

The structure of molecules in relation to their optical anisotropy

As is well known, the light scattered transversely when traversing a column of gas or vapour is not completely polarised, the defect of polarisation depending on the nature of the substance. The explanation of this phenomenon as developed by the late Lord Rayleigh, Born, Sir J J Thomson and others is that the molecules which scatter the light are optically anisotropic, that is, have different refractivities in different directions, and are oriented arbitrarily in space. From the point of view of dispersion-theory, the interpretation usually given is that the electrons responsible for the refraction of light are anisotropically bound in the molecule.

This way of regarding the matter, though perhaps not formally incorrect, does not hold out much hope of progress in interpreting the experimental results, owing to the scantiness of our knowledge regarding the manner in which the dispersion-electrons are bound in complex molecules. Recently, under the writer's direction, a series of accurate measurements have been made in his laboratory of the scattering of light in some thirty different gases and vapours by Mr A S Ganesan, and in more than sixty different transparent liquids (chiefly organic compounds) by Mr S Krishnan, and the empirical knowledge thus accumulated of the relation between light-scattering and chemical constitution emphasised the unsatisfactoriness of the position of the subject on the theoretical side. Thus, for example, the observations showed that molecules containing elongated chains of CH_2 groups and therefore highly unsymmetrical in shape are, optically, much more nearly *isotropic* than benzene, toluene and other compounds of the aromatic series.

These and other results stand in need of explanation, and it is the purpose of this note briefly to indicate a method of dealing with the matter which is at least a useful working hypothesis. The suggestion is that the optical anisotropy of the molecule is due, in the main, to the mutual influence of the electric doublets induced by the external field in its constituent atoms, the latter, individually, being themselves more or less completely isotropic. A similar idea has recently been used very successfully by W L Bragg to explain the doubly-refractive character of substances in the solid crystalline state, e.g. calcite and aragonite.

Following up the working hypothesis indicated, Dr K R Ramanathan has, at the suggestion of the writer, calculated the degree of optical anisotropy to be expected theoretically for the molecules of a number of substances in the gaseous state and obtained most encouraging results. The fullest test of the theory will be

that furnished by the series of organic vapours studied; the detailed calculations necessary for this purpose have been undertaken. Qualitatively, it is not difficult to see that the closer packing of the atoms in the benzene rings compared with that in the chain compounds would enhance their mutual influence, and that, consequently, the greater anisotropy exhibited by the compounds of the aromatic series is what we should expect on the hypothesis suggested.

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