CHAPTER 1

GENERAL THEORY OF MOLECULAR POLARIZABILITIES
1.1 OPTICAL POLARIZABILITY

When a beam of light is incident on a transparent material medium of refractive index different from that of the surrounding, the medium gets polarized. Suppose a light wave of electric intensity \( E = E_0 \cos 2\pi vt \) goes past a molecule in the medium. It induces an optic moment in the molecule and the molecule behaves like an oscillating dipole, since the incident light vector \( E \) is oscillatory. The molecule is said to be 'polarized'. The induced moment \( P \) is considered to be proportional to the strength of the incident electric field \( E \) and is given by the relation (1.1),

\[
P = \alpha E \quad \ldots \quad (1.1)
\]

\( \alpha \), the constant of proportionality is the moment induced in the molecule per unit incident field and is called the 'polarizability' of the molecule. In the case of isotropic molecules \( \alpha \) has the same value in all directions and it is a scalar, but in the case of anisotropic molecules it will have different values in different directions and hence it has to be regarded as a tensor of the second order.

Suppose an alternating electric field of intensity \( E = E_0 \cos 2\pi vt \) is imposed on a molecule. If an electron, in that molecule, attached elastically to the nucleus is initially at an equilibrium distance 'r' from the centre, the displacing force \( Ee \) on the electron will be balanced by a restoring force \( Ksr \) where 'e' is the charge of the electron and
'K' is the force constant. The induced moment $\mathbf{S}_\mu$ will be e. $\mathbf{S}_\mu$. Therefore, when $E = 1$, $\mathbf{S}_\mu = \frac{e^2}{K}$ by definition becomes the polarizability $\alpha$ of the molecule and possesses the dimensions of volume.

An electron so held would oscillate with the natural frequency

$$\nu_0 \cdot \text{Hz} = \frac{1}{2\pi} \left( \frac{K}{m} \right)^{1/2}$$

in the absence of an external field, provided damping is neglected. Here 'm' is the mass of the electron.

Accordingly, $\alpha$ can be written as (1.2)

$$\alpha = \frac{e^2}{K} = \frac{e^2}{4\pi^2 \nu_0^2 m} \quad \ldots \quad (1.2)$$

Under the influence of the light beam, of frequency $\nu$, the electron will execute forced vibrations. If we take the polarization of the dielectric into consideration, the general equation for molar refraction 'R' is well known as (1.3).

$$R = \left( \frac{n_0^2 - 1}{n_0^2 + 2} \right) \frac{M}{\rho} = \frac{Ne^2}{3\pi m} \sum_k \left( \nu_{0k}^2 - \nu^2 \right)^{-1}$$

$$\quad \ldots \quad (1.3)$$

The summation extends over 'k' kinds of oscillators in the medium, each vibrating with its own natural frequency $\nu_{0k}$. The symbols $n$, $N$, $M$ and $\rho$ refer to the refractive index, Avagadro...
number, molecular weight and density respectively.

If the medium has a single type of oscillators, then

\[ R = \frac{4}{3} \pi N \alpha \]  

... (1.4)

At infinite wavelength, the molar refraction 'R' in the above equation can be written as 'R_\infty' and is identified with the electronic polarization E_p of the molecule, and

\[ \alpha = \frac{3}{4} \pi N R_\infty = 0.3964 \frac{E_p}{10^{-24}} \text{ cm}^3 \]  

... (1.5)

According to Bhagavantam, the molecular polarizability '\alpha' can be written as (1.6).

\[ \alpha = \left( \frac{e^2}{m} \right) \left( \frac{1}{\omega^2 - \omega_0^2 + iq\omega} \right) \]  

... (1.6)

taking into consideration the damped equation of motion of the electron subjected to the influence of an external oscillating field. Theoretically therefore, polarizability should be a function of the incident frequency. However in practice \( \omega \ll \omega_0 \) except when measuring the refractive index 'n' near the absorption bands. As such '\alpha' may be regarded as a constant and hence equations (1.2) and (1.6) become equal in the limiting case.
From a comparison of polarizability with that of the conducting sphere of radius 'a' in electrostatics, the former can be identified with the cube of molecular radius. However, it is known that no expression based on $r^3$ fits all the known facts. Experimental evidence shows that ionic refractions are proportional to the fourth rather than the third power of the ionic radius 'r'. While Wasatjerna suggested the expression

$$R_{\text{ion}} = \frac{1}{K} r^4$$

(1.7)

for Kordes proposed the expression (1.8),

$$R_{\text{ion}} = 0.606 r^{4.5}$$

(1.8)

based on Pauling's univalent radii. Good agreement has been noticed between the values of $R_{\text{ion}}$ so evaluated by (1.8) and those estimated earlier by LeFevre. From the exhaustive experimental work of Dalgarno, on atomic and ionic polarizability, it has been noticed by LeFevre that the polarizability and $r^3$ are not simply related. Actually an empirical relation of the form $r^{4.5}$ seems to be more satisfactory, although dimensionally it is incorrect.
1.2 PRINCIPAL AND BOND POLARIZABILITIES

1.2.1 Anisotropy in polarizability

As noted earlier the induced dipole moment of a molecule can be written as (1.1).

\[ P = \alpha E \] 

\( \alpha \), the polarizability of a molecule, can be treated as a scalar only in certain special cases like isotropic systems. The polarizabilities of monoatomic ions and atoms are generally believed to be independent of field direction. The same is assumed for undistorted quasi-spherical molecules like methane and carbon tetrachloride.

But, according to Silberstein\(^6\), when two isotropic atoms A and B are held together as in a diatomic molecule, the resulting system A-B is not isotropically polarizable. If a unit field acts successively along and perpendicular to the line of centres A-B, it will induce primary moments parallel and perpendicular to the line of centres respectively in both the atoms A and B. The secondary moments induced by these primary moments will act in such a direction so as to increase the polarizability along the line of centres and decrease perpendicular to it. Thus polarizability of A-B assumes the anisotropic character. The case of hydrogen molecule \( \text{H}_2 \) is a good example in this context.
In general, a vast majority of the molecules are optically anisotropic, and therefore the polarizability \( \alpha \) acquires the directional property. It is regarded as a tensor of the second rank. Adopting a rectangular space fixed coordinate system, the nine tensor components, hereafter referred to as \( b' \)'s, are written in the matrix form (1.9).

\[
\alpha = \begin{bmatrix}
b_{xx} & b_{xy} & b_{xz} \\
b_{yx} & b_{yy} & b_{yz} \\
b_{zx} & b_{zy} & b_{zz}
\end{bmatrix}
\] ...

(1.9)

For optically inactive molecules \( \alpha \) is a symmetric tensor, i.e., \( b_{xy} = b_{yx} \); \( b_{yz} = b_{zy} \); \( b_{zx} = b_{xz} \), so that only six independent elements are present in its matrix. This concept of anisotropy in polarizability of a molecule is amply borne out from experiments on light scattering and other allied phenomena.

1.2.2 Principal polarizabilities

For every molecule three mutually perpendicular directions \( OX', OY', OZ' \) (Fig. 1.1) can be fixed in it such that when the incident field acts along any one of them, the corresponding induced moment also acts along that direction, and equations such as (1.10)
Fig. 1.1. Molecule in coordinate frames of references
\[ P_x' = b_1 E_x', \]
\[ P_y' = b_2 E_y', \]
\[ P_z' = b_3 E_z', \]

hold good. In this representation all the non-diagonal terms of the tensor components vanish and the diagonal terms \( b_1 \), \( b_2 \) and \( b_3 \) are called the 'Principal Coefficients of Polarizability'. Alternatively it is convenient to visualize the molecule geometrically as a polarizability ellipsoid with three orthogonal semi-axes. The latter can be identified with \( b_1 \), \( b_2 \) and \( b_3 \) which measure the moments induced when unit field acts respectively collinear with them. The equation of the ellipsoid is written as

\[
\frac{x^2}{b_1^2} + \frac{y^2}{b_2^2} + \frac{z^2}{b_3^2} = 1
\]

and the points represented by the coordinates lie on the surface of the ellipsoid.

In spherically symmetrical molecules the directions of action of the inducing field and induced moments are always collinear whereas in less symmetrical molecules the directions of action of induced moments depend on the orientation of the molecule in the field. In a general case it has been shown by Lefevre that if a unit field acts at an angle \( '8' \) with the \( b_1 \)-direction in the \( b_1-b_2 \) plane then components induced in the two
Fig. 1.2. Molecular polarizability ellipsoid
directions \( b_1 \) and \( b_2 \) are \( b_1 \cos \theta \) and \( b_2 \sin \theta \) respectively. The direction of the resultant induced moment naturally differs from that of the incident field as shown in Fig. (1.2) and in fact will make an angle \( \tan^{-1} \left( \frac{b_2}{b_1} \tan \theta \right) \) with the \( b_1 \) direction. The principal coefficients of polarizability \( b_1, b_2 \) and \( b_3 \) appear in many fields of study such as optical and electrical phenomena and in particular refractivity, light scattering, dielectric polarization and Kerr effect.

1.2.3 Bond polarizabilities

Mayer and Otterbein advanced a suggestion that individual chemical bonds may be associated with polarizabilities along their length and in the two perpendicular (transverse and vertical) directions. Accordingly, each chemical bond may be described as a polarizability ellipsoid with three coefficients designated by \( b_L \), \( b_T \) and \( b_V \) as its semi-axes. \( b_L \) is known as the longitudinal link polarizability, \( b_T \) is the link polarizability in the plane of the molecule or group containing the link and at right angles to it, and \( b_V \) is the one normal to the plane. These are assumed to constitute the molecular polarizability in an additive manner.

As an example, if we consider \( XY_2 \) bent symmetric molecule with \( \angle XY = 2\theta \), each bond \( XY \) will have the coefficients of polarizability \( b_{XY}^L, b_{XY}^T, b_{XY}^V \). Then the principal coefficients of polarizability of the molecule can be expressed
in terms of the bond polarizabilities as follows.

\[ b_{1}^{xy} = 2 \left( b_{L}^{xy} \cos^2 \theta + b_{1}^{xy} \sin^2 \theta \right) \]
\[ b_{2}^{xy} = 2 \left( b_{1}^{xy} \cos^2 \theta + b_{L}^{xy} \sin^2 \theta \right) \] ... (1.11)

and

\[ b_{3}^{xy} = 2 b_{V}^{xy} \]

The mean molecular polarizability \( \alpha_{M} = \frac{1}{3}(b_{1} + b_{2} + b_{3}) \) takes the form (1.12).

\[ \alpha_{M} = \frac{2}{3} \left( b_{L} + b_{1} + b_{V} \right)^{xy} \] ... (1.12)

Numerical values of these semi-axes for many bond ellipsoids have been estimated by Sachsse, Wang, Denbigh, LeFevre, and Bunn and Daubeney based on the arguments quoted by LeFevre. Their arguments simplify the above equation to (1.13).

\[ \alpha_{M} = \frac{2}{3} \left( b_{L} + 2b_{1} \right)^{xy} \] ... (1.13)

provided the molecule possesses cylindrical symmetry. If the atom x is carbon, then the cylindrical symmetry is lost and this necessitates certain approximations to be made. One such approximation is to assume that the C-H bond is isotropically polarizable in all cases. With these considerations LeFevre School has estimated the bond polarizabilities of various
bonds. A few of these are recorded in the recent article of LeFevre. Taking methane as a specific example, the details are discussed by Purnachandra Rao, Rama Murthy and Subbaiah. Though LeFevre School has adopted C-H bond to be isotropically polarizable ($b_L = b_T = b_V = 0.064 \times 10^{-23} \text{ cm}^3$), increasing evidences from the works of Chantry and Plane, Rama Murthy and Amos and Crispin are exhibiting the anisotropy of the C-H bond and it needs a re-estimation.

1.2.4 Application to stereo-structural problems

The application of bond polarizabilities to the structural studies of a simple $XY_2$ bent symmetric molecule has been described in the last section. The method is similar even to the other types of molecules except that the problem becomes increasingly complicated as one attempts larger molecules. If a given molecular formula can be represented by more than one structural formula then its stereochemical structural problem is solved as follows:

1) For each of the proposed structures, the principal polarizabilities are theoretically evaluated and compared with the experimental values obtained from light scattering measurements, and

2) From the estimated principal polarizabilities, molar Kerr constants are determined theoretically and are compared with the experimentally determined $K$ values.

From these two methods the most probable conformation
can be judged. However from these procedures it is clear that for either work an a priori estimation of $b_1$, $b_2$ and $b_3$ is required which can be done by fixing up a convenient set of rectangular coordinate axes $X$, $Y$ and $Z$ in each of the various alternatives of the proposed structures. The details of the estimation are described by Eckert and LeFevre. The problem finally turns out to be an eigenvalue-eigenvector problem of the standard type which can be solved by modern computers to yield the principal coefficients of polarizability for each of the proposed conformation.

The different sets of $b_i$ values thus calculated for various proposed structures of the same molecule can be compared with the experimental values if available. Otherwise from these sets of $b_i$'s and from a knowledge of the direction cosines of the components of the resultant dipole moments, the molar Kerr constants can be calculated using the approximate expressions given by LeFevre and LeFevre. A comparison of the theoretical results with the experimentally measured values of $\mu K$ will at once show the choice of the most favoured conformation out of the various plausible structures. This procedure has been extensively applied by LeFevre and his school for simple as well as complicated molecules. LeFevre's recent reviews list out the molecules for which the conformational analysis by this method has been successfully carried out.
REFERENCES


6 Silberstein, L. Phil. Mag., 33, 92, 215 and 521 (1917).


8 Sachsse, G. Physik. Z., 36, 357 (1935).


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