XXXIX. *The Optical Anisotropy of some simple Inorganic Gaseous Compounds.*

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Introduction.

FROM the time that Lord Rayleigh discovered the imperfection of polarization of the transversely scattered light in gases, it has been the hope of physicists that some time or other it would lead to important knowledge regarding the structure of atoms and molecules. In his recent work on the doubly refracting properties of typical inorganic crystals, W. L Bragg † has made use of the idea of the mutual influence of the polarization of the different atoms of the crystals, and has deduced results which are in general agreement with observation. In this work, Bragg assumes with Wasastjerna that the atoms are in an ionized condition : that is, they have given up or taken in a sufficient number of electrons so that the electronic structure of each ion approaches closely that of the nearest inert gas. He further assumes that each ion by itself can be considered optically isotropic.

One of the authors has recently shown that the optical anisotropy of some of the common inorganic gases ‡ which is evidenced by the imperfection of polarization of the transversely scattered light in these gases, can be likewise explained if we take into account the mutual influence of the

* Communicated by the Authors.
† Proc. Roy. Soc. A, vol. cv. p. 370 (1924).
‡ Proc. Roy. Soc. A, vol. cvii. p. 684 (1925).

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polarizations of the different atoms in the molecule. The work has later been extended to the organic molecules benzene and cyclohexane, but in all the cases that have been hitherto examined the gases are of the "homo-polar" or shared-electron type.

With a view to getting some idea of the optical anistropy of the "hetero-polar" molecules, experiments have been made on a few simple hydrides. The inert gases are known to possess a high degree of symmetry, and the experiments of Lord Rayleigh * on argon and of Capannes and Lépape on xenon and krypton † show that the optical anistropies of these molecules are very small, the values of the imperfection of polarization of the transversely scattered light in these gases being respectively ·0046, ·0055, and ·0055. Hydrides of elements adjoining the inert gases, like those of the halogens, would, it is believed, assume electronic structures similar to those of the inert gases, with perhaps a slight deformation of the symmetrical structure caused by the presence of the hydrogen nuclei. The gases CH_4, NH_3, H_2O may be expected to approach neon, while SiH_4, PH_3, H_2S, and HCl would approach argon.

In the following paper the results obtained with ammonia, sulphuretted hydrogen, and hydrochloric acid are described and discussed.

Experimental.

The apparatus employed was of the usual type, being a rectangular metal cross-tube of 5 cm. internal diameter. Each arm of the cross was 27 cm. in length. The tube was coated inside with black enamel which on heating gave a hard glassy coating. Three ends of the cross were closed with plane glass plates sealed on with sealing-wax or hard paraffin, while the fourth end was closed with a metal cap. An oblique metal plate with a uniform glassy coating of black enamel was placed near the closed end so as to reflect away any stray light which might reach that end. Suitable blackened metallic apertures were placed in the different arms so as to shut out stray light. The cross was also provided with two side tubes, one to serve as an inlet for the gas and the other to serve as an exit.

After drying and cleaning, the apparatus was exhausted by means of a pump and the dry dust-free gas was slowly let in. During the experiment a continuous stream of the

* Proc. Roy. Soc. A, vol. xcviii. p. 57 (1920).
† *Comptes Rendus*, clxxix. p. 325 (1924).

gas was kept running. The measurements of depolarization were made in the usual manner by means of a Wollaston double-image prism of quartz and square-ended nicol with a small low-power reading telescope placed behind the nicol.

The pure gases were prepared in the following manner :—

(a) *Hydrochloric acid gas.*

By the action of strong sulphuric acid on sodium chloride. The gas was dried by passing over fresh phosphorus pentoxide.

(b) *Hydrogen sulphide.*

By heating antimony trisulphide with concentrated hydrochloric acid. It was found that free evolution of gas was helped by mixing the antimony sulphide with clean sand. The gas was first bubbled through water to remove the acid spray and then dried over phosphorus pentoxide.

(c) *Ammonia.*

By warming a concentrated solution of ammonia. The gas was passed through a lime tower to remove moisture.

Usually for observations on the scattering of light in gases, the dust particles that are invariably present are removed by slow passage through a tube packed with cotton-wool. As it was, however, found that cotton-wool was slowly attacked by HCl, it was replaced throughout the experiments by clean dry asbestos wool, which was found to be a good substitute.

Error due to convergence of the Incident Rays.

Before discussing the experimental results, it is worth while to consider a source of error which, while unimportant when measuring the imperfection of strongly depolarizing substances, becomes of considerable importance when small values of depolarization are measured *. When the incident beam is focussed by means of a lens, and the imperfection of polarization is measured in a direction perpendicular to the average direction of the beam, the value obtained would be different from what it would be if the beam were strictly parallel. The error would be greater the greater the convergence of the beam. To find its amount, consider a beam of plane polarized light with its electric vector parallel to OZ moving along the X-axis. When observed along OY, let the Z-component of the intensity of the scattered light be A and the X-component B ; then, when the incident light

* Lord Rayleigh, Proc. Roy. Soc. A, vol. xcv. p. 161.

is unpolarized, the components will be A + B and 2B respectively. If the direction of observation be changed by an angle θ, the principal components in a plane perpendicular to the scattered ray will become A + B and B $(1 + \cos^2\theta)$ + A $\sin^2\theta$ respectively, and thus the observed ratio of the weak component to the strong will be

$$\rho_\theta = \frac{A\sin^2\theta + B(1+\cos^2\theta)}{A+B} = \frac{2B + (A-B)\sin^2\theta}{A+B},$$

which differs from ρ, the value in a transverse direction, by $(A-B)\sin^2\theta/(A+B)$.

In our present case, $\sin\theta$ varies from $-a/d$ to a/d where $2a$ is the aperture of the lens, and d is the distance from the lens at which the rays are focussed *.

We have, therefore, to find the average values of ρ_θ when θ varies through this range. A simple integration and averaging give for the ratio of the weak component to the strong in a direction perpendicular to the average direction of the beam

$$\frac{H}{V} = \frac{2B + (A-B)\sin^2\theta/2}{A+B}.$$

In the case of a gas producing an imperfection of polarization of 0·01 in a strictly perpendicular direction, the error caused by the non-parallelism of the incident rays will be as much as ·0038 when θ is 5° and ·0014 when θ is 3°.

Similar errors will be caused by a wrong adjustment of the double-image prism and by the direction of observation not being exactly perpendicular to the incident beam. The former error can be avoided by a careful adjustment of the double-image prism; the latter is usually small in visual observations, but it is one to be borne in mind when measurements are made photographically where the temptation is to use a large aperture in order to secure economy of light.

Results.

The observed value of the ratio of the weak component to the strong in the transversely scattered light in each of the gases HCl, H_2S, and NH_3 was found to be the same, namely ·010. The measurements were repeated on different days, and consistent results were obtained. There was no evidence of fog formation in any of the cases. In changing from one gas to another the whole apparatus was overhauled and

* With the small angles usually employed, the distinction between $\sin\theta$ and $\tan\theta$ may be dropped.

thoroughly cleaned, and the inside of the tube was repainted. The maximum angular divergence of the rays from the axis was measured to be 3°·8, and hence the error due to the non-parallelism of the incident rays was ·002. If we subtract this from the value obtained above, we get for all the three gases the corrected value ·008.

It is remarkable that the values of ρ for all these gases should be so low, and that they should all be equal to each other. They are also of the same order of quantities as the values obtained for the inert gases. As mentioned above, Lord Rayleigh obtained the value ·0046 for argon, which, however, has not been corrected for the non-parallelism of the incident rays. Lord Rayleigh estimated the extreme divergence of the incident rays from the axis to lie between 3° and 4°, and the angle subtended by the aperture of the camera was of the same order. The corrected value would be only about ·0025. Whether this residual effect does exist or not is worth re-examination.

It is now generally believed that in hydrochloric acid gas the electron belonging to the hydrogen atom has gone over to the chlorine atom to form one of its outermost orbits, thus completing the argon configuration, and similarly in sulphuretted hydrogen the two electrons from the hydrogen atoms have been transferred to the outermost orbits of sulphur. The smallness of depolarization of these gases supports this view. Likewise in ammonia, the additional electrons belonging to the three hydrogen atoms may be looked upon as having been transferred to the nitrogen to complete the neon configuration. Although no measurement of the depolarization of the transversely scattered light in neon are available, it may be expected to be small.

The cases of carbon monoxide and nitrogen are interesting. Langmuir and others have suggested that the configurations of the outer electrons of these gases are similar. If that is so, we expect that the optical anisotropies of the two gases should be nearly the same. Visual measurements made with sunlight at Calcutta show that carbon monoxide shows a depolarization of 3·4 per cent., while for nitrogen Lord Rayleigh * obtained the value 4·06 per cent. by the photographic method. On the other hand, if we calculate the depolarization of nitrogen from the visual measurements of Raman and Rao † on air (4·37) and oxygen (8·4), we obtain the value 3·5 per cent. For purposes of comparison

* Proc. Roy. Soc. A, vol. xcvii. p. 435 (1920).
† Phil. Mag. vol. xlvi. p. 427 (1923).

it is better to choose the values obtained by the same method, and the closeness of the values obtained by the visual method is very striking.

Summary.

In the foregoing paper, measurements of the depolarization of the light scattered by the gases hydrogen chloride, sulphuretted hydrogen, and ammonia are described, and the results obtained are discussed in their relation to the structure of the molecules. The depolarization in a direction perpendicular to the incident beam was in all cases the same, namely ·008, indicating a high degree of optical symmetry. The value of the anisotropy supports the view that in these gases the electrons belonging to the hydrogens have gone over to the outer orbits of the heavier atoms, in order to complete the electronic structure characteristic of the nearest inert gas. It is also pointed out that the values of the depolarization of nitrogen and carbon monoxide, both obtained visually, have practically the same value, supporting the view that the configurations of the outer electrons of these molecules are similar. The error caused in the measurement of the depolarization of the light scattered by substances owing to the non-parallelism of the incident light is discussed.