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Reversal of Circular Polarisation in Raman Scattering

BY

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ABSTRACT

A classical theory of the scattering of circularly polarised light by rotating molecules is worked out. In the forward direction a part of the total Rayleigh scattering proportional to $(2\mu^2 - \frac{5}{90}\gamma^2)$, is circularly polarised in the same sense as the incident light and a part proportional to $\frac{2}{15}\gamma^2$ is unpolarised. In the rotational Raman scattering in each branch, a part given by $\frac{1}{12}\gamma^2$ is circularly polarised in a *reverse* sense and the other part given by $\frac{1}{30}\gamma^2$ is unpolarised.

In the transverse direction the results are identical with those obtained when unpolarised incident light is used.

The case of strongly depolarised vibration lines which show the phenomenon of reverse circular polarisation in the forward scattering is briefly discussed. The conclusions are supported by the recent experiments of Bär and Hanle.

1. *Introduction.*

In a previous paper[1] the author has dealt with the problem of the scattering of plane polarised and unpolarised light by an assembly of randomly oriented, but freely rotating and vibrating diatomic molecules, on purely classical considerations. The results obtained are shown to exhibit a

[1] Ind. Jour. Phys., 6, 331 (1931).

general correspondence with those derived on the basis of the quantum theory of the scattering of light. Recently however Bär[2] and Hanle[3] have independently used circularly polarised light in the investigation of the Raman scattering and reported certain interesting results, amongst which the reversal of the sense of circular polarisation after being scattered in the forward or backward direction exhibited by some of lines may specially be mentioned here. The present writer has conducted similar experiments with carbon disulphide and found that the two principal lines which are well polarised in the transverse scattering show normal circular polarisation in the forward direction. The wings accompanying the Rayleigh lines which are usually attributed to rotational Raman effect exhibited in part circular polarisation of a reverse sense. Similar results have been obtained by Bär in the case of benzene.

It is well known that energy and linear momentum are conserved when photons and molecules exchange these quantities in mutual collisions. In two recent communications[4] it was shown that an extension of this rule to the case in which an exchange of angular momentum takes place between a spinning photon, and a rotating molecule leads to a very natural explanation of some of the results obtained with circularly polarised light, affording at the same time a simple interpretation of the peculiar selection rules found valid in Raman scattering. The existence of a spin of the photon in either sense is the quantum analogue of right and left handed circularly polarised light and as such it is obviously of importance to consider the results that are to be expected in the scattering of circularly polarised light. In the present paper, it is proposed to investigate the problem in a purely classical

[2] Helv. Phys. Acta, *4*, 130 (1931).

[3] Naturwiss., *19*, 375 (1931).

[4] Sir C. V. Raman and S. Bhagavantam, Nature, *128*, 114 (1931) and Sir C. V. Raman, Nature, *128*, 545 (1931).

way as is done in the case of the plane polarised or unpolarised light.

2. *Rotating Molecules: Forward Scattering.*

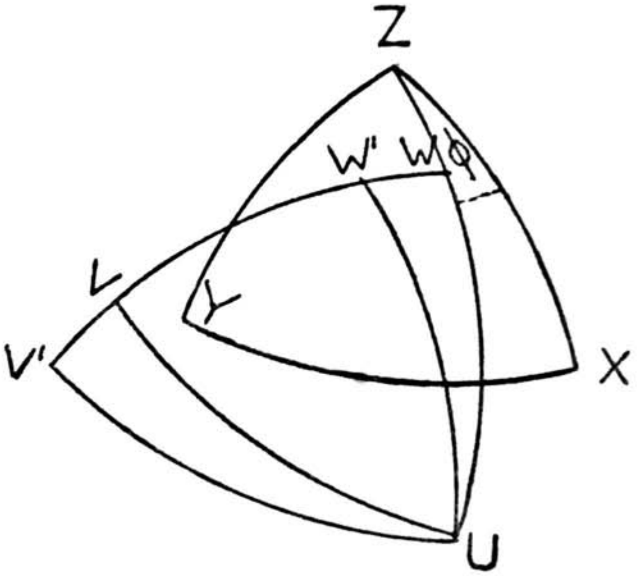

Fig. 1

OX, OY and OZ in fig. (1) represent rectangular axes fixed in space, where O is the centre of a unit sphere. OW is the axis of symmetry of the molecule and OU and OV are mutually two perpendicular axes in the plane of symmetry. The diagram represents one arbitrary orientation of the molecule specified by the arc ZW denoted by θ and the azimuthal angle ϕ. We shall consider the case of a circularly polarised beam, incident along XO, and specified by a vibration E sin $2\pi nt$ along OZ and E cos $2\pi nt$ along OY. A and C are coefficients characteristic of the molecule and are related to μ and γ through the equations

$$\mu = \frac{2A+C}{3} \quad \text{and} \quad \gamma = C - A.$$

The necessary cosines are

$\cos ZU = -\sin\theta$ $\cos XU = \cos\theta\cos\phi$ $\cos YU = \sin\phi\cos\theta$

$\cos ZV = 0$ $\cos XV = -\sin\phi$ $\cos YV = \cos\phi$

$\cos ZW = \cos\theta$ $\cos XW = \sin\theta\cos\phi$ $\cos YW = \sin\theta\sin\phi$

$\cos ZW' = \cos\theta\cos 2\pi\nu t$

$\cos YW' = \cos\phi\sin 2\pi\nu t + \sin\theta\sin\phi\cos 2\pi\nu t$

$\cos XW' = -\sin\phi\sin 2\pi\nu t + \sin\theta\cos\phi\cos 2\pi\nu t$

where W′ represents the position of W after an interval of time t if the molecule begins to rotate about the OU axis with an angular velocity $2\pi\nu$.

The procedure is the same as that given in the previous paper and follows, in the general outlines, the one given by Lord Rayleigh. The incident vibration is resolved along the axes of the molecule and the induced moments are resolved back to any desired direction. The final intensities are obtained by averaging the trigonometric functions involved of the angles θ and ϕ for random orientation; with due regard to the phases of the various amplitudes.* The following expressions give the induced vibrations for a stationary molecule.

$$\mu_{oz} = (A\sin^2\theta + C\cos^2\theta)\, E\sin 2\pi nt \quad \ldots \quad (1)$$

$$\mu_{oy} = (A\sin^2\phi\cos^2\theta + A\cos^2\phi + C\sin^2\theta\sin^2\phi)\, E\cos 2\pi nt \quad \ldots \quad (2)$$

$$\mu_{oy} = (C - A)\,(\sin\theta\cos\theta\sin\phi)\, E\sin 2\pi nt \quad \ldots \quad (3)$$

$$\mu_{oz} = (C - A)\,(\sin\theta\cos\theta\sin\phi)\, E\cos 2\pi nt \quad \ldots \quad (4)$$

(1) and (2) represent the vibrations in the scattered light that are parallel to the vibrations in the incident light while (3) and (4) represent those that are perpendicular to the

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* The average values adopted are the same as those that are given in a previous paper by the author; *loc.cit.*

vibrations in the incident light. (1) and (2) may be respectively written in the form

$$\{\mu+\gamma\,(\cos^2\theta-\tfrac{1}{3})\}\ \mathrm{E}\sin 2\pi\, nt$$

$$\{\mu+\gamma\,(\sin^2\theta\sin^2\phi-\tfrac{1}{3})\}\ \mathrm{E}\cos 2\pi\, nt.$$

With the introduction of a rotation of the molecule, these vibrations split into two parts, one having the original frequency and the other altered frequencies. They will, as before, respectively constitute the Rayleigh and the Raman scattering and the expressions for them may be written out as

$$\text{Rayleigh}\left\{\begin{array}{ll} \mu_{oz}=\left\{\mu+\gamma\left(\dfrac{\cos^2\theta}{2}-\dfrac{1}{3}\right)\right\}\mathrm{E}\sin 2\pi\, nt & (5)\\[2ex] \mu_{oy}=\left\{\mu+\gamma\left(\dfrac{1}{6}-\dfrac{\cos^2\theta\sin^2\phi}{2}\right)\right\}\mathrm{E}\cos 2\pi\, nt & (6)\end{array}\right.$$

$$\text{Raman}\left\{\begin{array}{ll} \mu_{oz}=\dfrac{\gamma\cos^2\theta}{4}\{\sin 2\pi\,(n+2\nu)t+\sin 2\pi\,(n-2\nu)t\} & \ldots\ (7)\\[2ex] \mu_{oy}=\dfrac{\gamma}{4}(\sin^2\theta\sin^2\phi-\cos^2\phi)\ \{\cos 2\pi\,(n+2\nu)t+\cos 2\pi\,(n-2\nu)t\} & \end{array}\right.$$

$$+\frac{\gamma}{2}\sin\theta\sin\phi\cos\phi\ \{\sin 2\pi(n+2\nu)t-\sin 2\pi\,(n-2\nu)t\}\quad (8)$$

In order to interpret the above expressions, we will consider the process of an actual experiment. If a quarter wave plate is introduced in such a way that it retards the OX vibration by quarter of an oscillation and the light is then allowed to pass through a nicol with its vibration axis placed parallel to the internal bisector of the principal vibrations, only that part of the light which is circularly polarised in the same sense as the incident beam will be allowed to pass through. On the other hand if the quarter wave plate retards the OZ oscillation, the nicol in the same position will only allow that part of the light which is circularly polarised in a reverse sense. If some of the light is however unpolarised, equal parts of it will pass through the nicol in the two cases and hence unpolarised light may be interpreted as a mixture of two equal beams of circularly polarised light of opposite sense with uncorrelated phases and *vice versa*.

The result of applying the above operations to the amplitudes (5) and (6) leads to a change of $\cos 2\pi nt$ into $\sin 2\pi nt$ in the first case and the part that is circularly polarised in the same sense as the incident light is allowed to go through the nicol. The total intensity of this part is obtained by adding together $1/\sqrt{2}$ times each of the amplitudes and averaging the square of the resulting amplitude for all values of θ and ϕ. In the second case, $\sin 2\pi nt$ is retarded and changed to $-\cos 2\pi nt$ and only the part which is reversely circularly polarised is allowed to pass through the nicol. The total intensity of this part is obtained by subtracting from one another $1/\sqrt{2}$ times each of the amplitudes and averaging the square of the resulting amplitude for all values of θ and ϕ. In this case it is actually found that this latter part is less than the former unreversed part and the difference between the two amounting to $\left(2\mu^2 - \frac{1}{45}\gamma^2\right) E^2$, is separated out as a residual normally circularly polarised light and the rest having an intensity $\frac{1}{15}\gamma^2 E^2$ is interpreted as unpolarised light.

Similar treatment of the Raman terms (7) and (8) shows that out of an aggregate intensity of $\frac{1}{15}\gamma^2 E^2$ for each of the increased and diminished sets of frequencies, only $\frac{1}{30}\gamma^2 E^2$ is circularly polarised in the reverse sense whereas the rest is unpolarised.

The perpendicular components (3) and (4) may be dealt with in a similar manner, and separated into the Rayleigh and Raman terms by introducing the rotation of molecules. We have

$$\text{Rayleigh}\begin{cases}\mu_{oy}=\dfrac{\gamma}{2}\,(\cos\theta\sin\phi\sin\theta)\,\mathrm{E}\sin 2\pi\,nt\\[2ex] \mu_{oz}=\dfrac{\gamma}{2}\,(\cos\theta\sin\theta\sin\phi)\,\mathrm{E}\cos 2\pi\,nt\end{cases}$$

$$\text{Raman}\begin{cases}\mu_{oy}=\dfrac{\gamma}{4}\,(\cos\theta\cos\phi)\{\cos 2\pi(n-2\nu)t-\cos\;2\pi(n+2\nu)t\}\\[2ex] \qquad+\dfrac{\gamma}{4}\,(\cos\theta\sin\theta\sin\phi)\{\sin 2\pi(n+2\nu)t+\sin 2\pi(n-2\nu)t\}\\[2ex] \mu_{oz}=\dfrac{\gamma}{4}\,(\cos\theta\cos\phi)\{\sin 2\pi(n+2\nu)t-\sin 2\pi(n-2\nu)t\}\end{cases}$$

$$+\frac{\gamma}{4}\,(\cos\theta\sin\theta\sin\phi)\{\cos 2\pi(n+2\nu)t+\cos 2\pi(n-2\nu)t\}.$$

It is clear that the Rayleigh parts having identical amplitudes at all instants will give rise to a beam of total intensity $\frac{1}{30}\gamma^2\mathrm{E}^2$ wholly circularly polarised, the sense being the reverse of that of the incident light.

The Raman scattering terms show that all the light appears as circularly polarised in the *reverse* sense. The total intensity may easily be seen to be $\frac{1}{20}\gamma^2\mathrm{E}^2$. Summarising all the results we get in the forward direction

$$\text{Rayleigh scattering}\begin{cases}\left(2\mu^2-\dfrac{5}{90}\gamma^2\right)\mathrm{E}^2\text{(normal circular)}\\[2ex] \dfrac{2}{15}\gamma^2\mathrm{E}^2\text{(unpolarised)}\end{cases}$$

$$\begin{matrix}\text{Raman scattering}\\ \text{(Rotational)}\end{matrix}\begin{cases}\dfrac{1}{12}\gamma^2\mathrm{E}^2\text{ (reversed circular)}\\[2ex] \dfrac{1}{80}\gamma^2\mathrm{E}^2\text{ (unpolarised)}\end{cases}$$

It is interesting to note that $\frac{5}{7}$ of the Raman scattering is circularly polarised in a reverse sense whereas the rest is unpolarised. The reason for this is clear if we consider the groups of molecules rotating about the OX, OY and OZ axes separately. In the latter two cases the Raman radiations are restricted to XZ and XY planes respectively and in the forward direction the molecules rotating about the OY axis give an effective component along OZ and those that are rotating about the OZ axis give an effective component along OY. The two are not in phase relationship with each other and hence we get unpolarised light. The intensity in each case will only be derived from the parallel componets. On the other hand the molecules rotating about the OX axis give both OY and OZ components which will be in phase relation with each other and recombine to give circularly polarised light. This consits of a part derived from the parallel components, equal in intensity to the above unpolarised light and the other part derived from the perpendicular components. A reversal of sense however occurs due to the fact that if we separate out the stationary or the average part of the induced doublet from the fluctuating part, the latter will have opposite phases in the two directions OZ and OY with respect to the incident vibrations.

3. *Rotating Molecules : Transverse Scattering.*

The expressions in this case corresponding to 1, 2, 3 and 4 of the case of forward scattering may be written as

$$\mu_{oz} = (\mathrm{A} \sin^2 \theta + \mathrm{C} \cos^2 \theta) \, \mathrm{E} \sin 2\pi \, nt$$

$$\mu_{oz} = (\mathrm{C} - \mathrm{A}) \, (\sin^2 \theta \sin \phi \cos \phi) \, \mathrm{E} \cos 2\pi \, nt$$

$$\mu_{ox} = (\mathrm{C} - \mathrm{A}) \, (\sin \theta \cos \theta \cos \phi) \, \mathrm{E} \sin 2\pi \, nt$$

$$\mu_{oz} = (\mathrm{C} - \mathrm{A}) \, (\sin \theta \cos \theta \sin \phi) \, \mathrm{E} \cos 2\pi \, nt.$$

Separating them into the Rayleigh and Raman parts, by introducing the rotation of the molecule as before and writing them out in the same order, we have for the Rayleigh terms

$$\mu_{oz} = \left\{ \mu + \gamma \left(\frac{\cos^2\theta}{2} - \frac{1}{3} \right) \right\} \mathrm{E} \sin 2\pi\, nt$$

$$\mu_{ox} = -\frac{\gamma}{2} (\cos\phi \sin\phi \cos^2\theta)\ \mathrm{E} \cos 2\pi\, nt$$

$$\mu_{ox} = \frac{\gamma}{2} (\sin\theta \cos\theta \cos\phi)\ \mathrm{E} \sin 2\pi\, nt$$

$$\mu_{oz} = \frac{\gamma}{2} (\sin\theta \cos\theta \sin\phi)\ \mathrm{E} \cos 2\pi\, nt.$$

Similar treatment shows that there is no circularly polarised light in these expressions and all the light is either partially polarised or unpolarised. The aggregate intensity of the Rayleigh scattering will therefore be $\frac{1}{30}\gamma^2\mathrm{E}^2$ and $\left(\mu^2 + \frac{7}{180}\gamma^2\right)\mathrm{E}^2$ in the X and the Z directions respectively.

The Raman terms in the same order will be given by

$$\mu_{oz} = \frac{\gamma}{4} \cos^2\theta\ \{\sin 2\pi(n+2\nu)\,t + \sin 2\pi\,(n-2\nu)t\}$$

$$\mu_{ox} = \frac{\gamma}{4} \cos\phi \sin\phi\ (1+\sin^2\theta)\ \{\cos 2\pi(n+2\nu)\,t + \cos 2\pi\,(n-2\nu)t\}$$
$$+ \frac{\gamma}{4} \sin\theta\ (\cos^2\phi - \sin^2\phi)\{\sin 2\pi\,(n+2\nu)t - \sin 2\pi\,(n-2\nu)t\}$$

$$\mu_{ox} = -\frac{\gamma}{4} (\cos\theta \sin\phi)\ \{\cos 2\pi\,(n-2\nu)t - \cos 2\pi(n+2\nu)t\}$$
$$+ \frac{\gamma}{4} (\cos\theta \sin\theta \cos\phi)\{\sin 2\pi\,(n+2\nu)t + \sin 2\pi(n-2\nu)t\}$$

$$u_{oz} = \frac{\gamma}{4} (\cos\theta \cos\phi)\ \{\sin 2\pi(n+2\nu)\mathrm{t} - \sin 2\pi\,(\mathrm{n}-2\nu)t\}$$
$$+ \frac{\gamma}{4} (\cos\theta \sin\theta \sin\phi)\{\cos 2\pi(n+2\nu)t + \cos 2\pi\,(n-2\nu)t\}$$

It is easily shown that the first two terms give rise to only partially polarised light whereas the latter two give thicknesses of the bubble. The calculated values are given in Table I. I/a^2 is obviously the ratio of the observed intensity of transmission to the intensity which would be observed if the bubble were removed and the analyser rotated through 90°, so as to have its axis parallel to that of the polariser; in the table it is expressed as a percentage.

TABLE I.

Radial distribution of intensity for the diagonal positions.

$\frac{I}{a^2} \times 100$

Thickness / $\theta =$	60°	70°	75°	80°	85°	88°	89°	90°
42 A. U. (=1 unit layer of soap film)	0·0	0·1	0·2	0·6	2·1	6·7	6·2	0
84 A. U. (=2 unit layers)	0·2	0·5	0·9	2·0	5·5	4·8	...	0
168 A. U. (=4 unit layers)	0·6	1·5	3·0	5·3	6·7	1·8	...	0
252 A. U. (=6 unit layers)	1·3	3·2	5·0	7·1	5·2	0·6	...	0
420 A. U. (=10 unit layers)	2·7	5·7	7·1	6·6	2·1	...	...	0
840 A. U. (=20 unit layers)	5·1	7·2	6·1	3·1	0·4	...	...	0
1260 A. U. (=30 unit layers)	5·6	7·0	5·0	2·0	0·2	...	...	0
1680 A. U. (=40 unit layers)	5·0	7·2	5·5	2·3	0·3	...	...	0

One significant result emerges from the values exhibited in the above table, *viz.*, that in the case of *black* bubbles the illumination is confined practically to the edge of the bubble. It is true that theoretically the illumination at the edge itself is zero. But this has no practical significance since the vibrational Raman scattering are respectively proportional to $\left(\mu'^2 + \frac{7}{45}\gamma'^2\right)$ and $\frac{2}{15}\gamma'^2$. The expressions are similar to the ordinary type of the Rayleigh scattering except that μ' and γ' now represent the variations of μ and γ themselves for a unit variation in the nuclear distance. The true vibrational scattering is however given only by $\left(\mu'^2 + \frac{7}{180}\gamma'^2\right)$ and $\frac{1}{30}\gamma'^2$ and the bulk of the unpolarised light, as in the Rayleigh scattering, is contained as wings on either side arising from a simultaneous rotation and vibration of the molecules. It is obvious that with increasing γ', the intensity of the very nearly unpolarised rotational wings as well as the intrinsic depolarisation of the true vibrational scattering increase simultaneously. The aggregate vibrational scattering becomes more and more imperfectly polarised. On this view an appreciable part of the strong depolarised vibration lines, particularly in the case of polyatomic molecules with large moments of inertia, has a rotational origin. This part will therefore show a reversal of circular polarisation in accordance with the foregoing considerations. These results appear to be supported by the recent work of Bär and Hanle who find that in benzene, carbon tetrachloride and chloroform, the lines that are badly polarised in the transverse direction are just those that show the phenomenon of reverse circular polarisation in the forward direction. The lines that are well polarised in the transverse direction do not show the reversal of circular polarisation.

The above considerations however imply that the imperfectly polarised vibrational lines should be very much spread out in the manner of rotational wings, a conclusion which is not in accordance with experimental facts, although it may be noted that such lines are usually broad and diffuse to a certain extent. Even in the absence of the requisite spreading, quite a large number of vibration lines of polyatomic molecules seem to be very imperfectly polarised.

As has already been pointed out in a previous paper, both the classical and the quantum theories lead to the result that the bulk of the unpolarised scattering is in the form of rotational wings, and the true Rayleigh and the vibration lines should show a very nearly complete polarisation. Closely connected with this is the question of the intensity of the rotational scattering and certain discrepancies noticed by the author[5] between the experimental and the theoretical values seem to suggest a failure of the theory. The above discrepancies may perhaps be attributed to the fact that the existence of a spin of the light quantum has not been taken into account in the above theories.

In conclusion the author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest and guidance in the work.

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[5] *Loc. cit.*