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## The molecular scattering of light

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*The colour of the sea*

In the history of science, we often find that the study of some natural phenomenon has been the starting-point in the development of a new branch of knowledge. We have an instance of this in the colour of skylight, which has inspired numerous optical investigations, and the explanation of which, proposed by the late Lord Rayleigh, and subsequently verified by observation, forms the beginning of our knowledge of the subject of this lecture. Even more striking, though not so familiar to all, is the colour exhibited by oceanic waters. A voyage to Europe in the summer of 1921 gave me the first opportunity of observing the wonderful blue opalescence of the Mediterranean Sea. It seemed not unlikely that the phenomenon owed its origin to the scattering of sunlight by the molecules of the water. To test this explanation, it appeared desirable to ascertain the laws governing the diffusion of light in liquids, and experiments with this object were started immediately on my return to Calcutta in September, 1921. It soon became evident, however, that the subject possessed a significance extending far beyond the special purpose for which the work was undertaken, and that it offered unlimited scope for research. It seemed indeed that the study of light-scattering might carry one into the deepest problems of physics and chemistry, and it was this belief which led to the subject becoming the main theme of our activities at Calcutta from that time onwards.

The theory of fluctuations

From the work of the first few months, it became clear that the molecular scattering of light was a very general phenomenon which could be studied not only in gases and vapours but also in liquids and in crystalline and amorphous solids, and that it was primarily an effect arising from molecular disarray in the medium and consequent local fluctuations in its optical density. Except in amorphous solids, such molecular disarray could presumably

be ascribed to thermal agitation, and the experimental results appeared to support this view. The fact that molecules are optically anisotropic and can orientate freely in liquids was found to give rise to an additional type of scattering. This could be distinguished from the scattering due to fluctuations in density by reason of its being practically unpolarized, whereas the latter was completely polarized in the transverse direction. The whole subject was critically reviewed and the results till then obtained were set out in an essay published by the Calcutta University Press in February 1922.

The various problems requiring solution indicated in this essay were investigated with the aid of a succession of able collaborators. It is possible to mention briefly only a few of the numerous investigations which were carried out at Calcutta during the six years 1922 to 1927. The scattering of light in fluids was studied by Ramanathan over a wide range of pressures and temperatures with results which appeared to support the "fluctuation" theory of its origin. His work also disclosed the remarkable changes in the state of polarization which accompany the variations of intensity with temperature in vapours and in liquids. Liquid mixtures were investigated by Kameswara Rao, and furnished optical proof of the existence in such systems, of simultaneous fluctuations of density, composition, and molecular orientation. Srivastava studied the scattering of light in crystals in relation to the thermal fluctuations of density and their increase with temperature. Ramdas investigated the scattering of light by liquid surfaces due to thermal agitation, and established a relation between surface-tension and surface-opalescence. He also traced the transition from surface-opalescence to volume-opalescence which occurs at the critical temperature. Sogani investigated X-ray diffraction in liquids, in order to connect it with their optical behaviour, and test the application of fluctuation theory to X-ray scattering.

#### *The anisotropy of molecules*

As stated above, the state of polarization of the light scattered in fluids is connected with the optical anisotropy of the molecules. Much of the work done at Calcutta during the years 1922 to 1927 was intended to obtain data concerning this property and to establish its relations with various optical phenomena. Krishnan examined a great many liquids, and by his work showed very clearly the dependence of the optical anisotropy of the molecule on its chemical constitution. Ramakrishna Rao studied the depolariza-

tion of scattered light in a very large number of gases and vapours, and obtained information of high importance for the progress of the subject. Venkateswaran studied the scattering of light in aqueous solutions to find the influence on it of electrolytic dissociation. Ramachandra Rao investigated liquids having highly elongated molecules and also highly polar substances over a wide range of temperatures, and discovered the influence of molecular shape and molecular association on the depolarization of scattered light in liquids.

The interpretation of the observations with liquids involved the development of a molecular theory of light-scattering in dense media which was undertaken by Ramanathan, myself, and Krishnan. A revised opalescence formula was derived which differed from that of Einstein and yielded results in better agreement with observation. Krishnan and myself also published a series of investigations showing how the optical anisotropy of the molecules deduced from light-scattering could be utilized to interpret the optical and dielectric behaviour of fluids, and also the electric, magnetic, and mechanical birefringence exhibited by them. The conclusions derived from these studies enabled a connection to be established between the molecular anisotropy observed in fluids and the optical, electric, and magnetic anisotropy exhibited by solids in the crystalline state.

### *A new phenomenon*

The investigations referred to above were in the main guided by the classical electromagnetic theory of light, the application of which to the problems of light-scattering is chiefly associated with the names of Rayleigh and of Einstein. Nevertheless, the possibility that the corpuscular nature of light might come into evidence in scattering was not overlooked and was in fact elaborately discussed in the essay of February 1922 which was published at least a year before the well-known discoveries of Compton on X-ray scattering. While our experiments in the main appeared to support the electromagnetic theory of light, evidence came to hand at a very early stage of the investigations of the existence of a phenomenon which seemed to stand outside the classical scheme of thought. The scattering of light in transparent fluids is extremely feeble, much weaker in fact than the Tyndall effect usually observed in turbid media. It was experimentally discovered that associated with the Rayleigh-Einstein type of molecular scattering, was another and still

feebler type of secondary radiation, the intensity of which was of the order of magnitude of a few hundredths of the classical scattering, and differed from it in not having the same wavelength as the primary or incident radiation. The first observation of this phenomenon was made at Calcutta in April 1923 by Ramanathan who was led to it in attempting to explain why in certain liquids (water, ether, methyl and ethyl alcohols), the depolarization of scattered light varied with the wavelength of the incident radiation. Ramanathan found that after exhaustive chemical purification and repeated slow distillation of the liquid in vacuum, the new radiation persisted undiminished in intensity, showing that it was a characteristic property of the substance studied and not due to any fluorescent impurity. Krishnan observed a similar effect in many other liquids in 1924, and a somewhat more conspicuous phenomenon was observed by me in ice and in optical glasses.

*The optical analogue of the Compton effect*

The origin of this puzzling phenomenon naturally interested us, and in the summer of 1925, Venkateswaran attempted to investigate it by photographing the spectrum of the scattered light from liquids, using sunlight filtered through colour screens, but was unable to report any decisive results. Ramakrishna Rao in his studies on the depolarization of scattering during 1926 and 1927 looked carefully for a similar phenomenon in gases and vapours, but without success. This problem was taken up again by Krishnan towards the end of 1927. While his work was in progress, the first indication of the true nature of the phenomenon came to hand from a different quarter. One of the problems interesting us at this time was the behaviour in light-scattering of highly viscous organic liquids which were capable of passing over into the glassy state. Venkateswaran undertook to study this question, and reported the highly interesting result that the colour of sunlight scattered in a highly purified sample of glycerine was a brilliant green instead of the usual blue. The phenomenon appeared to be similar to that discovered by Ramanathan in water and the alcohols, but of much greater intensity, and, therefore, more easily studied. No time was lost in following up the matter. Tests were made with a series of filters transmitting narrow regions of the solar spectrum and placed in the path of the incident beam, which showed that in every case the colour of the scattered light was different from that of the incident light, and was displaced from it towards the red. The radiations were

also strongly polarized. These facts indicated a clear analogy between the empirical characters of the phenomenon and the Compton effect. The work of Compton had made familiar the idea that the wavelength of radiation could be degraded in the process of scattering, and the observations with glycerine suggested to me that the phenomenon which had puzzled us ever since 1923 was in fact the optical analogue of the Compton effect. This idea naturally stimulated further investigation with other substances.

The chief difficulty which had hitherto oppressed us in the study of the new phenomenon was its extreme feebleness in general. This was overcome by using a 7-inch refracting telescope in combination with a short-focus lens to condense sunlight into a pencil of very great intensity. With these arrangements and using complementary light-filters in the path of the incident and scattered beams, as was done by Ramanathan in 1923, to isolate the modified radiations, it was found that they could be readily observed in a great many liquids, and that in many cases they were strongly polarized. Krishnan, who very materially assisted me in these investigations, found at the same time that the phenomenon could be observed in several organic vapours, and even succeeded in visually determining the state of polarization of the modified radiations from them. Compressed gases such as CO, and N<sub>2</sub>O, crystalline ice, and optical glasses also were found to exhibit the modified radiations. These observations left little doubt that the phenomenon was really a species of light-scattering analogous to the Compton effect.

#### *The spectroscopic characters of the new effect*

Thanks to the vastly more powerful illumination made available by the 7-inch refractor, the spectroscopic examination of the effect, which had been abandoned in 1925 as indecisive, now came within the reach of direct visual study. With a Zeiss cobalt-glass filter placed in the path of the incident beam and one or other of a series of organic liquids as the scattering substance, a band in the blue-green region was observed by me in the spectrum of the scattered light, separated by a dark interval from the indigo-violet region transmitted by the filter. *Both* of these regions in the spectrum became sharper when the region of transmission was narrowed by the insertion of an additional filter in the incident beam. This suggested the employment, instead of sunlight, of the highly monochromatic radiations given by a mercury arc in combination with a condenser of large aperture and a cobalt-glass filter.

With these arrangements the spectrum of the scattered light from a variety of liquids and solids was visually examined, and the startling observation was made that the spectrum generally included a number of sharp lines or bands on a diffuse background which were not present in the light of the mercury arc.

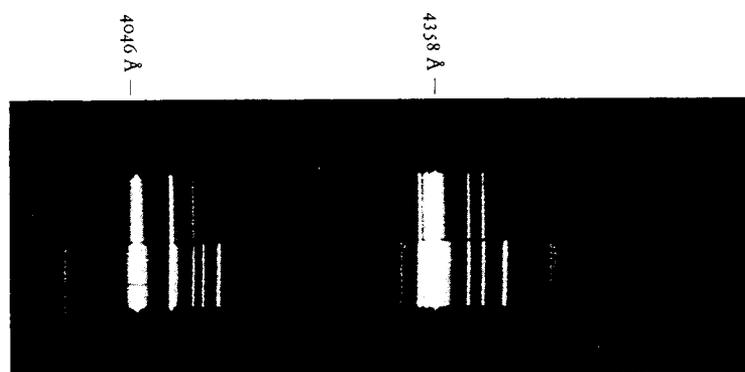


Fig. 1. Spectrum of carbon tetrachloride.

The quartz mercury lamp was so powerful and convenient a source of monochromatic illumination that, at least in the case of liquids and solids, photographing the spectrum of scattered light was found to present no extraordinary difficulties. The earliest pictures of the phenomenon were in fact taken with a portable quartz spectrograph of the smallest size made by the firm of Hilger. With a somewhat larger instrument of the same type, Krishnan obtained very satisfactory spectrograms with liquids and with crystals on which measurements of the desired precision could be made, and on which the presence of lines displaced towards the violet was first definitely established. The experimental difficulties were naturally greater in the case of gases or vapours, though they could be lessened by working with the substance under pressure. With an improvised instrument of large aperture (F/1.8), Ramdas obtained the first spectrograms with a gaseous substance (ether vapour) at atmospheric pressure.

In interpreting the observed phenomena, the analogy with the Compton effect was adopted as the guiding principle. The work of Compton had gained general acceptance for the idea that the scattering of radiation is a unitary process in which the conservation principles hold good. Accepting this idea it follows at once that, if the scattering particle gains any energy

during the encounter with the quantum, the latter is deprived of energy to the same extent, and accordingly appears after scattering as a radiation of diminished frequency. From thermodynamic principles, it follows that the reverse process should also be possible. Adopting these ideas, the actual observations could be interpreted, and the agreement of the observed displacements with the infrared frequencies of the molecules made it clear that the new method opened up an illimitable field of experimental research in the study of the structure of matter.

*Interpretation of the effect*

It appears desirable to emphasize that though the conservation principle of Compton is useful in interpreting the effects disclosed by experiment, it is by itself insufficient to explain the observed phenomena. As is well known from studies on molecular spectra, a gaseous molecule has four different species of energy of increasing orders of magnitude, namely those corresponding to translatory motion, rotation, vibration, and electronic excitation. Each of these, except the first, is quantized and may be represented by an integer in an extended sequence of quantum numbers. The aggregate energy of a molecule may, therefore, assume any one out of a very large number of possible values. If we assume that an exchange of energy occurs in the collision between the molecule and the quantum, and limit ourself to the cases in which the final energy of the molecule is less than that of the incident quantum, we arrive at the result that the spectrum of the scattered light should contain an immense number of new lines and should in fact rival in its complexity the band spectrum of the molecule observed in the emission or absorption of light. Nothing more different from what is actually observed can be imagined than the foregoing picture. The most conspicuous feature revealed by experiment is the beautiful simplicity of the spectra of even complicated polyatomic molecules obtained in light-scattering, a simplicity that is in striking contrast to the extreme complexity of their emission or absorption spectra. It is this simplicity that gives to the study of light-scattering its special significance and value. It is clear that the effect actually observed was not and could not have been foreseen from an application of the conservation principles.

The general principle of correspondence between the quantum and classical theories enunciated by Niels Bohr enables us, on the other hand, to ob-

tain a real insight into the actual phenomena. The classical theory of light-scattering tells us that if a molecule scatters light while it is moving, rotating or vibrating, the scattered radiations may include certain frequencies, different from those of the incident waves. This classical picture, in many respects, is surprisingly like what we actually observe in the experiments. It explains why the frequency shifts observed fall into three classes, translational, rotational and vibrational, of different orders of magnitude. It explains the observed selection rules, as for instance, why the frequencies of vibration deduced from scattered light include only the fundamentals and not the overtones and combinations which are so conspicuous in emission and absorption spectra. The classical theory can even go further and give us a rough indication of the intensity and polarization of the radiations of altered frequency. Nevertheless, the classical picture has to be modified in essential respects to give even a qualitative description of the phenomena, and we have, therefore, to invoke the aid of quantum principles. The work of Kramers and Heisenberg, and the newer developments in quantum mechanics which have their root in Bohr's correspondence principle seem to offer a promising way of approach towards an understanding of the experimental results. But until we know much more than we do at present regarding the structure of molecules, and have sufficient quantitative experimental knowledge of the effect, it would be rash to suggest that they afford a complete explanation of it.

#### *The significance of the effect*

The universality of the phenomenon, the convenience of the experimental technique and the simplicity of the spectra obtained enable the effect to be used as an experimental aid to the solution of a wide range of problems in physics and chemistry. Indeed, it may be said that it is this fact which constitutes the principal significance of the effect. The frequency differences determined from the spectra, the width and character of the lines appearing in them, and the intensity and state of polarization of the scattered radiations enable us to obtain an insight into the ultimate structure of the scattering substance. As experimental research has shown, these features in the spectra are very definitely influenced by physical conditions, such as temperature and state of aggregation, by physico-chemical conditions, such as mixture, solution, molecular association and polymerization, and most essentially by

chemical constitution. It follows that the new field of spectroscopy has practically unrestricted scope in the study of problems relating to the structure of matter. We may also hope that it will lead us to a fuller understanding of the nature of light, and of the interactions between matter and light.

*Some concluding remarks*

From a physical point of view, the quantitative study of the effect with the simplest molecules holds out the largest hope of fundamental advances. The beautiful work of McLennan with liquefied gases, and of R. W. Wood and Rasetti are pioneer investigations in this field which command the highest admiration. The quantitative study of the effect with crystals of the simplest possible chemical constitution is naturally of great importance. The case of the diamond, which has been investigated by Ramaswamy, Robertson, and Fox, and with especial completeness by Bhagavantam, is of special interest. Very surprising results have been obtained with this substance, which may be the pathway to a fuller understanding of the nature of the crystalline state. I should also like to draw attention to the work of Krishnamurti, who has traced a remarkable dependence of the intensity of the spectral lines observed in scattering on the nature of the chemical bond, and followed the transition from the homopolar to the heteropolar type of chemical combination. Krishnamurti's observation that the paramagnetism of crystals apparently influences the observed intensity of the displaced lines is one of the most remarkable ever made in this new field of research.