

The Structure of Molecules in Relation to their Optical Anisotropy.—Part I.

By K. R. RAMANATHAN, M.A., D.Sc., Assistant Lecturer in Physics,
University College, Rangoon.

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One of the most significant facts relating to the scattering of light in gases is the imperfection of polarisation of the light scattered in a direction perpendicular to the incident beam. The late Lord Rayleigh* and Born† explained this phenomenon as being due to the optical anisotropy of the molecule, that is, to the fact that the polarisation induced in a molecule depends on its orientation with respect to the electric vector in the incident light. Lord Rayleigh's theory does not go into the question as to how the anisotropy arises, but merely assumes that there are in each molecule three principal directions of vibration, along which the induced polarisations are different. If A, B, C are the moments induced in a molecule when its three principal directions are respectively along the direction of the electric vector in the incident light, then the ratio of the weak component to the strong in the transversely scattered light is given by

$$r = \frac{2(A^2 + B^2 + C^2) - 2(AB + BC + CA)}{4(A^2 + B^2 + C^2) + AB + BC + CA} \quad (1)$$

We now possess reliable measurements of the imperfection of polarisation in many gases and vapours, from the work of Lord Rayleigh‡ and of Raman and Rao.§ Recently there has been carried out at Calcutta further measurement of the same quantity, in a series of organic vapours, by Mr. A. S. Ganesan.|| Some of these results are collected together in Table I.

An examination of the table shows clearly the influence of the nature of the

* Rayleigh, 'Phil. Mag,' vol. 35, p. 373 (1918).

† Born, 'Verh. Deutsch. Phys. Gesell.,' vol. 20, p. 16 (1918).

‡ 'Roy. Soc. Proc.,' A, vol. 97, p. 435 (1920); vol. 98, p. 57 (1920); vol. 102, p. 190 (1923).

§ 'Phil. Mag.,' vol. 46, p. 427 (1923). Measurements have also been made by Gans ('Ann. der Physik,' vol. 65, p. 97 (1921)), and J. Cabannes (Jour. de Physique,' vol. 4, p. 429 (1923)).

|| Not yet published.

Table I.

	$\frac{\text{Weak component}}{\text{Strong component}}$ in per cent.	Author.
Argon	0.46	R.
Mercury.....	Approximately complete	R.
Helium	< 6.5	R.
Hydrogen	3.83	R.
	3.6	R. and R.
Oxygen	9.4	R.
	8.4	R. and R.
Nitrogen	4.06	R.
CO	3.4	Randdas at Calcutta (not previously published).
CO ₂	11.7	R.
	10.6	R. and R.
N ₂ O	15.4	R.
	14.3	R. and R.
CS ₂	12.0	R. (earlier work).
	16.7	G.
Octane	2.7	G.
Benzene.....	6.6	G.
CCl ₄	1.9	G.

R. = Lord Rayleigh. R. and R. = Raman and Rao. G. = Ganesan.

molecule on the value of the imperfection. Sir J. J. Thomson* has made suggestive attempts at connecting the variation of r with the departure of the shape of the molecule from spherical symmetry, but although among the mono-, di- and triatomic gases the value of the imperfection increases in general with the number of atoms in the molecule, this is by no means always the case. For example, octane, which is supposed to have a long molecule, shows even less imperfection than any of the diatomic gases in the table. It is, however, significant that in the case of the monatomic molecules, the imperfection is very nearly zero, and that among the polyatomic molecules, the smallest value of the imperfection is obtained for carbon tetrachloride, a molecule in which the chlorine atoms are presumably arranged at the corners of a regular tetrahedron.

The last-mentioned example suggests that a new way of approaching the problem is by considering the mutual influence of the different atoms composing a molecule. For example, in a diatomic molecule, when the electric vector is parallel to the line of centres of the atoms, the resultant polarisation would, owing to the mutual influence of the polarisations induced in each atom, be greater than if the atoms were far away from each other, while when the electric vector is perpendicular to the line of atomic centres, the polarisation

* 'Journal of the Franklin Institute,' vol. 195, p. 743 (1923).

would be smaller. On this view, a diatomic molecule must necessarily be anisotropic. With molecules containing more atoms, the anisotropy will depend on the nature and arrangement of the constituent atoms, and it may well be small even with long molecules. The recent success of Prof. W. L. Bragg* in explaining the double refraction of calcite and aragonite on somewhat similar lines makes it worth while to examine how far we can explain the observed effects by considering the mutual influence of the atoms.

Diatomic Molecules.

We shall assume that each atom by itself is isotropic, and that when placed in a periodic electric field behaves like a vibrating doublet placed at some point within the atom which we may call its "optical centre." Considering first the case of a diatomic gas like hydrogen in which both atoms are similar, let e be the charge on each equivalent doublet, m the mass of the vibrator and x the displacement. When the electric field E acts parallel to the axis of the molecule, the total electric intensity acting on one of the charges will be $E + 2ex_1/d^3$ where d is the distance between the optical centres of the atoms. Hence

$$m\ddot{x}_1 + fx_1 = e(E + 2ex_1/d^3)$$

where f is the restoring force on each charge per unit displacement.

When the periodicity of the electric intensity is introduced through the factor $\cos pt$

$$ex_1 = \frac{e^2/m}{n^2 - p^2 - 2e^2/md^3} E, \quad (2)$$

where $n^2 = f/m$.

The electric moment for the two atoms together is

$$AE = 2ex_1.$$

Similarly, when the electric field acts perpendicular to the axis of the molecule,

$$BE = 2ex_2 = \frac{2e^2/m}{n^2 - p^2 + e^2/md^3} E.$$

When the molecules are oriented at random, the average value of $2ex$ will be given by

$$\overline{2ex} = \left(\frac{A}{3} + \frac{2B}{3} \right) E$$

* W. L. Bragg, 'Roy. Soc. Proc.,' A, vol. 105, p. 370 (1924). Reference may also be made to a series of interesting papers by Dr. Silberstein in 'Phil. Mag.,' January, 1917, on "Molecular Refractivity and Atomic Refraction," etc.

and the refractivity

$$\begin{aligned}\mu^2 - 1 &= 4\pi\nu \left(\frac{A}{3} + \frac{2B}{3} \right) \\ &= \frac{4\pi\nu e^2}{3m} \left\{ \frac{2}{n^2 - p^2 - 2e^2/md^3} + \frac{4}{n^2 - p^2 + e^2/md^3} \right\},\end{aligned}$$

where ν is the number of molecules per unit volume. Writing

$$\frac{4\pi\nu e^2}{m(n^2 - p^2)} = R_0$$

and

$$\frac{1}{2\pi\nu d^3} = k,$$

it is easy to put this into the convenient form

$$\mu^2 - 1 = \frac{2R_0}{3} \left\{ \frac{1}{1 - R_0k} + \frac{2}{1 + \frac{1}{2}R_0k} \right\}. \quad (3)$$

The optical anisotropy which may be defined as A/B is given by

$$\frac{A}{B} = \frac{1 + \frac{1}{2}R_0k}{1 - R_0k}. \quad (4)$$

We shall now consider a few simple cases.

1. *Hydrogen*.—From our assumption of the isotropy of each atom, the molecule should have spheroidal symmetry. We can therefore write in equation (1) $B = C$, and we get

$$r = \frac{2(A^2 + B^2 - 2AB)}{4A^2 + 9B^2 + 2AB}.$$

Taking r for hydrogen to be 3.7 per cent. and solving, we get

$$A/B = 1.66 \text{ or } 0.543.$$

Consistently with our physical assumptions we adopt the first value, and from (4) we calculate $R_0k = 0.3047$. Using this value in (3) and taking R to be 0.0002812 (Cuthbertson's value for 0.486 μ), we get

$$\begin{aligned}R &= 1.328 \times 10^{-4} \\ \text{and } k &= 2.293 \times 10^3,\end{aligned}$$

leading to a value $d = 1.37 \times 10^{-8}$ cm.* This may be compared with the value of the molecular radius calculated from mean free path phenomena 1.34×10^{-8} cm.†

* ν has been assumed to be 2.708×10^{19} per c.c.

† Jeans, 'Dynamical Theory of Gases,' second edit., p. 341.

2. *Nitrogen*.— $r = 4.06$ per cent. $A/B = 1.696$. $R_0k = 0.3169$ from (4). Taking R to be 0.0006024 for 0.486μ and using (3), $R_0 = 2.832 \times 10^{-4}$,

$$k = 1.119 \times 10^3 \quad \text{and} \quad d = 1.90 \times 10^{-8} \text{ cm.}$$

while the kinetic theory free path value of the "radius" of a nitrogen molecule is 1.90×10^{-8} cm.

3. *Oxygen*.—For this gas we shall take $r = 8.9$ per cent., the average of the values obtained by Rayleigh and by Raman and Rao.

The corresponding value of $A/B = 2.211$ and $R_0k = 0.4466$.

$$\text{Taking } R = 0.000547 \text{ for } 0.486\mu \text{ and } R_0 = 2.384 \times 10^{-4}, \\ k = 1.874 \times 10^3 \quad \text{and} \quad d = 1.46 \times 10^{-8} \text{ cm.,}$$

while the mean free path value of the molecular radius is 1.81×10^{-8} cm. As will be noticed, while the kinetic theory diameter of an oxygen molecule is somewhat less than that of a nitrogen molecule, the distance between the optical centres seems to be much smaller in the former case.

Triatomic Molecules.

Turning now to the case of a triatomic molecule like N_2O , CO_2 , or CS_2 , we can calculate its refractivity and optical anisotropy provided we know the structure of the molecule, the refractivities of the constituent atoms and the distance apart of the optical centres. For example, in the case of N_2O , let us suppose that the atomic centres are in a straight line, the oxygen being at the centre and let e_1 denote the charge on the equivalent doublet in the nitrogen atom, m_1 the mass of the vibrator and f_1 the restoring force per unit displacement. Let similar symbols with suffixes 2 denote the corresponding quantities in the oxygen atom. Then, when the electric field is parallel to the length of the molecule, the equations of motion of the charges in the nitrogen and oxygen atoms are respectively

$$m_1\ddot{x}_1 + f_1x_1 = e_1 \left\{ E + \frac{2e_2x_2}{d^3} + \frac{2e_1x_1}{8d^3} \right\} \\ m_2\ddot{x}_2 + f_2x_2 = e_2 \left\{ E + \frac{4e_1x_1}{d^3} \right\}, \quad (5)$$

where d is the distance between the optical centres of the oxygen and nitrogen atoms.

Introducing the periodicity of the electric intensity through the factor $\cos pt$ and solving for e_1x_1 and e_2x_2 , we get

$$e_1x_1 = \frac{R_1}{4\pi v} \frac{1 + R_2k}{1 - R_1k/8 - 2R_1R_2k^2} F, \quad (6)$$

where

$$R_1 = \frac{4\pi\nu e_1^2}{m_1(n_1^2 - p^2)} \quad R_2 = \frac{4\pi\nu e_2^2}{m_2(n_2^2 - p^2)} \quad \text{and} \quad k = \frac{1}{2\pi\nu d^3},$$

and

$$e_2 x_2 = \frac{R_0}{4\pi\nu} \frac{1 + 15/8 R_1 k}{1 - R_1 k/8 - 2R_1 R_2 k^2} E.$$

The total moment along the length of the molecule is

$$2e_1 x_1 + e_2 x_2 = \frac{2R_1 + R_2 + 31/8 R_1 R_2 k}{1 - R_1 k/8 - 2R_1 R_2 k^2} \frac{E}{4\nu} = AE, \text{ say.}$$

Similarly, when the electric intensity is perpendicular to the line of atomic centres, the equations of motion are

$$m_1 \ddot{x}_1 + f_1 x_1 = e_1 \left(E - \frac{e_2 x_2}{d^3} - \frac{e_1 x_1}{8d^3} \right),$$

$$m_2 \ddot{x}_2 + f_2 x_2 = e_2 \left(E - \frac{2e_1 x_1}{d^3} \right).$$

Solving,

$$e_1 x_1 = \frac{R_1}{4\pi\nu} \frac{1 - R_2 k/2}{1 + R_1 k/16 - \frac{1}{2} R_1 R_2 k^2}$$

and

$$e_2 x_2 = \frac{R_2}{4\pi\nu} \frac{1 - 15/16 R_1 k}{1 + R_1 k/16 - \frac{1}{2} R_1 R_2 k^2}$$

and the corresponding moment is

$$2e_1 x_1 + e_2 x_2 = \frac{1}{4\pi\nu} \frac{2R_1 + R_2 - 31/16 R_1 R_2 k}{1 + R_1 k/16 - \frac{1}{2} R_1 R_2 k^2} E$$

$$= BE.$$

As in the case of the diatomic molecules the refractivity is given by

$$\mu^2 - 1 = 4\pi\nu \left(\frac{A}{3} + \frac{2B}{3} \right) = R, \text{ say,}$$

$$= \frac{1}{3} \frac{2R_1 + R_2 + 31/8 R_1 R_2 k}{1 - R_1 k/8 - 2R_1 R_2 k^2} + \frac{2}{3} \cdot \frac{2R_1 + R_2 - 31/16 R_1 R_2 k}{1 + R_1 k/16 - \frac{1}{2} R_1 R_2 k^2}, \quad (7)$$

and the optical anisotropy as we have previously defined is

$$A/B = \frac{2R_1 + R_2 + 31/8 R_1 R_2 k}{1 - R_1 k/8 - 2R_1 R_2 k^2} \cdot \frac{1 + R_1 k/16 - \frac{1}{2} R_1 R_2 k^2}{2R_1 + R_2 - 31/16 R_1 R_2 k}. \quad (8)$$

To calculate A/B, we require to know R_1 , R_2 and k . We have no direct means of determining any of these quantities, but let us tentatively assume that the refractivities R_1 and R_2 appropriate to the nitrogen and oxygen atoms are the same as in the respective molecules of N_2 and O_2 . The known

refractivity of N_2O will then enable us to calculate k from equation (7). The equation can be put in the form of a bi-quadratic :—

$$k^4 R \delta^2 - k^3 (R \gamma \delta + \beta \delta) - k^2 (5R \delta - 3\alpha \delta + 2R \gamma^2 + 2\beta \gamma) - k (2R \gamma - 2\alpha \gamma) + 4 (R - \alpha) = 0,$$

where

$$\alpha = 2R_1 + R_2 \quad \beta = 31/8 R_1 R_2$$

$$\gamma = R_1/8 \quad \text{and} \quad \delta = 2R_1 R_2.$$

Taking

$$R = 10.28 \times 10^{-4} \quad (\text{for } \lambda = 0.480 \mu)$$

$$R_1 = 2.832 \times 10^{-4}$$

and

$$R_2 = 2.384 \times 10^{-4},$$

the equation becomes

$$1874k_1^4 - 492.4k_1^3 - 389k_1^2 - 1.58k_1 + 8.928 = 0,$$

where

$$k_1 = k \times 10^{-4}.$$

The only root of this equation consistent with our physical assumptions is

$$k = 0.1460 \times 10^4, \text{ which leads to a value of } d = 1.59 \times 10^{-8} \text{ cm.}$$

From (8),

$$A/B = 2.80,$$

and hence $r = 14.1$ per cent., while the value experimentally obtained by Lord Rayleigh was 15.7 per cent. and that obtained by Raman and Rao was 14.3 per cent. Without laying too great stress on the numerical agreement, it seems to show that the general idea of the method is correct.

Carbon Dioxide.

We shall now take up the case of carbon dioxide. Since we have no direct means of determining the refractivity to be attributed to carbon in the molecule of carbon dioxide, we have to derive it from some other source. We may take the refractivity of carbon as derived from saturated organic compounds, but since it is likely that even there its value is likely to be influenced by the proximity of the neighbouring atoms, it is better to derive it from a source where the influence of the neighbouring atoms vanishes. In a crystal of diamond there is regular tetrahedral symmetry, and each carbon atom is bound by one electron each to its four nearest neighbours. We may adopt the value of the atomic refractivity of carbon in diamond for our present case, since here also all the four outer electrons of carbon are presumably bound up with the neighbouring oxygen atoms.

The refractive index of diamond for 0.480μ is 2.4370^* and taking its density to be 3.514 ,

$$\frac{\mu_1^2 - 1}{\mu_1^2 + 2} \cdot \frac{M}{\rho} = 2.124,$$

where M is the atomic weight of carbon and ρ is the density of diamond. The corresponding value of $\mu^2 - 1$ for free carbon atoms at 0°C and 76 cm. pressure is given by

$$2.124 = \frac{\mu^2 - 1}{3} \cdot \frac{2.016}{8.987 \times 10^{-5}},$$

where 2.016 is the molecular weight and 8.987×10^{-5} is the density of hydrogen.

Hence
$$R_2 = \mu^2 - 1 = 2.841 \times 10^{-4}.$$

Using our previous value of R for the oxygen atom from its value in the oxygen molecule, and making use of equation (7), we obtain the appropriate biquadratic:—

$$1663k_1^4 - 392k_1^3 - 322k_1^2 - 0.865k_1 + 5804 = 0, \quad \text{where } k_1 = k \times 10^{-4},$$

in which the refractive index of CO_2 at N.T.P. has been assumed to be 1.000453 . The physically relevant root of the equation gives

$$k = 0.1284 \times 10^4 \quad d = 1.66 \times 10^{-8} \text{ cm.},$$

and hence
$$A/B = 2.42.$$

The imperfection of polarisation in a direction transverse to the incident light comes out as 10.8 per cent., which may be compared with Rayleigh's experimental value 11.7 per cent., and Raman and Rao's value 10.6 per cent.

The distance between the optical centres of the two nitrogen atoms in nitrous oxide is thus $3.18 \times 10^{-8} \text{ cm.}$, and the corresponding distance between the centres of the two oxygen atoms in CO_2 is $3.32 \times 10^{-8} \text{ cm.}$ Viscosity measurements indicate that the mean free-path size of the two molecules N_2O and CO_2 is practically the same. Since the size of the nitrogen molecule is larger than that of the oxygen molecule, the increased distance between the atomic centres in CO_2 is compensated by the smaller size of the oxygen atoms.

Carbon Disulphide.

We may expect that carbon disulphide has a constitution similar to carbon dioxide, and if we know the atomic refractivity of sulphur, we can calculate

* Landolt-Börnstein, 'Tabellen' (Martens), 1923 Edition, p. 918.

the anisotropy of carbon disulphide, and hence the imperfection of polarisation of the transversely scattered light in its vapour. We may adopt the following empirical method of calculating the refractivity of sulphur. The refractivity of H_2S for 0.486μ is 13.12×10^{-4} , and since the refractivity of hydrogen is small compared with that of sulphur, we may to a first approximation obtain the value for sulphur by subtracting the refractivity of H_2 from that of H_2S . We thus get $R = 10.31 \times 10^{-4}$. Using the same value for the refractivity of carbon as in carbon dioxide,

$$R_2 = 2.841 \times 10^{-4}.$$

We do not possess data for the refractivity of carbon disulphide vapour at wave-length 0.486μ , but from its refractivity for 0.589μ and its dispersion in the liquid state, we can easily calculate $\mu^2 - 1$, for 0.486μ . We thus get

$$R = 30.70 \times 10^{-4}.$$

Making a similar calculation as in the two preceding cases,

$$k = 7.18 \times 10^2 \quad \text{and} \quad d = 2.02 \times 10^{-8} \text{ cm.},$$

and $A/B = 2.61$, and $r = 12.5$ per cent.

The imperfection of polarisation obtained photographically by Lord Rayleigh in his earlier work was 12 per cent., while that obtained visually by Ganesan at Calcutta was 16.7 per cent. The latter value is probably entitled to greater weight, as in this case the illumination of the vapour was limited to a time just sufficient for the observation to be taken, and thus the chance of formation of clouds was reduced to a minimum. The difference between the observed and calculated values is no doubt to be attributed to the uncertainty in the values of the atomic refractivity.

The general agreement, however, in the three cases investigated makes it fairly certain that a large part of the optical anisotropy of gaseous molecules arises from the mutual action of the atoms of the molecule. It is thus of great importance to extend the investigation to the case of other molecules, particularly in the organic region, where the influence of the structure of the molecule on the anisotropy stands out conspicuously.

Summary.

In the foregoing paper, the view is put forward that the optical anisotropy of gaseous molecules, as revealed by the polarisation of the light scattered from them, is due to the mutual action of the doublets induced by the incident light in the different atoms constituting the molecule. It is assumed that each atom by itself is isotropic.

From the known refractivity and polarisation of the scattered light in hydrogen, nitrogen and oxygen, the atomic refractivities and distances between the optical centres in the molecules are deduced. These distances are consistent with the size of atoms deduced from the kinetic theory.

The investigation is extended to the three triatomic gases, N_2O , CO_2 and CS_2 , and an expression is deduced for the imperfection of polarisation of the transversely scattered light in terms of the atomic refractivities of the different atoms and the distances apart of the optical centres. The calculated values of the imperfection are in satisfactory agreement with experiment.

I have great pleasure in acknowledging my indebtedness to Prof. C. V. Raman, at whose suggestion the above work was taken up, for his kind interest and helpful advice.
