SCATTERING OF LIGHT IN OPTICAL GLASSES.

By R. S. Krishnan.
(*From the Department of Physics, Indian Institute of Science, Bangalore.*)

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1. *Introduction.*

The constitution and structure of glass have long been a puzzling problem. It is, nevertheless, true to say that there has been comparatively little work done of a fundamental or theoretical nature. This is no doubt due to the meagre knowledge we possess concerning the constitution of glass. It is obvious that glasses do not consist of crystallites which can be recognised as such by the naked eye even when assisted by powerful microscopes. Glasses are usually described as supercooled liquid or as an amorphous solid ; the word amorphous as used by the workers on glass is taken to mean that no crystallites can be detected by the ordinary laboratory methods. From its state of aggregation one is led to believe that glass is a supercooled liquid for it exhibits a series of thermodynamic characteristics of such a condition. Data on specific heat, surface tension, melting point, viscosity and dielectric strength indicate that the material is of high molecular weight or highly associated. But on the other hand as regards its elastic properties, glass behaves more or less like a hard rigid solid.

X-ray diffraction by glasses has been studied in detail by numerous investigators beginning with Debye and Scherrer. The lack of obvious crystallinity makes it clear that sharp diffraction patterns are unlikely to be obtained. Most glasses exhibit broad and diffuse bands similar to those obtained in the case of ordinary liquids. Randall and Rooksby[1] tried to explain the different bands on the basis of minute crystals or groups of atoms regularly arranged over a very small volume. But such a view regarding the constitution of glass does not find support from other directions.

It has long ago been pointed by Prof. Raman[2] that a study of the scattering of light in glasses would enhance our knowledge regarding the nature of glass and amorphous substances in general, to a considerable extent. The present

[1] J. T. Randall and H. P. Rooksby, *Journ. Soc. Glas. Techn.*, 1933, 17, 287.
[2] C. V. Raman, *Molecular Diffraction of Light*, 1922.

Lord Rayleigh[3] was the first to demonstrate the existence of an internal scattering of light in common glasses. The degree of depolarisation was found to be of the same order of magnitude as that usually observed in gases. He was inclined to attribute the scattering in glasses to spherical inclusions of diameter not small compared with the wavelength of light and explained the finite depolarisation of the scattered light as due to the appreciable size of these inclusions. It is well known that opal glasses owe their diffusing properties to the fact that they contain in suspension small crystals which can be observed under an ordinary microscope, of refractive index and absorption coefficient different from those of the glassy matrix. But it is hard to believe that such inclusions may also exist in optical glasses. Prof. Raman[4] has reported the measurements of intensity and depolarisation of light scattered by a series of optical glasses. The closest examination by him under a powerful microscope with dark ground illumination failed to indicate the presence of any visible inclusions. Consequently he came to the conclusion that the scattering in these glasses was really molecular in origin. He found that the scattering power of glass approximated to that of a liquid and not to that of a crystal.

The observations of the above-mentioned investigators on the scattering of light in glass did not carry us far into the more intricate problem concerning the constitution of glass, for they studied the Rayleigh radiation with incident unpolarised light alone. In order to get more comprehensive and fundamental information regarding the state of aggregation or dispersion of molecules in any scattering medium, it is essential to make a comparative study of the state of polarisation of the scattered light with the incident light in different states of polarisation, (namely, unpolarised, vertically polarised and horizontally polarised). This fact has often been stressed by the author in recent papers[5] in these *Proceedings*. If glass is an aggregate of molecular clusters, the light scattered transversely when the incident light is polarised with electric vector horizontal, will no longer be completely unpolarised as in the case of an ordinary liquid or gas but will be partially polarised with the horizontal component stronger than the vertical component to an extent depending upon the size of the clusters present. The object of the present investigation is to make a more detailed study of the scattering of light in a series of optical glasses of widely different composition and to discuss the bearing of the results on the constitution of glass.

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[3] R. W. Strutt, (Lord Rayleigh), *Proc. Roy. Soc.*, 1919, **95**, 476.

[4] C. V. Raman, *Journ. Optical Soc. America*, 1927, **15**, 185.

[5] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1934-5, 1, 211; 717; 782; 915. 1935, 2, 221.

2. *Specimens Examined.*

TABLE I.

Serial No.	Melting No.	Glass contains traces of Al_2O_3, Fe_2O_3, As_2O_3 and oxides in :		Density
		more than 10%	less than 10%	
1	25188	SiO_2, B_2O_3, Al_2O_3, K_2O	Na_2O, F	2·3
2	18415	SiO_2, B_2O_3, K_2O	Al_2O_3	2·3
3	16776	SiO_2, K_2O	Al_2O_3, Na_2O, CaO	2·4
4	23975	SiO_2, B_2O_3, ZnO	Al_2O_3, Na_2O	2·5
5	24906	SiO_2, B_2O_3	Na_2O, K_2O, BaO	2·5
6	22601	SiO_2, B_2O_3, Sb_2O_3	Al_2O_3, Na_2O, K_2O	2·7
7	23125	SiO_2, Na_2O, PbO	ZnO	2·7
8	22638	SiO_2, PbO	Na_2O, K_2O	2·9
9	24464	SiO_2, ZnO, BaO	B_2O_3, Na_2O, K_2O, PbO	3·1
10	19510	SiO_2, PbO	Na_2O, K_2O	3·2
11	23355	SiO_2, B_2O_3, BaO	Al_2O_3, Na_2O	3·3
12	20672	SiO_2, PbO	B_2O_3, Na_2O, K_2O	3·4
13	22986	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·5
14	23441	SiO_2, PbO	Na_2O, K_2O	3·9
15	23497	SiO_2, BaO, PbO	Na_2O, K_2O, ZnO	3·9
16	23850	SiO_2, PbO	Na_2O, K_2O	4·4
17	23590	SiO_2, PbO	Na_2O, K_2O	5·1

Table I gives the list of seventeen optical glasses and also their composition and density as furnished by the manufacturers. These glasses were manufactured and were presented to Prof. C. V. Raman by Messrs. Schott and Gen. in Jena (Germany). They are in the form of rectangular slabs (3 cm., 3 cm., 2 cm.) with all the faces excluding the two end faces well polished. The list comprises a representative collection of optical glasses of widely different densities and composition.

3. *Preliminary Observations.*

The specimen to be examined was kept immersed in dust-free distilled water contained in a rectangular cell. The cell was suitably blackened on the outside excepting for three windows. A narrow beam of sunlight reflected by a single mirror Foucault Heliostat was focussed by means of a

long focus lens. At the focus the light passed through the specimen. The track inside the glass was intensely coloured blue when viewed in the transverse direction. It was of uniform colour and intensity throughout. When the track inside the specimen was viewed in the direction of the incident beam with the aid of a microscope no visible speck was observed, the track being throughout homogeneous.

On examining the light scattered transversely with a double-image prism, the two components observed were very different in colour and intensity, showing thereby that the scattered light was strongly but not completely polarised. The vertical component which was very much more intense was a rich blue in colour. The difference in colour is indicative of a weak fluorescence. Suitable colour filters were introduced in the path of the incident beam to exclude fluorescence. It was found that with an orange filter in the path of the incident beam, the two components of the scattered light were identical in colour for all the specimens.

Table II gives the colours of the vertical and horizontal components of the light scattered transversely by the different optical glasses when a narrow beam of unpolarised white light is passed through them. The refractive index of each specimen for the yellow line of sodium was measured with the aid of a Pulfrich Refractometer.

4. Measurement of Depolarisation.

The light from a 25 ampere projection lantern was condensed on a small square aperture (of edge 2 mm.). A long focus lens (aperture=4 cm.) served to condense the light emerging out of the aperture on to the glass to be examined which was placed at a distance of about 50 cm. from the lens. A double-image prism was placed in the path of the incident beam by the side of the lens. The scattered light was viewed through another double-image prism. It was found that the fourth image which was the horizontal component of the scattered light arising from the horizontal component of the incident beam was found to be distinctly brighter than either of the middle two equal anisotropic components. This indicated at once that the optical heterogeneity of the glassy medium should no longer be identified as due to the individual molecules, but due to small groups of molecules. Using incident unpolarised light, light polarised with electric vector, vertical and horizontal respectively, the three depolarisation factors ρ_u, ρ_v and ρ_h of the scattered light corresponding to the three cases were measured using a double-image prism and a nicol, with the orange filter in the path of the incident beam. ρ_u and ρ_v are defined as the ratio of the horizontal component to the vertical component, while ρ_h is defined as the ratio of the vertical component to the horizontal component.

TABLE II.

S. No. as in Table I	Density	Refractive Index μ_D	With incident unpolarised white light		
			Colour of the transversely scattered light	Colour of the vertical component of the same	Colour of the horizontal component of the same
1	2·3	1·4670	Bluish green	Greenish blue	Yellowish green
2	2·3	1·4925	Bluish white	Blue	Greenish yellow
3	2·4	1·5022	Greenish blue	Blue	Greenish yellow
4	2·5	1·5095	Deep blue	Deep blue	Yellowish brown
5	2·5	1·5269	Green	Bluish green	Yellowish green
6	2·7	1·5294	Blue	Blue	Brown
7	2·7	1·5370	Blue	Blue	Green
8	2·9	1·5449	Blue	Blue	Green
9	3·1	1·5697	Blue	Blue	Yellowish brown
10	3·2	1·5698	Blue	Blue	Greenish yellow
11	3·3	1·5892	Blue	Blue	Yellowish green
12	3·4	1·5983	Blue	Blue	Orange
13	3·5	1·6163	Blue	Blue	Yellowish brown
14	3·9	1·6473	Blue	Blue	Indigo-blue with a pink tinge
15	3·9	1·6498	Blue	Bluish white	Indigo-blue with a pink tinge
16	4·4	1·7130	Blue	Blue	Indigo-blue with a pink tinge
17	5·1	1·7850	Greenish blue	Greenish blue	Greenish yellow

The errors arising from the finite angle of convergence of the incident beam were calculated using Ananthakrishnan's formulæ.[6] The actual angle of convergence of the beam inside the specimen was equal to $4/50 \times 2/3$ radian. For this particular angle of convergence the corrections for ρ_u and ρ_v were 0·00035 and 0·00017 respectively. Since the observed values of ρ_u and ρ_v were of the order of 0·03 to 0·01 the correction factors could be neglected. In the same way the correction for ρ_h could also be neglected in comparison with the observed value of ρ_h. The values of ρ_u, ρ_v and ρ_h for the glasses examined are given in Table III.

[6] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1935, 2, 133.

5. Intensity Measurements.

For the measurement of the relative intensity of scattering in these glasses, the photo-electric method was employed. The method consists in allowing the scattered light to fall on a photo-cell which was connected to a direct current valve bridge amplifier. For very weak intensities the deflections of the galvanometer in the amplifier circuit was a direct measure of the intensity of light falling on the photo-cell. Relatively low scattering power in these glasses especially with an orange filter in the path of the incident beam necessitated recourse to sunlight. A parallel beam of sunlight reflected by a single mirror Foucault Heliostat was condensed by means of a long focus photographic lens provided with an iris diaphragm. At the focus the light passed through the specimen of optical glass contained in the cell of water.

TABLE III.

S. No. as in Table I	Refractive index μ_D	With orange filter in the path of the incident beam					
		ρ_v %	ρ_u %	ρ_h (observed) %	ρ_h (calculated) %	$\Delta\rho_u = \rho_u - \frac{2\rho_v}{1+\rho_v}$	Intensity relative to ether = 1
1	1·4670	12·7	26	78	77	3·5	0·8
2	1·4925	12	24	82	81	2·6	1·0
3	1·5022	3·5	8·1	72	72	1·3	1·9
4	1·5095	0.46	1·2	68	62	0·3	3·3
5	1·5269	3·6	8·1	80	75	1·05	0·9
6	1·5294	3·5	7·5	85	82	0·7	1·2
7	1·5370	2·4	5·2	78	82	0·5	2·1
8	1·5449	3·0	6·1	91	91	0·3	2·1
9	1·5697	2·1	4·8	81	75	0·7	1·8
10	1·5698	3·3	7·0	88	84	0·6	1·3
11	1·5892	2·1	4·6	80	82	0·5	1·6
12	1·5983	3·3	7·0	83	84	0·6	1·6
13	1·6163	1·6	3·7	80	74	0·5	2·4
14	1·6473	2·3	5·2	75	76	0·7	..
15	1·6478	2·0	4·5	77	77	0·6	1·9
16	1·7130	2·5	5·3	87	85	0·4	1·8
17	1·7850	2·8	5·9	87	86	0·5	2·2

The whole arrangement was set up inside a dark cabin. The photo-cell was enclosed in a suitable box and was placed in front of the specimen in such a way that when the screen in front of the photo-cell was raised, only the light scattered by the specimen in the exact transverse horizontal direction entered the photo-cell. One of the glasses was kept as the standard for comparison of intensities of scattering. With the orange filter in the path of the incident beam,the glasses were placed inside the cell of water at the focus of the incident beam one after another in quick succession and the corresponding deflections of the galvanometer in the amplifier circuit were recorded. In order to avoid errors arising from the variations in intensity of the incident beam, the readings with the standard glass were taken before and after each one of the glasses was examined. Finally the scattering power of the standard glass was compared with that of pure dust-free ether contained in a double bulb. From the galvanometer deflections the scattering power of each specimen was calculated in terms of that of ether. The values are given in Table III.

6. *Discussion of Results.*

The sixth column in Table III gives the values of ρ_h calculated from the observed values of ρ_u and ρ_v applying the general Reciprocity Relation

$$\rho_u = (1 + {}^1/\rho_h) / (1 + {}^1/\rho_v) \quad .. \quad .. \quad .. \quad (1)$$

The agreement between the calculated and the observed values of ρ_h is quite satisfactory.

Almost all the glasses examined are fluorescent. But this fluorescence is rather weak unlike that in ordinary viscous liquids. The colour of the fainter component is found to be largely influenced by this fluorescence and consequently it varies from glass to glass. On spectroscopic examination it is found that this weak fluorescence is mainly due to a Raman effect together with a faint continuous fluorescence band superposed on it. This continuous band which extends over several hundred Angstrom units is found to change its position for different specimens.

The light scattered by these glasses is strongly polarised as is seen from the low value of ρ_u. The rather high value of ρ_u for glasses 1 and 2 may be due to the higher anisotropy of the scattering elements in them. It is to be noted that for all the glasses, the value of ρ_h is definitely less than 100%. This furnishes us for the first time positive evidence for the existence of molecular aggregates in glass, the size of which is not excessively small compared with the wavelength of light. The depolarisation ρ_u arises not only from the anisotropy of the scattering elements but also from their finite size. To a first approximation the anisotropic part of ρ_u can be considered

to be equal to $2\rho_v/(1+\rho_v)$. The difference $\Delta\rho_u$ between the observed value of ρ_u and $2\rho_v/(1+\rho_v)$ represents the depolarisation due to finite size. Values of $\Delta\rho_u$ are given in Table III. $\Delta\rho_v$ is of the order of 0·6%. That this value of $\Delta\rho_u$ is definite but small indicates that the molecular aggregates are not of large size.

Coming to the intensity of scattering, it is seen that the scattering power of glass is of the same order of magnitude as that of an ordinary liquid or liquid mixture, and not as that of an ordinary crystal. A close scrutiny of the figures in Table III reveals the fact that glasses which possess high scattering power give low depolarisation values. Of all the glasses examined the intensity of scattering is maximum for the glass marked 4. The values of ρ_u, ρ_v and ρ_h for this glass are 1·2%, 0·46% and 62%. They are the lowest observed. It can be inferred from this that in addition to the density scattering and orientation scattering, there may exist composition scattering also in glasses as in the case of liquid mixtures. The transverse scattering due to composition fluctuations is in general completely polarised. In spite of the appreciable size of the molecular clusters in glass, the value of ρ_u is diminished by the presence of this composition scattering. Glass can therefore be considered as a mixture of anisotropic molecular aggregates.

The influence of composition of the glass on the depolarisation value and intensity of scattering is very striking. The value of ρ_h is found to diminish with increasing percentage of acidic oxides such as silicon dioxide (SiO_2), boric oxide (B_2O_3), etc., in glass, whereas the value of ρ_h tends to increase as the proportion of basic oxides such as Na_2O, K_2O, PbO etc., increases. In other words, the tendency for the formation of large molecular aggregates is greater for glasses containing more of acidic oxides especially boric oxide and less of basic oxides than for glasses which contain more of basic oxides and less of acidic oxides. Glasses numbered 4, 5, 8, 10, 16 and 17 are illustrative of the above conclusions. The regularity in the dependence of scattering on composition makes it clear that the scattering phenomenon observed in optical glasses is not due to accidental inclusions but is an intrinsic property of glass.

The conclusions of the author regarding the constitution of glass fully substantiate the remarks made by G. Hagg[7] in his paper on the "Nature of Vitreous State". His remarks can be summarised in a few words as follows :—Glass is an aggregate of large groups. A melt will show tendency for glass formation if it contains large and irregular groups of molecules. The only oxides which are known in the vitreous state are B_2O_3, SiO_2, P_2O_3,

7 G. Hagg, *Journ. of Chem. Phys.*, 1935, 3, 42.

P_2O_5, GeO_2, As_2O_3 and As_2O_5. A melt containing any one of these oxides will easily tend to become glassy on cooling. Glass forming tendency is largest for boric oxide (B_2O_3), which cannot even be obtained in crystalline form. The glass forming ability of the melt will decrease when it is getting more basic.

7. *Conclusion.*

Important information concerning the constitution of glass and the nature of the vitreous state in general may be expected to result from a detailed study of the Raman spectra as they offer a unique method of investigating these substances which give no X-ray pattern and which will not yield to the usual physico-chemical method of approach. Notwithstanding the inherent difficulties, considerable progress has been made in this direction by Gross and Romanova,[8] Hollaender and Williams,[9] Bhagavantam[10] and by Kujuinzelis.[11] The Raman lines obtained from glasses are in general broad and diffuse. In addition to these diffuse lines, there is a general background scattering. Consequently the interpretation of the Raman spectra obtained has not been easy. The broadening of the lines as well as the frequency shifts are attributed to the influence of polymerisation. It appears possible that a connection may exist between the width of the Raman bands and the clustering tendency disclosed by the present investigation. Further experimental work in this direction appears desirable.

In conclusion the author takes this opportunity to record his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., under whose guidance the present investigation was carried out.

8. *Summary.*

A comparative study has been made of the intensity and state of polarisation of the light scattered transversely by a series of seventeen glasses of optical quality with the incident light in different states of polarisation (namely, unpolarised, vertically polarised and horizontally polarised). A weak fluorescence was observed in all the glasses. Measurements of the depolarisation factors ρ_u, ρ_v and ρ_h were made with an orange filter in the path of the incident beam to eliminate fluorescence. ρ_u and ρ_v are found to be of the same order of magnitude as are usually observed in the case of gases. But on the other hand, ρ_h is found to be distinctly less than 100%

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8 E. Gross and M. Romanova, *Zeits. fur Phys.*, 1929, **55**, 744.

9 A. Hollaender and J. W. Williams, *Phys. Rev.*, 1929, **34**, 380; 1931, **38**, 1739.

10 S. Bhagavantam, *Ind. Journ. of Phys.*, 1931, **6**, 1.

11 Th. G. Kujuinzelis, *Zeits. fur Phys.*, 1935, **97**, 561.

showing thereby the existence of molecular aggregates of size not small compared with the wavelength of light. Since no visible inclusions are observed it is concluded that the scattering in glass is really an internal phenomenon. Measurements of the relative intensity of scattering in these glasses were also made employing the photo-electric method. The influence of composition of the glass on the formation and the size of the molecular aggregates formed is fully discussed. It is found that the tendency for the formation of molecular aggregates increases with an increasing percentage of acidic oxides especially boric oxide, whereas it diminishes when the glass gets more and more basic.