

THE MOLECULAR SCATTERING OF LIGHT IN BENZENE, VAPOR AND LIQUID

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ABSTRACT

Scattering of sunlight by benzene, vapor and liquid, from 35° to 283° C.—The intensity of the light scattered at right angles was determined relative to that scattered by liquid ether at 35° C, by photometric comparison with the aid of reflecting prisms and a sectored disc. The relative intensity increased with the temperature at an accelerated rate; for the liquid, from 3.2 at 35° to 102 at 283° and, for the saturated vapor, from 0.95 at 182° to 11.9 at 267°. The scattered light is not completely polarized. The *imperfection of polarization* was measured by use of a double-image prism and a nicol. The ratio of the weaker to the stronger component, r , was found to decrease from 7.2 to 0.9 per cent for the vapor and from 43 to 2.8 per cent for the liquid as the temperature was raised from 35° to 280°. *Comparison with theories.* This imperfection has been attributed to the anisotropy of the molecules by Rayleigh, Born and others. The theory as extended by Raman to the general case of fluids leads to the relation $Sr/\rho(1+r) = \text{const.}$, where S is the intensity and ρ the density. This is found to agree satisfactorily with the observations for both vapor and liquid. Since for the vapor, the intensity S increases with the temperature much more rapidly than the density, the Rayleigh law is not valid. The Einstein-Smoluchowski formula shows much better agreement, although, when calculated values of the refractive index and compressibility are inserted, it gives for the scattering in the vapor values which are 20 per cent or more too high.

Formula for isothermal compressibility of a saturated vapor is derived from Dietrici's equation of state. It is found to give the observed values for ether, isopentane and CO₂ in the temperature range 0.8 to 0.96 T_c if an arbitrary numerical factor 1.25 is used. Introducing this gives, for this range $(dp/d\rho)_t = 2.5\rho(\rho_c - \rho)^2/(2\rho_c^2\rho - \rho^2\rho_c)$.

1. INTRODUCTION.

IN his recent experiments on the molecular scattering of light in gases and vapors¹ Lord Rayleigh noticed the interesting fact that the light scattered in a direction perpendicular to the incident beam was not perfectly polarized. A similar effect has been observed but in a much more marked degree by W. H. Martin² in the light scattered by dust-free liquids. When we compare a liquid like ether and its vapor at the ordinary temperature in this respect, we find a large difference. Ether vapor at the ordinary temperature shows an imperfection of 1.7 per cent,

¹ Proc. Roy. Soc. A., Vol. 94, p. 453, 1918.

² Martin, Journal of Physical Chemistry, Vol. 24, 1920, p. 478, and Jan., 1922.

while liquid ether shows 8 per cent. The imperfection of polarization in gases has been explained^{1, 2} on the assumption of anisotropy of the molecules; the imperfection in liquids is no doubt to be attributed to the same cause. The general theory of light-scattering in liquids has been discussed by Prof. C. V. Raman,³ who has also put forward an explanation⁴ of the increased imperfection of polarization of the scattered light in this case and suggested a quantitative connection between the intensity of the transversely scattered light, its state of polarization and the density of the fluid. A brief account of this theory is given in the course of the paper. The experiments described here were undertaken with a view to securing data regarding the intensity and polarization of the transversely scattered light both in the liquid phase and the saturated vapor phase of a suitable substance over a large range of temperatures. Benzene was chosen owing to the large value of its imperfection of polarization at ordinary temperatures. The result of the experiments has been to confirm the general validity of the explanation suggested.

2. EXPERIMENTAL ARRANGEMENTS.

The apparatus used in the work is the same as that used by the author in an investigation on the intensity of the light scattered in ether.⁵ The benzene was sealed in a stout-walled uniform glass bulb of about 1.2 inches internal diameter and the bulb was mounted in the center of an iron cross-tube (diameter 1.5 inches and each arm of the cross 15 inches long). The ends of the tube were closed with glass windows and it could be heated electrically by passing a current through a coil of nichrome wire wound uniformly over it. Temperatures could be maintained steady for long intervals of time to within half a degree. The benzene used was Merck's pure grade and was distilled five or six times in vacuo in the manner described by Martin.⁶

The intensity of the scattered light was determined by comparing the luminosity of a track of sunlight passing through it with a similar track in liquid ether kept in a rectangular glass bottle at the room temperature. The sunlight was focussed by two exactly similar lenses of the same focal length and provided with adjustable apertures at the center of the benzene bulb and at the center of the ether bottle. By means of two totally-reflecting prisms, the two tracks were brought

¹ Lord Rayleigh, *Phil. Mag.*, Vol. 35, p. 373, 1918.

² Born, *Deutsch. Phys. Gesell.*, Vol. 19, p. 243 (1917), and Vol. 20, p. 16 (1918).

³ "Molecular Diffraction of Light," Calcutta University Press, 1922.

⁴ *Nature*, July, 1922, page 11.

⁵ *Proc. Roy. Soc.*, Vol. 102, p. 154, 1922.

⁶ *Loc. cit.*

side by side and their luminosities compared visually by means of a rotating sector disc photometer.

The polarization of the light scattered at right angles to the incident beam was measured by means of a double-image prism and nicol. The double-image prism was mounted at the same height as the benzene bulb with its axis horizontal and pointing towards the bulb. It was first adjusted so that the two images of the horizontal track in the benzene were obtained in the same horizontal line and side by side with each other. The nicol was now inserted behind the double-image prism and so oriented that the vertical component was extinguished. On either side of this position, there is a position when the two images would be equal in intensity. If we denote the angle between these two equality-positions by 2θ , the ratio of the intensity of the horizontal component to that of the vertical is given by $\tan^2 \theta$.

3. RESULTS.

The results regarding the scattering in the saturated vapor of benzene and in liquid benzene are collected in the following two tables.

TABLE I.

Scattering in Saturated Benzene Vapor.

S_t = Scattering at t° C.

S_e = Scattering in liquid ether at 35° C.

ρ_t = density at t° C.

r = Ratio of weak component to strong in the transversely scattered light.

Temperature t° .	$\frac{S_t}{S_e}$ Observed.	$\frac{S_t}{S_{182}}$	$\frac{\rho_t}{\rho_{182}}$	r (in per cent).	
				Observed.	Calculated.
35				7.2	
100				6.2	
182	0.95	1.00	1.00	3.5	3.2
204	1.56	1.64	1.48	3.4	2.8
228	3.00	3.15	2.25	2.5	2.2
247	4.9	5.14	3.00	2.0	2.0
267	11.9	12.5	4.5	1.5	1.2
280				0.9	

It will be seen that the intensity of scattering in both the saturated vapor and in the liquid increases rapidly with temperature becoming very large as we approach the critical temperature, and that in the case of the vapor, the increase is much more than in proportion to the density. The imperfection of polarization shows a diminution with increasing temperature tending to a very small value as we approach the critical point. In the last column of the two tables are shown the values of

imperfection of polarization calculated in the manner indicated in the next section.

TABLE II.

Scattering in Liquid Benzene.

Temperature t° C.	$\frac{S_i}{S_s}$	r.	
		Observed.	Calculated.
35.....	3.2	43	44
125.....	3.67	32	31
182.....	5.48	19	16
205.....	7.21	14	10.3
228.....	11.0	9.5	7.0
268.....	20.5	3.0	2.9
280.....		2.8	
283.....	102		

4. POLARIZATION OF THE TRANSVERSELY SCATTERED LIGHT.

The theory of light-scattering by gases consisting of isotropic molecules as developed by the late Lord Rayleigh and the general theory of scattering of fluids as developed by Einstein on the lines of Smoluchowski's work, based on the idea of accidental deviation of density in the fluid, predict a perfect polarization of the light scattered in a direction at right angles to the incident beam. Einstein's expression for the fraction of the incident light scattered per unit solid angle in a transverse direction by unit volume of a homogeneous fluid is given by

$$\frac{\pi^2 RT\beta}{18 N\lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2, \quad (1)$$

where T , β are the temperature and compressibility of the fluid, R is the gas-constant per gram-molecule, N the Avogadro-number, λ is the wave-length of the incident light and μ is the refractive index of the fluid. This reduces to Rayleigh's law in the case of gases obeying Boyle's law and experiments at Calcutta on a number of substances both in the liquid and vapor states have established the general validity of this law.

In the case of most media, however, the transversely scattered light is only imperfectly polarized. This imperfection has been attributed to the anisotropy of the molecules and the general case has been recently discussed by Raman. In such a medium, there is an extra scattering which is for the most part unpolarized, due to the anisotropy of the molecules. If Ω_0 denote the scattering arising from the fluctuations of density, $4\Omega_1$ the unpolarized scattering arising from molecular anisotropy and Ω_2 the polarized scattering due to the same cause, the ratio of the weak

component to the strong in the transversely scattered light is given by

$$r = \frac{2\Omega_1}{\Omega_0 + \Omega_2 + 2\Omega_1} \quad (2)$$

In the case of a gas obeying Boyle's law, Ω_2 has the value $\frac{1}{3}\Omega_1$. The extra contribution from molecular anisotropy leads to an increased scattering in the ratio

$$\frac{6(1+r)}{6-7r} \quad (3)$$

We shall assume this to be true generally.

If the molecules have absolutely random orientations, Ω_1 should be proportional to the number of molecules per unit volume. Since in the case of liquids and vapors, on rise of temperature, Ω_0 increases at a much larger rate than the density (in liquid the density actually decreases), the ratio $2\Omega_1/(\Omega_0 + \frac{1}{3}\Omega_1)$ should get smaller and smaller and reach a minimum value at the critical point where the value of Ω_0 is a maximum. We can easily deduce a quantitative relation between the intensity of the transversely scattered light and its imperfection of polarization. From equation (2), when $\Omega_2 = \frac{1}{3}\Omega_1$,

$$\Omega_0 = \frac{6-7r}{3r} \Omega_1,$$

and since $\Omega_1 = k\rho$, where ρ is the density of the substance,

$$\Omega_0 = \frac{6-7r}{3r} k\rho,$$

and the total scattering

$$\begin{aligned} S &= \Omega_0 + \frac{13}{3} \Omega_1 \\ &= \frac{1+r}{r} \cdot 2k\rho; \end{aligned}$$

$$\therefore \frac{S}{\rho} \frac{r}{1+r} = 2k, \text{ a constant.} \quad (4)$$

In the last column of Tables I. and II. are given the values of r calculated from this relation. The constant k was calculated from the intensity and polarization of the transversely scattered light in saturated benzene vapor at room temperature. The imperfection of polarization was measured in an apparatus similar to that used by Lord Rayleigh, the vapor being illuminated by means of a strong beam of sunlight. The value of r was found to be 7.2 per cent as against Lord Rayleigh's value 6 per cent. The intensity at the room temperature was calculated, assuming the validity of the Rayleigh law of scattering (to which the

Einstein law reduces when the vapor is sufficiently rare) and applying the correction for the admixture with unpolarized light. The agreement between the calculated and observed values is satisfactory.

5. CALCULATION OF THE INTENSITY OF THE TRANSVERSELY SCATTERED LIGHT.

For calculating the intensity of the transversely scattered light according to the Einstein-Smoluchowski formula, the refractive index and the compressibility of the medium have to be known. The refractive index can be calculated, using Lorentz's relation $(\mu^2 - 1)/(\mu^2 + 2)\rho = 0.3423$ ¹ for benzene (for the F line). There are no data for the compressibility of the liquid² or the vapor for the temperatures at which these experiments were made, but the compressibility of the vapor can be calculated from Dietrici's equation of state, viz.,

$$p = \frac{RT}{v - b} e^{-\frac{a}{RTv}} \quad (5)$$

with an empirical correction which can be determined in the manner described below. From (5)

$$\frac{1}{\beta} = -v \left(\frac{dp}{dv} \right)_t = p \left\{ \frac{v}{v - b} - \frac{a}{RTv} \right\}$$

Putting in the values of a and b in terms of the critical constants $b = v_c/2$ and $a/RT = 4b = 2v_c$, this reduces to

$$-v \left(\frac{dp}{dv} \right)_t = p \left\{ \frac{2v}{2v - v_c} - \frac{2v_c}{v} \right\} = \frac{2p}{v} \frac{(v - v_c)^2}{(2v - v_c)}, \quad (6)$$

where v is the specific volume of the saturated vapor and v_c is the critical volume (volume of 1 gram of the substance at the critical point).

To test the applicability of this equation, the values of the compressibility of the saturated vapors of ether, isopentane and carbon dioxide were calculated and the values compared with the actual values obtained from the isothermal curves. The actual value of the compressibility is found to be larger than that given by equation (6), the ratio of the actual compressibility to that derived from (6) lying in the neighborhood of 1.25 over a large range. This ratio is plotted against the reduced temperatures. The points for the three different substances lie practically on the same curve, and from 0.8 T/T_c to 0.96 T/T_c the ratio lies near 1.25. In order to calculate the isothermal compressibility

¹ Landolt-Bornstein Tabellen, 1912, p. 1031.

² Except for the liquid up to 100°. For this case, the observed values of the scattering agree with the calculated.

of the saturated vapor of a substance for which the necessary isothermal pressure volume data are not available, we may multiply the compressibility given by equation (6) by the corresponding factor obtained from the curve. Calculating in this way, I find that the scattering in benzene vapor at 267° C. is 10 times that of liquid ether at 35° , while the observed value is 11.9 times. At other temperatures, the observed values are even higher than the calculated ones. This may be due either to the inapplicability of the above method of calculating the compressibility, or to the presence of a trace of impurity in the benzene which would give rise to an additional concentration scattering. The writer hopes to repeat the intensity measurements with carefully purified benzene.

This does not, however, in any way invalidate the main conclusion of the paper, namely, the proportionality of the unpolarized part of the scattered light to the density. The theoretical basis for this rests upon the assumption of the random character of the orientation of the molecules and the agreement of the experimental and theoretical values of the imperfection of polarization supports the assumption. This relation may not be true in the case of all liquids; with liquids whose molecules behave like electrical di-poles, the orientations are certainly not likely to be *at random*. Experiments on the polarization of the transversely scattered light with other liquids and over a large range of temperature are likely to furnish valuable information on the mutual influence of molecules in liquids.

In conclusion, I have much pleasure in recording my thanks to Prof. C. V. Raman under whose inspiring guidance the work described above was carried out in the laboratory of the Indian Association for the Cultivation of Science.

210 BOWBAZAAR STREET,
CALCUTTA,
August, 1922.

ADDENDUM.

A question has been raised as to the mean wave-length to be adopted in calculations when using composite light like sunlight for scattering experiments. In the above paper, the wave-length of the F line has been adopted. The influence of the wave-length of the incident light enters in two ways: (1) directly in the λ^{-4} factor and (2) indirectly through its influence on μ . When comparing two substances as regards their scattering, the effect of the first and dominant factor is identical in the two cases; that of the second depends on the dispersive powers of

the two substances. The values of $(\mu^2 - 1)^2(\mu^2 + 2)^2$ for liquid benzene and liquid ether at 20° C have been tabulated below:

Liquid Benzene at 20° C.

λ .	C 6,563 A.	D 5,893 A.	F 4,861 A.	G' 4,340 A.
μ	1.4965	1.5011	1.5133	1.5236
$(\mu^2 - 1)^2(\mu^2 + 2)^2$	27.76	28.22	30.48	32.53

Liquid Ether at 20° C.

λ .	C 6,563 A.	D 5,893 A.	F 4,861 A.	G' 4,340 A.
μ	1.3519	1.3538	1.3580	1.3607
$(\mu^2 - 1)^2(\mu^2 + 2)^2$	10.05	10.16	10.56	10.77

In benzene, the more dispersive substance, the difference between adopting the wave-length of the F line and that of the G' line, for example, comes to nearly 6 per cent. At higher temperatures and for the vapor, the effect would be less and when we remember that our standard of comparison, ether, has itself a higher refractive index towards the violet, the difference between adopting the values of μ_F and $\mu_{G'}$ reduces to 4 per cent.

As regards the intensity of the scattered light in different parts of the spectrum, it will depend partly on the distribution of energy in the incident light and partly on the law of scattering. Adopting Abbot's values for the energy-distribution in sunlight, and assuming that the energy in the scattered light is proportional to λ^{-4} , the following are the relative values of the scattered energies:

λ in A.U.	Incident Energy I in Arbitrary Units.	$I\lambda^{-4}$.
6,000.....	5,050	3.9×10^{21}
5,400.....	5,700	6.7 "
5,200.....	5,900	8.1 "
5,000.....	6,080	9.7 "
4,800.....	6,250	11.8 "
4,400.....	5,820	15.5 "
4,000.....	4,350	17.0 "
3,800.....	3,750	18.0 "
3,500.....	2,700	18.0 "

The effect of the dispersion of the substance is to increase the relative importance of the radiations of shorter wave-length and more for a substance of larger than for one of smaller dispersion.

We have now to consider the visual effect of the scattered light. For ordinary luminosities, the maximum visual effect is produced by rays in the neighborhood of 5,500 A; but for the weak luminosities such as we here deal with, owing to the Purkinje effect, the region of maximum sensitiveness is shifted towards the blue, the shift being a function of the luminosity. Taking everything into account, the effective wave-length of the scattered light is probably a little farther on toward the violet than F; but considering the uncertainties in our knowledge of the luminosity-curves for weak illuminations and the smallness of the error when we use *scattered light for comparison*, the error introduced by adopting the wave-length of the F line for the calculations is not of a serious nature.

CALCUTTA,

November 28, 1922.