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The electrical polarity of molecules

On attempting to correlate the electrical double-refraction (Kerr effect) of gases and vapours which has been measured by Leiser, Hansen and Szivessy, with the optical anisotropy of the molecules determined from observations on light-scattering, it is found that electrically polar molecules generally exhibit a Kerr effect which is very large in relation to their optical anisotropy. This indicates that the orientative action of the field on the molecule in such cases is chiefly due to the permanent electric doublet present in it, and is much larger than would be the case if the molecules were non-polar. In the case of molecules having an axis of optical symmetry to which the electric doublet is parallel, or is inclined at some known angle, it is possible to calculate the permanent electric moment from the value of the Kerr constant and the constant of depolarisation of the scattered light. Conversely, if the moment is known, the inclination of the electric doublet to the optic axis can be found. For example, in the case of the simple dipole molecule HCl, we may assume the optic axis to be parallel to the doublet.

The constant of depolarisation as recently measured by Ramanathan is 0·010, and the Kerr constant from the measurements of Hansen $= 0{\cdot}90 \times 10^{-10}$. From this, considering the orientative action of the field to be due only to the permanent doublet, we find its moment to be $1{\cdot}06 \times 10^{-18}$ electrostatic units, while if the orientative couple on the induced doublet is also taken into account as in the case of non-polar molecules, the value of the permanent moment comes out to be $1{\cdot}04 \times 10^{-18}$. The recent determination by Zahn from dielectric constant measurements gives $1{\cdot}03 \times 10^{-18}$, thus showing good agreement.

When the optical ellipsoid of the molecule has three unequal axes, measurements of the factor of depolarisation and of the Kerr constant are by themselves insufficient for an accurate determination of the electric moment. But if the moment is known from measurements of the dielectric constant, the data mentioned are of much assistance in fixing the position of the axis of the doublet. For example, if the Kerr constant of a substance is negative, we can assert definitely that the axis of the permanent doublet does not coincide with the longest axis of the optical ellipsoid. It is interesting to note in this connexion that, so far as is known, all substances having a negative Kerr constant are polar.

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