CHAPTER I

Molecular Polarizability-
an Introduction
1.1. Molecular Polarizability

When a beam of light is incident on a transparent material medium of refractive index different from that of its surroundings, the medium gets polarized. If a light wave of electric intensity \( E \) goes past a molecule in the medium, it induces an optic moment in the molecule. The molecule is said to be polarized. The moment induced per unit incident field is called the polarizability of the molecule.

Let 'r' be the equilibrium distance of an elastically attached electron in the molecule from the centre. Then the displacing force "Ee" on the electron will be balanced by a restoring force 'K\( \delta r \)'. Here 'e' is the charge on the electron and 'K' is the force constant. The induced moment \( \delta \mu \) will be equal to e\( \delta r \). From the definition of polarizability when \( E=1 \), \( \delta \mu = e^2/K \). Therefore \( \delta \mu \) becomes the polarizability '\( \alpha \)' of the molecule. Since the charge has the dimensions \( M^{1/2} L^{3/2} T^{-1} \) and the force constant \( MT^{-2} \), the polarizability will have the dimensions of volume.

In the absence of an external field the electron of mass 'm' so held would oscillate with a natural frequency \( \nu_0 \) Hz which is given by

\[
\nu_0 = \frac{1}{2 \pi} \sqrt{\frac{k}{m}}
\]

Provided damping is neglected. Accordingly \( \alpha \) is given by

\[
\alpha = \frac{e^2}{k} = \frac{e^2}{4\pi^2 \nu_0^2 m} \quad \text{(1.1)}
\]

The electric vector in a light beam is oscillatory. Under the influence of the light beam of frequency \( \nu \), the electron behaves like on oscillating dipole, and will execute forced vibrations.
According to Lorentz\(^1\) and Partington\(^2\), taking into consideration the polarization of the dielectric, the general equation for molar refraction \(R\) may be written as

\[
R = \frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{Ne^2}{3\pi n} \sum_k \left[ \frac{\omega_0}{\omega_0^2 - \omega^2} \right]^4
\]

The summation extends over \(k\) kinds of oscillators in the medium, each vibrating with its natural frequency \(\omega_0k\). The symbols \(n\), \(N\), \(M\) and \(\rho\) represent the refractive index, Avagadro number, molecular weight and density respectively.

If the medium has only a single type of oscillators, then we have from equations 1.1 & 1.2

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

At infinite wavelength, molar refraction \(R\) becomes \(R_\infty\), which is defined as the electronic polarization of the molecule.

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

According to Bhagavantam\(^3\) the molecular polarizability \(\alpha\) can be written as

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

Taking into account the effect of damping on the motion of the electron subjected to an oscillating electric field. Here \(\omega_0 = 2\pi \nu_0\), \(\omega = 2\pi \nu\) and \(q\) is the damping term. Theoretically therefore polarizability should be a function of the incident light frequency. However \(\nu\) is very small compared to \(\nu_0\) except when measuring \('n'\), the refractive index, near absorption bands, therefore, \(\alpha\) may be regarded as a constant. In the limiting case equations 1.5 & 1.1 become identical.
It is known that a conducting sphere of radius ‘a’ when placed in an electric field of intensity ‘E’ would acquire an electric dipole moment $a^3E$. On an analogy the polarizability of a molecule might therefore be identified with the cube of molecular radius.

According to Debye polarizability of a molecule is proportional to the cube of the molecular radius. However no expression based on $r^3$ fits all the known facts. Experimental evidence shows that refractions of ions are proportional to the fourth power of the ionic radius. Wasatjerna gave the expression.

$$R_{\text{ion}} = \frac{1}{k} \cdot r^4$$  \hspace{1cm} (1.6)

Where $k$ is a constant, nearly unity and depends on the column of the periodic table to which the ion belongs. But Kordes connected refractions with univalent radii listed by Pauling and gave the relation.

$$R_{\text{ion}} = 0.606r^{4.5}$$  \hspace{1cm} (1.7)

Good agreement is found between the values of $R_{\text{ion}}$ so calculated and estimated by LeFevere.

Dalgarno’s exhaustive study of the determination of atomic and ionic polarizability suggested that an empirical relation of the form $r^{4.5}$ seems to be more satisfactory. However dimensionally it is not correct.

1.2. Principal and Bond Polarizabilities

1.2.1. Anisotropy in Polarizability

When a beam of light passes through a transparent material medium the moment induced in the molecule has been shown to be proportional to the strength of the incident field. It is indicated as

$$P = \alpha E$$  \hspace{1cm} (1.8)
Where $\alpha$ is a constant of proportionality, called the polarizability of the molecule. In certain special cases such as isotropic systems it is treated as a scalar of constant magnitude. In general a vast majority of molecules are optically anisotropic. Therefore polarizability acquires directional property. It is regarded as a tensor of second rank. Choosing rectangular space fixed coordinate system, the nine tensor components, referred to as ‘b’s’ are written in matrix notation as

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

for optically inactive molecules, $\alpha$ is a symmetrical tensor, i.e., $b_{xy} = b_{yx}, b_{xz} = b_{zx}$ and $b_{yz} = b_{zy}$, so that only six independent elements are present in this matrix.

### 1.2.2. Principal Polarizabilities

For every molecule three mutually perpendicular directions $ox'$, $oy'$ and $oz'$ Fig (1) can be fixed in it such that the directions of $E$ & $P$ are collinear. Then

$$P_x' = b_{xx} E_x$$
$$P_y' = b_{yy} E_y$$
$$P_z' = b_{zz} E_z$$

hold good. In this representation all the non-diagonal terms vanish and the diagonal terms $b_{xx}, b_{yy} & b_{zz}$ are called the principal coefficients of polarizability represented by $b_1, b_2$ and $b_3$.

According to Gans & Bottcher\textsuperscript{10} a molecule can be geometrically visualized as a polarizability ellipsoid possessing three orthogonal semi-axes $b_1, b_2, & b_3$. The equation of the ellipsoid is written as

$$\frac{X^2}{b_1^2} + \frac{Y^2}{b_2^2} + \frac{Z^2}{b_3^2} = 1$$
Fig. 1.1: Molecule in coordinate frames of references
The points are represented by the coordinates on the surface of the ellipsoid. All these points on the surface of the ellipsoid may be viewed as the end points of moment vectors induced when unit field is successively applied to the molecule in all possible orientations.

In spherically symmetric molecules, the directions of action of the inducing field and induced moments are always collinear. In less symmetric molecules, the directions of moments depend on the orientation of the molecule in the field i.e., the field induces component moments parallel and perpendicular to itself. When the field acts parallel to any one of the semi-axes $b_1$, $b_2$, or $b_3$ the perpendicular components of the induced moments in each case will be zero and the parallel components are known as principal coefficients of polarizability.

In a general case if a unit field acts at an angle $\theta$ with the $b_1$ direction (fig 2) in the $b_1$-$b_2$ plane, the two moments $b_1 \cos \theta$ & $b_2 \sin \theta$ will be induced mutually at $90^0$. The direction of the resultant induced moment will be at an angle $\tan^{-1} \left( \frac{b_2}{b_1} \tan \theta \right)$ with the $b_1$ direction.

These principal coefficients of polarizability $b_1$, $b_2$, & $b_3$ are found to be essential, to study the phenomena such as refractivity, light scattering, dielectric polarization and Kerr effect. In practise they are evaluated from quantitative measurements made in the above fields.

### 1.2.3. Bond Polarizabilities

Mayer and Otterbein\(^1\) suggested that individual chemical bonds can be associated with polarizability components along their lengths and in two perpendicular (transverse and vertical) directions. Accordingly each chemical bond may be described as a polarizability ellipsoid with three coefficients designated by $b_L$, $b_T$, & $b_\perp$ 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 $b_\perp$ is one normal to the plane. These link polarizabilities are assumed to constitute the molecular polarizability in an additive manner.
Fig. 1.2: Molecular polarizability ellipsoid
Numerical values of these semi-axes for many bond ellipsoids have been estimated by Sachsee, Wang, Denbigh, LeFevre and LeFevre and Bunn and Daubery.

As an example if we consider \( xy_2 \) bent symmetric molecule with \( \gamma \hat{e}_y = 2\theta \), each bond will have the coefficients of polarizability \( b_{L}^{XY} \), \( b_{T}^{XY} \), \( b_{V}^{XY} \). Then the principal coefficients of polarizability of the molecule can be expressed in terms of the bond polarizabilities as follows.

\[
\begin{align*}
    b_{1}^{XY} &= 2\left[ b_{L}^{XY} \cos^2 \theta + b_{T}^{XY} \sin^2 \theta \right] \\
    b_{2}^{XY} &= 2\left[ b_{T}^{XY} \cos^2 \theta + b_{L}^{XY} \sin^2 \theta \right] \\
    b_{3}^{XY} &= 2b_{V}^{XY}
\end{align*}
\]  

Then the mean molecular polarizability of the molecule is given by

\[
\alpha = \frac{2}{3} \left[ b_{L} + b_{T} + b_{V} \right]^{XY}
\]  

Assuming that the single bonds & triple bonds satisfy the cylindrical symmetry condition i.e. \( b_{L} \neq b_{T} = b_{V} \) the above equation can be simplified as

\[
\alpha = \frac{2}{3} \left[ b_{L} + 2b_{T} \right]^{XY}
\]  

However the equation (1.12) remains the same for double bonds \( [b_{L} \neq b_{T} \neq b_{V}] \)

In general, if a molecule contains \( n_1, n_2, \ldots, n_i \) similar bonds then the mean polarizability of the molecule can be written as

\[
\alpha = \sum_{i=1}^{n_i} \frac{n_i}{3} \left[ (b_{L} + b_{T} + b_{V}) \right]_i
\]  

If the atom \( x \) is carbon, then the cylindrical symmetry is lost and this leads to certain approximations to be made. One such approximation is to assume that C-H
bond is isotropically polarizable in all cases, with these considerations Le Fevre has estimated the polarizability of various bonds.

Though Le Fevre school has adopted C-H bond to be isotropically polarizable \((b_L \approx b_T \approx b_V = 0.064 \times 10^{-23} \text{ cm}^3)\) evolving evidences from the works of Chanty and Plane\(^{17}\), Amos and Crispin\(^{18}\), Subbaiah\(^{19}\) are establishing the anisotropy of the C-H bond.

**1.2.4. Application to stereo-structural problems**

Bond polarizability studies can be extended to the structural elucidation of simple as well as macromolecules. If a given molecular formula can be represented by more than one structural formula, then its stereo-chemical structural formula 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 experiments.

2) From the estimated principal polarizabilities molar Kerr constants are determined theoretically and compared with the experimental values.

By these two methods the most probable conformation can be predicted.

For calculating \(b_1\), \(b_2\) & \(b_3\) in each case, a set of rectangular axes \(x, y \& z\) is chosen. After choosing the appropriate set of bond polarizabilities, a unit electric field is imagined to act, for instance, along the \(x\)-direction and the induced moments \(b_{xx}, b_{yx}\) & \(b_{xz}\) are computed. Then the process is repeated for the field in the other two directions. Then cubic equation,

\[
\begin{vmatrix}
   b_{xx} - \lambda & b_{xy} & b_{xz} \\
   b_{yx} & b_{yy} - \lambda & b_{yz} \\
   b_{zx} & b_{zy} & b_{zz} - \lambda
\end{vmatrix} = 0
\]

is solved to obtain the principal polarizability coefficients \(b_1, b_2 \& b_3\) of the molecule. This permits the calculation of the direction, which locate these \(b\)'s within the axes chosen. This data can be verified with the experimental values if available; otherwise
the molar Kerr constant $m_K$ is evaluated using appropriate equations given by Le Fevre and Le Fevre. This procedure has been applied for the structural conformation studies of many simple and complicated molecules by Le Fevre school.

According to Le Fevre\textsuperscript{8}, "The present application of anisotropic polarizabilities, made on the basis of theoretical arguments of Lorenz, Lorentz, Born, Gans, Debye and others have where solutes are concerned – advantages both in their foundations and in the qualitatively expressible nature of the conclusions they can provide."

### 1.3. Hyperpolarizability

#### 1.3.1. Introduction

According to Debye\textsuperscript{4} the polarizability of a molecule is proportional to the first power of the field. Sutton\textsuperscript{20} pointed out that at very high voltages polarizability is an increasing function of the field intensity. Coulson et al\textsuperscript{21} suggested that the low field polarizability $b_0$ shall not be affected by fields less than $10^8$ V cm$^{-1}$ thus revealing the fact that direct observation of hyper polarizability requires the application of voltages above the dielectric break down.

According to Buckingham and Pople\textsuperscript{22}

$$
\mu_{\text{induced}} = b_0 E + \frac{1}{2} a E^2 + \frac{1}{6} c E^3
$$

When the above relation was applied to spherically symmetric molecules for which 'a' in the above equation is zero, a value of $c = 12.2 \times 10^{-36}$ esu turned out for the hyper polarizability constant. Further it was proved that the low field polarizability of this molecule shall not be altered by fields less than about, $10^7$ Vcm$^{-1}$. This result concurs with Coulson's estimates. With the field strengths commonly applied in all these experiments which are of the order of $10^4$ V cm$^{-1}$ the detection of hyper polarizability in common molecules becomes impossible. It is assumed that it might exist among randomly coiled polymers which exhibit large Kerr constants.
1.3.2. Recent trends in Hyperpolarizabilities

The phenomenon of hyperpolarizability has been studied by applying it to
1. Isotropic media and
2. Conjugated and non-conjugated organic liquids.

A naturally isotropic medium, when subjected to a dc electric field gets polarized and gains the ability to generate the second harmonic of light. Terhune et al observed such a dc electric field induced second harmonic generation in the calcite crystal, which has a centre of inversion. Mayor\textsuperscript{24} investigated second harmonic generation in non-dipolar substances like H\textsubscript{2}, O\textsubscript{2}, CCl\textsubscript{4}; as well as in dipolar substances CO, CHCl\textsubscript{3} and other methyl and ethyl halogen derivatives. Kielich\textsuperscript{25} has derived a theory to explain the second harmonic generation in naturally isotropic media placed in a dc electric field. Kielich and his co-workers\textsuperscript{26} studied this parameter as a function of temperature or oscillation frequency of the laser light or the applied electric field. He reported the non-linear third order polarizabilities of some molecules in the liquid state.

Conjugated organic molecules contain certain number of free or delocalized electrons. These electrons give rise to nonuniformity in charge distribution. These electrons contribute to large non-linear polarizability values. Levine and Bethea\textsuperscript{27} measured the second (\(\beta\)) and third order (\(\gamma\)) hyperpolarizability of a few conjugated as well as nonconjugated organic liquids. Their reported value of third order polarizability (\(\gamma\)) is 40 x 10\textsuperscript{-36} esu and the second order polarizability (\(\beta\)) is 20 x 10\textsuperscript{-31} esu for nitrobenzene measured as a solute in benzene. Their measurements on nitromethane which is a non-conjugated compound confirmed that the delocalized \(\pi\)-electrons present in conjugated molecules are more effective in contributing to hyperpolarizability than localized electrons in non-conjugated compounds. They have given the details of experimental technique to measure the second and third order hyperpolarizabilities in liquids using Laser light and pointed out the following advantages in experimenting with liquids.

1. The difficulties, such as crystal growing cutting etc., and structural determination by X-ray diffraction techniques met with in solids, can be avoided.
2. Many of the highly conjugated organic molecules which may have large non-linear polarizabilities generally tend to decompose when they are vapourised. Therefore they can be studied in liquid state with appropriate solution techniques.

3. The second harmonic signal in the liquid phase will be two orders of magnitude larger than that observed in gaseous phase.

They have extended these studies to benzene, carbon tetrachloride, carbon disulphide and to several other simple compounds like alkenes and concluded that the third order hyperpolarizability also obeys the additive law.
References
