PHOTOELECTRIC PHOTOMETRY OF LIGHT SCATTERING IN FLUIDS.

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1. Introduction.

ALTHOUGH the study of the molecular scattering of light has received a new orientation with the discovery of the Raman Effect in 1928, it is widely recognised that the older field of research still retains a place of great importance. The intensity and depolarisation of the " Rayleigh Radiation " (apart from its spectral character) have formed the subject of extensive measurements by a number of workers, and the results of the measurements have been in the great majority of cases correlated with the optical polarisability and anisotropy of the molecules which play the leading rôle in the phenomena of light scattering. The anisotropy of the molecules causes the intensity of the transversely scattered light to be greater than that indicated by the earlier theories, besides giving rise to its characteristic depolarisation, and the recognition of these facts led to the correction of the original Einstein expression for the intensity by the introduction of a factor called the factor of anisotropy. The want of good agreement between the observed and calculated values of the intensity in a number of cases necessitated later a more careful examination of the Einstein expression, and it was recognised that Einstein's method of calculating the mean square of the fluctuations in dielectric constant in a small volume element by differentiating the Lorentz equation is not justified. Finally, Raman and Krishnan[1] have worked out a theory in which they take into consideration a new factor called 'the anisotropy of the polarisation field' acting on a molecule, and arrive at a slightly different expression for the intensity which shows better agreement with the experimental values.

2. Survey of the Experimental Methods.

The earliest quantitative studies of light scattering in liquids are those of Martin[2] in 1920. Two years later, Martin and Lehrman[3] undertook a

[1] *Phil. Mag.*, 1928, **5**, 498.
[2] *Jour. of Phys. Chem.*, 1920, **24**, 478.
[3] *Ibid.*, 1922, **26**, 75.

combined study of the scattering of light by dust-free liquids with improved experimental technique. Ramanathan in 1923 and Raman and Rao[4] in the same year have studied a few liquids, but by far the greatest part of the experimental data on light scattering in liquids, we owe to Dr. Krishnan[5] at Calcutta. Cabannes and Daure[6] in 1927 have made an accurate study of the scattering of light by liquid benzene, and Rama-chandra Rao[7] in the same year has studied the scattering of light by a few liquids at high temperatures. The experimental technique adopted in the study of light scattering falls into two classes, of which that of Martin and Lehrman on the one hand, and of Krishnan on the other may be taken as typical.

Martin and Lehrman experimented with the liquid in a pyrex cross with sealed-in flat ends, so that the error due to the change in the divergence of the beam was completely eliminated. The source of light was a tungsten arc pointolite lamp, the light from which was rendered parallel by means of a lens and passed through the liquid. The intensity of the scattered light was measured photometrically, using as comparison source the light scattered from a piece of paper illuminated from behind.

Krishnan's method consisted in focussing a beam of sunlight at the centre of a bulb containing the dust-free liquid by means of a long focus telescope objective of small aperture, and comparing the intensity of the track, viewed in a transverse direction with the light diffused by a secondary source such as a block of Jena glass in close proximity to the bulb by the aid of an Abney rotating sector photometer. To eliminate as far as possible errors that might be caused by the change in divergence of the beam due to the action of the liquid sphere, the latter was kept immersed in a rectangular tank containing liquid of very nearly the same refractive index,—water in the case of liquids of low refractive index, and a mixture of carbon-di-sulphide and benzene in the case of highly refracting liquids.

Regarding his results on intensity measurements, Krishnan has the following remark in his paper :—" as the two portions of the track compared had to be separated by a few millimeters....the comparison was by no means as accurate as in the case of polarisation measurements."

3. Photoelectric Photometry.

The increased sensitivity and accuracy of the photoelectric method for photometric work has been widely recognised of late, and the photoelectric

4 *Phil. Mag.*, 1923, **45**, 625.

5 *Ibid.*, 1925, **1**, 697.

6 *C.R.*, 1927, **184**, 520.

7 *Ind. Jour. of Phys.*, 1927, **2**, 7.

cell as a precise instrument for photometry is acquiring a rapidly growing importance. The photoelectric currents, though very feeble, are easily measurable on a sensitive galvanometer or electrometer, or in the absence of either of these, the feeble currents are readily amplified by the use of thermionic vacuum tubes, and read on less sensitive and more robust instruments, such as the milli- or the micro-ammeter. Photoelectric methods have got the advantage that they obviate the necessity of a dark room for photometric work. The eye " an instrument that will work with almost equal precision in illuminations differing in a ratio of 10,000 to 1 " cannot be susceptible to small differences in illumination. Secondly, the eye is absolutely insensitive to the spectral character of two lights so long as both of them have got the same colour. But the emission curve of no cell coincides with the visibility curve of the eye, and so two lights which are equal to the eye will not in general be equal to the cell, unless they are of the same quality. The state of polarisation of the light, however, has got little influence on the photoelectric current. Apart from these facts, the photoelectric method is objective, whereas all visual methods are subjective in nature. These few remarks are sufficient to show that while possessing most of the qualities of the eye, the photocell possesses additional characteristics which give it a place of much greater importance in photometric work.

Although the photocell has been used for the comparison and measurement of feeble light intensities, such as measurement of absorption and fluorescence spectra, polarimetric work and stellar photometry, the author is not so far aware of any attempt to use it in the field of light scattering. It was therefore of interest to see what information the photoelectric method could furnish in this region, and how far the results of photoelectric photometry would be compatible with those of visual photometry.

4. Choice of the Photocell.

The photocell employed in the present work was the Osram CMG8 (gas filled) cell, manufactured by the General Electric Co., Ltd., of England. It consists of a cylindrical glass bulb containing two electrodes. The anode is a rectangular wire, the cathode, a light sensitive surface, being formed of a vee-shaped plate of specially prepared caesium on a silver oxide base. Externally the cathode is connected to a screw cap on the top of the bulb, while the anode is joined to the anode pin of the valve base with which the cell is fitted. The interior of the bulb is filled with argon. Although vacuum cells have got the advantage that the intensity of the incident light is directly proportional to the saturation current over a wide range, gas-filled

cells are much more sensitive for small illuminations owing to the amplifi-
cation produced by gas filling. Moreover the study of gas-filled cells has
shown that for feeble intensities of illumination, the linearity of the current-
illumination characteristic is perfectly valid, if the applied voltage is not
too near the discharge voltage.[8] This was in fact tested to be true for the
cell used in the present work by a method to be described later.

5. Mounting of the Cell.

The cell was mounted on a valve holder which was fixed on a baseboard
of bakelite $\frac{1}{2}$ inch thick, and 4 inches square. It was covered up with a
cylindrical dome of brass in which was cut a slit $(1 \cdot 4 \times 4)$ cm. on the milling
machine, for the admission of light to the cell. By the aid of two brass
rings sliding over this cylindrical cover, the aperture allowing light on to
the sensitive vane of the photocell could be adjusted to any desired size.
The interior of the brass cover was painted dull black to avoid reflection
and stray light. The lead to the cathode was taken through an ebonite
plug at the top which was further insulated from the metallic cover by
means of molten sulphur poured into the interstices. The brass cover, in
addition to its being a light-tight chamber, served also the important
purpose of an electrical shield, protecting the cell from stray external
electrical disturbances.

6. The Amplifier and its Working.

The scattered light in the great majority of cases is too feeble to excite
a photoelectric current capable of direct measurement on an ordinary mirror
galvanometer, especially when the source of illumination is artificial, as was
the case in the present work. The only two ways open therefore are (1)
the use of an electrometer such as the Compton type, possessing extremely
high current sensitivity, or (2) the amplification of the feeble currents to
render them measurable on an ordinary instrument. The latter method
was employed in the present work.

The type of direct current amplifying circuit employed is the well-
known Valve Bridge Amplifier, first described by Wynn-Williams[9] and later
on improved and modified by Razek and Mulder,[10] Eglin,[11] Du Bridge,[12] and
a number of others. A detailed theoretical treatment of this type of ampli-
fying circuit is given by Nottingham.[13] Although the original circuit of

[8] See Campbell and Ritchie, *Photoelectric Cells*, 1929, p. 70.

[9] *Phil. Mag.*, 1928, **6**, 324.

[10] *Jour. Opt. Soc. Amer.*, 1929, **19**, 390.

[11] *Ibid.*, 1929, **18**, 393.

[12] *Phys. Rev.*, 1931, **37**, 392.

[13] *Jour. Frank. Inst.*, 1930, **209**, 287.

Wynn-Williams has been very much modified in detail, the principle employed is the same in all forms of Bridge Amplifier circuits. Without going into details a brief description of the amplifier may not be out of place.
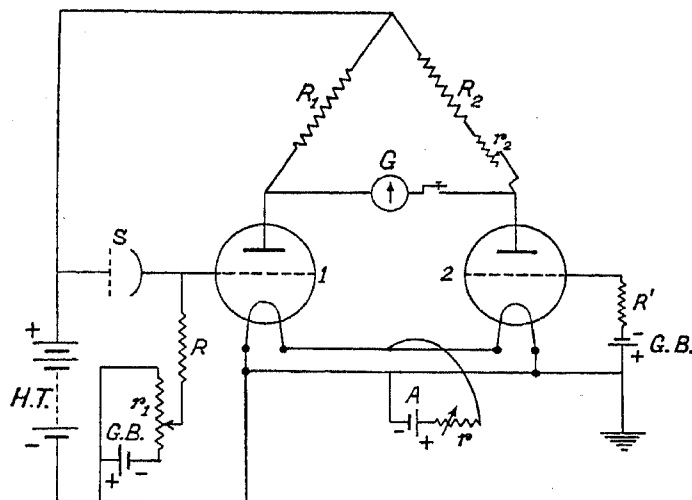

FIG. 1.

1, 2	..	L610 Marconi Dull Emitter Valves.
R_1, R_2	..	10000 ohm resistances.
R, R'	..	20 meg ohm grid leaks.
r_1	..	Varley Potentiometer (1200 ohms).
r_2	..	Adjustable rheostat (400 ohms).
r	..	Filament rheostat (5 ohms).
A	..	Filament battery (6 volts).
H. T.	..	High tension battery (115 volts).
G. B.	..	Grid bias battery (2 volts).
S	..	Osram CMG8 Photocell.
G	..	Microammeter.

It must be stated that the form of the valve bridge circuit employed was the simplest type possible without the elaborate controls, described in all papers dealing with the subject. In fact the purpose of these controls is to overcome the disturbances in the bridge balance, arising from slight fluctuations in the voltage of the H. T. and filament batteries. But by the use of good storage batteries it was found that the disturbance due to this cause was not serious.

Although special kinds of valves have been designed recently[14] for use in bridge amplifier circuits, the valves employed in the present work were the dull emitter general purpose valves, Type L610, manufactured by the M.O. Valve Company, Ltd., of England. The nominal rating for these valves is Filament volts, 6·0 max., Filament current, 0·1 amp., Anode

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[14] Du Bridge, *loc. cit.*

volts, 150 max. From a supply of about two dozen of these valves, two were chosen which were fairly well matched. The amplifier unit was built up inside a wooden box soaked in molten paraffin, in order to ensure good insulation. The box front was a sheet of ebonite on which were fixed rheostats, potentiometers, and all requisite connecting terminals. All connections, wherever possible, were soldered to avoid troubles arising from bad contact. The whole amplifying unit was enclosed in a metallic case for shielding it as far as possible from stray electrical disturbances. Protection from mechanical vibrations was secured by supporting the box on rubber props. The lead to the photocell was taken out through a tube of quartz and formed a shielded lead cable outside the metallic case. The photocell formed a separate unit, the connecting lead being made as short as possible by placing the amplifier quite adjacent to the optical system. The H. T. battery was common for the amplifier and the photocell.

In actual working, the tubes were run on the filament saturation portion of the characteristic so that changes in filament voltage were relatively unimportant as regards the plate current. In practice it was found that after switching on the various connections, two to three hours elapsed before a steady state was attained. Balance could be secured, first by adjusting the potentiometer r_1 controlling the grid bias of one of the valves, and more delicately and accurately by adjustment of the variable rheostat r_2, in one of the arms of the bridge. The grids of both the valves were maintained at a negative bias.

The principle of working consists in bringing the bridge to balance with the photocell in the dark. When the cell is then illumined, the photoelectric current flowing across the leak R produces a small change in the grid potential of the first valve, and the balance is disturbed. It has been shown by Wynn-Williams,[15] that for small changes in the grid potential the current through the galvanometer is directly proportional to the change in potential, i.e., to the main photoelectric current. If the photoelectric current varies directly as the intensity of the light falling on the cell, and this is the case when the illumination is feeble, the deflection of the galvanometer is a direct measure of the intensity of the light falling on the cell.

7. The Optical System.

The molecular scattering of light being a comparatively feeble phenomenon, it is necessary to have a very intense source of illumination. Sunlight has been extensively employed for this purpose, but the cloudy

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[15] *Proc. Camb. Phil. Soc.*, 1927, **23**, 811.

skies of Bangalore necessitated recourse to a source of artificial illumination. A 1000 c.p. tungsten arc pointolite lamp formed a suitable source for the experiments. The light from this was condensed by means of a short focus
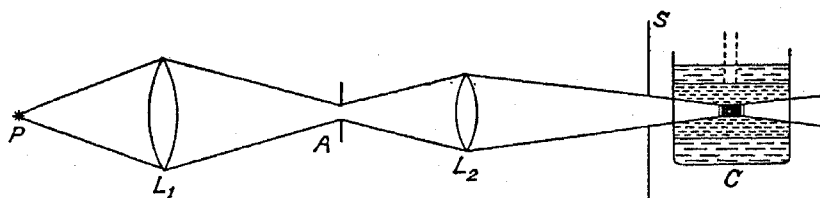

FIG. 2.

condenser L_1 of about 10 cms. aperture on a sharp-edged square hole A (7×7) mm. distant 20 cms. from L_1 so that the hole was uniformly illuminated. An image of this luminous aperture was formed by a second condenser L_2 of 5 cms. aperture at the centre of a rectangular glass cell C, (10×9×5) cm., containing distilled water. The distance of L_2 from the centre of the cell was 24 cms., and the distance of L_2 from A, 17 cms. The glass vessel was painted dull black excepting for three openings, two for the entry and exit of the beam of light, and the third for the admission of light to the photocell. This latter aperture was rectangular (8×8) mm. and was exactly opposite to the focus of the track in the liquid. The track of the beam of light in the glass cell was very nearly parallel in the neighbourhood of the focus, to which of course the observation was confined.

The photoelectric cell was placed inside a box painted dull black, at one end of which was mounted the rectangular glass vessel, the scattered light having access to the cell through an aperture at the end of the box, which could be opened or shut off at will by means of a shutter controlled by a string. The aperture in the brass shield of the photocell through which the scattered light entered the cell measured (1·4×1·4) cm. The distance of this aperture from the centre of the focus of the beam was 7 cms.

8. Experimental Technique.

(a) *Purification of the liquids.*—The liquids studied were all purified from dust by vacuum distillation in the usual way. Instead of the usual double bulb, however, a slight modification was effected. A cylindrical tube of pyrex, about 7·5 cms. long and 3·5 cms. diameter, was taken and pyrex flats were sealed to its ends. The size of the cylindrical glass cell so obtained was such that it would just fit inside the rectangular glass tank containing distilled water. This was connected to a pyrex bulb and the liquid was distilled from the bulb into the cylindrical cell, which was finally painted dull black excepting for the two ends and a small portion in the centre. In the actual experiment the latter was immersed in the rectangular

glass tank, and adjusted so that the beam of light traversed along its axis. There was very little distortion of the track.

(b) *Testing the linearity of the amplifier.*—The first essential step in the experiment was to test out how far the response of the amplifier was linear, *i.e.*, to ascertain whether the deflections registered by the galvanometer in the bridge circuit when light of a certain small intensity was allowed to fall on the photocell could be taken to be directly proportional to the intensity of the incident light. For this purpose, the following procedure was adopted, which enabled a two-fold verification of the result.

A series of metallic plates about $4\frac{1}{2}$ inches square were taken, and circles were drawn on them, the diameter of these circles being the same as the aperture of the lens L_1. The area within this circle was next drilled through to get holes of equal size, uniformly distributed over the whole area, the total number of holes alone differing from plate to plate. By interposing these plates immediately in front of the lens L_1 (which was uniformly illumined over its whole aperture), the intensity of the incident track could be cut down in any known ratio. Three liquids, having fairly large intensities of scattering, CS_2, C_6H_5Cl, and C_6H_6 were taken and the deflections produced when the scattered light from each of them was allowed to fall in succession on the photoelectric cell were recorded, the incident light being of maximum intensity. The intensity of the incident light was then cut down by interposing the perforated plates one after another in front of L_1 and the deflections in each case were again noted. The results are given in the table below :—

Intensity of incident beam	Deflection in scale divisions			Number of holes / Deflection			$CS_2 : C_6H_5Cl : C_6H_6$
	CS_2	C_6H_5Cl	C_6H_6	CS_2	C_6H_5Cl	C_6H_6	
Full	>250 (out of range of the instrument)	110	74	..	..	..	.. : 1·49 : 1
Plate with 187 holes in front of L_1	108	43	28	1·71	4·35	6·61	3·86 : 1·54 : 1
Do. 147 holes ..	87	33	22	1·69	4·45	6·68	3·95 : 1·50 : 1
,, 97 ,, ..	58	20	14·5	1·67	4·85	6·69	4·00 : 1·38 : 1
,, 45 ,, ..	28	10·5	7·0	1·60	4·18	6·43	4·00 : 1·50 : 1
Mean ..				1·67	4·46	6·60	3·95 : 1·48 : 1

The results in the last four columns show that within the limits of experimental errors, the deflection of the galvanometer is directly proportional to

the intensity of the light falling on the photocell; and as the range of intensities covered by the above table comprises the whole field of scattering in the liquids investigated in the present work, the conclusion was drawn that in every case the deflection registered by the galvanometer when the scattered light from the liquid was allowed on the photocell, was a true measure of the intensity of the light falling on the latter.

9. Experimental Results.

The following table gives the results of experiments in the case of a few liquids :—

Liquid	Deflection in scale divisions	Relative Intensities (Benzene=1)		
		Author	Krishnan[16]	Martin and Lehrman[16]
Benzene	74	1	1	1
Carbon-di-sulphide	>250	3·95	4·12	4·54
Chlorobenzene	110	1·49	1·30	1·46
Acetic acid	38	0·51	0·38	....
Ether (ethyl)	30	0·40	0·32	0·35
Methyl alcohol	20	0·27	0·25	0·19
Ethyl alcohol	17	0·23	0·18	0·20

The results are in fairly good agreement with those of visual photometry. Indeed, small deviations are to be expected when it is remarked that no special care was taken for drying and chemical purification of the liquids. Moreover the optics of the arrangement, particularly in regard to the divergence of the incident beam on entering the liquid, and that of the scattered light before it enters the photocell, probably require a detailed examination, which has not been made in the present work. The results should therefore be considered only of a preliminary nature. But they clearly show the possibility of applying the photoelectric method with success in the field of light scattering.

10. Sources of Error.

As has been recognised from long time since, the main source of error in the study of ' Rayleigh Scattering ' is fluorescence. This is caused to a

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[16] Taken from Cabannes, *La Diffusion Moléculaire de la Lumèire.*

large extent by the presence of impurities, but in a smaller degree it is attributed to the photochemical action of the light on the medium. The latter type of fluorescence persists even after the most careful and thorough purification of the liquids, and is in fact largely responsible for the continuous background often present in most photographs of Raman spectra. Fluorescence for most practical purposes, however, can be avoided by using freshly distilled liquids; and putting suitable filters in the track of the incident beam. The vibration lines arising from the modified Raman scattering are too feeble to produce any sensible effect. The rotation wings accompanying the true Rayleigh scattering have their origin in the anisotropy of the molecules and are in fact taken into account in all intensity and depolarisation measurements.

11. Conclusion.

The photoelectric method of measuring the intensities of scattering promises to offer a new method for the measurement of depolarisation, the validity of which depends on the experimentally known fact that the state of polarisation of the incident light has no influence at all on the photo-electric current. If, therefore, a suitably mounted nicol is interposed in the path of the scattered light before it enters the photocell, then the ratio of the minimum and maximum deflections of the galvanometer when the nicol is rotated will give the depolarisation value of the light scattered by the liquid. Alternatively, the incident light could be polarised first horizontally and then vertically and the knowledge of the photoelectric currents in the two cases should be capable of yielding the value for the depolarisation. Of course, for the measurement of small depolarisation values a very sensitive and robust outfit would be necessary and the use of an electro-meter which will directly give the primary photoelectric current would be preferable to an amplifying system.

In conclusion, the author wishes to record his indebtedness to Sir C. V. Raman, Kt., F.R.S., N.L., for suggesting the problem and for valuable guidance in the course of the work.

Summary.

The paper deals with a photoelectric method for measurement of the intensities of scattering in liquids, which is much quicker and more convenient than the visual methods hitherto employed. Results of the measurements in the case of a few liquids show good agreement between the results of photoelectric and visual photometry. The possibility of extending the method to depolarisation measurements is outlined.