Proc. Indian Acad. Sci. A 14 228–234 (1941)

New methods in the study of light scattering*

Part I. Basic ideas

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Received August 14, 1941

1. Introduction

The scattering of light in material media may be considered from two distinct points of view: The first is that of the colloid chemist or biologist, the opalescence or Tyndall effect exhibited by whose media is related to the number, size and structure of the particles dispersed in them. The other point of view is that of the spectroscopist investigating the scattering of light in transparent substances and its relation to the molecular structure and the state of molecular aggregation. There is obviously a wide difference in the aims and methods of study adopted by these two groups of workers. This should not be permitted, however to obscure the essential similarities in the phenomena with which they are concerned. We have only one to mention some specific examples, viz., optical glass, phenol-water mixtures, protein solutions and rubber dissolved in organic solvents, to realise the futility of setting out any rigid line of demarcation between "colloid" or turbid media, and "molecular" or transparent ones. Any such distinction must be conventional rather than logical. It will be realised, therefore, that the exchange of ideas and methods between the two fields of research should be of great importance for the progress of both.

2. The reciprocity relation

An important step in the unification of colloid and molecular optics was taken by Dr R S Krishnan (1934–1939) in his investigations at this Institute which established the "Reciprocity Relation" in the scattering of light and developed

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*This paper reproduces the substance of a lecture delivered to the Indian Academy of Sciences at Bangalore on the 23rd September 1939.

experimental methods based on its validity. This relation may be stated as follows: Consider a *parallel beam of plane-polarised light passing horizontally through an isotropic substance*, and let the scattered light be observed in a horizontal direction transverse to the incident beam. The intensity and state of polarisation of the transversely scattered light would evidently depend on the azimuth of polarisation of the incident light. Krishnan's discovery was that, irrespective of the nature, size and shape of the particles of the scattering substance, $H_v = V_h$. These symbols represent respectively, the intensity of the horizontal vibration in the scattered light when the vibration in the incident light is vertical, and the intensity of the vertical vibration in the scattered light when that of the vibration in the incident beam is horizontal. A direct experimental proof of this result is furnished by the arrangement represented schematically in figure 1. A beam of unpolarised light is divided by means of a double-image prism into two beams of *equal intensity* in which the electric vibrations are respectively vertical and horizontal. These beams enter the observation vessel containing the colloidal substance, and their tracks (which, in general, appear of unequal intensity) are viewed transversely through a double-image prism suitably held.

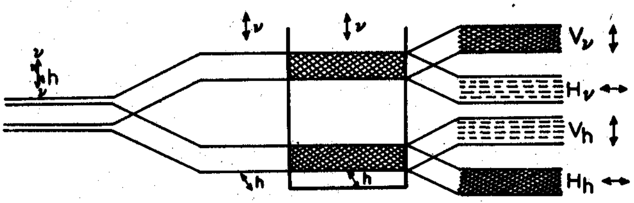

Figure 1. Demonstration of reciprocity principle in light scattering.

We then see four tracks which may be designated as V_v, H_v, V_h and H_h respectively, the meaning of these symbols being clear from the figure. The equality of intensity of H_v and V_h in all cases is then directly evident to observation. The relative intensity of the four components V_v, H_v, V_h and H_h depends greatly on the size, shape and structure of the particles scattering light.

If the particles are very small, spherical and isotropic,

$$V_v \neq 0, H_v = V_h = H_h = 0. \tag{1}$$

If the particles are not small but are spherical and isotropic,

$$V_v \neq 0, H_v = V_h = 0, H_h \neq 0. \tag{2}$$

If the particles are very small but are not spherical and isotropic,

$$V_v \neq 0, H_v = V_h = H_h \neq 0. \tag{3}$$

If the particles are neither small nor spherical and isotropic,

$$V_v \neq 0,\ H_v = V_h \neq 0,\ H_h = 0. \tag{4}$$

The experimental facts stated in (1), (2), (3) and (4) are readily explained on the basis of the electromagnetic theory of light. The relations stated in (1) follows immediately from the fact that the particle in the conditions stated is equivalent to a simple Hertzian oscillator or electric dipole. The relationships stated in (2) follow immediately from the theory of scattering by spherical isotropic particles developed by Mie (1908). The radiations from the particle may be regarded as the result of the summation of a series of partial vibrations, *viz.*, a first electric, a first magnetic, a second electric, a second magnetic, a third electric, a third magnetic vibration and so on. The first and third electric vibrations, and the second and fourth magnetic vibrations in this sequence give a finite value for V_v and zero values for H_v, V_h, and H_h, while the first and third magnetic vibrations and the second and fourth electric vibrations give a zero value for V_v, H_v, V_h and a finite value for H_h. The superposition of these radiations gives the result stated in (2). The scattering of light by a very small ellipsoidal particle averaged for all orientations of the particle with respect to the field gives the result stated in (3). The relation $H_v = V_h$ is seen to be valid both in case (2) and in case (3). Hence, if the radiation from particles which are neither small nor spherical and isotropic is regarded as a superposition of the types of radiations considered in these two cases, the result $H_v = V_h$ must be valid also in the general case. Krishnan (1938) has given a different argument which also leads to the same result.

3. The Krishnan effect

From the foregoing considerations, it follows that in the general case $V_h < H_h$. In other words, *if the incident beam is polarised with the electric vibration horizontal, the light scattered transversely would exhibit a partial polarisation in which the horizontal vibration is more intense than the vertical.* This is the Krishnan effect. The actual magnitude of the partial polarisation would be determined by the extent to which radiations of the types envisaged in (2) and (3) respectively enter, in other words by the relation between the size and the optical anisotropy of the particle. In the electromagnetic theory, the amplitude of the first electric radiation is proportional to the cube of the radius of the particle, while those of the first magnetic and the second electric radiations are proportional to its fifth power. Hence, the larger the size of the particle and the smaller its optical anisotropy, the greater would be the partial polarisation and the more readily, therefore, would it be detectable. *Vice versa,* the smaller the particle, and the larger its optical anisotropy, the more difficult of detection would be the partial polarisation of the transversely scattered light. The formulae of the electromagnetic theory also indicate that the ratios of the amplitude of the higher partial radiations relatively to the lower ones involve the wavelength of the light. This is evident since the ratios must evidently be dimensionless numbers, such as $a^2/\lambda^2, a^2/\lambda^4$, etc., where a and λ are respectively the radius of the particle and the wavelength of the radiation. Hence, for relatively small particles, the effect now under discussion must rapidly become more pronounced as the wavelength of the light is diminished.

4. A sensitive method of observation

The partial polarisation of the scattered light referred to above may be readily demonstrated in a variety of cases. A Nicol which can be rotated polarises the light entering the colloid. The track of the beam passing through the observation vessel is viewed transversely through a double-image prism suitably held. It will then be noticed that as the Nicol is rotated and the direction of vibration in the incident beam turns round from the vertical to the horizontal position, the two images of the track seen alter in their relative intensity, the one which is stronger in the first case becomes the weaker in the second case. In other words, $V_v > H_v$ but $V_h < H_h$. The same effect can be shown in a more striking way by viewing the track through a Babinet compensator instead of through a double-image prism. As the polarising Nicol is rotated, the fringes seen in the compensator shift their position, indicating that the partial polarisation of the scattered light alters to a state in which the horizontal component instead of the vertical one is the more intense. As a means of detecting the partial polarisation, this technique is obviously more sensitive than observation through a double-image prism or a measurement of the depolarisation ratio which were the methods employed by Krishnan. A partial polarisation of only a few per cent is detectable by the Babinet compensator. Hence, the range of the investigation is extended by its use to cases in which the difference of intensity between V_h and H_h is extremely small. Moreover, since the fringes in the Babinet compensator can be photographed, it becomes possible to extend the investigations into the ultra-violet region of the spectrum where, as already remarked, the magnitude of the partial polarisation is expected to become much larger.

The sequence of changes in the appearance of the field of the compensator as the polarising Nicol is rotated may be readily followed. It is evident that, since $V_v > H_v = V_h < H_h$, the fringes would be most marked when the vibrations in the incident light are vertical; their visibility would diminish and reach a minimum value at an oblique setting of the Nicol and increase again to a second maximum when the vibrations are horizontal. The setting of the Nicol at which the compensator fringes have the minimum visibility would evidently depend on the ratio V_v/H_h. The fringes seen in the compensator appear on a background of uniform illumination due to the unpolarised or "anisotropic" part of the light scattering. The larger this is, the smaller would be the visibility of the fringes for all settings of the Nicol, and in particular at the setting in which the vibrations transmitted by it are horizontal. The sensitiveness of the method therefore diminishes with the increasing optical anisotropy of the particles arising from their non-spherical shape or structure.

5. Ellipticity of the scattered light

As was shown by Mie, we cannot expect to observe an elliptic polarisation in the light scattered by particles of any size, if the incident light is *unpolarised*. The position would, however, be altered, if the incident light is *plane polarised* in an arbitrary azimuth and the particles of the colloid are spherically symmetric and of uniform size. For, the incident vibration can then be resolved into vertical and horizontal components in a determinate phase relation, and the scattered radiations V_v and H_h arising respectively from these components would also be coherent, the phase relations between them being specifiable and the same for all the particles in the colloid. Unless, therefore, the relationship of phase is one of identity, the resulting radiation would be elliptically polarised. This would be indicated in the Babinet compensator by the position of the fringes which would correspond neither to a vertical nor a horizontal vibration but would be intermediate. In other words, when the Nicol polarising the incident beam is turned round from the vertical to the horizontal, the compensator fringes would shift continuously from one position to the other, remaining visible all the time. An effect of this kind should be easily noticeable when the particles in the medium are of the requisite type, e.g., a cloud of water drops suspended in air or a dilute emulsion of one liquid in another. On the other hand, if the particles in the medium are of such a nature that there is no definite relation of phase between the components V_v and H_v, then no elliptic polarisation should be detectable. In such a case, the compensator fringes would vanish at some particular setting of the Nicol, and re-appear in an altered position when the Nicol is rotated further in either direction.

6. Applications of the method

The sequence of changes observed in the position and visibility of the compensator fringes as the polarising Nicol is turned round is thus closely connected with the structure of the medium scattering the light, and affords an insight into the mechanism of such scattering. In this connection, reference may be made to two very interesting papers by Dr Hans Mueller (1938) who has discussed the theory of the Krishnan effect from a standpoint which is very different from that set out above.

The technique described in the present paper would evidently be applicable to a great variety of cases and should be capable of yielding interesting results. In particular, the increased sensitiveness should enable the Krishnan effect to be looked for even in cases where it is undetectable with the methods previously employed, e.g., colloids of the smallest particle size and even pure liquids. Preliminary work on these lines has been carried out with pure liquids and with liquid mixtures by Mr T A S Balakrishnan and on selected colloidal solutions and emulsions by Mr Darbara Singh. Their results are described in a series of papers appearing in these *Proceedings* under the same title (Parts II, III, IV and V).

Summary

A method is described, based upon the use of a Nicol for polarising the incident beam in any desired azimuth and of a Babinet compensator for observing the transversely scattered light which enables the Krishnan effect to be very conveniently studied. The sensitiveness of the arrangement permits its use for the observation of the effect in cases where the methods previously employed are not delicate enough. It is pointed out that the magnitude of the effect would be enhanced by using ultra-violet radiation, the compensator fringes being recorded photographically. The same arrangement can also be employed for detecting and measuring the elliptic polarisation of the scattered light when the particles scattering the light are uniform and spherically symmetrical. The wide field of utility of the method in the study of light scattering is indicated.

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