

A New Radiation^{1*}

Prof C V Raman F R S

(Plate XII)

1. Introduction

I propose this evening to speak to you on a new kind of radiation or light-emission from atoms and molecules. To make the significance of the discovery clear, I propose to place before you the history of the investigations made at Calcutta which led up to it. Before doing so, however, a few preliminary remarks regarding radiation from atoms and molecules will not be out of place.

Various ways are known to the physicist by which atoms or molecules may be caused to emit light, as for instance, heating a substance or bombarding it with a stream of electrons. The light thus emitted is usually characteristic of the atoms or molecules and is referred to as *primary* radiation. It is also possible to induce radiation from atoms and molecules by illuminating them strongly. Such light-emission is referred to as *secondary* radiation. The familiar diffusion of light by rough surfaces may be cited as an example of secondary radiation, but strictly speaking, it hardly deserves the name, being an effect occurring at the boundaries between media of different refractive indices and not a true volume-effect in which all the atoms and molecules of the substance take part. The first case discovered of secondary radiation really worthy of the name was the phenomenon of fluorescence whose laws were elucidated by the investigations of Sir George Stokes. This is a familiar effect which is exhibited in a very conspicuous manner in the visible region of the spectrum by various organic dye-stuffs. I have here a bottle of water in which an extremely small quantity of fluorescein is dissolved. You notice that when placed in the beam of light from the lantern, it shines with a vivid green light, and that the colour of the emission is not altered, though its brightness is changed, by placing filters of various colours between the bottle and the lantern. A violet filter excites green fluorescence strongly, while a red filter has but little effect.

Another kind of secondary radiation whose existence has been experimentally recognised more recently is the scattering

of light by atoms and molecules. It is this scattering that gives us the light of the sky, the blue colour of the deep sea and the delicate opalescence of large masses of clear ice. I have here a large bottle of a very clear and transparent liquid, toluene, which as you notice contains hardly any dust particles, but the track of the beam from the lantern passing through it is visible as a brilliant blue cone of light. This internal opalescence continues to be visible even after the most careful purification of the liquid by repeated distillation in vacuo. A similar opalescence is shown, though much less brightly, by dust-free gases and vapours, and also by solids. A large clear block of ice shows a blue colour in the track of the beam when sunlight passes through it. The blue opalescence of blocks of clear optical glass is also readily demonstrable. The molecular scattering of light is thus a phenomenon common to all states of matter.

During the past seven years, the scattering of light in transparent media has been the subject of intensive experimental and theoretical investigation at Calcutta, and it is the researches made on this subject that have led to the discovery which I shall lay before you this evening. One important outcome of our researches has been to show that while light-scattering is in one sense a molecular phenomenon, in another sense it is a bulk-effect having a thermal origin. It is the thermal agitation of the molecules which causes them to be distributed and orientated in space with incomplete regularity, and it is the local fluctuations in the properties of the medium thus arising which give rise to optical heterogeneity and consequent diffusion of light. The subject of light-scattering is thus a meeting ground for thermodynamics, molecular physics and the wave-theory of radiation. That the combination of theories in such diverse fields of physics gives us predictions which have been experimentally verified, is one of the triumphs of modern physics.

2. A new phenomenon

While the quantitative investigations made at Calcutta have in the main substantiated the thermodynamic-wave-optical theory of light scattering, indications appeared even in our earliest studies of a new phenomenon which refused to fit in with our pre-conceived notions. Thus, in some observations

¹Inaugural Address delivered to the South Indian Science Association on Friday, the 16th March, 1928, at Bangalore.

^{*}Reprinted from Indian Journal of Physics Vol. 2, 387-98 (1928)

made by me [1] with the assistance of Mr. Seshagiri Rao in December, 1921, it was found that the depolarisation of the light transversely scattered by distilled water measured with a double-image prism and Nicol increased very markedly when a violet filter was placed in the path of the incident light. More careful investigations made with dust-free liquids [2] in 1922, confirmed this effect and showed it to exist also in methyl and ethyl alcohols, and to a lesser degree in ether. It was also noticed that the colours of the scattered light from the different liquids studied did not match perfectly. An important advance was made when Dr. Ramanathan [3] working at Calcutta in the summer of 1923, investigated the phenomenon more closely and discovered that it was not a true dependence of the depolarisation on the wave-length of the scattering radiation but was due to the presence in the scattered light of what he described as "a trace of fluorescence." This was shown by the fact that the measured depolarisation depended on whether the blue filter used was placed in the path of the incident beam or of the scattered light, being smaller in the latter case. Accepting the explanation of the effect as "weak fluorescence," it naturally became important to discover whether it was due to some impurity present in the substance. Dr. Ramanathan tested this by careful chemical purification followed by repeated slow distillation of the liquid at the temperature of melting ice. He found that the effect persisted undiminished.

The investigation of this species of "weak fluorescence" has ever since 1923 been on our programme of research at Calcutta. Krishnan, [4] who investigated 60 liquids for light scattering in the spring and summer of 1924, made systematic studies of the phenomenon, and found that it was shown markedly by water, ether, all the monohydric alcohols and a few other compounds. He pointed out that the liquids which exhibit the effect have certain family relationships amongst themselves, and that they are also substances whose molecules are known to be polar. The chemical importance of the subject led to Mr. S. Venkateswaran attempting to make a fuller study of it in the summer of 1925, but without any special success. The research was discontinued at the time but was resumed by him later in the current year (January, 1928). The remarkable observation was made that the visible radiation which is excited in pure dry glycerine by ultra-violet radiation (sunlight filtered through Corning glass G. 586) is *strongly polarised*.

The possibility of a similar effect in gases and vapours was also borne in mind and repeatedly looked for by the workers at Calcutta. The feebleness of the scattering in gases and vapours, and the infructuousness of the earlier efforts in this direction, however discouraged progress.

3. Its Universality

Though the phenomenon was described in the paper of Dr. Ramanathan and Mr. Krishnan as a "feeble fluorescence," the impression left on my mind at the time was that we had here an entirely new type of secondary radiation distinct from what is usually described as fluorescence. The publication of the idea

was however discouraged by the belief then entertained that only a few liquids exhibited the effect and by the supposition that it was unpolarised in the same way as ordinary fluorescence in liquids. Indeed, a chemical critic might even have asserted that the effect was in each case due to a trace of dissolved fluorescent impurity present in the substance which our efforts at purification had failed to remove. Early this year, however, a powerful impetus to further research was provided when I conceived the idea that the effect was some kind of optical analogue to the type of X-ray scattering discovered by Prof. Compton, for which he recently received the Nobel Prize in Physics. I immediately undertook an experimental re-examination of the subject in collaboration with Mr. K. S. Krishnan and this has proved very fruitful in results. The first step taken in the research was to find whether the effect is shown by all liquids. The method of investigation was to use a powerful beam of sunlight from a heliostat concentrated by a 7" telescope objective combined with a short focus lens. This was passed through a blue-violet filter and then through the liquid under examination contained in an evacuated bulb and purified by repeated distillation in vacuo. A second filter of green glass was used which was complementary in colour to the blue-violet filter. If it were placed in the track of the incident light, all illumination disappears, while, if it be placed between the bulb and the observer's eye, the opalescent track within the liquid continued to be visible, though less brightly. All the liquids examined (and they were some 80 in number) showed the effect in a striking manner. There was therefore no longer any doubt that the phenomenon was universal in character; with the bulb of toluene on the lantern, you see that the effect is readily demonstrable. The cone of light vanishes when I place the violet and green filters together, but it appears when I transfer the latter to a place between my audience and the observation bulb.

Now the test with the complementary filters is precisely that ordinarily used for detecting fluorescence and indeed was first suggested by Stokes in his investigations on the subject. You may therefore rightly ask me the question how does this phenomenon differ from fluorescence? The answer to the question is, firstly, that it is of an entirely different order of intensity. A more satisfactory proof was however forthcoming when Mr. Krishnan and myself examined the polarisation of this new type of radiation and found that it was nearly as strong as that of the ordinary light scattering in many cases, and is thus quite distinct from ordinary fluorescence which is usually unpolarised.

This is shown for the case of toluene in Figures. 1 and 2 in Plate XII. Figure 1 is a photograph of the scattering by toluene of sunlight filtered through a blue-violet glass. It was taken through a double-image prism of Iceland spar with an exposure of 3 seconds. Figure 2 is a picture with an additional complementary filter of green glass interposed in front of the camera lens. The exposure necessary is now increased greatly by the insensitiveness of the plate to green light, and had to be

as much as 25 minutes. It will be noticed that the polarisation of the track as shown by the difference in brightness of the two polarised images is quite as prominent in Figure 2 as in Figure 1.

I may also mention that Mr. Krishnan and myself have succeeded in detecting the new radiation and observing its partial polarisation in a number of organic vapours and also in the gases CO_2 and N_2O . The problem in these cases is one of securing sufficient intensity of scattering for the effect to be detectable through the complementary filter. This can be secured by heating up the substance in a sealed bulb or by using steel observation-vessels for containing the compressed gases, so as to obtain sufficient density of the scattering molecules. The question of the background against which the track is observed is also of great importance.

The new type of secondary radiation is also observable in crystals such as ice, and in amorphous solids. It is thus a phenomenon whose universal nature has to be recognised.

4. Line-Spectrum of New Radiation

That the secondary radiation passes the complementary filter and yet is strongly polarised to an extent comparable with the ordinary molecular scattering, is clear evidence that we have in it an entirely new type of secondary radiation which is distinct from either the ordinary scattering or the usual type of fluorescence. A striking and even startling confirmation of this view is furnished by an examination of its spectrum. Preliminary observations with sunlight filtered through a combination which passes a narrow range of wave-lengths, showed the spectrum of the new radiation to consist mainly of a narrow range of wave-lengths clearly separated from the incident spectrum by a dark space. This encouraged me to take up observations with a monochromatic source of light. A quartz mercury lamp with a filter which completely cuts out all the visible lines of longer wave-length than the indigo line 4,358 A.U. was found to be very effective. When the light from such a lamp was passed

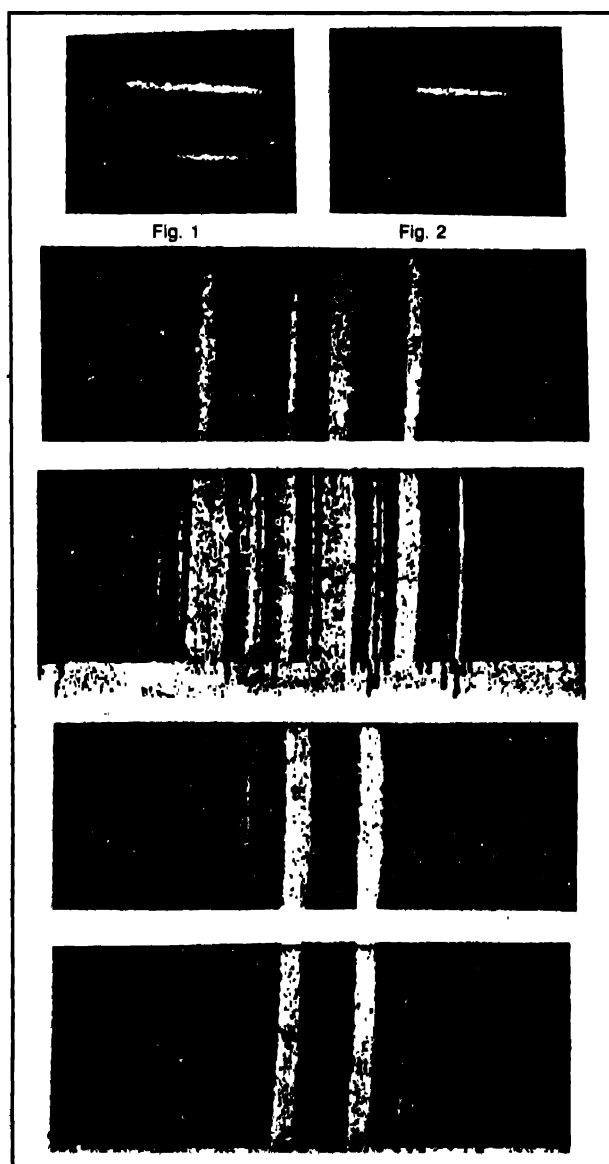


PLATE XII

Polarisation of Scattering
 Fig. 1 Unmodified
 Fig. 2 Modified

Fig.3(1) Incident Spectrum

◀ Fig. 3 (2) Scattered Spectrum

Fig. 4 (1) Incident Spectrum

◀ Fig. 4 (2) Scattered Spectrum

through the bulb containing a dust-free liquid, and the spectrum of the scattered light was observed through a direct-vision spectroscope, it was found to exhibit two or more sharp bright lines in the blue and green regions of the spectrum. These lines are not present in the spectrum of the incident light or in the unfiltered light of the mercury arc and are thus manufactured by the molecules of the liquid.

Figures 3(1) and 3(2), and Figures 4(1) and 4(2) show the phenomenon. They are spectrograms taken with a small Hilger quartz instrument of the scattering by *liquid* benzene. Fig. 3 was taken with the light from the quartz mercury arc filtered through a blue glass which allows the wavelengths from about 3,500 A.U. to 4,400 A.U. to pass through. Figure 3(1) represents the incident-spectrum and Figure 3(2) the scattering spectrum, and the latter shows a number of sharp lines not present in Fig. 3(1). These are indicated in the figure. Figures 4(1) and (2) similarly represent the incident and scattered spectra with benzene liquid, the filter used being a potassium permanganate solution. Here again the new lines which appear are indicated in the figure. Visual observations were also made using a quinine sulphate solution together with the blue glass as a filter and thus cutting off all the radiations except 4,358 A.U. from the incident spectrum. Some of the modified lines then disappear, leaving only those of longer wave-length. It is thus clear that each line in the incident spectrum gives rise to at least two lines in the scattered spectrum, one in the original or unmodified position, and a second in a shifted position of longer wave-length. There is thus a striking analogy with the Compton effect in the X-ray region.

There has, as yet, not been sufficient time for photographing the spectra from a large number of liquids, or even for measuring the photographs already obtained. Visual observations have however been made with a large number of liquids. There is an astonishing similarity between the spectra obtained with different liquids. When only the 4,358 line was used, most liquids showed in the spectrum of the scattered light, a bright line in the blue-green region of the spectrum (about 5,000 A.U.), whose position was practically the same for chemically similar liquids such as pentane, hexane and octane for instance. There was, however, a recognizable difference in the position of the modified line when other liquids such as benzene or water were used. When the 4,047 line of the mercury arc was let in by removing the quinine sulphate solution, a second modified line in the blue region of the spectrum was seen with most liquids.

Photographs obtained so far with benzene and toluene suggests that there may be several modified lines, and that each modified line may be a doublet in some cases. In many liquids, the scattered spectrum shows in addition to sharp lines also an unmistakable continuous spectrum accompanying it. Carbon disulphide behaves in an exceptional manner, showing a diffuse band.

Observations already made show that the new lines in the scattered spectrum are usually markedly polarised; they also

suggest that a continuous spectrum, when present, is less markedly polarised.

5. Nature of the New Radiation

The discovery set out above naturally opens up an array of problems for investigation. The most pressing question is, how is the modified scattered radiation, as we may call it, generated by the molecules of the liquid? As a tentative explanation, we may adopt the language of the quantum theory, and say that the incident quantum of radiation is partially absorbed by the molecule, and that the unabsorbed part is scattered. The suggestion does not seem to be altogether absurd and indeed such a possibility is already contemplated in the Kramers-Heisenberg theory of dispersion. If we accept the idea indicated above, then the difference between the incident and scattered quanta would correspond to a quantum of absorption by the molecule. The measurement of the frequencies of the new spectral lines thus opens a new pathway of research into molecular spectra, particularly those in the infra-red region.

If a molecule can take up part of the incident quantum of radiation and scatter the remaining part, then it might also be capable of adding a quantum of its own characteristic frequency to the incident radiation when scattering it. In such a case we should expect a modified line of *increased* frequency. Such a result appears to be shown in Figure 3(2) of Plate XII, as a solitary line in the extreme left of the photograph. This result, however, requires to be confirmed by more photographs and with other liquids. So far it would appear that a degradation of frequency is more probable than an enhancement. It is too early to speculate at present on the origin of the continuous radiation observed in some cases, whether it is due to changes in the molecule itself, or whether it arises from inelastic collisions of the second kind within the liquid resulting in *partial* transformation of the incident quantum of radiation into translatory kinetic energy of the molecules. When further data are obtained, it should be possible to express a definite opinion on this point, and also on the role played by the solvent in the explanation of ordinary fluorescence.

6. Relation to Thermodynamics

As explained in the introduction, the ordinary scattering of light can be regarded equally well as a molecular effect, and as a bulk effect arising from the thermodynamic fluctuations of the whole medium. The question arises whether the new type of secondary radiation is exclusively a molecular effect or not, and whether it is related in any way to thermo-dynamics. The question is obviously one to be answered by experiment and theory conjointly. The comparative study of the effect at different temperatures and in different states of aggregation of matter is obviously of great importance in this connection. It has already been remarked that the effect is observable in gases and vapours and indeed it is found possible to determine its intensity and polarisation in the gaseous state. It is also of great interest to remark that the solid crystal ice also shows the sharp modified

lines in the scattered spectrum in approximately the same positions as pure water. The only observations made with amorphous solids are with optical glass. Here the modified scattered spectrum consists of diffuse bands and not sharp lines. Whether this is generally true for all amorphous solids, and whether any changes occur at low and high temperatures remains to be determined by experiment.



Raman with his instrument.

7. Coherent or Non-coherent Radiation ?

An important question to be decided in the first instance by experiment is whether the modified scattered radiations from the different molecules are incoherent with each other. One is tempted to assume that this must be the case, but a somewhat astonishing observation made with liquid carbon dioxide contained in steel observation vessels gives us pause here. It was found on blowing off the CO_2 by opening a stopcock, a cloud formed within the vessels which scattered light strongly in the ordinary way. On viewing the cloud through the complementary filter, the scattered radiation of modified frequency also brightened up greatly. This would suggest that the assumption of non-coherence is unjustifiable. Further, some qualitative observations suggest that the modified scattering by a mixture of carbon disulphide and methyl alcohol also brightens up notably at the critical solution temperature.

Quantitative observations are necessary to decide the very fundamental question here raised.

8. Possible X-ray Analogies

If a quantum of radiation can be absorbed in part and scattered in part in the optical region of the spectrum, should not similar phenomena also occur in X-ray scattering ? The type of scattering discovered by Prof. Compton may possibly be only one of numerous other types of scattering with modified frequencies, some with a line spectrum and some in the nature of continuous radiation. The extreme ultra-violet region of the spectrum may also furnish us with numerous examples of the new type of radiation, which clearly occupies a position intermediate between scattering and fluorescence.

9. Conclusion

We are obviously only at the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and wave-theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics and chemistry. It all remains to be worked out.

I have to add in conclusion that I owe much to the valuable co-operation in this research of Mr. K. S. Krishnan, and the assistance of Mr. S. Venkateswaran and other workers in my laboratory.

The line spectrum of the new radiation was first seen on the 28th February, 1928. The observation was given publicity the following day.

(Issued separately, 31st March, 1928)

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