is *widely* different for different wave-lengths.

It is not difficult to find the cause of this rotation since all the optical parts of the spectrograph are of crystalline quartz. First considering the prism, it is of the Cornu type consisting of two equal prisms of right- and left-handed quartz. For the ray for which the deviation by the prism is a minimum, the distance traversed in the two halves will be exactly the same and hence the rotations will compensate each other. Even for a wave-length for which the ray inside the prism deviates most from the previous track, calculation shows that the difference in thickness of right-handed and left-handed material traversed by it would, for prisms of the size used, be small even near the base; and the consequent rotation is only a few degrees. Thus the enormous rotations actually observed must be due to the lenses, and

are quite understandable since the rotation for quartz is about 21° per mm. for the D-line and very much more shorter wave-lengths. The rotation by the camera lens would not of course affect the relative intensities of the two components reaching the photographic plate, but that by the collimating lens would evidently determine the plane of polarisation at incidence on and emergence from the first and second prism faces respectively and hence the loss by reflection. The alternation in intensity observed on the photographic plate is a necessary consequence.

But this rotation would depend on what *part* of the collimating lens the ray is traversing ; experimentally the ratio of the two components transmitted does depend to some extent on the size of the aperture used in front of the camera lens and also on the position of the source of light in front of the spectrograph.

These limitations of the quartz spectrograph do not seem to have been recognised.

4. *Experimental Method adopted in the Present Measurements.*

From what has been said at the end of the last section it will be clear that the ratio of the intensities of the two vibrations, besides being different for different wave-lengths, also depends on the portion of the collimating lens of the spectrograph through which they traverse. This latter fact makes the calibration of the quartz instrument to some extent uncertain. Of course in a glass spectrograph or one of fused silica parts, the polarisation of the instrument for any given wave-length is exactly determinable. But the glass spectrograph can be used only over a limited range of the spectrum while fused quartz prisms and lenses are not usually available. For this reason it seemed desirable to use the ordinary quartz spectrograph and design a method of measurement which would be *independent of the polarisation of the instrument.*

The following experimental arrangement satisfies this condition. The principle of the method is essentially the same as in the well-known Cornu method of measuring partially polarised light which has been so frequently used in light scattering, with this difference, *viz.*, the scattered light after passage through the double image prism and nicol is analysed spectroscopically. A narrow horizontal beam of light from a mercury arc is sent through the liquid. The double image prism is placed in the path of the transversely scattered light and so oriented as to deviate in a vertical plane the rays passing through it. Immediately behind it is the nicol and further behind, a lens which focusses the two images of the track formed by passage through the double image prism, on the slit of the spectrograph. The two images will naturally fall one above the other crossing the length of the slit, and will correspond to vibrations in the scattered light which were initially vertical and horizontal respectively. On taking a spectrogram with the slit fairly open, a separate pair of tracks appears on the plate for each incident wave-length. By suitably rotating the nicol, the two tracks can be adjusted for equality of density on the photographic plate for any given mercury line and thus the depolarisation of the scattered light for the wave-length calculated. In Fig. 2, Plate VI, is reproduced one such picture (enlarged about $2\frac{1}{2}$ times) obtained with benzene liquid with an exposure of about 15 mins.

In this arrangement the window through which the scattered light passes from the liquid to the double image prism is of fused silica. All the other parts may be of *crystalline* quartz. Because in the first place the incident light being perfectly unpolarised, any lens or plate of crystalline material interposed normally in its path does not affect the nature of its polarisation. On the observation side also, *after leaving the nicol* the light corresponding to either of the two images of the track is plane polarised in the same direction determined by the orientation of the nicol, and hence any further passage

through either the crystalline lens used to focus them on the slit, or through the parts of the spectrograph will not affect their *relative* intensities. Thus the polarisation of the instrument is completely eliminated.

There are also other advantages in this arrangement. The source of light need not be steady, since any fluctuation in its intensity would not alter the relative intensities of the two images. Also the influence of stray light from the background, whose polarisation would in general be different from that of the liquid scattering, on the measurement of the latter, is eliminated; since the images are here viewed against a background which is of the same intensity for both.¹⁰

5. Results.

Coming to the actual measurements on benzene it may be mentioned at the outset that the present measurements extend only to about 3100 A.U. on the ultra-violet side, since a double-image prism transparent to shorter wave-lengths was not available to us. When such a prism is available we hope to extend the measurements as far as the transparency of the liquid would allow.

The spectrogram reproduced in Fig. 2, Plate VI, shows tracks for the three prominent mercury wave-lengths: $\lambda 3650$, $\lambda 4047$ and $\lambda 4358$. The tracks for the green and yellow lines on one side, and for the 3341 and 3130 doublet on the other, are not shown in the picture, because when the tracks for these wave-lengths are of reproducible intensity, those for the other three are highly over-exposed. The actual values obtained for different wave-lengths are given in column 2 of the following table.

¹⁰ See J. Cabannes, "La diffusion moléculaire de la lumière," Paris, 1929, p. 102.

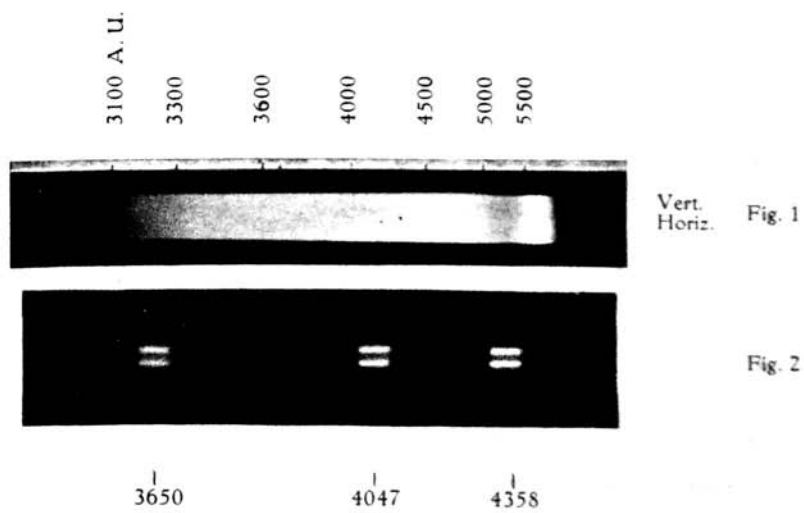


TABLE I.

Values for the depolarisation factor for liquid benzene
at 25°-28°C.

λ in A.U.	Cornu method with quartz spectrograph.	Cornu method with inci- dent monochromatic light.	With a glass spectro- graph and only a nicol.
5790 } 5769 }	0.40 ₅	...	0.43
5461	0.40 ₅	0.41	0.42
4358	0.40 ₅	0.41	0.41
4047	0.40 ₅	...	0.41
3650	0.41 ₀	0.42	0.41
3341	0.41 ₀
3132 3126	0.41 ₀

6. Other Methods

The values have been verified by other methods which are not however so accurate. For example instead of analysing the scattered light spectroscopically as has been done in the above measurements, the incident light was rendered monochromatic by interposing in its path suitable filters, and the scattered light after passing through the double prism and nicol, was photographed directly. The "Zeiss monochromator filters," B and C, served to transmit the 5461 line and the 4358 group respectively. For the 3650 group a Corning glass filter was used. The values obtained by this method are given in column 3 of Table I.

In this method the Raman radiations are not eliminated; their effect on the values, however, is not likely to be appreciable. (See section 2.)

Measurements have also been made, by the method discussed in Section 3, with a glass spectrograph specially constructed for the purpose, the scattering being analysed merely by a nicol placed in front of the slit of the spectrograph. The instrument was of course calibrated for its polarisation. A mercury lamp running at a constant voltage of 110 from a storage battery served as the source of illumination. The values obtained by this method are given in the last column of Table I.

In this method any residual stray light which could not be completely eliminated is likely to affect the values, especially for the longer wave-lengths. The high values for the yellow and the green are evidently to be attributed to this cause. Also in this method the accuracy of the measurements depends on the steadiness of the source.

Considering the above uncertainties in the latter two methods their results must be considered as fully confirming the values obtained by the Cornu method with spectral analysis, which are more reliable. They show unambiguously that over the range of wave-lengths investigated the *depolarisation factor for liquid benzene has practically the same value.*

7. *Scattering by Benzene Vapour.*

The constancy in the value of the depolarisation of liquid scattering for different wave-lengths and the consequent suggestion, at least at first sight, that the optical anisotropy of the benzene molecule is presumably also constant, makes an investigation of the scattering in the vapour state extremely desirable. Here the experimental difficulties are naturally very much greater. Some preliminary measurements have been made on the vapour at a pressure of one atmosphere at the temperature of boiling of the liquid. The values must be considered as very approximate. They seem to show that

when we pass from the green to about 3600 A.U. the depolarisation factor increases from 0.041 to about 0.047 in contrast with the behaviour of the liquid where the value *remains constant* over a much larger spectral range. We shall postpone discussion about the significance of these results till more accurate values for the vapour have been obtained.

Summary

The paper describes the results of measurements on the dispersion of polarisation of the light scattered by benzene both in the liquid state and in the state of vapour. It is found that while the depolarisation factor for the liquid remains constant over a wide range of the spectrum, the value for the vapour increases appreciably as we proceed towards the ultra-violet.