On the polarization of the light scattered by gases and vapours

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1. Introduction

The work of Lord Rayleigh[†] and others has shown conclusively that the light scattered transversely by gases is not in general perfectly polarized, but shows a defect of polarization which at the ordinary temperature and pressure is characteristic of each gas. This result is of great interest, and has been interpreted as due to the optical anisotropy of the scattering molecules, which is different for different gases. Observation shows that with monatomic gases such as argon the scattered light is almost completely polarized, while more complex molecules show a very marked imperfection of polarization. The exact measurement of the state of polarization of the scattered light for different gases, and of its variations with temperature, pressure, and the frequency of the incident light, is an experimental problem of the first importance. Preliminary measurements were published by Rayleigh, Cabannes, and Gans. These disagreed considerably among themselves; the most reliable data that have so far appeared are those obtained in Rayleigh's own later work, in which some very careful measurements were made with special precautions to secure accuracy. The table given below collects the data referred to, the last column showing Rayleigh's definitive measurements. The figures give the ratio of the weak to the strong component of polarization as a percentage.

^{*}Communicated by the Authors.

[†]Rayleigh, Proc. Roy. Soc. vol. xcv, p. 155; vol. xcvii, p. 435; vol. xcviii, p. 57. Cabannes, Ann. der Phys., tome xv, pp. 1-150. Gans, Ann. der Phys., lxv, p. 97 (1921).

	Rayleigh I	Cabannes	Gans	Rayleigh II
Argon		0.8		0.46
Hydrogen	1.7	1 to 2		3.83
Nitrogen	3.0	2.5 to 2.8	3.0	4.06
Air	4.2	3.7 to 4.0		5.0
Oxygen	6.0	5·1 to 5·4	6.7	9.4
Carbon dioxide	8.0	9.5 to 9.9	7.3	11.7
Nitrous oxide	14.0		12.0	15.4

Rayleigh in his experiments used a photographic method. Each measurement required several exposures, each of several hours' duration. Direct visual measurements of the state of polarization, if they were possible, would obviously be much more expeditious, and would enable a large number of gases and vapours to be examined. It was with the object of determining whether accurate measurements were possible by visual methods and to find the influence of the frequency of incident radiation that the present work was undertaken, and the paper describes the results so far obtained.

While dealing with this subject, it should be mentioned, as has been already remarked by one of us elsewhere, that in the case of dense gases and vapours not obeying Boyle's law, the state of polarization of the scattered light should not be independent of the temperature and pressure. In fact, when the scattering is greater than in proportion to the density, the scattered light should be more perfectly polarized. Observations with carbon dioxide under pressure, ether, benzene, and pentane vapours entirely confirm this indication of theory.

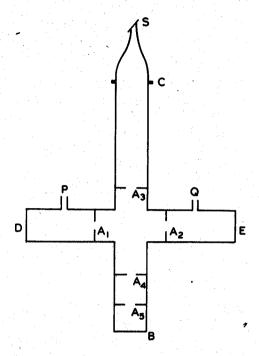
2. Experimental arrangements

In order that visual measurements might be possible, very intense illumination is obviously required. This was obtained with the aid of a powerful optical combination of an astronomical telescope of 18 cm aperture and 200 cm focal length and a converging lens placed beyond its focus. A beam of sunlight which fills the object-glass of the telescope and passes through the combination is converged by it into an extremely intense beam of a few millimetres diameter but of small angle. With such intense illumination, the scattering of light by gases and vapours becomes a very conspicuous phenomenon, and is of a brilliant sky-blue colour. With the help of a double-image prism it is easy to observe visually that the transversely scattered light is not completely polarized.

As in Rayleigh's experiments, the gas is contained in a vessel in the form of a cross-tube, the primary beam passing along one arm and the scattered beam

being observed in the perpendicular direction. For accurate work the most important thing is of course the adequate blackness of the background, against which the faint light under investigation is to be observed. It is essential that special attention should be given to the way in which the far end of the vessel against which the observations are made is constructed. It must be so arranged as to send back exceedingly little or, better still, no light at all. For, if the back of the tube returns any light, serious error will be introduced, for the visibility of the fainter track of the two seen through the double-image prism would be greatly diminished. In fact, preliminary experiments with a cross in which the background was not perfect gave invariably values for the intensity of the weaker component of polarization which were much too small. In his final experiments Rayleigh used a curved horn blown out of dark green glass and fitted to the far end of the observation tube. Any light which fell into the mouth of the horn was reflected internally from side to side towards the end away from the observing side. As such a horn was not available to us, other expedients had to be tried. The final arrangement adopted was to use a dark green conical glass bottle with its bottom cut out. The neck was ground down obliquely at an angle of 45°, and to this was cemented a dark glass plate. It was found that this gave quite a good background, and the use of sunlight, which gives beams of relatively small divergence, is specially favourable for avoiding stray illumination.

The cross-tube was made of zinc, and was 7 cm in diameter. The arm to which the conical bottle was attached was about 36 cm in length, and the other three arms were 25 cm in length. The metal parts were all soldered together. The primary beam entered through the plate-glass window D, and passing through the circular diaphragms A₁ and A₂ of diameter 2 cm, fell on the window E. The laterally scattered light was observed through the window B. A diaphragm was placed at A₃ so as to cut off any stray light getting inside. Apertures A₄ and A₅ served to cut off from view any stray light that fell on the edges of A3 and which tended to make these edges luminous as seen from the window. C is the glass bottle fixed to the observation arm. S is the dark glass plate cemented to the bottle at an inclination of 45°. The glass bottle was painted dead black outside and wrapped in black cloth as an additional precaution. The inside of the cross was completely painted dead black. The glass windows were fixed in position by screwing brass caps on to the ends of the tube. Thick rubber washers were placed between the metal and the glass so as to distribute the pressure and to make the whole air-tight. The ends of the cap were further coated with a cement made of a mixture of rosin and wax so as to prevent any leakage. The air-tightness of the whole apparatus was tested, and it was found that there was a leakage of about 10 cm of mercury in one hour. It was, however, thought not advisable to spend time in making it more perfectly air-tight, as the gas could be passed for a sufficiently long time to ensure that all air was driven out, and also as the observations were all made visually in a short time. P and Q are the ends for the entrance and exit of the stream of gas.



As mentioned above, brilliant sunlight concentrated by an 18 cm aperture object-glass combined with a short focus lens was used. By suitable diaphragms stray light can be entirely cut off and prevented from entering the cross-tube. In order to make quantitative observations and to determine the ratio of the two components of polarization of scattered light, it is very essential that the eye should be properly screened from all outside light and must be able to see only the two patches of light. For this purpose a small dark room made of thick canvas stretched on wooden supports was built up in front of the observation window of the cross-tube. A hole of just the size of the diameter of the cross-tube admitted a little of the observation arm of the cross into the room and the photometric apparatus—that is, the double-image prism and the nicol—were mounted within it. The room could be made perfectly dark, and when the eye had been for some time accustomed to the darkness, the two patches of light seen through the double-image prism could be easily made out. Even in the case of hydrogen. which scatters only about a fourth as much as air, there was no great difficulty experienced in seeing the two tracks.

The method employed to measure the imperfection of polarization was to use the double-image prism and a square-ended nicol. The double-image prism when properly oriented gave the two images, which had intensities in the same ratio as the polarized components of the scattered light. These two intensities were then equalized by the nicol. This method is very convenient, as continuous adjustments can be made. In working with the prisms, there are, as pointed out by Rayleigh, two possible sources of error. One is, that it might be possible that, starting with the unpolarized light, the double-image prism would not produce two images of equal intensity within the desired limits of accuracy, and hence the ratio of the intensities with partially polarized light could not be taken as a true measure of the constitution of the light; and the second is, that it might be possible that the $\tan^2\theta$ law does not hold. For accurate determination it is therefore very essential to know that these sources of error do not conspire to produce errors beyond the desired limit of accuracy.

The following method was therefore adopted to test the behaviour of the



prisms. A ground-glass screen was illuminated by an electric lamp, and a black screen with a rectangular aperture was placed in front of it. The aperture gave perfectly unpolarized light, and could be viewed through the double-image prism and nicol to be tested. In front of the double-image prism another nicol was mounted to polarize the light in any desired orientation, and the test was carried out by determining the ratio of the vertical and horizontal components of polarization of the beam transmitted through it in different orientations. Both nicols were mounted at the centres of accurately divided circles so that their orientations could be read off very accurately. Preliminary tests with the unpolarized light showed that the double-image prism produced images of practically equal intensity. The double-image prism was then adjusted so that the two images were just touching each other and were in a line. This secured that the direction of vibrations in the images were approximately horizontal and vertical. The polarizing nicol was then mounted in front of the double-image prism, and the orientations in which one of the two images vanished were noted. They differed by 90°, as was to be expected. The nicol was then set at a definite orientation ϕ with the vertical, the double-image prism remaining fixed, and the ratio of the intensities of the vertical and the horizontal components in the beam passed by it was determined by rotating the second nicol and equalizing the brightness of the two images. The ratio was found to be $\tan^2 \phi$ without appreciable error.

Measurements were also made with a few vapours of organic liquids such as benzene, ether and pentane. These have a large vapour-pressure at ordinary temperatures, and consequently also a large scattering power, and were also found to have no tendency to form fogs or decompose under the action of light. As

these vapours either act on or are absorbed by the paint used inside the crosstube, another cross-tube of the same dimensions was used. The inside was not painted with any substance, but was merely chemically blackened. The background in this case was not of course as perfect as in the cross-tube used for the gases; but as the vapours have relatively a very large scattering power, it was thought that the background could not have introduced any appreciable error.

3. Preparation and supply of gases and vapours

The gases experimented upon were oxygen, hydrogen, carbon dioxide, nitrous oxide and air. Of these, oxygen and carbon dioxide were bought in compressed cylinders and were nearly quite pure. As hydrogen and nitrous oxide could not be had in cylinders at Calcutta, they were prepared in the laboratory in the usual way. Hydrogen was prepared from pure H_2SO_4 and pure zinc in a Kipp's apparatus. The gas was passed in succession through potassium hydroxide and strong sulphuric acid. Nitrous oxide was prepared by heating ammonium nitrate, with the usual precautions. The gas was passed in succession through potassium hydroxide and strong sulphuric acid. During the whole time of observation the gases were passed at a slow rate so as to get always fresh gas under observation and thus avoid the formation of any fog, though there was no evidence of such formation. The cross was first exhausted, and the gas was then allowed to stream. In each case, before any observations were taken the gas was allowed to pass for a sufficiently long time to ensure that all air had been driven out. The gases were dried over phosphorus pentoxide before they entered the cross.

As the dark glass plate cemented to the bottle was not meant to stand any outward pressure, precautions had to be taken in filling the cross with the gas to see that at no time did the pressure inside exceed one atmosphere. To do this the entrance-tube was connected to a glass T-tube. Through one arm the gas was allowed to stream, and the other arm was connected to a long narrow tube dipping in mercury. Thus the pressure in the cross-tube could be registered, and at the same time, if the pressure inside exceeded one atmosphere, the gas could escape freely. As soon as the pressure was one atmosphere the manometer-tube was closed and the exit-tube opened.

In the case of vapours the cross-tube was connected to a small quantity of pure liquid and exhausted. The tube was filled with the vapour by the evaporation of the liquid.

4. Adjustments and results

The cross was mounted in position and the two lenses arranged to give a beam of light parallel to the axis of the cross-tube. The adjustments could be made by

observing the patches of light at the two windows. The double-image prism and the nicol were mounted in front of the observation window so as to be in the direction of the axis of the tube. The double-image prism was so adjusted that the duplicate images were just touching and in continuation of each other. The patch of light under observation was nearly rectangular, and was of fair width. As stated before, a slight error in setting the double-image prism involves only a negligible error in the measurements. To set the double-image prism accurately in position, measurements of the ratio of the intensities were made near and on either side of the correct position of the double-image prism by altering its position slightly and by trial the position which gave the minimum ratio was determined. This gave the correct position for the double-image prism.

Before starting the measurements, the blackness of the background was tested when the light was on by pumping out all the gas. Further, of the gases chosen, hydrogen scattered least, and showed an imperfection of polarization of less than 4%. The weaker component due to hydrogen should thus be excessively feeble. It was found that even this faint track could be easily seen as a bright patch against a perfectly dark background, provided of course the eye was sufficiently accustomed to darkness. There was thus no reason to suspect that the background was defective in any way. Measurements were accordingly made with confidence. In the case of vapours, the scattered light was many times brighter than in gases, and the observations were distinctly more easy.

A large number of readings (not less than fifty) were taken for each gas and the mean of all these was taken to calculate the ratio. The following table gives the final results.

Ratio of weak to strong component in percentages

	Authors	Rayleigh's later results	Rayleigh's earlier results
H ₂	3.6*	3.83	
O_2	8.4	9.4	
CO ₂	10-6	11.7	
Air	4.37	5.0	
N ₂ O	14-3	15.4	
Benzene	6.8		6.0
Pentane	2.8		1.2
Ether	3.0		1.7

^{*}It may be remarked that the imperfect polarization determined visually for H₂ agrees very closely with the value deduced by Havelock from dispersion theory (*Proc. Roy. Soc.*, May, 1922, p. 164). *Philos. Mag. S. 6*, Vol. 46, No. 273, Sept. 1923, 2F.

It will be seen from the above figures that the values obtained for the imperfection of polarization of gases are much higher than any of those of previous investigations except those obtained in Rayleigh's final work, and that in the case of the five gases studied, Rayleigh's final values are distinctly higher than ours. The cause of the discrepancy is not entirely clear. It will be noticed that Rayleigh worked with an arc lamp and by photographic photometry, whereas we used the visual region of the spectrum and direct eve observation. To determine whether a difference in the effective wavelength has an effect on the state of polarization, a series of observations were made with colour filters. The effect was carefully looked for in carbon dioxide, oxygen and air. For getting different wavelengths. Wratten colour filters were interposed in the path of the light, and, as before, a large number of readings were taken for each colour. It was found that throughout the visible region the polarization was practically constant, and it would seem therefore that the difference cannot be attributed to this cause. We are of opinion that the visual method is particularly direct and simple, and that the results given by it are entitled to considerable weight. In regard to the three vapours studied. Rayleigh's results obtained in his earlier work are, we think, decidedly too low.

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