INVESTIGATION OF SCATTERING OF LIGHT BY POLAR MOLECULES

BY
NELSON KIIO MULLA

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DECLARATION

I declare that the work presented in this thesis is my original work and has never been presented in this form or any other form in this University or any other for a degree or any other award.

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APPROVAL

This thesis has been submitted with my approval as the university supervisor.

Signature _____, Date 12th Nov 96

Prof. H. S. Subramhanyam.

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DEDICATION

This thesis is dedicated to my parents Mr. Shadrack. Mulla Ndetei and Mrs. Tabitha Mulla.

ABSTRACT

This thesis reports a theoretical and experimental investigation of the scattering of light by polar molecules which are oriented in an external electric field. The stress is more on the theoretical part and less on experimental study as a laser source of high power demanded by the theory is not available. The oriented polar molecules under study are in some respects similar to nematic liquid crystalline medium.

Motivation for the investigation is therefore from the study of scattering of light by liquid crystalline PAA (p-azoxyanisole) by chatelain [1,2] and Subramhanyam et al [5]. The orientation in this case is not likely to be very high.

Expressions for intensity components of the light scattered as a function of the angle θ_s, θ_s being the angle between direction of observation of scattered light and the direction of light incident on the scatterer, have been derived for various orientations of the applied static electric field relative to direction of incident light.

The analysis of the expressions has led to certain relationships between the expressions for the intensity components corresponding

to different states of polarization of incident and scattered light as well as the orientation of the applied electric field. Analysis has also led to an expression for the depolarization factor

$$\rho = \frac{H_H}{V_H}$$

in various cases, which expression for strictly transverse direction (i.e, direction at right angles to direction of incidence) takes a simple and useful form. This expression involves the dipole moment as well as the optical anisotrophy of the scattering molecule. Infact the depolarization factor turns out to be slightly different from unity, which is of course the value in the absence of the external field.

Though this depolarization factor is very slightly different from unity, we were able to determine the same to a satisfactory accuracy experimentally for one particular orientation of the applied electric field which of course was the most convenient orientation. We could therefore provide a method of calculating the dipole moment, or optical anisotropy if one of them is known which we have illustrated through our calculations of dipole moment in the case of ethyl alcohol. Limitations of our experimental investigations and suggestions for further investigations are also discussed.

PREFACE

The present thesis submitted for the M.sc degree of Egerton University incorporates the results of experimental and theoretical investigations we carried out on the scattering of light by polar molecules subjected to external electric field. Numerous experimental and theoretical investigations have been carried out on scattering of light, by crystals, liquids and gases. While the molecules are closely packed in the case of solids, they are randomly oriented and free to rotate in the case of gaseous assembly of molecules. Even though the arrangement of molecules in liquids is different either from that in solids or gases, we can extend the theory which we have developed in the case of gases easily to the case of liquids. The motivation for this study has emerged from the Chatelain's study on the scattering of light [1,2] in the nematic phase of liquid crystalline p-azoxyanisole (PAA). Chatelain's theory of light scattering in nematic liquid crystals is modified and extended to obtain expressions for intensities of the scattered light for different states of polarization of incident light by Subramhanyam et al [3]. We realized that the polar molecules oriented in an external electric field is analogous in some respects to a nematic liquid crystal and hence this investigation has been taken up. The primary concern in this thesis is the theoretical as well as experimental study of light by polar molecules oriented by external electric field. The source of scattering is the oscillating electric dipole induced in the

molecule by the external electric field even though oscillating quadrupole are also induced. This is because the intensity due to the oscillating quardrupole is several orders of magnitude less than that of the former.

The moments of the oscillating dipoles involve concepts referred to as polarizabilities. The expressions for the intensities of the scattered components, the depolarization ratios are all obtained through a study of polarizability and how it modifies under different circumstances.

In the light of the above, Chapter 1 of this thesis is devoted to a general and brief discussion of polarizabilities. The basic equations involved are also useful for our theoretical investigation of intensities of scattered components and depolarization ratios.

Chapter 2 of this thesis presents a general survey of the well known ideas with regard to scattering of light, with a particular reference to Rayleigh scattering. After a brief discussion of Thomson, Compton, Brillouin and Raman scattering, we have presented the fluctuation theory of scattering. We have concluded this Chapter with calculation of intensities and depolarization ratios in the case of Rayleigh scattering and a qualitative discussion of application of Rayleigh scattering.

As already mentioned the polar molecules oriented in an external electric field being analogous to nematic liquid crystals as far as scattering of light is concerned, we have made a brief discussion of light scattering in nematic liquid crystals studied

by Chatelain and its modification by Subramhanyam et al in the introductory part of the Chapter 3.

In the second part of Chapter 3 we have taken up a theoretical investigation of light scattering by gaseous assembly of polar molecules and have obtained expressions for fractional intensities of scattered light for different states of polarization of the incident light when the gaseous assembly of molecules is subjected to external electric fields. These various components are denoted here by H_H, V_H, V_V, and H_V, whose meaning we have explained in the text. We have shown quantitatively that expressions for H_H, V_H, H_V, and V_V are different for different direction of the applied field, i.e (i) applied electric field perpendicular to the scattering plane, (ii) applied electric field along direction of the incident light and (iii) applied electric field perpendicular to the incident direction and in the scattering plane. Further, expressions for the various components clearly show that they are functions of angle of scattering θ_s, $\hat{b}$ and $\hat{a}$ which respectively involve optical anisotropy and the dipole moment of the scattering molecules. We have concluded the chapter by showing how the expressions could easily be modified for the case of liquid assembly of molecules which is our main concern.

In chapter 4, we have used the expressions for fractional intensities which we have derived in Chapter 2, made some valid approximations and proceeded to obtain expressions for the depolarization factor (denoted by ϱ) given by

$$\varrho = H_H / V_H .$$

It is seen that ℓ involves the optical anisotropy and dipole moment of the scattering molecules. Further it is also seen that its value changes, it is slightly different from unity when molecules are subjected to external electric field while it has value unity with zero field. We have also given a sketch description of the apparatus, and experimental procedure which we have employed for the experimental determination of the depolarization factors in the same Chapter. We have also briefly discussed the limitations of the experiment in this Chapter only.

Chapter 5 not only gives a detailed interpretation of the results, but also details of numerical calculations concerning the optical anisotropy and dipole moment in the case of ethyl_alcohol based on our expression for ℓ and its experimental determination. We end the Chapter by summarising our conclusions. We have also discussed the limitations of our study and come forward with some recommendations for further investigations in this field.

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CHAPTER 1

LITERATURE REVIEW: POLARIZABILITY

When an assembly of molecules is subjected to external electric field E, which may be of the incident visible radiation, oscillating dipoles are induced in the assembly of molecules. An electric dipole is formed when a pair of charges of equal magnitude and opposite sign are separated by a given distance due to action of the applied electric field.

The phenomena of acquiring of dipole moment by an atom in an external electric field E is called polarization. The dipole moment induced is given by the relation;

$$P = \alpha E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1.0)$$

where P is the dipole moment or polarization and α is the polarizability which is the measure of ease with which a material gets polarized.

Polarizability is characterized by definite type of the changes of the particle under the action of applied field. All types of polarizablity can be reduced to two main types:

i) Elastic displacement of charges in the atoms and molecules under the action of the field E, and

ii) the orientation of the permanent dipoles in the direction of the applied field.

If electron distribution is unsymmetrical in a molecule, it will have a so-called permanent dipole. During vibration, the magnitude of this change results in the formation of dipole oscillating at the frequency of vibration. If the electron distribution is

symmetrical in a molecule it has no permanent dipole in it's equilibrium state configuration, it is possible for unsymmetrical vibrations to disturb the symmetry of the electron distribution and produce dipole which again oscillate with the frequency of the vibration. Electric dipoles may also be induced in the molecules by an external electric field, and such dipoles can oscillate and emit radiation. The frequecy of the dipoles are related to frequency of the applied electric field and frequency of the molecular vibration. If the electric field is an oscillating one, as for example in electromagnetic radiation, induced dipoles result which oscillate at the frequency of the electric field and also at frequencies which are beat frequencies between the electric field frequency and molecular frequency [6]. Since in the course when the dipole is being induced a particle undergoes changes, depending on the type of polarizability, it is conventional to consider the total polarizability of the medium as consisting of 3 distinctive components [24] arising from;

(i) Electric polarizabilty resulting from displacement of the electrons relative to the atomic nuclei,

(2) Orientation polarizability arising due to orientation of the permanent electric dipole moments of the molecules in the electric field, and

(3) Ionic polarizability arising due to displacement of ions from their equilibrium positions by the applied electric field.

We will now take up a brief discussion of the different types.

1.1. Electronic polarizability(α_e)

All types of polarizability can be reduced to two main types as earlier on stated in section [1.0]. Now considering electronic polaizability denoted by α_e, in this case the polarizability is characterised by the elastic displacement of the electronic charge cloud relative to the nuclei when the atom or molecule is acted upon by an electric field E.

Electron polarizability exists in all atoms or molecules of both polar and non-polar dielectrics. The magnitude of polarizability referred to one mole of dielectric substance is given by the relation [14];.

$$P_e = \frac{4}{3}\pi N\alpha_e$$

where P_e is the electronic polarization, and α_e is the electronic polarizability of the dielectric, and since P_e is of dimensions (el) and E is of dimensions (el^{-2}) (e,is the charge, and l is length), then, from the relation, $P = \alpha E$, we can rewrite, $\alpha_e = P_e/E = e(l)/el^{-2} = l^3$. α is seen to have dimensions (l^3), i.e those of a volume. Therefore, α_e increases with increase in volume of electron charge cloud, further the electron is, from the nucleus, the greater is its mobility and more highly it is subjected to the action of an electric field. Hence highest polarizability is possesed by the valence electrons, since feebly bound by the nucleus.

If we strictly take non-polar molecule subjected to an electric field, the electrons and nuclei are displaced and a dipole is generated. The vectorial sum of all the dipole moments of the

molecule in the unit volume is essentially the vector P introduced in the preceding section.

Dependance of polarization and refractive index on the frequency of field can easily be determined by first finding the displacement r of each of charged particle from the equilibrium position.

Now considering electrons in a molecule as harmonic oscillator, to a good approximation, electrons behave as if they are bound to an equilibrium position by a quasi-elastic restoring force [19].

$$Q = -qr.$$

Hence if m denotes the mass of the electron, it's equation of motion is;

$$m\ddot{r} + qr = eE \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.1)$$

Let ω be the angular frequency of the incident field given by

$$E = E_o e^{-i\omega t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

and take as trial solution of (1.2) the expression

$$r = r_o e^{-i\omega t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.3)$$

then the required solution

$$r = eE/m(\omega^2_o - \omega^2). \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.4)$$

where $\omega_o = \sqrt{(q/m)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.5)$

is called the resonace (or absorption) frequency. According to (1.4) the electron oscillates with the frequency of the incident field. Each electron contributes to the polarization a moment P = er. There will also be contribution from the nuclei; but since the nuclear masses are heavy in comparison with the masses of the

electrons, their contributions can be neglected.

Now, assuming there is only one effective electron in a molecule wih resonance frequency ω_o, we obtain for the total polarization P the expression

$$\vec{P} = Np = Ner = \frac{Ne^2}{m} \frac{\vec{E}'}{(\omega_0^2 - \omega^2)} \quad \ldots\ldots\ldots\ldots (1.6)$$

Now, the electric dipole moment $\vec{P}$ established under the influence of the field is proportional to the effective field, $\vec{E}_{Loc}$ where $\vec{E}_{Loc}=E+4\pi p$, and therefore, from (1.0)

$$\vec{P} = N\vec{E}_{loc} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.7)$$

Comparison of (1.6) with (1.7) gives

$$N\alpha e = Ne^2/m(\omega^2_o - \omega^2) \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.8)$$

Expressing the density of polarizability in terms of atomic parameters, it turns out that the quantity α_e is not a constant as it ought to be if ε denotes the static dielectric constant from **Lorentz-Lorenz formula** [18]

$$\alpha_e = \frac{3}{4\pi N} \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{3}{4\pi N} \frac{(n^2-1)}{(n^2+2)} \quad \ldots\ldots\ldots\ldots\ldots (1.9)$$

It can easily be shown that, the explicit dependance of the refractive index on frequency is given by;

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3} \frac{Ne^2}{m(\omega_0^2 - \omega^2)} \quad \ldots\ldots\ldots\ldots\ldots (1.10)$$

For a gas, n is close to unity so that we set $n^2 + 2 \sim 3$ in the denominator on the left-hand side and obtain

$$n^2 - 1 \sim 4\pi N\alpha = \frac{4\pi N e^2}{m(\omega_0^2 - \omega^2)} \qquad (1.11)$$

It is seen that n is an increasing function of the frequency, the dispersion is then said to be normal.

Now, if we assume that there are many frequencies, even in systems with the same kind of molecules; (1.10) and (1.11) must then be more generally expressed as,

$$\frac{4\pi N\alpha}{3} = \frac{n^2-1}{n^2+2} = \frac{4\pi N e^2}{3} \sum_k \frac{f_k}{\omega_k^2 - \omega^2} \qquad (1.12)$$

where, Nf_k is the number of electrons corresponding to the resonance frequeny ω_k.

Now, for isotropic molecules, (CCL_4, SF_6) with strictly spherical symmetrical spatial distribution of the electron cloud, all three components of the polarizabilities are equal [6] i.e

$\alpha = \alpha_1 = \alpha_2 = \alpha_3$ and for such molecules (1.12) enables us to calculate α. Howeve,r for anisotropic medium, α's will be different i.e polarizability along the direction of valence bond is always greater than along the other directions. In such cases there is need to obtain neccessary expressions for different components of polarizability and also involve experimental methods to determine the same.

1.2. Orientation polarizability (α_o)

Behaviour in an electric field of a polar dielectric, the molecules which posses a permanent dipole moment μ_o, differs from the behaviour of a non-polar dielectric. While for the molecules of the later the deformation polarizability is the only effect of the action of the applied field, in the case of the polar molecules in addition to the deformation polarizability there is another one caused by orientation of the permanent dipoles in an external electric field E called Orientation polarizability, denoted by α_o.

So, in a molecule assuming all α's are independent of one another then,

$$\alpha = \alpha_e + \alpha_{io} + \alpha_{or} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.13)$$

where α_e, α_{io}, and α_{or} is the electronic, ionic and orientation polarizabilities respectively.

Orientation polarization has its origin in the torque which the electric field exerts on the permanent moment P of the molecule i.e under action of field, dipoles are oriented, and in the absence of the electric field a free molecule with moment μ_o possesses not only translational but also rotational and vibrational motion because of random motion (distribution) of mean dipole moment of all molecules with a small physical volume, will be zero.

Application of electric field leads to orientation of the dipoles in the direction of the field and to the appearance in the polar dielectric of non-zero moment.

This resultant dipole moment will be higher under otherwise

identical conditions, the higher the strength of the field, higher the permanent dipole moment of the molecule.

In electric field, the molecule of a polar substance will strive to take up such a position such that the dipoles are arranged parallel to direction of applied field E. Such an orientation of the dipoles will normally make a non-zero angle (θ) with the direction of the applied field even on very high field strength of the order of 10^5V/cm, then potential energy obtained [6] is

$$U = -U_o E\cos\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.14)$$

P.E is small if $\theta$is small and minimum at $\theta = 0$. In a static field, E, rotational force which tends to turn the axis of the dipole in the direction of the field acts on a molecule with a dipole moment μ_o. The rotational moment T of this force is

$$T = \mu_o E\sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.15)$$

This force is opposed by rotational thermal motion of molecule, which tends to restore random distribution, hence a statistical equation is set up.

Since rotational movement of molecule is a function of temperature, rotational polarization (P_{or}) must depend on temperature.

Establishment of P_{or} when electric field is applied to a polar dielectric takes place slowly, it depends on the dimension of the molecule and viscosity of the medium [14].

Debye laid the theory for behaviour of polar dielectrics in an electirc field [6]. Debye showed that the connection between the

identical conditions, the higher the strength of the field, higher the permanent dipole moment of the molecule.

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dipole moment of the molecule μ_o, and it's orientation polarizability α_{or} for this mean electric dipole moment of the molecule in the direction of the applied field.

According to Debye, molecules which rotate, that which are found in a quantum state where quantum number J is non-zero, contribute nothing to polarization since the mean value of projection of the dipole moment P_o in the direction of field is zero (as it is, more over, on all spatial directions). In ground state, J = 0, where the molecule is not rotating, it has in the field E, a potential energy,

$$U=-E_o . p_o =-E_o\mu_o\cos\theta ,$$

θ being the angle P_o makes with E_o and it is subjected to a torque which tends to orient P_o parallel to E_o, thus polarising the medium, however this tendency is opposed by thermal agitation. The thermal equilibrium of the assembly of the molecules is governed by Boltzman's expression. In the absence of field E, the number dN of the total number N (molecules per unit volume) P_o lies in the solid angle the $d\Omega$ and is proportional to this angle. Since all orientaions are possible, thus

$$dn = \frac{N}{4\pi} d\Omega \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.16)$$

In pressence of field, the number becomes

$$[N/4\pi]\exp(-W/KT)d\Omega, \quad W = - E_oP_o\cos\theta$$

$$- \frac{N}{4\pi}\exp\left(\frac{P_oE_o\cos\theta}{KT}\right)d\Omega$$

$$= \frac{N}{4\pi}(\exp U\cos\theta)d\Omega$$

Mean value of useful moment $\bar{P}$ is given by;

$$\bar{P} = \int \frac{N\exp(U\cos\theta)p_o\cos\theta d\Omega}{N\exp(\cos\theta)d\Omega} \quad \ldots\ldots (1.18)$$

But $d\Omega = 2\pi \sin\theta d\theta d\phi$, Hence

$$\bar{P} = P_o \frac{\int_0^{\pi} \exp(U\cos\theta)\cos\theta\sin\theta d\theta}{\int_0^{\pi} \exp(U\cos\theta)\sin\theta d\theta} \quad \ldots\ldots (1.19)$$

(This is langevin-Debye function)

When $P_oE_o << KT$, $\exp(U\cos\theta) = 1 + U\cos\theta$.

Then,

$$\bar{P} = P_oU/3$$

$$= P_o^2E_o/3KT, \quad \text{but, } \mu_o = P_o$$

$$= \mu^2{}_oE_o/3KT, \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.20)$$

where, $\mu_o = P_o$ is the dipole moment of the molecule.

From above equation (1.20) and (1.0) it can easily be shown through comparison of the two above equations that Orientation polarizability, α_{or}, is given by;

$$\alpha_{or} = \mu_o^2/3KT, \quad \ldots\ldots\ldots\ldots (1.21)$$

which is the Debye solution for orientation polarizability, α_{or}. Debye formula describes the dependency of the dielectric constant of polar dielectric not only on the distortion polarization of the molecule but also on the magnitude of the permanent dipole moment and its orientation in the electric field, thus Debye

formula is;

$$\bar{P} = [4/3][\ \pi N(\alpha_e + \alpha_a + \alpha_{or})]$$

$$= [4/3][\pi N(\alpha_e + \alpha_a + \mu^2_o/3KT],$$

where α_e, α_a, μ_o are the electronic, atomic polarizability and dipole moment respectively. Debye formula can be applied to polar gases at low pressure and extremely dilute solution of polar molecules.

1.3. Ionic polarizability (α_{io})

The component of total polarizability corresponding to ionic polarization (denoted by α_{io}) is fully presented all the way from zero frequency (static field) upto microwave.

However in the visible region the Ionic polarization drops to zero owing to the fact that at such high frequency of electric fields the ions suffer very little oscillatory displacements from their equilibrium positions due to the electric field. So, ultimately in the optical region we ignore this contribution.

CHAPTER 2

SCATTERING OF LIGHT

This thesis is mainly concerned with scattering of light by polar molecules, the optical anisotropy and dipole moment of the scattering molecules. So, at the outset we take up for general consideration certain concepts and establish some basic ideas concerning the scattering of light.

According to classical theory of electromagnetic radiation, electric and magnetic dipoles, quadrupoles and multipoles oscillating with a given frequency radiate electromagnetic radiation of that frequency. Light scattering phenomena may be given a classical explanation interms of e.m radiation produced by such entities induced in a scattering system by the electric and the magnetic fields of incident radiation.

When beam of light traverses a material medium(transparent) it's intensity is reduced partly by absorption and partly by scattering. The oscillating electric field of light traversing any real medium induces oscillating electric dipole moment in the particles composing it, provided the frequency of the induced oscillations is far from the natural frequency of the electrons. They inturn act as secondary sources of radiation, and scatter light of same frequency.

2.1. The induced dipole moment: Some general consideration [15].

For the majority of the systems, we need to consider only an induced electric dipole moment **P** which is related to the electric field **E** of the radiation by the power series

$$\mathbf{P} = \mathbf{P}^{(1)} + \mathbf{P}^{(2)} + \mathbf{P}^{(3)} + \ldots,$$

where

$$\mathbf{P}^{(1)} = \alpha.(\mathbf{E}) \qquad (2.1)$$

$$\mathbf{P}^{(2)} = \frac{1}{2}\beta.(\mathbf{EE}) \qquad (2.2)$$

and

$$\mathbf{P}^{(3)} = \frac{1}{2}\gamma.(\mathbf{EEE}) \qquad (2.3)$$

In these equations **P** and **E** are vectors with units of **Cm** and **Vm-1**, respectively, α, β, and γ, which relate **P** and **E**, are tensors. Since in general the direction of the induced dipole is not the same as that of the electric field producing it: i.e each component of $\mathbf{P}^{(1)}$ is a different linear combination of the components of **E**, each component of $\mathbf{P}^{(2)}$ is a different linear combination of **EE**, and so on. In classical picture, equations (2.1) to (2.3) are to be understood to imply that the tensors are <u>real and symmetric</u>. α is termed the polarizability tensor and is a second-rank tensor whose components have units of $Cv^{-1}m^{2}$; β is the hyperpolarizability tensor and is a third-rank tensor whose components have units $Cv^{-2}m4$; γ is termed the second hyperpolarizability tensor and is a fourth-rank tensor whose components have units of $Cv^{-3}m^{4}$. The polarizability α, β and γ can be regarded as measures of the ease with which electrons can be displaced to produce an electric dipole moment under the action of an electric field. The tensors α, β and γ can

be time-dependent, and hence the time dependence of the induced dipoles can be different from that of the electric field terms E, EE , etc.

Typical orders of magnitude for components of α, β, and γ, are as follows; α, $10^{-40}cv^{-1}m^{2}$; β, $10^{-50}cv^{-2}m^{3}$; and γ, $10^{-61}cv^{-1}m^{4}$. For such values ,if the contribution to the induced dipole from $P^{(2)}$ is to reach one percent of that from $P^{(1)}$ an electric field intensity of the order of $10^{9}vm^{-1}$ is required ; and electric field intensity must rise to about $10^{10}vm^{-1}$ for contribution from $P^{(3)}$ to be one percent of that from $P^{(1)}$ term.It will be recalled that , as far as electromagnetic radiation is concerned ,such electric field intensities are reached only in focused giant-pulse Laser beams. Since Rayleigh and Raman scattering are observed quite readily with very much lower electric field intensities, we may expect to be able to explain Rayleigh and Raman scattering interms of linear induced dipole moment $P^{(1)}$ only, and this will indeed prove to be the case.

The first order term $p^{(1)}$ will be found to have the correct frequency dependency for Raleigh and Raman scattering scattering. The second order term $P^{(2)}$ does not include any induced dipoles whose frequencies correspond to normal Rayleigh and Raman scattering, but it can give rise to non-linear Raman and Rayleigh scattering, termed hyper Raman and hyper Rayleigh scattering which have a different frequency dependence. Although the third order term $P^{(3)}$ include induced dipoles with the correct frequency dependency for Rayleigh and Raman scattering, the contributions

from such dipoles is quite negligible. $P^{(3)}$ also gives rise to yet another kind of non-linear Rayleigh and Raman scattering, known as second hyper Rayleigh and Raman scattering, which still have different frequency dependence.

This thesis will be devoted to normal Rayleigh scattering arising from linear induced dipoles. So, for majority of the systems including the polar molecules considered by us the linear induced dipoles is described by the equation of the form,

$$\vec{P} = \alpha.\vec{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.3)$$

2.2. Types of scattering

2.2.1 Scattering by free electrons

Free electrons form the simplest type of scatterers. When photon energy ,$h\nu$, is sufficiently small (much smaller than the electron rest energy $m_o c^2$) the only scattering process that can occur for this scatterer is elastic scattering, giving changes in the direction but not in the frequency of the scattered photons. The physical mechanisms and cross-section for this scattering process is called **Thomson scattering**, in this case $h\nu$ (ν being the incident frequency) $<< m_o c^2$. This model gives the scattering cross-section as a function of photon energy and angle of scattering. At higher energies, i.e when $h\nu << m^o c^2$, the scattering is usually called **Compton scattering** [10,12]. This model leads to change in energy of the scattered photon. Let us now take up an elaborate discussion of the two models.

2.2.2. Thomson scattering

If we treat the radiation passing through a medium of free electrons classically and express the electric field as

$$\vec{E} = \hat{i}_x E_o \cos(\omega t - kz) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.4)$$

we see that an electron with Z-coordinates Z_o, mass m_o and charge, -e has the equation of motion:

$$m_o(d^2x/dt^2) = -eE_o\cos(\omega t - kz_o), \quad \ldots\ldots\ldots\ldots (2.5)$$

In the absence of any damping forces, the solution of the above equation is

$$x = x_o\cos(\omega t - kz_o) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

where

$$x_o = eE_o/m_o\omega^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.7)$$

The electron therefore acts as a Hertzian dipole, and it re-radiates at the same angular frequency ω, with a mean power given by Larmor formula [12].

$$\bar{P}_{rad} = \frac{e^2}{6\pi\varepsilon_o c^3}\left(\overline{\frac{d^2x}{dt^2}}\right) = \frac{e^4 E_o'^2}{12\pi\varepsilon_o m_o^2 c^3} \quad \ldots\ldots\ldots\ldots (2.8)$$

Where P_{rad} is the power radiated. This power can only come from the incident radiation, and so the intensity of the incident beam is reduced in passing through the medium. The net effect is therefore that some part of the incident radiation (initially travelling in the z direction) reappears as radiation of the same frequency, but travelling in a different direction. This type of scattering is called **Thomson scattering.**

For classical treatment of Thomson scattering to be valid, the length x_o of the oscillating dipole must be much smaller than the wavelength of the scattered radiation, otherwise the dipole will not be considered as a Hertzian dipole. The condition is [12],

$$x_o/\lambda = \frac{eE_o}{(m_o\omega^2\lambda)} << 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.9a)$$

The second condition is that the energy of the dipole must be much larger than the energy $h\nu$ of the photons that comprise the field, thus allowing us to treat the re-radiation as a continous process i.e

$$\frac{(1/2m_o(dx/dt)^2}{h\omega} = \frac{e^2E_o^2}{2m_oh\omega^2} \gg 1 \quad \ldots\ldots\ldots\ldots\ldots \quad (2.9b)$$

combining the two conditions (2.9a) and (2.9b), we find that

$2m_oh\omega^3 << e^2E_o^2 << (m_o\omega^2\lambda)$

or equivalently,

$$h\omega << \frac{e^2E_o^2}{2m_o\omega^2} << 2\pi^2m_oc^2$$

hence the second condition,

$$h\omega << m_o^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.10)$$

Thomson scattered light is commonly seen by naked eyes during a total eclipse of the sun . Light from the sun reaches the earth after being Thomson scattered by electrons in the sun's corona then appear's as a bright ring surrounding the eclipsed sun.

2.2.3 Compton scattering

If the condition (2.10) is not satisfied, then it is more appropriate to consider scattering process in terms of individual photon-electron collisions. This represents an extreme example of inelastic scattering of light, in which scattering of X-rays by electrons is considered. The electrons and the scattered X-ray are observed at various angles of scattering, say θ and ϕ respectively with reference to incident light. The dependence of the wavelength difference on the angle θ is given by **Compton formula of scattering** (see for example "Optics " by Moller .K .D [10])

$$\lambda_2 - \lambda_1 = h/mc(1-\cos\theta) \quad \ldots\ldots\ldots\ldots \quad (2.11)$$

where m is the mass of the scatterer λ_1, and λ_2' are the initial and final wavelengths of the photon respectively. The quantity

$$\lambda_c = h/moc = 2.426 \times 10^{-12} m$$

is known as Compton wavelength of the electron. Compton in his many experiments managed to show that energy and momentum are conserved in a photon_electron scattering process, so giving the correct interpretation for the scattered X-rays of increased wavelength.

2.2.4 Brilloun Scattering.

The scattering of light by the acoustical modes is called **Brilloun scattering.** In this scattering process, the incident wave in the crystal may take away energy from the incident light, lowering the frequency of the scattered light. But also the wave in the crystal may add energy to the light, raising the frequency

of the scattered light. Using the phonon picture we can say that a phonon is 'created' by the incident light and that the scattered light has a smaller frequency. The reverse process is "annihilation" of a phonon and results in a higher frequency of the scattered light. The process can be explained by the equation

$$h\nu = h\nu' + h\Omega,$$

which describes conservation of energy. The primed quantity belong to scattered light. Ω being equal to $(\omega - \omega')$, which describes the angular frequency of the modes [12].

2.2.5. Scattering in gases and liquids

When the scattering occurs and the internal energy of the atom or molecule is not altered the process is called **Rayleigh scattering.** In this case the atom is not exited from it's equilibrium position, also the frequency of the scattered light is unaltered and hence is the same as that of the incident radiation.
Rayleigh scattering being the central point of our discussion, an elaborate discussion of the same will be presented in the next sub-section.

The scattering and absorption of the photons by the atoms and molecules of the transparent medium also results in a very tiny proportion of the molecules interacting inelastically with the incident photon and as a consequence the vibrational, rotational, and in some cases even the electronic energy of the molecule increasing or decreasing resulting in the scattered light with

change in frequency which is the well known **Raman scattering.** As we are not concerned with this type of scattering in our thesis we would only give a brief account of the same in this subsection. Raman scattering results from a change due to incident light in the vibrational, rotational, and electronic state of the molecule. Now polarization P induced in a molecule by an electric field as already seen (2.4), is given by

$\vec{P} = \alpha\vec{E}$

Here α is the elastic polarizability of the molecule.

In the case of isotropic molecules P is proportional to E, and are along the same direction. Hence α is the scalar. However most of the molecules being generally anisotropic, α is a tensor referred to as polarizability tensor. α being a symmetric tensor it has a maximum of six distinct components all of which are real.

Since the rotational and vibrational motions continuously change the electronic distribution of the molecule, it is likely that the polarizability α as a whole or one of it's components undergo a change during vibration.

Polarizability α can be written as a series [23]:

$$\alpha = \alpha_e + (d\alpha/dQ)_e Q + 1/2(d^2\alpha/dQ)_e Q^2 + - -, \quad \ldots\ldots\ldots \quad (2.12)$$

where α_e is the polarizability of the molecule in it's equilibrium position, and $Q = (r - r_e)$ where r is the internuclear distance at a given instant (r_e being the equilibrium nuclear distance). If the molecule is vibrating with frequency ν_e then Q itself must be a function of time. We write

$$Q = Q_e \sin 2\pi\nu_e t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.13)$$

Neglecting all but the 1st two terms in (2.12) , We have,

$$\alpha = \alpha_e + (d\alpha/dQ)_o Q_o \sin 2\pi \nu_o t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.14)$$

Assuming that the molecule is subjected to an oscillating electric field E as already mentioned of the type

$$E = E_o \sin 2\pi \nu_o t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.15)$$

The induced dipole moment $\vec{P}$ takes the form

$$\vec{P} = \alpha_o E_o \sin(2\pi \nu_o t) + 1/2 (d\alpha/dQ)_o Q_o E_o [\cos 2\pi(\nu - \nu_o)t - \cos 2\pi(\nu + \nu_o)]$$

The above equation contains three frequencies, ν, $\nu - \nu_o$, $\nu + \nu_o$. If we regard the time varying dipole $\vec{P}$ as a Hertzian dipole, we see that it emmits radiation at the three frequencies. The overall effect is that the incident radiation is scattered both elastically (i,e scattered radiation has a frequency $\nu_s = \nu$,) and inelastically (i.e $\nu_s = \nu - \nu_o$, stokes scattering, or $\nu_s = \nu + \nu_s$, anti-stokes scattering, ν_s being the frequency of scattered radiation). However, our main interest is elastic scattering i.e **Rayleigh scattering**, in which frequency is essentially unchanged, (i.e $\nu_s = \nu$).

2.2.6. Rayleigh scattering.

Rayleigh scattering does not involve a change in the internal state of the molecule. Now, taking scattering in gases when mean free path r of the molecule is large compared with the wavelength of the light, scattering in this case takes place independently at each molecule. In this case each molecule acts as a seperate dipole radiating independently, and the total scattering intensity is proportional to the square of the vector sum of the amplitudes of the contribution of all the dipoles, this theory is called the

interference theory of light scattering. In this theory, each molecule acts as a scattering center, i.e radiating dipole, taking energy from the incident radiation and reradiating a spherical wave, the dipole moments reradiating are induced by the incoming light and they each reradiate a wave at slightly different times. These waves must travel slightly different paths relative to the observation point. As a result , they arrive at a given point, say p (point of observation) with different phase constants.

Considering the scattering from two particles, (**Fig.2.1**) the particles are seperated by the distance R_{12} and have the distance r_1 and r_2 from the point of observation p, which is located in the direction of the incident light [10].

Superposition of the two waves is described by equation

$$E_{scat} = Ae^{i(\omega t+\Phi 1)} + Ae^{i(\omega t+\Phi 2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.16)$$

Where E_{scat} is the scattered electric field. Hence intensity $I_{(o)}$ of the scattered beam is,

$$I(\theta) = |E_{scat}|^2 = 4A^2\cos^2[(\Phi_1-\Phi_2)/2]$$

$$= 2I'[1+\cos(\Phi_1-\Phi 2)] \quad \ldots\ldots\ldots\ldots \quad (1.17)$$

where I' is the single particle scattering intensity ($A^2 = I'$).

For interference effects ,the intensity I(o) can be larger than 2I' for certain values of $(\Phi_1-\Phi_2)$. If the collection of the two particles varies in a random way, we obtain for $\cos(\Phi_1-\Phi_2)$ all possible values of between +1 and -1. Average of $\langle\cos(\Phi_1-\Phi_2)\rangle = 0$. For a collection of particles, the intensity depends on the angle θ, and is found to be

$$I_{(\theta)} = \tfrac{1}{2}I_0(1+\cos\theta) \quad \ldots\ldots\ldots\ldots \quad (1.19)$$

where Io is the forward scattered intensity (i.e for θ = 0).

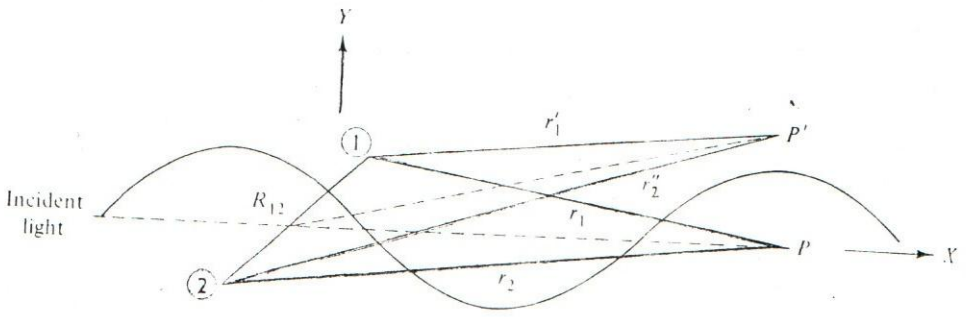


Fig.2.1: Scattering from two particles. The incident wave has a large wavelength compared to the diameter of the particles.

The particles are assumed to be randomly oriented and the dipoles illuminated by unpolarized light. When the particles have dimensions greater than wavelength of light in the medium of the incident light, the difference in phase between the scattering of the dipole in different parts of the particle becomes large enough for destructive inteference to occur, hence no scattering results. If molecules were all alike and were arranged in a lattice exactly, the resultant amplitude would vanish giving no scattreing, e.g in crystal cases. Observation of scattered light intensity are ussually as a function of angle θ of scattering relative to the incident beam [9,11].

2.3. Fluctuation theory of Rayleigh scattering

In this theory, the opposite of limiting case applies, i.e seperation between the dipoles is smaller than wavelength of the incident light, i.e $r << \lambda$, then Rayleigh scattering in gases assumes two parts, one due to the irrengularities in the orientation of the molecules (called fluctuation of anisotropy) The other part is scattering by fluctuation in the gas density (called isotropic scattering). The orientation of the molecules is entirely changed by a few collisions i.e after a time of the order of mean free path τ. Hence, the scattering by flunctuation of an isotropy results in the appearance of a relatively broad line with its peak at $\omega' = \omega$ and width $\sim h/\tau$. The scattering by flunctuation of density gives a much sharper line superimposed on the other.

The scattering by density fluctuation is scalar scattering since the density ρ is scalar, so is the change $\delta\varepsilon$ in the permitivity resulting from a change in ρ. The change in permitivity in fluctuations of anisotropy, on the other hand, is described by a symmetrical tensor $\delta\varepsilon_{ik}$ with zero trace. The latter property follows from the fact that the effect must vanish on averaging over all directions. Thus the scattering by anisotropy fluctuations is a symmetric scattering [11].

The polarizability of isotropic molecule is proportional to its volume and hence the total scattering is dependent on the of concentration of the particles and the square of their volume, thus exclusion of any large impurities in particular dust is therefore

essential for accurate measurement of the scattering from any system.

Rayleigh scattering in a liquid is due to thermodynamic fluctuations (of density or temperature) relaxation times, i.e scattering in liquids is considered to arise from purely statistical random fluctuations in the local concentration of the molecules in small elements of the volume. Liquids have a high degree of order hence scattering cannot be explained through inteference theory. Equally in crystals, there is no scattering of light due to destructive inteference of light radiated from one particle with that of the other.

According to Einstein, [11,12] the magnitude of these fluctuations is determined by the energy change involved, they can be calculated with the aid of the fluctuation theory explained and can be shown that the extinction coefficient h, derived by Rayleigh (1881) is given by

$$h = 2w^4(n-1)^2/3\pi c^4 N \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.20)$$

where N is the number of particles per unit volume.

Now, using equation below

$$h = \frac{(w)^4}{(16\pi c^4)} V\langle \delta\varepsilon_{ik}^2 \rangle_v \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.21)$$

where $\langle \ldots. \rangle_v$ denotes the mean square fluctuation in volume. ε_{ik} is the permitivity tensor. h is the extinction coefficient defined as the ratio of total intensity of light scattered in all direction per unit volume of he scattering medium to the incident light flux

density. Substituting $\delta\varepsilon_{ik} = \delta\xi\delta_{ik}$ in (2.21) gives

$$h = [\omega^4/16\pi c^4]V\langle\delta\xi^2\rangle \quad \ldots\ldots\ldots\ldots\ldots \quad (2.22)$$

If $\delta\rho$ and δT are the density and temperature respectively, then

$$\delta\xi = (\partial\xi/\partial\rho)_s\delta\rho + (\partial\xi/\partial T)_\rho\delta T \quad \ldots\ldots\ldots\ldots \quad (2.23)$$

According to known results, the fluctuation of density and temperature are statistically independent (i.e $\langle\delta\rho\delta T\rangle = o$), and their mean squares are;

$$\langle(\delta T)^2\rangle_v = T^2/\rho c_v V, \qquad \langle(\delta\rho)^2\rangle_v = (\rho T/V)(\partial\rho/\partial p)_T$$

where c_v is the specific heat per unit mass. Thus we have,

$$h = \frac{\omega^4}{16\pi c^4}\left[\rho T(\partial\rho/\partial p)_T(\partial\varepsilon/\partial\rho)_T + \frac{T^2}{\rho C_v}(\partial\varepsilon/\partial T)_\rho^2\right] \quad \ldots\ldots (2.25$$

a formula first derived by **A.EINSTEIN (1910)**

This can be expressed in terms of other thermodynamic derivetives. Taking as indepedent variables another pair of statistically indepedent quantities, the pressure **p** and the entropy **s** per unit mass, we write

$$\delta\xi = (\partial\xi/\partial p)_s\delta p + (\partial\xi/\partial s)_p\delta s \quad \ldots\ldots\ldots\ldots \quad (2.25)$$

and use the familiar expressions for the fluctuatons i.e $\langle(\delta s)^2\rangle_v = c_p/\rho V$, $\langle(\delta P)^2\rangle_v = \rho TU^2/V$,

where U is the adiabatic velocity of sound in the medium, also writing, $U^2 = \partial p/\partial s$, With further substitutions,

$$(\partial\xi/\partial s)_p = (\partial\xi/\partial T)_p(\partial T/\partial s)_p = T/C_p(\partial\xi/\partial T)_p \quad \ldots\ldots\ldots \quad (2.27)$$

$$(\partial\xi/\partial p)_s = (\partial\xi/\partial\rho)_s\frac{1}{U^2}$$

We obtain Einsteins formula in the form

$$h = \frac{\omega^4}{16\pi c^4}\left[\frac{T^2(\partial\varepsilon/\partial T)_\rho^2}{\rho c_p}\right] + \frac{\rho T}{U^2}(\partial\varepsilon/\partial\rho)_s \quad \ldots\ldots\ldots\ldots (2.28)$$

For gases, formula (2.28) becomes much simpler, because the permitivity of a gas (at optical frequencies) is almost independent of temperature, an hence the first term in the brackets can be neglected. The density dependence is such that, ε-1, is proportional to ρ, and hence,

$$\rho(\partial\varepsilon/\partial\rho)_T \equiv \varepsilon - 1 \equiv 2(n^2-1), \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.29)$$

where $n = \sqrt{\varepsilon}$ is the refractive index of the material. But from the equation of state of a perpect gas, i.e $(1/\rho)(\partial\rho/\partial p)_T = 1/NT$, Where N is the number of particles in unit volume .We find that,

$$h = 2\omega^4(n^2-1)^2/3\pi c^4 N \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.30)$$

This formula was first derived by Rayleigh (1881) [11]. The formula derived enables us to consider scattering macroscopically as occuring at fluctuational inhomogenities in the medium. Now since all scattering phenomena is based on the fact that light consists of e.m.waves or short oscillating electric dipole forces which induces dipole moments in the molecules, which inturn reradiates light as scattered light. Of interest is the scattered intensity of the emitted light as a function of the various angles the dipole makes with the direction of the emission. The intensity distribution of a vibrating dipole is represented as

$$I = constant\ \frac{P^2}{\lambda^4}\cos^2\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.31)$$

Where P is the dipole moment; and θ is the angle between the direction of emitted (scattered) light and incident light. λ is the wavelength of the incident beam.

Emitted light from the dipole is polarized in the plane containing the axis of the dipole. In the case where light is not polarized (e.g light from the sun), the induced dipoles are in all directions of propagation.

The expression (2.31) for intensity, explains why the sky appears blue. This is well explained by the inverse fourth power of the wavelength (λ), reffered as Rayleigh law of scattering. It applies for example to the scattering of visible light by the earths atmosphere, since the relevant frequencies of Nitrogen (N_2) and Oxygen (O_2) molecules lie in the ultra-violet region. Blue light has a wavelength approximately half that of Red light and therefore scattering cross_section is approximately 16-times that of red light, causing the sky to appear blue. The sky becomes more and more violet (and also darker) as the observer's height increases, because the only shortest wavelength visible photons have a high enough probability of being scattered towards the observer [10].

2.4. Intensity calculations in Rayleigh scattering

Now considering induced dipole moment P in a molecule by an electric field E of light wave plane polarized in the **xz** plane, then this linear induced dipole moment will be given by relation [3,9],

$$\vec{P} = \alpha.\vec{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.32)$$

where P is the linear induced dipole vector at some time t, α is the time dependent polarizability tensor defined also as [14],

$$\alpha = \alpha_o + Q_k \cos(\omega_k t + \delta_k) \quad \ldots\ldots\ldots\ldots\ldots \quad (2.33)$$

where Q_k is the normal coordinate amplitude, and $\vec{E}$ is the electric field vector at time t. Variation of electric field intensity with time is given by

$$\vec{E} = E_o \cos(2\pi c/\lambda)t \quad \ldots\ldots\ldots\ldots\ldots \quad (2.34)$$

where λ is the wavelength of the light in the medium, c is the velocity of light. Then equation (2.34) can be rewritten as

$$\vec{P} = \alpha\vec{E} = \alpha E_o \cos(2\pi c/\lambda)t \quad \ldots\ldots\ldots\ldots \quad (2.35)$$

The oscillating dipole will then reradiate secondary waves without frequency change, say at an angle θ to the direction of the incident wave-front, Fig.2.2. The amplitude of the secondary wave will depend on the amplitude of the induced moment, $1/c(d\alpha/dt)$, projected perpendicular to the directin of the op in the pz plane and inversily as the distance of the point of observation r_s, provided r_s is much greater than wavelength λ, i.e $r_s >> \lambda$

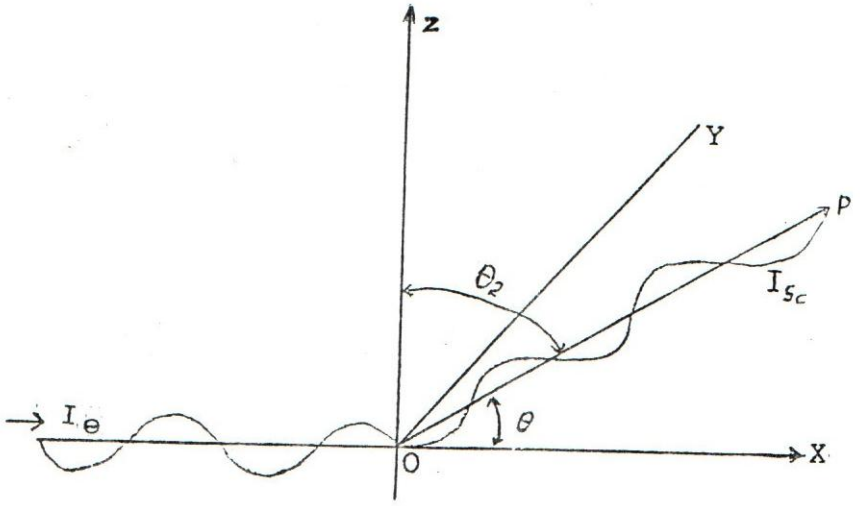


Fig.2.2. Oscillating dipole, radiating secondary waves without frequency change.

Then, reradiated seconary wave will be

$$E_{scat} = \frac{\alpha E_0}{r_s}\left(\frac{2\pi}{\lambda}\right)^2 \sin\theta_E = \frac{4\pi^2\nu^2 E_0 \alpha}{r_s c^2}\sin\theta \qquad (2.16)$$

Since intensity I is proportional to the square of the amplitude of the reradiated secondary wave, the intensity of the scattered radiation I_s is given by,

$$I_s = \frac{16\pi^4\alpha^2 E_0^2}{\lambda^4 r_s^2}\sin^2\theta \qquad (2.17)$$

Now since the power of the scattered intensity from a freely rotating induced dipole will be determined by space_averaged value of the square of the induced dipole, we shall require the average of the squares of the tensor components over all the orientations of the system fixed axes relative to a set of space_fixed axes which we shall here denote by x, y ,and z, hence one can define in molecule a coordinate system O X'Y'Z' of principle axes along which P is parallel to E and one has,

$P_x = \alpha_x E_x$, $P_y = \alpha_y E_y$, $P_z = \alpha_z E_z$. where α_x, α_y, α_z are principal polarizabilities of the molecule outside the principal direction, and the vectors E and P do not coincide and the molecule is optically anisotropic, Fig.(2.3) [6].

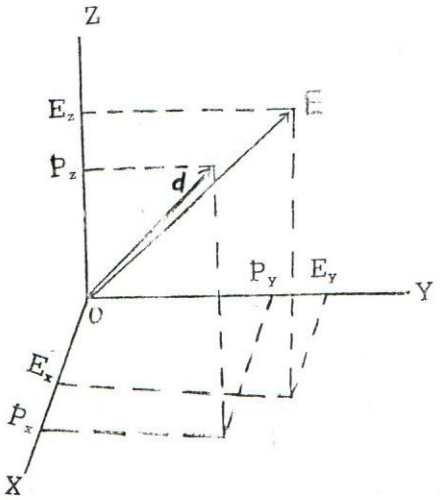


Fig.2.3: Optically anisotropic molecule.

When E takes on all possible directions in OX'Y'Z' system its tip describes a sphere, the tip of P describes an ellipsoid with the axes OX, OY, and OZ called the polarizability ellipsoid of the molecule.

Molecules which do not have a symmetry axis greater than two (e.g H_2O, SO_2) have a polarizability ellipsoid with 3-unequal axes (i.e $\alpha_x \neq \alpha_y \neq \alpha_z$). Molecules which have an axis of order at least equal to three (e.g $POCL_3$) have an ellipsoid of revolution about its axis ($\alpha_x = \alpha_y = \alpha_z$). Monoatomic molecules (e.g inert gas) or those with several axes of order three (e.g CCL_4, SF_6) have a polarizability sphere and these are optically isotropic

($\alpha_x = \alpha_y = \alpha_z$).

The mean polarizability of these symmetric optically isotropic molecules is (see G.Placzek, [16] also D.A long [15]) given by,

$$\alpha = 1/3[\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2.38)$$

where a is the mean polarizability.

On the other hand, optical anistrophy δ is defined by

$$\delta^2 = 1/2\{(a_{xx}-a_{yy})^2+(a_{yz}-a_{zz})^2+(a_{zz}-a^{xx})^2+6(a_{xy}+a^2_{yz}+a^2_{zz})\}$$

The invariance of these combinations under rotation may be established using the equation below and the properties of direction consines.

$$a_{xy} = \Sigma a_{x'y'} \cos(xx')\cos(yy') \quad \ldots\ldots\ldots\ldots\ldots \quad (2.39)$$

where direction Cosines, Cos(xx'), are the cosines of angle between axis **x** and **x'** axis etc, in which x',y',z' is another cartesian system (Fig.2.4)

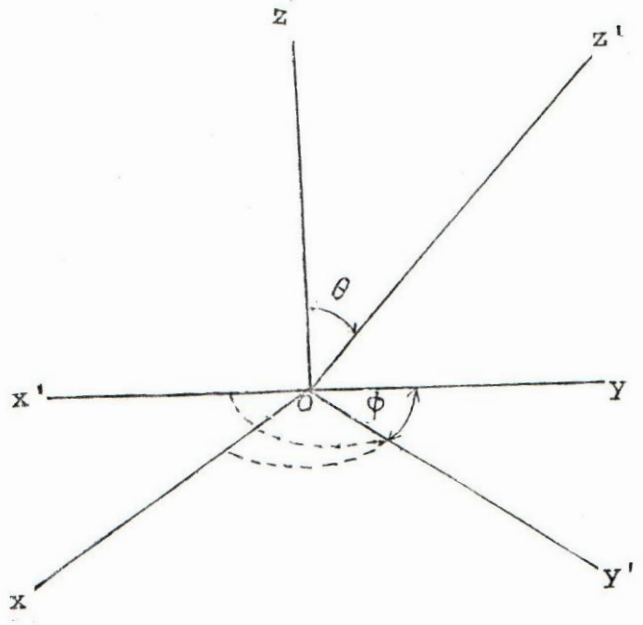


Fig.2.4: Cartesian cordinates.

Now, if two of the principal values of polarizability are equal, i.e $\alpha_{yy} = \alpha_{zz}$, then we have

$$|\delta| = |\alpha_{zz} - \alpha_{yy}| \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.40)$$

and if all three values are equal then

$$\delta = 0$$

Hence these enables us to see that, δ as its name is indeed a measure of the anisotropy of polarizability. The invariant α is clearly a measure of the average polarizability.

Now using equation (2.40) and average of the squares of the tensor components over all orientations of the system-axis, we find that,

$$\bar{\alpha}^2_{yx} = \bar{\alpha}^2_{yy} = \bar{\alpha}^2_{zz} = \frac{45\alpha^2 + 4\delta^2}{45} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.41)$$

$$\bar{\alpha}^2_{yx} = \bar{\alpha}^2_{yz} = \bar{\alpha}^2_{zx} = \frac{\delta^2}{15} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.42)$$

$$\overline{\alpha_{xx}\alpha_{yy}} = \overline{\alpha_{yy}\alpha_{zz}} = \overline{\alpha_{zz}\alpha_{xx}} = \frac{45\alpha^2 - 2\delta^2}{45} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.43)$$

Now, given defination above, one can find depolarozation factor for a perfect gas of anisotropic factor for a perfect gas of anisotropic molecules [14].

Let oxyz be the laboratory co-ordinates system and O'X'Y'Z' the principal axis system of the molecule. With incident light linearly polarized along OZ the components of the E - field along the molecular axes are

$E_x = E\sin\theta$, $E_y = 0$, $E_z = E\cos\theta$,

and the components of the induced moments are

$P_x = \alpha_x E\sin\theta$, $Py = 0$, $P_z = \alpha_z E\cos\theta$.

In the oy direction, the scattering is due to the P_x and P_z components. Therefore,

$$P_x = P_x(\cos(Xox) + P_z\cos(Zox)$$

$$=[-\alpha_x\sin\theta\cos\theta\cos\Phi + {}_z\cos\theta\sin\theta\cos\Phi]E \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.44)$$

$$P_z = P_x \cos(Xoz) + P_z \cos(Zoz)$$

$$= [\alpha_x\sin^2\theta + \alpha_z\cos^2\theta]E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.45)$$

The above equations can be rewritten as,

$$P_x = \delta\sin\theta\cos\theta\cos\Phi E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.46)$$

$$P_z = [(\alpha_z - \alpha_x)\cos^2\theta - \alpha_x]E$$

$$=[\ \alpha + \delta(\cos^2\theta - 1/3)]E \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.47)$$

Then, taking (2.39) and (2.40) into account,

$$\alpha_x = \alpha - \frac{(\alpha_z - \alpha_x)}{3} = \alpha - \frac{\delta}{3} \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.48).$$

The intensity I_z is proposional to NP^2_z, i.e

$$I_z \propto NP_z^2,$$

N being the number of molecules per unit volume and P_z^2 the mean-square of the projection of the molecular moment on oz.

Similarly, on ox projection,

$$I_x \propto NP_x^2$$

Because of torsional nature of α, then θ is made to vary from 0 to $\pi/2$

$$\bar{P}_z^2 = \frac{\int P_z^2 dN}{\int dN} = (\alpha + 4\delta^2/45)E^2 \quad \ldots\ldots (2.49$$

$$\bar{P}_x^2 = \frac{\int_0^{\pi/2} \delta^2 \cos^2\theta E^2 . N \sin\theta d\theta \int_0^{2\pi} \cos^2\phi d\phi}{\int_0^{\pi/2} N \sin\theta d\theta \int_0^{2\pi} d\phi} \quad \ldots\ldots (2.50)$$

The integral in θ has the value

$$\frac{\cos^4\theta \sin^4\theta}{5} + \frac{1}{5}\left[-\frac{1}{3}\cos\theta(\sin^2\theta + 2)\right]_0^{2\pi} = \frac{2}{5}$$

Since mean value of $\cos^2\theta = 1/2$, then equation (1.50) becomes,

$$P_x^2 = \frac{\delta^2 E^2}{15} \quad \ldots\ldots (2.51)$$

Where P_x^2 is the mean square of the projection of the molecular moment on o.

2.5. Depolarization ratio

Information regarding symmetry of normal modes can often be obtained from Raman experiments if we can determine the degree of depolarization ρ_n, of the scattered light [20].

If a molecule is excited by unpolarized light, the scattering at

right angles to the incident light will be atleast partially polarized. The degree of polarization depends on the way in which the polarizability ellipsoid varies during the vibration. It is also possible, and infact more confinient, to excite molecules using polarized light, for example, polarized laser light. Fig.2.5 shows the incident and scattered radiation.

The incident light is along the x_axis, and the direction of observation is perpendicular to the x_axis in the yz plane. ρ_n is define as

$$\rho_n = \frac{I_y}{I_z} \qquad (2.52)$$

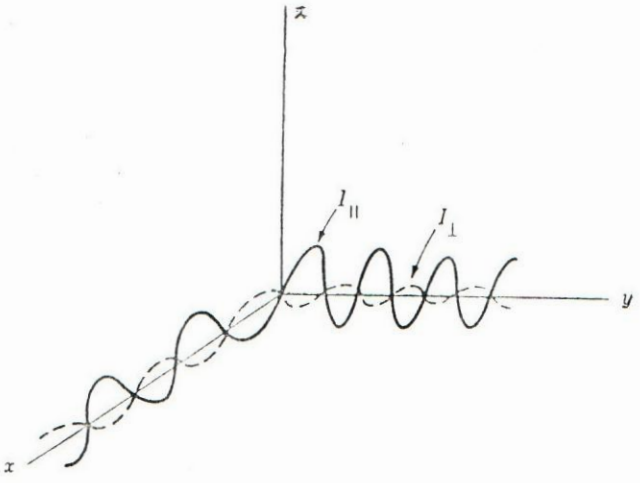


Fig.2.4. The parallel and perpendicular components of the scattered radiation. The incident radiation is along the x_axis and the molecule is situated at the origin.

where I_z is the intensity of the scattered light parallel to the xy plane and I_x is that parallel to zy plane. The maximum value of ρ_n is 6/7. A Raman line is characterized as polarized or depolarized according to the value of ρ. We have

$$\begin{aligned} \rho &= 0 - 6/7 \quad \text{polarized,} \\ &= 6/7 \qquad \text{depolarized.} \end{aligned}$$

Only totally symmetric vibration can yield polarized Raman lines. A reading of 6/7 is of course ambigous, but usually these lines can determine whether they are polarized.

Now we have [6],

$$P_x^2 = I_x, \quad \text{and} \quad P_z^2 = I_z \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.53)$$

Therefore,

$$\rho_p = \frac{(\delta^2 E^2)}{15} / (\alpha^2 + \frac{4\delta^2}{45}) E^2$$

$$= \frac{3\delta^2}{45\alpha^2 + 4\delta^2} \qquad \ldots\ldots\ldots\ldots (2.54)$$

where ρ_n is the depolarization factor for perpendicular case. This value is for $E=E_x$, where E_z is electric field parallel to xy plane.

For $E = E_y$, then OX, and OZ axes play the same role as OX for E_z, and P_z^2 and P_z^2 are equal and have their value given by,

$$P^2_x = P^2_z = \delta^2 E/15 \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2.55)$$

Therefore from equation (2.56) depolarization ratio ρ_{II}, is a unit i.e

$$\rho_{II} = 1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1.56)$$

If the incident light is natural (unpolarized), the scattered intensities excited by the incoherent vibrations E_z and E_y add, from

which the depolarization factor in natural light is,

$$\varrho_n = \frac{2I_x}{I_x+I_y} = \frac{6\delta^2}{45\alpha+7\delta^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.57)$$

Where ϱ_n is depolarization for natural light.

It can be seen that depolarization cannot be determined directly by measuring the ratio of scattered intensities $I_{\parallel}/I_{\perp}$ [15]. In order to determine the depolarization, the illumination is done along the z-axis using radiation plane polarized with $Ex \neq 0$, $E_y=E_z=0$, and total radiant intesity scattered along x-axis is given by

$$^{\parallel}I_{\perp(\pi/2)} + {}^{\parallel}I_{\parallel(\pi/2)}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.58a)$$

Secondly, illumunation is done along the x-axis, i.e

$$^{\perp}I_{\perp(\pi/2)} + {}^{\perp}I_{\parallel(\pi/2)}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.58b)$$

Then the ratio of equation (2.58a) to (2.58b) yields $\varrho_n(\pi/2)$(Rayleigh), defined by equation (1.57). The mean value of the equilibrium polarizability tensor α, can never be zero, since all the molecular systems are polarized to some extend; the anisotropy, δ will however be zero for isotropic systems. Thus for Rayleigh scattering, we have two cases, for

(i) isotropic case we have,

$$\alpha_s = \delta = 0,$$

Therefore, using equation (2.54), (2.56) and (2.57) we have,

$$\varrho_p = \frac{3\delta^2}{45\alpha^2+4\delta^2} = 0,$$

$$\varrho_n = \frac{6\delta^2}{45\alpha^2+7\delta^2} = 0,$$

Hence, $\varrho_n = \varrho_p = 0$. Also

$$\varrho_u = 1$$

And for anisotropic case, the derived polarized tensor can be zero i.e a =0, hence equations (2.58) and (2.61) becomes,

$$\varrho_n = \frac{6\delta^2}{7\delta^2} = \frac{6}{7},$$

$$\varrho_p = \frac{3\delta^2}{4\delta^2} = \frac{3}{4}$$

Since $\varrho_u(\pi/2)$ is always unity, it yields no useful information. Conventionally, a Rayleigh line is said to be polarized when $\varrho_p(\pi/2)=3/4$; or $\varrho_n=6/7$; polarized when $0<\varrho_p<3/4$ or $0<\varrho_n<6/7$; and completely polarized when $\varrho_p(\pi/2) =\varrho_n(\pi/2)=0$. Symmetry information obtained from such random oriented molecules is such that, it enables us to distinguish between those vibrations which preserve the equilibrium molecular symmetry (e.g $\varrho_p(\pi/2)<3/4$), and those which do not (e.g $\varrho_p(\pi/2) =3/4$).

In the above case, the formulae we have used for Rayleigh scattering in assembly of molecules have been derived on the assumption that all orientations are equally possible [14]. Strictly then, these equations apply only to gases at low pressure. Same formulas may ussually be applied to liquids, but in such systems the assumption of no preffered orientation may not always be correct.

2.6. Importance of Rayleigh scattering

In this subsection, the importance of scattering of light, in particular Rayleigh scattering will be outlined point by point. Light scattering is a widely utilized phenomena in our every day life. It is greatly used as a diagnostic tool for studying fundamental properties of polar materials such as dynamics of phase transitions in the materials.

Rayleigh ratio plays a very important role in determination of molecular weight of materials ranging from any simple particles (molecules) to colloids, e.g polymers etc. It's also a relative simpler method of determining the extensions in space of the polymer molecules from the angular distribution of the light. Light scatterring has been widely applied in variety of high polymer's substances which provided results which have greatly assisted in the understanding of the behaviour of long chain molecules in solution, e.g Glycogen, polysterene, e.t.c.

Also for larger molecules (e,g colloids etc) it can be used to distinguish between various possible models (shapes). It has further advantage in responding instantaneously to change in the shape and size of macromolecule and therefore be used to obtain kinetic data otherwise inaccessible. Also if the composition of sample is known, the number of molecules per unit volume can be found.

Further Rayleigh scattering could also be employed as an important tool for determining some thermodynamical parameters and the heterogeneity or othewise, of some samples.

Proteins, Viruses, Ovalliumin, Lactoglobulin, Polysterene, Starch, Amylopectin, Tobacco-mosaic virus are some of the substances investigated by studying Rayleigh scattering on them.
Also in display industry, light scattering is quite applicable, e.g in T.V's, Calculators ,Overhead projectors, etc.

It provides a rapid and unambigious way to show difference in behaviour of similar polymers, otherwise difficult to detect by other methods, like viscosity and osmotic pressure which are less consistent.

2.7. Application of Rayleigh scattering in liquid crystals

Rayleigh scattering theory has been employed to study the scattering of light in various phases of the liquid crystalline medium.

To give a specific example, Chatelain [1,2] has applied the same in the nematic phase of p-azoxyanisole (PAA). The intensity data thus obtained are analyzed by Subramhanyam et al [3] by modifying the theoretical expressions by an empirical form factor to represent the effect of the orientation correlation between neighbouring volume elements. From the analysis it emergies that the volume elements have a radius of about 800A. Also they could estimate the average value of $\cos^2\theta$, θ being the angle between the optic axis and the orientation direction in a volume element of the liquid crystal, which information goes a long way as this can lead to determination of orientational order parameter of liquid crystalline materials. Subramhanyam et al found the value of $\cos^2\theta$

to be equal to 0.508, where as the same calculated from the well established statistcal theory of orientational order by Chandrasekar et al [19] was 0.49.

Further Maier and Saupe [22] also used the Rayleigh scattering theory together with necessary corrections for the existence of the dispersion and repulsion forces between the long molecules of the nematic liquid crystals and were able to calculate the dipole moments and optical anisotropy for nematic liquid crystals.

CHAPTER 3

THEORETICAL CONSIDERATIONS

3.1. Theory part I: Rayleigh scattering in liquid crystalline p-azoxyanisole(PAA)

As mentioned in the preface the motivation for our study is the one of light scattering (Rayleigh scattering) by nematic liquid crystalline medium, hence a brief discussion of some of the salient features of this study is given in what follows.

The scattering of light in the nematic phase of p_azoxyanisole at 125°c was investigated by Chatelain [1,2] in detail, using plane polarized incident light with the electric vector lying (i) in the plane of scattering and (ii) perpendicular to it. In each case the scattered light was analyzed and intensities of the H and V components with the electric vectors normal to the plane of scattering were determined mainly over the range of angles of scattering from 8° to 50°. The intensities of the different components may be denoted here by H_H, V_H, V_V and H_V, the respective subscripts H and V being used to denote that the incident electric vector is in the plane of scattering or normal to it. In his studies Chatelain made use of oriented specimens corresponding to two cases, wherein the optic axis of the medium was lying (i) normal to the plane of scattering and (ii) in the plane of scattering. A striking angular anisotropy in the intensities of the scattered light, analogous to that encountered with colloidal

scattering was observed with regard to all the components. Further, at small angles it was observed that the intensity V_v was several times greater than H_v. Falgulrattes [3] who studied the intensity V_v for various angles of scattering in the case of nematic liquid parabutoxy-benzoic acid, found the intensity to be large at small angles.

A theory of scattering in nematic liquid crystals was proposed by Chatelain [4] on the basis of the following assumptions. The intensity of scattering due to fluctuations in orientation (anisotropic scattering) is large compared to that arising from density fluctuations so that the later part (isotropic scattering) may be neglected. The molecules are arranged with their long axes parallel to one another in the form of "baquets" bundles which are spherical volume elements whose size is small compared to the wavelength of light, and phase correlation exists between the scattered waves from the molecules with a volume element. The different volume elements in the medium have different orientations for their optic axes and the orientation distribution function is assumed to be of the form $e^{-\beta\theta^2}$, where θ is the angle between the orientation axis of a volume element and the optic axis of the medium. Also the values of θ are restricted so that $0 \leq \theta \leq \theta_0$. Besides, Chatelain has also considered the case when the molecules may not form "paquets" but have an orientation distribution given by $e^{-\beta\theta^2}$. The results of the theory proposed by him gave the right order of magnitude for the depolarisation factor at small angles. However, detailed comparison of the intensities of the scattering

for different angles, from the stand points of theory and experiment have not been made.

Chatelain has dealt with only the case corresponding to the optic axis of the medium lying normal to the plane of scattering. Later Subramhanyam et al [5] theoretically considered on the basis of an approach similar to his, but without using any specific distribution function, three cases of interest viz, where the optic axis of the medium lies (i) normal to the plane of scattering, (ii) along the direction of the incident light and (iii) in the plane of scattering and in a direction perpendicular to that of the incident light. An analysis of intensity data of Chatelain was also carried out by them with the aid of the results of the theory, and in conjunction with a simple empirical relation to represent some of the effects which is not possible to treat theoretically. From their analysis of Chatelains intensity data Subramhanyam et al have shown that the volume elements in the nematic PAA have a volume of about 800Å. They were also successful in calculating the average value of $\cos^4\theta$ to a considerable accuracy, θ being the angle between the optic axis of the nematic medium and the orientation of the nematic liquid crystal.

Again, as already mentioned in the preface, scattering of polar molecules which are oriented in external electric field is analogous in some respects to a nematic liquid crystal. In our theoretical investigation therefore we are guided by some concepts employed by Chatelain et al [1,2] and Subramhanyam et al [5], even though our procedure to obtain expressions for scattered

intensities and depolarization ratio are very different. We now proceed to give an elaborate discussion of our original contribution.

3.2. Part 2, Theoretical considerations

The phenomena of light scattering is associated with the oscillating electric moment (induced by an incident light field) in the molecule of the medium. In particular, in the case of fluids, the scattered light can be regarded as made up of two components corresponding to (i) isotropic scattering arising due to the density fluctuations (ii) anisotropic scattering arising due to the fluctuations in the orientation of the optically anisotropic molecules. The induced electric moments P_x, P_y, P_z due to incident light wave of electric vector components E_x, E_y, E_z are given by terms of type

$P = \Sigma_y \alpha_{xy} E_y$, where the α's are the elements of the polarizability tensor and x, y, z are the space fixed cartesian axes. If we take x', y', z' as the principal axes of the polarizability ellipsoid of the molecule (capable of rotation), then the induced moments are expressible by the relation, viz.,

$$P_{x'} = AE_{x'}, \quad P_{y'} = BE_{y'}, \quad P_{z'} = CE_{z'}$$

Here, A, B, and C are the principal polarizabilities of the molecule, $E_{x'}$, $E_{y'}$ and $E_{z'}$ are the components of the incident electric vector along the three principal axes.

Here, the molecules under consideration are assumed to posses an axis of rotational symmetry such that their polarizability

ellipsoid cuts the surface of the sphere of unit radius drawn, with O the origin of coordinate systems as centre at X', Y', and Z' as shown in Fig.1. For a particular position θ, ϕ of the molecule, the direction cosines of the angle between the different axes are given by the following well known expressions [8] given in Table 3.1 below:

TABLE 3.1: Direction cosines.

	X	Y	Z
X'	$\cos\theta\cos\phi$	$\cos\theta\sin\phi$	$-\sin\theta$
Y'	$-\sin\phi$	$\cos\phi$	0
Z'	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$

The intensities of the scattered light are discussed here for three cases, viz., (i) applied electric field perpendicular to the scattering plane, (ii) applied electric field along the direction of the incident light and, (iii) applied electric field perpendicular to incident direction and in the scattering plane. The intensities of the different horizontal and vertical components are denoted here by H_H, V_H, V_V and H_V the respective subscripts H or V being used to denote that the incident electric vector is in the horizontal plane of scattering or normal to the plane of scattering. Here V_V and H_H for a general angle of scattering arise due to (i) the average polarizability of the molecule and (ii) its

optical anisotropy. On the other hand, H_v and V_H arise entirely due to its optical anisotropy. In order to calculate V_V, H_H, V_H, and H_v, in all the cases, it is necessary at the outset to calculate the corresponding induced,

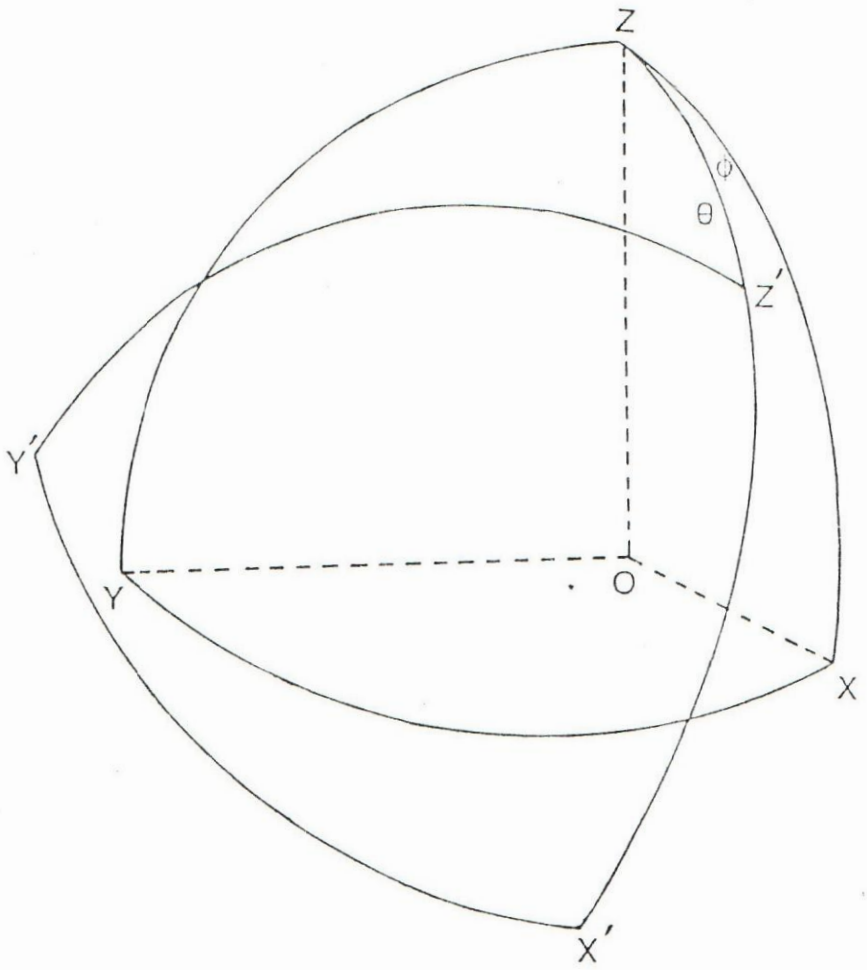


Fig.3.1: Sphere of Unit radius

dipole moment and hence the average of its squares as discussed in the following.

If $\hat{a}_m$ denotes the unit vector along the principal axis Z' (corresponding to the polarizability C) of the m^{th} molecule, the induced moment of the m^{th} molecule can be shown to be given be given by

$$\vec{P}_m=(\vec{E}.\hat{a}_m)(C-A)\hat{a}_m+A\vec{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

where E is the applied electric field due to the incident light. Now if $\hat{a}_m$ is along z', Fig.3.2,. Equation (3.1) is derived as follows.

In general, $\hat{a}_m = \hat{i}\sin\theta\cos\phi + \hat{j}\sin\theta\sin\phi + \hat{k}\cos\theta$

Hence, $\hat{a}_m . \hat{k} = \cos\theta$, but dipole moment $\vec{P}$ is given by the relation,

$$\vec{P}_m = \alpha . \vec{E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

$$\vec{P}_m = (\vec{P}.\hat{a}_m)\hat{a}_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

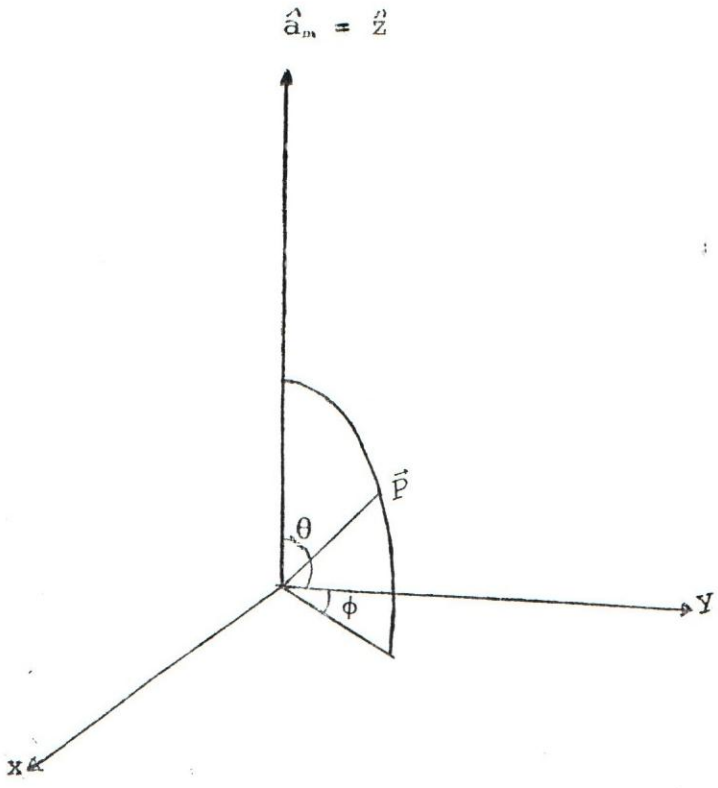


Fig.3.2:

$$\begin{pmatrix} p_{x'} \\ p_{y'} \\ p_{z'} \end{pmatrix} = \begin{pmatrix} A & 0 & 0 \\ 0 & C & 0 \\ 0 & 0 & C \end{pmatrix} \begin{pmatrix} E_{x'} \\ E_{y'} \\ E_{z'} \end{pmatrix}$$

Thus from the above matrix,

$$\vec{P} = p_{x'}\hat{x}' + p_{y'}\hat{y}' + p_{z'}\hat{z}'$$

$$= (AE_{x'})\hat{x}' + (CE_{y'})\hat{y}' + (CE_{z'})\hat{z}' \quad \ldots\ldots\ldots\ldots$$

On assuming B = C.

Since we are considering a_m along z' axis, then the above equation (3.4) becomes,

$$\vec{P} \cdot \hat{a}_m = CE_{z'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5a)$$

Hence, from (3.2)

$$\vec{P}_m = (CE_{z'})\hat{a}_m = [C(\vec{E}.\hat{a}_m)]$$
$$= [(C-A+A)(\hat{a}_m.\vec{E})]\hat{a}_m$$
$$= (\vec{E}.\hat{a}_m)(C-A)\hat{a}_m + A\vec{E}) \quad \ldots\ldots\ldots\ldots \quad (3.5b)$$

Which is the derivation of equation (3.1). If $\vec{E}$ is represented by $E_o\hat{b}$, where $\hat{b}$ is the unit vector along $\vec{E}$, the resolved component of P_m along the vibration direction of the scattered light, the vector unit along which is represented by $\hat{o}$ (expressible in terms of the unit vectors $\hat{i}$, $\hat{j}$, $\hat{k}$, along x, y, and z axes, and the angle of scattering θ_s), is therefore

$$\vec{P}_m.\hat{o} = E_o[\delta(\hat{a}_m.\hat{b})(\hat{a}_m.\hat{o}) + A(\hat{b}.\hat{o})] \quad \ldots\ldots\ldots\ldots (3.6)$$

Here we have written δ for the optical anisotropy (C-A). We further have

$$\overline{(\vec{P}_m.\hat{o})^2} = E_o^2[\delta^2\overline{(\hat{a}_m.\hat{b})^2(\hat{a}_m.\hat{o})} + A^2\overline{(\hat{b}.\hat{o})^2}$$
$$+ 2A(C-A)\overline{(\hat{a}_m.\hat{b})(\hat{a}_m.\hat{o})(\hat{b}.\hat{o})}] \quad . \quad . \quad . \quad (3.7)$$

$A(C - A)$ in the above equation (3.7) can be substituted by $\delta(\alpha - 1/3\delta)$, where $\alpha = (C + 2A)/3$ is the mean polarizability of the molecule. The general expression for the components of the fractional intensity of the scattered light per unit volume in the case of a gas at low pressure wherein the scattering centres are assumed to be independent is given by [6,7]

$$\left(\frac{4\Pi^2}{r\lambda^2}\right)^2 E_o^2 N_g \frac{\int_0^{\pi}\int_0^{2\pi} \frac{1}{E_o^2}(P_m.\hat{o})^2 f(\theta)\sin\theta d\theta d\phi}{\int_0^{\pi}\int_0^{2\pi} f(\theta)\sin\theta d\theta d\phi} \quad \ldots\ldots(3.8)$$

Here, N_g is the number of molecules per unit volume of the gas; r is the distance between the point of observation and the scattering centre and λ is the wavelength of light. $f(\theta)$ in equation (3.5) is given by

$$f(\theta) = \exp(-U/KT) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3.9)$$

U in equation (3.9) is the potential energy of the molecule at θ, ϕ in the external electric field E_c. If we assume that the molecule possesses a permanent electric dipole moment μ° along the Z'-axis (axis of polarizability C), the potential energy of the molecule in the static electric field consists of the energies due to the permanent and induced moments and is given by (see for example, "Light scattering" by Bhagavantam [8]).

$$U = [-\mu_o E_c \cos ZZ' - \frac{1}{2}(\bar{A}(E_c\cos ZX')^2 + \bar{B}(E_c\cos ZY')^2 + \bar{C}(E_c\cos ZZ')^2] \quad \ldots\ldots(3.10)$$

Here E_c is the applied electric field the direction of which is chosen as the Z axis. $\bar{A}$, $\bar{B}$, and $\bar{C}$ are the principal electric moments induced in the molecule by unit external static electric field acting respectively along X', Y', and Z'.We assume here, $\bar{A} = \bar{B}$. Writing $\bar{A}E_c^2/2KT = b_1$, $\bar{B}E_c^2/2KT = b_2$ and $\bar{C}E_c^2/2KT = b_3$ and substituting the values of cos(ZX'), cos(ZY')..etc from Table 3.1 and also assuming that the quantity;

$[b_1\cos^2 zx' + b_2\cos^2 zy' + b_3\cos^2 zz']$ is small enough to allow the approximation $e^x = 1 + x$, $f(\theta)$ in equation (3.9) may be expressed as, $f(\theta) = [\exp(\mu_o E_c \cos\theta/KT](1 + b_1\sin^2\theta + b_3\cos^2\theta)$

$$= [\exp(a\cos\theta)](1 + b_1\sin^2\theta + b_3\cos^2\theta), \quad . \quad (3.11)$$

On using this value of $f(\theta)$ and evaluating the denominator in (3.8), taking $a = \mu_o E_c/kT$. Then,

$$\int_0^{\pi}\int_0^{2\pi} e^{a\cos\theta}[1 + b_1\sin^2\theta + b_3\cos^2\theta]\sin\theta d\theta d\phi$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} e^{a\cos\theta}[1 + b_1\sin^2\theta + b_3\cos^2\theta]\sin\theta d\theta$$

$$= 2\pi[\int_0^{\pi} e^{a\cos\theta}(1 + b_1\sin^2\theta + b_3\cos^2\theta)\sin\theta d\theta]$$

$$= 2\pi[(\int_0^{\pi} e^{a\cos^2\theta}\sin\theta d\theta) + (b_1\int_0^{\pi} e^{a\cos\theta}\sin^3\theta d\theta)$$

$$+ (b_3\int_0^{\pi} e^{a\cos\theta}\cos^2\theta\sin\theta d\theta)]$$

$$= 2\pi[\frac{2\sinh a}{a} + \frac{2b_1\sinh a}{a}(\frac{2}{3} + \frac{2a^2}{45} + \frac{4a^2}{945} + \ldots)$$

$$+ \frac{2b_3\sinh a}{a}(\frac{2}{3} + \frac{2a^2}{45} - \frac{a^4}{945} + \ldots)]$$

$$= \frac{4\pi\sinh a}{a}[1 + \frac{(b_3+2b_1)}{3} + (\frac{2a^2}{45} - \frac{4a^2}{945})(b_3-b_1)] \ldots (3.12)$$

For purpose of calculation of the intensities here we neglect the terms involving a^2 and a^3 in (3.9). Hence the denominator integral

is approximated as equal to;

$$\frac{4\pi \sinh a}{a}[1+(b_3+2b_1)/3]$$

for all cases. Further, since $[b_3+2b_3]/3$ is small, we can write $[1+(b_3+b_1)/3]^{-1}$ as $[1-(b_3+b_1)/3]$, if necessary.

For the purpose of calculation of intensities in the various cases it is necessary to evaluate the numerator of (3.9) separately as the directions of $\hat{\mathbf{b}}$ and $\hat{\mathbf{o}}$ are different in various cases. The details regarding the directions of $\hat{\mathbf{b}}$ and $\hat{\mathbf{o}}$ for the various cases in terms of $\hat{\mathbf{i}}$, $\hat{\mathbf{j}}$, $\hat{\mathbf{k}}$ and θ are given in **Table 3.2.** By using the corresponding values of $\hat{\mathbf{b}}$ and $\hat{\mathbf{o}}$ from **Table 3.2,** it is found that the expressions for intensities in the various cases involve the averages

$$\overline{(\hat{a}_m\cdot\hat{k})^2},\quad \overline{(\hat{a}_m\cdot\hat{i})^2},\quad \overline{(\hat{a}_m\cdot\hat{k})^4},\quad \overline{(\hat{a}_m\cdot\hat{i})^4},$$
$$\overline{(\hat{a}_m\cdot\hat{i})^2(\hat{a}_m\cdot\hat{k})^2},\quad \overline{(\hat{a}_m\cdot\hat{i})^2(\hat{a}_m\cdot\hat{k})^2}$$

(the bar represents the average of the quantity, e.g

$$\chi = \frac{\int_0^{\pi}\int_0^{2\pi} \chi f(\theta)\sin\theta d\theta d\phi}{\int_0^{\pi}\int_0^{2\pi} f(\theta)\sin\theta d\theta d\phi} \quad)$$

TABLE 3.2: Directions of $\hat{b}$ and $\hat{o}$

Direction of the applied Static electric field, $\hat{k}$	Direction of incident light	Scattered component	$\hat{b}$	$\hat{o}$
Case I: Normal to the plane of scattering	$\hat{i}$	V_H	$\hat{j}$	$\hat{k}$
	$\hat{i}$	H_H	$\hat{j}$	$\hat{j}\cos\theta_s - \hat{i}\sin\theta_s$
	$\hat{i}$	V_V	$\hat{k}$	$\hat{k}$
	$\hat{i}$	H_V	$\hat{k}$	$\hat{j}\cos\theta_s - \hat{i}\sin\theta_s$
Case II: Along the direction of the incident light	$\hat{k}$	V_H	$\hat{j}$	$\hat{i}$
	$\hat{k}$	H_H	$\hat{j}$	$\hat{j}\cos\theta_s + \hat{k}\sin\theta_s$
	$\hat{k}$	V_V	$\hat{i}$	$\hat{i}$
	$\hat{k}$	H_V	$\hat{i}$	$\hat{j}\cos\theta_s + \hat{k}\sin\theta_s$
Case III: In the scattering plane and Perpendicular to the directionof incident light	$\hat{i}$	V_H	$\hat{k}$	$\hat{j}$
	$\hat{i}$	H_H	$\hat{k}$	$\hat{k}\cos\theta_s + \hat{i}\sin\theta_s$
	$\hat{i}$	V_V	$\hat{j}$	$\hat{j}$
	$\hat{i}$	H_V	$\hat{j}$	$\hat{k}\cos\theta_s + \hat{i}\sin\theta_s$

Note: θ_s, in the above is the scattering angle.

The expression for the intensities in the different cases involve one or more of the above seven averages. Each of the above seven averages involves a numerator integral and denominator integral. The expression for the denominator integral which is the same in all the seven averages has already been given and is equal to;

$$\frac{4\pi sinha}{a}\left[1+\frac{b_3+2b_1}{3}\right]$$

The numerator integral in the above involves one or more of the seven averages. Therefore at the outset we have worked out the seven averages one by one. As an illustration we have shown how the value for average $\overline{(\hat{a}_m.\hat{k})^2}$ is worked out, i.e using equation (3.8), the expression for numerator intergral is worked out below (3.13). Now using, $x = \overline{(\hat{a}_m.\hat{k})^2} = \cos^2\theta$, and also $f(\theta) = e^{a\cos\theta}\,[1 + b_1\sin^2\theta + b_3\cos^2\theta]$, from equation (3.10), and substituting these values of x and $f(\theta)$ in the numerator expression (equation (3.8)), this gives,

$$\int_0^{2\pi}\int_0^{\pi} xf(\theta)\sin\theta d\theta$$

$$= \int_0^{2\pi}\int_0^{\pi} \overline{(\hat{a}_m \cdot \hat{k})^2} f(\theta)\sin\theta d\phi d\theta$$

$$= \int_0^{\pi}\int_0^{2\pi} e^{a\cos\theta}\cos^2\theta\,[1+b_1\sin^2+b_3\cos^2\theta]\sin\theta d\theta d\phi$$

$$= \int_0^{2\pi} d\phi \int_0^{\pi} e^{a\cos\theta}\cos^2\theta[1 + b_1\sin^2\theta + b_3\cos^2\theta]\sin\theta d\theta$$

$$= 2\pi[(\int_0^{\pi} e^{a\cos\theta}\cos^2\theta\sin\theta d\theta) + b_1(\int_0^{\pi} e^{a\cos\theta}\cos^2\theta\sin^2\theta d\theta)$$

$$+ b_3(\int_0^{\pi} e^{a\cos\theta}\cos^4\theta\sin\theta d\theta)]$$

$$= 2\pi[(\frac{2\sinh a}{3a}|1+\frac{2a^2}{15}|)+(\frac{4b_1\sinh a}{15a})+(\frac{2b_3\sinh a}{5a})]$$

$$= \frac{4\pi\sinh a}{a}\frac{1}{3}[1 + \frac{2a^2}{15} + \frac{1}{5}(3b_3 + 2b_1)] \quad \ldots\ldots\ldots$$

In exactly similar way all the remaining six averages mentioned above have been worked out and are tabulated in Table 3.3. It has to be mentioned that in these evaluations terms of the order higher than a^2 are left out which will not alter the final expressions for all practical purposes.

When once we have obtained the various averages we proceed to calculate the resulting expressions for intensities in the various cases.

$\bar{\bar{x}}$	$\int_0^{\pi} \int_0^{2\pi} \times f(\theta)\sin\theta \, d\theta \, d\phi$ (*)
$(\hat{a}_m.\hat{k})^2$	$\frac{4\pi \sinh a}{a} \frac{1}{3} \left[\frac{1+2a^2}{15} + \frac{1}{5} (3b_3+2b_1) \right]$
$(\hat{a}_m.\hat{k})^4$	$\frac{4\pi \sinh a}{a} \frac{1}{5} \left[\frac{1+4a^2}{21} + \frac{1}{7} (5b_3+2b_1) \right]$
$(\hat{a}_m.\hat{i})^2$	$\frac{4\pi \sinh a}{a} \frac{1}{3} \left[\frac{1-a^2}{15} + \frac{1}{5} (b_3+4b_1) \right]$
$(\hat{a}_m.\hat{i})^4$	$\frac{4\pi \sinh a}{a} \frac{1}{5} \left[\frac{1-2}{7} a^2 + \frac{1}{7} (b_3+6b_1) \right]$
$(\hat{a}_m.\hat{k})^2(\hat{a}_m.\hat{i})^2$	$\frac{4\pi \sinh a}{a} \left[\frac{1}{15} \left(\frac{1+a^2}{21}\right) + \frac{4b_1}{105} (1-2a^2) + \frac{b_3}{35} \left(1+\frac{25}{9} a^2\right) \right.$
$(\hat{a}_m.\hat{i})^2(\hat{a}_m.\hat{j})^2$	$\frac{4\pi \sinh a}{a} \frac{1}{15} \left[\frac{1-2}{7} a^2 + \frac{1}{7} (b_3+6b_1) \right]$
$(\hat{a}_m.\hat{k})^2(\hat{a}_m.\hat{j})^2$	$\frac{4\pi \sinh a}{a} \left[\frac{1}{15} (1+a^2) + \frac{4b_1}{105} (1-2a^2) + \frac{b_3}{35} \left(1+\frac{25}{9} a^2\right) \right]$

(*) terms of order higher than a^2 are left out.

Again as an illustration let us see how we calculate V_H in the Case I i.e direction of applied static electric field normal to the plane of scattering (see Table 3.2).In this case, as can be seen from the Table 3.2,

$\hat{\delta} = \hat{k}$. Hence the intensity expression according to (3.8) is given by;

$$I = \left(\frac{4\pi^2}{r\lambda^2}\right)^2 \frac{\int_0^{\pi}\int_0^{2\pi} \frac{1}{E_o}(\hat{p}_m.\hat{k})^2 f(\theta)\sin\theta d\theta d\phi}{\int_0^{\pi}\int_0^{2\pi} f(\theta)\sin\theta d\theta d\phi} \quad \cdots (3.14)$$

In the equation above, the denominator has already been evaluated and shown to be equal to

$$\frac{4\pi\sinh a}{a}\left[1+\frac{b_3+2b_1}{3}\right]$$

In the numerator of the intensity expression above we have $\overline{(\hat{p}_m.\hat{k})^2}$ which according to equation (3.5b) turns to be ;

$$\overline{(\hat{p}_m.\hat{k})^2} = E_o^2[\delta^2(\hat{a}_m.\hat{b})^2(\hat{a}_m.\hat{k})^2 + A^2(\hat{b}.\hat{k})^2 + 2A(C-A)(\hat{a}_m.\hat{b})(\hat{a}_m.\hat{k})(\hat{b}.\hat{k})$$

In the case where we are now evaluating i.e V_H case I (see Table 3.2);

$\hat{b} = \hat{j}$, then we have $(\hat{b}.\hat{a}) = (\hat{j}.\hat{k}) = 0$

Therefore,

$$\overline{(\hat{P}_m \cdot \hat{k})^2} = E_o^2 \delta^2 \, \overline{(\hat{a}_m \cdot \hat{j})^2 (\hat{a}_m \cdot \hat{k})^2}$$

Substituting from Table (3.3) we have

$$\overline{(\hat{P}_m \cdot \hat{k})^2} = E_o^2 \delta^2 \frac{4\pi \sinh a}{a} \left[\frac{1}{5}\left(1 + \frac{a^2}{21}\right) + \frac{4b_1}{105}(1-2a^2) + \frac{b_3}{35}\left(1+\frac{25a^2}{9}\right)\right] \quad \ldots \quad (3.17)$$

If we equate the above derived expression to A′, i.e $\overline{(\mathbf{p}_m.\mathbf{k})^2} = A$, Then, the expression for intensity V_m will then become;

$$I = \frac{\left(\frac{4\pi^2}{r\lambda^2}\right)^2 E_o^2 N_g \times A'}{\frac{4\pi \sinh a}{a}\left[1+\frac{b_3+2b_1}{3}\right]} = \frac{K^2 A}{\frac{4pi \sinh a}{a}\left[1+\frac{b_3+2b_1}{3}\right]}$$

Substituting the value of A′, from equation (3.17), we have

$$-k^2\delta^2\left[\frac{1}{15}\left(1+\frac{a^2}{21}\right)+\frac{4b_1}{105}(1-2a^2)+\frac{b_3}{35}\left(1+\frac{25a^2}{9}\right]\right. \times \left[1-\frac{b_3+2b_1}{3}\right]$$

[where we have written k^2 for $[4\pi^2/r\lambda^2]\ E_o^2 N_g$]

$$-k^2\delta^2\left[\frac{1}{15}\left(1+\frac{a^2}{21}\right)+\frac{2}{315}(b_3-b_1)\right]$$

leaving out terms involving b_3b_1, b_3a^2, b_1a^2, b_1^3 and b_3^2. So the final

expression for the intensity turns out to be;

$$\frac{k^3\delta^3}{15}\left[1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right] \quad . \quad . \quad . \quad (3.18)$$

where $\Delta b = (b_3 - b_1)$, and $\delta = C - A$.

As a second illustration we show how we evaluated expression for H_H of Case I (see Table 3.2).

According to Table 3.2 for this case also,

$$\hat{D} = \hat{j}, \quad \hat{O} = \hat{j}\cos\theta_s - \hat{i}\sin\theta_s$$

Hence,

$$\overline{(\hat{P}_m \cdot \hat{O})^2} = \cos^2\theta_s \overline{(\hat{P}_m \cdot \hat{j})^2} + \sin^2\theta_s \overline{(\hat{P}_m \cdot \hat{i})^2}$$

$$\overline{(\hat{P}_m \cdot \hat{j})^2} = E_0^2 \left[\delta^2 \overline{(\hat{a}_m \cdot \hat{b})^2 (\hat{a}_m \cdot \hat{j})^2} + A^2 \overline{(\hat{b} \cdot \hat{j})^2} + 2A(C-A) \overline{(\hat{a}_m \cdot \hat{b})(\hat{a}_m \cdot \hat{j})(\hat{b} \cdot \hat{j})} \right]$$

$$\overline{(\hat{P}_m \cdot \hat{i})^2} = E_0^2 \left[\delta^2 \overline{(\hat{a}_m \cdot \hat{b})^2 (\hat{a}_m \cdot \hat{i})^2} + A^2 \overline{(\hat{b} \cdot \hat{i})^2} + 2A(C-A) \overline{(\hat{a}_m \cdot \hat{b})(\hat{a}_m \cdot \hat{i})(\hat{b} \cdot \hat{i})} \right]$$

The expression for the intensity of the H_H component (case I) turns out to be,

$$= \frac{k^2 \left[\cos^2\theta_s \overline{(\hat{P}_m \cdot \hat{j})^2} + \sin^2\theta_s \overline{(\hat{P}_m \cdot \hat{i})^2} \right]}{\frac{4\pi \sinh d}{d} \left[1 + \frac{b_3 + 2b_1}{3} \right]}$$

On substituting the expression for the concerned average and again writing;

$$\frac{1}{\left[1+\frac{b_3+2b_1}{3}\right]} = \left[1-\frac{b_3+2b_1}{3}\right]$$

Leaving out terms ivolving b_1b_3, b_3^2, b_1^2, b_1a^2, b_3a^2, and so on, we get for H_H the expression;

$$k^2\left[\cos^2\theta_s\left((\bar{\alpha})^2+\frac{4\delta^2}{45}-\frac{(3C^2-4A^2+AC)(2a^2+4\Delta b)}{315}\right]\right.$$
$$\left.+\sin^2\theta_s\left[\frac{\delta^2}{15}\left(1-\frac{2a^2}{21}-\frac{4\Delta b}{21}\right)\right)\right]$$

In a similar way the expressions for intensities of two more components V_V and H_H for the case I, four expressions for case II, and four more expressions for case III are obtained. The intensity expressions for all the twelve scattered components are tabulated in the Table 3.4.

Thus we are now able to make some further conclusions, discussions and interpretations on the basis of expressions obtained by us for twelve components in the three cases.

Direction of the applied static electric field	Scattered components	Expressions for fractional intensity
Case I: Normal to the plane of scattering	V_H	$\frac{K^2\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)$
	H_H	$K^2\left[\cos^2\Theta_s\left\{(\bar{\alpha})^2+\frac{4}{45}\delta^2-\frac{(3C^2-4A^2+AC)}{315}(2a^2+4\Delta b)\right\}+\sin^2\Theta_s\left\{\frac{\delta^2}{15}\left(1-\frac{2a^2}{21}-\frac{4\Delta b}{21}\right)\right\}\right]$
	V_V	$K^2\left[(\bar{\alpha})^2+\frac{4}{45}\delta^2+\frac{(3C^2-4A^2+AC)}{315}(4a^2+8\Delta b)\right]$
	H_V	$\frac{K^2\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)$
Case II: Along the direction of incident light	V_H	$\frac{K^2\delta^2}{15}\left(1-\frac{2a^2}{21}-\frac{4\Delta b}{21}\right)$
	H_H	$K^2\left[\cos^2\Theta_s\left\{(\bar{\alpha})^2+\frac{4}{45}\delta^2-\frac{(3C^2-4A^2+AC)}{315}(2a^2+4\Delta b)\right\}+\sin^2\Theta_s\left\{\frac{\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)\right\}\right]$
	V_V	$K^2\left[(\bar{\alpha})+\frac{4}{45}\delta^2-\frac{(3C^2-4A^2+AC)}{315}(2a^2+4\Delta b)\right]$
	H_V	$K^2\left[\cos^2\Theta_s\frac{\delta^2}{15}\left(1-\frac{2a^2}{21}-\frac{4\Delta b}{21}\right)+\sin^2\Theta_s\frac{\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)\right]$
Case III: In the scattering plane and perpendicular to direction of incident light	V_H	$\frac{K^2\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)$
	H_H	$K^2\left[\cos^2\Theta_s\left\{(\bar{\alpha})^2+\frac{4}{45}\delta^2+\frac{(3C^2-4A^2+AC)}{315}(4a^2+8\Delta b)\right\}+\sin^2\Theta_s\left\{\frac{\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)\right\}\right]$
	V_V	$K^2\left[(\bar{\alpha})^2+\frac{4}{45}\delta^2-\frac{(3C^2-4A^2+AC)}{315}(2a^2+4\Delta b)\right]$
	H_V	$K^2\left[\cos^2\Theta_s\frac{\delta^2}{15}\left(1+\frac{a^2}{21}+\frac{2\Delta b}{21}\right)+\sin^2\Theta_s\frac{\delta^2}{15}\left(1-\frac{2a^2}{21}-\frac{4\Delta b}{21}\right)\right]$

We also notice that the intensities of the various scattered components are functions of angle of scattering θ_s (with exception of a few of them), Δb, ($= b_3 - b_1$) which involves E_c (applied static electric field), $\bar{A}$, $\bar{C}$, (principal electric moments in the molecule acted upon by external electric static field) and a ($= \mu_o E_c/KT$) which involves the dipole moment μ_o of the molecule, a also involves the temperature of the scatterer.

3.2. Expressions in the case of polar liquids

The expressions for the scattered components which we have obtained and tabulated in the **Table (3.4)** are for the gaseous assembly of scattering molecules. In what follows we show that the expressions are not very different in the case of polar liquids.

In Chapter 1 of our thesis we have shown that for the case of gaseous assembly (writing equation (1.11)) as

$n^2 - 1 = 4\pi N\alpha$ or $\alpha = \frac{1}{4\pi N}(n^2-1)$ . . . . . (3.21)

where as for (3.21) a liquid assembly of the molecules (writing equation (1.12)) the polarizability α is given by

$$\alpha = \frac{3}{4\pi N}\frac{(n^2-1)}{(n^2+2)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.22)$$

C, A_1 being principal polarizabilities of the molecule, C and A for the gaseous assembly have to be replaced by $C(n^2+2)/3$ and $A(n^2+2)/3$ according to equation (1) and (2) for the liquid phase.

Here all the twelve expressions tabulated in Table 3.4 remain valid for the case of liquid assembly of molecules provided we replace $\delta = (C-A)$ in each case by $\delta' = (C-A)[n^2 + 2)/3]$ and $\alpha = (C-2A)/3$ by $\alpha' = [(C + 2A)/3][(n^2+2)/3]$. Further E_c (which is involved in a, b_1, and b_3) is to be replaced by $E_c(\varepsilon+2)/3$ where ε and n respectively are the refractive index for the incident wavelength in the medium. The expressions for the intensities of the scattered copmonents will become more complicated at least for a few of them in the liquid phase. As the same set of expressions with δ, α, A, C, Δb respe-ctively replaced by δ', α', A', C', $\Delta b'$ (the primed quantities being equal to product of the unprimed quantities and $(n^2 + 2)/3$ or $(\varepsilon + 2)/3$ as already seen) hold good for the liquid phase. We have not given a separate table for the liquid phase. To be very exact we should also consider here the density fluctuations which we had ignored in the case of gases. However if one is interested in the ratio of intensities rather than the absolute intensities of each of the components the error involved in not considering the density fluctuations becomes negligible [23].

THEORETICAL AND EXPERIMENTAL STUDIES ON DEPOLARIZATION RATIO

4.0 Theoretical

The various expressions obtained by us for the intensities of the components of scattered light from the oriented specimen corresponding to three directions of the applied static electric field relative to the direction of incident radiation are already tabulated in Table 3.4 of Chapter 3. These expressions enable us to calculate the depolarization ratio in the three cases.

If the direction of propagation of incident light radiation is assumed to be along z-axis and if the direction of observation of the scattered light makes an angle $\theta_s (0<\theta_s<180)$, with direction of incidence the expression for the depolarization ratio 'ϱ' which is generally defined as ratio of the intensity of scattered light polarized perpendicular to the xy plane '$I_\perp$', to that polarized parallel to xy plane '$I_\parallel$ i.e. $\varrho = I_\perp/I_\parallel$ will now take the form $\varrho = H_H/V_H$ as as per the notation employed by us. We will now proceed to calculate the same in three cases.

Case I:

<u>Direction of the applied static electric field normal to the plane of scattering.</u>

Suppose we consider the strictly transverse direction of observation only i.e. $\theta_s = 90°$, then $Cos^2\theta_s = 0$ and $Sin^2\theta_s = 1$. The expression for ϱ takes the following form given by

(see Table 3.4)

$$\rho = \frac{k^2\delta^2[1 - \frac{2}{21}(a^2 - 4\Delta b)]}{\frac{k^2\delta^2}{15}[1 - \frac{1}{21}(a^2 + 2\Delta b)]}, \quad \text{from } \rho = \frac{H_H(\text{I Case})}{V_H(\text{I Case})}$$

In the absence of applied static electric field i.e. $E_c = 0$, we have

$a = \mu_o E_c/kT = 0$ and $\Delta b = b_3 - b_1 = (C - A)E_c^2/kT = 0$

where μ_o is the dipole moment, C and A are the polarizabilities or dipole moments per unit electric field (see chapter 3)

The numerical value of ρ will then turn out to be unity. In the presence of external electric field i.e we have

$E_c \neq 0$, Hence $a \neq 0$ and $\Delta b \neq 0$. However a and Δb are extremely small enough to allow us to simplify ρ as follows

$$\rho = (1 - \frac{2}{21}a^2 - \frac{4\Delta b}{21})(1 - \frac{a^2}{21} - \frac{2\Delta b}{21})$$

$$\approx 1 - \frac{1}{21}(2a^2 + 4\Delta b + a^2 + 2\Delta b)$$

$$\approx 1 - \frac{1}{21}(3a^2 + 6\Delta b) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.1)$$

Leaving out higher order terms.

Case II:

Applied static electric field along the direction of incident light. With the same approximations we have in this case

$$\rho = (1 + \frac{a^2}{21} + \frac{2\Delta b}{21})(1 + \frac{2a^2}{21} + \frac{4\Delta b}{21}), \quad \text{from } \rho = \frac{H_H(\text{II case})}{V_H(\text{II case})}.$$

$$\approx 1 + \frac{1}{21}(3a^2 + 6\Delta b) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4.2)$$

In the above evaluation we have taken $\cos^2\theta = 0$ and $\sin^2\theta = 1$.

Case III:

Applied electric field in the scattering plane and perpendicular to direction of the incident light. Following the same procedure and taking $\cos^2\theta = 0$, $\sin^2\theta = 1$ and $\rho = \frac{H_H \text{ (III case)}}{V_H \text{ (III case)}}$, then

$$\rho = \left(1+\frac{a^2}{2I}+\frac{2\Delta b}{2I}\right)\left(1-\frac{a^2}{2I}-\frac{2\Delta b}{2I}\right), \text{ from}$$

$$= 1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4.3)$$

It must be noted that in the derivation of expressions (4,1), (4,2) and (4,3) we have left out terms involving $(a^2)^2$ $(\Delta b)^2$ and $a^2\Delta b$ as they are negligible compared to Ist order terms.

Equations (4,1) and (4,2) clearly show that the depolarization ratio ρ is a function of 'a' and Δb. As 'a' and Δb both involve E_c the applied static electric field the numerical values of ρ should, not only depend on the direction of applied static electric field but also on the magnitude of the field. As the orientation of the molecules in the presence of the external electric field is not likely to be high in low fields one of the essential requirements for accurate experimental determination of ρ is that the field should be as high as possible, E_c should not exceed the dielectric strength. Secondly the intesity of the scattered light being a very small fraction of the incident
intensity it is very essential that laser radiation of as high power as possible should be employed.

4.1. Experimental

In order to test the validity of our theoretical expressions

already arrived at in the previous chapters as well as to determine dipole moment of a few liquids experimental investigation was undertaken. As already mentioned there are three possible cases in which the intensity of the scattered light can be measured and hence depolarization ratio calculated. Calculated values depend on the orientation of external electric field E_c, relative to direction of incident Light. The three cases are

Case (i). When applied electric field is perpendicular to the direction of incident light.

Case (ii). When applied electric field is along the direction of the incident light, and

Case (iii). When applied electric field is perpendicular to incident light and in the plane of scattering i.e along the direction of scattered light

However, we have only undertaken an experimental study of Case I, i.e. when applied electric field is perpendicular to the direction of incident light, as it is the only case which is practically convenient for us. We have not considered Case II and III due to practical inconveniences associated with them [see limitation in section (4.5)]. It must be mentioned that the two other cases can also be investigated in principle.

The three liquids chosen for our investigation were:

i) Methyl-chloride (ii) Ethyl-alcohol and

(iii) Cinnamaldehyde.

These three were chosen for the following reasons:

i) they have considerable values for their dipole moments,

ii) data leading to the calculation of their Optical anisotropy, hence Δb are readily available. We will see that the values of Δb are essential for the calculation of dipoloe moments.

4.2. Description of the Apparatus (Equipment)

In our investigation, we used the following listed materials and apparatus,

1. A Laser source, He-Ne gas Laser,
2. A sample holder, Glass chamber,
3. A signal processing system (detector),
4. Sample, (Details already mentioned)
5. Polarizers and analyzers,
6. EHT - power source for application of the field,
7. Spectrometer.

4.2.1. Laser Sources and Signal detectors

The Laser Source which we employed for our investigation is the He-Ne gas Laser, with a wavelength of 6250A°, and having typical pourer of 5mw (higher power Laser sources were not available). For scattered signal detection, we used sensitive Light Dependent Resistor (LDR), whose resistance varies proportionally to intensity of Light falling on it from the scattering sample. The resistance of the LDR in various cases were measured using a Digital Multimeter complimented by an Analog metre. Also to compliment the

LDR was a sensitive photocell. Hence the measured resistance of the LDR is a measure of the intensity of the scattered light.

4.2.2. Sample Preparation, and Glass Chamber

The liquids were highly purified through distillation and redistillation to ensure no suspension (particles) which may obscure the intensity of light scattered from the sample.

4.2.3. The Fabrication of the Chamber

A rectangular glass chamber to contain the liquids under investigation was fabricated. This is approximately base area 16-square centimetres and height 0.5 centimetres (i.e. 5mm), with a small opening at one corner on the top for introducing and pouring in the liquid under investigation. The upper and lower glass plates chosen are optically flat with accurate parallelism of its two surfaces. The parallelism was tested by making use of the autocollimation system. Method consists of viewing the reflected images of slit of the spectrometer from the surface of glass plates through the telescope of the spectrometer. The existence of any non-parallelism was indicated by the appearance of two reflected images from the same glass plate surface. The plates giving single image is hence chosen.

The edges of the cell were covered with dark material to avoid edge scattering, a dark background opposite to the direction of the outcoming scattered light was also created. A circular opening of the dimension slightly more than that of Laser beam was made at the

point of entry of incident beam through a dark covering on the glass cell, allowing the beam to fall on the liquid at the centre of the incident face, also a slit opening perpendicular to incident direction was also left which acts as outlet for the scattered light, (See Fig.4.1)

The chamber was placed between two parallel copper plates of the same surface area as the chamber plates and whose surfaces are perfectly in contact with the upper surface of the upper glass plate and lower surface of the lower glass plate.

Obviously the separation between the two copper plates is equal to the thickness of the chamber which includes the thickness of the upper and lower glass plates of the chamber. This in our experiment was exactly equal to 5 mm. Thus we could apply a required electric field between the upper and lower plates.

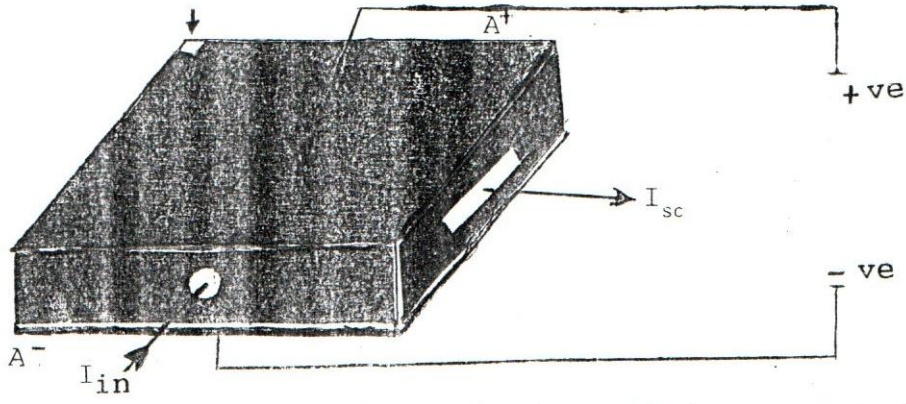


Fig.4.1. A rectangular glass chamber of base area 16-square centimetres and height 5 mm, between copper plates A^+ and A^-. I_{in}; Incident Light; I_{sc}; scattered light.

4.3. Experimental Procedure.

As stated in subsection (4.1.2) only three liquids were

considered, i.e. Ethyl-alcohol, Methyl Chloride, and Cinnamaldehyde. The rectangular chamber containing purified liquid was placed on spectrometer table, and the table height adjusted to allow the incident light to go through the circular hole (see Fig. 4.1) and irradiate the liquid (scatterer). Apart from providing a table to mount the chamber, the spectrometer also provides convenient means of measuring the angle of observation θ_s of scattered light. The detection and measurement of scattered light is done by mounting the light sensitive detector on the movable hand of the spectrometer (telescope) with the eye piece removed, whose rotation from the direction of incident light to the direction of observation of scattered light could be accurately measured and hence θ_s determined. We confined our measurement to strictly transverse direction, i.e. $\theta_s = 90$ (see Fig. 4.2) only. The Laser Light irradiating the sample could either be horizontally polarized or vertically polarized, denoted by H and V respectively. To achieve this, a polariser (P) whose vibration direction is known is placed between the Laser Source and the Sample (scatterer) and its orientation could be adjusted to make either H or V component fall on the scatterer.

Similarly an analyzer whose vibrational direction is also known in placed in between the outlet slit and the detector. Its orientation could also be adjusted such that the horizontal component (H) or Vertical Component (V) of the Scattered Light falls on the detector.

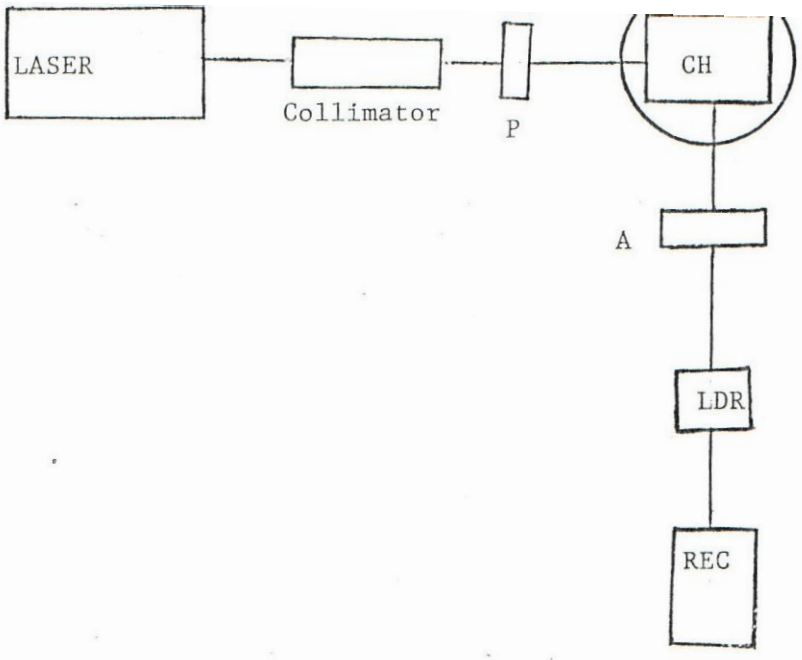


Fig. 4.2: Schematic layout of the experimental arrangement

Key:

C; Collimator, P; Polarizer,

CH; Chamber placed on prism Table of Spectrometer

A; Analyzer, LDR; Light Dependent Resistor

REC; Recorder.

If the vibration direction of the polarizer is horizontal and that of the analyzer is also horizontal then the component detected by the detector is H_H according to our rotation.

Similarly V_H, V_v and H_v could be detected.

As we need only components H_H and V_H for the determination of ρ the depolarization ratio we made an accurate study of H_H and V_H only. Obviously absolute values of the scattered intensity components could not be measured. The intensity of a particular component of scattered light is inversely proportional to the resistance of the LDR when that particular component falls on the

LDR. If the resistances of the LDR are R_1 and R_2 respectively corresponding to scattered components H_s and V_s respectively, then ρ is given by, $\rho = R_2/R_1$

A digital meter measuring the resistance accurate to $(1/100000)^{th}$ of an Ohm is employed to measure the resistance of LDR. The DC power supply employed could give an output voltage of slightly more than 20000 volts. Hence by applying a voltage of 20000 volts between the upper and lower plates of the Chamber through the parallel copper plates the Sample could be subjected to an applied static electric field of E_c = 40000 Volts/cm as the thickness of the chamber is 5 mm.

The whole set up was housed in a darkroom, and further to ensure that the incident light does not contribute any significant signal noise in our observation, the chamber and detector were covered with dark material after properly aligning the whole set up. This was aimed at ensuring only the scattered light was registered by the detector.

Repeated readings were taken and average calculated. The results are tabulated in Tables 4.1, 4.2 and 4.3 for the three liquids.

TABLE 4.1: Methyl-chloride

Trail No.	Resistance of LDR Corresponding to		Depolarization ratio $e = H_H/V_H = R_2/R_1$
	H_H R_2 ($m\Omega$)	V_H R_1 ($m\Omega$)	$\pm 10^{-5}$
1	18.3411	18.8520	0.9729
2	18.3353	18.8499	0.9727
3	18.3476	18.8548	0.9731
4	18.3410	18.8519	0.9729
5	18.3436	18.8526	0.9730
6	18.3306	18.8470	0.9726
7	18.3472	18.8519	0.9732
8	18.3490	18.8516	0.9728
9	18.3472	18.8519	0.9729
10	18.3411	18.8520	0.9729
			ρ^* =0.9729

ρ^* is the average of the depolarization ratio of the ten trials.

TABLE 4.2. Cinnamaldehyde

Trail No.	Resistance of LDR Corresponding to		Depolarization ratio $e = H_H/V_H = R_2/R_1$
	H_H R_2 (mΩ)	V_H R_1 (mΩ)	$\pm 10^{-5}$
1	11.0384	12.8728	0.8575
2	11.0412	12.8730	0.8577
3	11.0428	12.8734	0.8578
4	11.0443	12.8736	0.8579
5	11.0457	12.8738	0.8580
6	11.0442	12.8735	0.8579
7	11.0413	12.8731	0.8577
8	11.0399	12.8730	0.8578
9	11.0427	12.8733	0.8581
10	11.0472	12.8740	0.8581
			ρ^* =0.8578

ρ^* is the average depolarization ratio of the ten trials.

TABLE 4.3. Ethyl-alcohol

Trail No.	Resistance of LDR Corresponding to		Depolarization ratio $e = H_H/V_H = R_2/R_1$
	H_H R_2 ($m\Omega$)	V_H R_1 ($m\Omega$)	$\pm 10^{-5}$
1	16.3771	16.7614	0.97707
2	16.2912	16.6730	0.97710
3	16.2893	16.6717	0.97706
4	16.2991	16.6819	0.97705
5	16.3367	16.7200	0.97708
6	16.3565	16.7400	0.97709
7	16.2996	16.6821	0.97707
8	16.4859	16.6728	0.97707
9	16.2905	16.6723	0.97710
10	16.2902	16.6730	0.97704
			ρ^*=0.97707

ρ^* is the average depolarization ratio of the measurements.

4.4. Experimental Limitations

Experimental investigation of ρ' depolarization ratio is undertaken only for Case I, i.e. for a Case when applied electric field is perpendicular to direction of incident Light because it is practically convenient. The other two Cases, II and III were not done, for the following reasons:

i). For Case II, the applied electric field should be along the direction of the incident Light. This presents a problem in the sense that the copper plates would be in the path of the incident light hence would obstruct the incoming light, though this would somehow be solved by punching a hole through the plates to allow light to pass through this would further complicate our derived equation, because that would mean the applied filed is not uniform.

ii). For Case III, the applied field is perpendicular to incident light and in the plane of scattering, this also presents problem in the sense that the scattered light would be obstructed by the copper plates placed on its path; hence we have restricted our investigation to Case I only.

iii). Our investigation could not be extended to Liquid Crystals (LC) though LC study provided motivation for our investigation. LC study presents serious problems for the following reasons. LC is essentially a two dimensional crystal. Hence at the most, the thickness of the oriented LC specimen should be of the order of a fraction of a mm only. Hence one cannot enclose the Liquid Crystal in a Chamber of thickness 5 mm unlike in the case of non-LC polar liquids. The plates have to be separated by placing spacers of microthickness and a thin Layer of LC has to be enclosed between the plates. Applying an electric field of the order of 10000 to 20000 volts across two plates separated by a fraction of mm is, for all practical purposes equivalent to

shorting.

iv). Use of a laser source of much higher power is most desirable for an accurate investigation. Owing to non availability of the same the best among the available was employed.

RESULTS AND DISCUSSION

On a detailed examination of Table 3.4 of Chapter 3 where we have presented the expressions obtained by us for H_H, V_H, V_V, and H_V for 3 orientations of applied electric field relative to the direction of incident light, we can notice the following interesting relationships between intensities of the components.

(i) In the Case I, i.e when the applied electric field is perpendicular to the plane of scattering we notice that the vertical component of the scattered light when the vibration direction of the scattered light is horizontal is equal to horizontal component of the scattered light when the vibration direction of the incident light is vertical i.e $H_V = V_H$. In fact this confirms the well known reciprocity relation which was first explained by Peviin [29].

(ii) H_V (I Case) = V_H(III Case). This is to be expected because in the I case concerning H_V and III case concerning V_H the incident electric vector is along the direction of the applied static field and the direction of the electric vector of the scattered light is perpendicular to the direction of the applied field i,e the preferred direction of the orientation of the molecules of the medium.

(iii) Vertical component of scattered light when the incident electric vector is vertical have the same intensity both in II and

III cases i.e V_v(II case) = V_v(III case). This is in fact follows from the fact that in both V_v(II) and V(III) the incident and the scattered electric vector are transverse to the direction of the applied field.

(iv) In the derivation of the expressions for the various scattered components, we have used the averages of quantities like $\overline{(\hat{a}_s.\hat{k})^2}$, $\overline{(\hat{a}_s.\hat{k})^4}$, ...etc. Because of the combinations of different averages involved, the following equalities are also valid.

(1) $H_H(I) = \cos^2\theta_s V_v(II) + V_H(II)\sin^2\theta_s$

(2) $H_H(II) = \cos^2\theta_s V_v(II) + V_H(I)\sin^2\theta_s$

(3) $H_H(III) = \cos^2\theta_s V_v(I) + V_H(I)\sin^2\theta_s$

(4) $H_v(II) = \cos^2\theta_s V_H(II) + V_H(I)\sin^2\theta_s$

(5) $H_v(II) = \cos^2\theta_s V_H(I) + V_H(II)\sin^2\theta_s$

In fact above five relationships are useful to verify the validity of our experimental investigation of the intensities especially when the direction of observation is strictly transverse

i.e $\theta_s = 90°$

As already mentioned in Chapter 3 the expression for V_v and H_v which entirely arise due to anisotropic scattering are valid for liquid phase also provided we replace δ by δ' $[= \frac{(n^2 + 2)}{3}\delta]$

However, while calculating the depolarization ratio $\varrho = H_H/V_H$ δ cancels out and hence replacing δ by δ' becomes meaningful only when we intend to calculate absolute values of the intensity components.

Before we present the details of our calculations it is worthwhile to mention that the two expressions (4.1) and (4.2) i.e

$\rho = 1 + \frac{1}{21}(3a^2 + 6\Delta b)$ in case II relating the depolarization ratio ρ to the parameter a ($= \mu_o E_c/kT$) and the parameter $\Delta b=(b_3 - b_1) = \frac{(\bar{C}-\bar{A})E_c^2}{2kT}$ can lead to verification of the correctiness experimental values of ρ in case I and case II. However, this question will not arise in our thesis as we experimentally determine ρ in case I only.

Though we have determined ρ^* for 3 liquids in this case substitution of the same in (4.1) of Chapter 4, yields the value of $(3a^2 + 6\Delta b)$ only. If our intention is to determine "a" we should think of a means to accurately estimate Δb. Alternatively if a is known by other means b can be estimated from our studies however this is not our intention. In the following section we describe in brief how Δb is estimated by other accurate means. It may be noted that Δb involves $(\bar{C} - \bar{A})$ the optical anisotropy of the scattering molecule.

5.1. Calculation of Δb by calculating optical anisotropy

We have,

$$\Delta b = b_3 - b_1 = \frac{(\bar{C} - \bar{A})E_c^2}{2kT} \quad \text{.....(5.1)}$$

As we already know quantity $(\bar{C} - \bar{A})$ gives the difference in

dipole moments per unit applied field or the polarizabilities of the molecule, $\bar{C}$ being the polarizability component along the direction of the axis of molecule and B being that perpendicular to axis of the molecule.

Infact this difference ($\bar{C}$ - $\bar{A}$) is what is called the optical anisotropy.

Subramhanyam et al [24, 25] have provided a well established method for estimating ($\bar{C}$ - $\bar{A}$) for molecules based on so called bond polarizability data. The procedure will not be discussed here, but we take the example of CH_3CL and illustrate how ($\bar{C}$ - $\bar{A}$) is calculated on the basis of Subramhanyam et al's procedure. The molecular formula for CH_3CL is as given below.

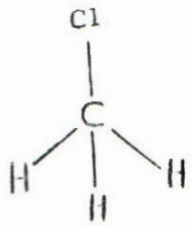


Fig.5.1. Methyl-chloride molecular structure

CH_3CL has a tetrahedral symmetry. The molecular axis is the one which passes through C-CL bond. Hence it makes an angle $\theta = 0$ with C-CL bond and 30° with each of the 3 CH bonds.

α_l and α_t, the longitudinal (along) and transverse (perpendicular) polarizabilities respectively for the bonds C-CL and CH are available from the literature [26, 27, 28]. The values in the case

of bonds relevant to our calculations are given in Table 5.1 below.

Table 5.1: Bond Polarizabilities

Bond/Group	α_l	α_t
C_H	0.82	0.60
C-CL	3.67	2.06
C-C	0.97	0.26
C=C	2.90	1.07
C=O	2.292	0.849
C_6H_6	12.31	6.35

α_l and α_t are in units of $10^{-24}cm^3$.

(The data is for λ = 5893Å. The λ we have used in our investigation is 6250Å. Discrepancy is ignored).

If θ is the angle which any bond makes with the molecular axis then

$\bar{C} = \Sigma\alpha_l\cos\theta$,

and $\bar{A} = \Sigma\alpha_t\sin\theta$, Σ indicating the summation over all the involved bonds.

Accordingly for CH_3CL, θ being equal to 0° for C-CL bond and 30° for C-H bond.

$\bar{C} = 3.67\cos0 + (0.82\cos30°)3 = 5.8004$

$\bar{A} = 2.06\ \sin0 + (0.60\sin30°) = 0.9$

Hence, $(\bar{C} - \bar{A}) = 4.90042 * 10^{-24} cm^3$

Similarly taking the case of ethyl alcohol, it's (C - A) value is accurately estimated by subramhanyam et al [26] and the value is $4.150 * 10^{-24} cm^3$. We make use of this data.

The third liquid investigated is Cinnamaldehyde as already mentioned, it's structural formula is given below

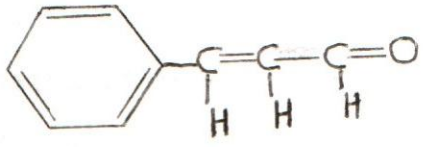


Fig.5.2: Cinnamaldehyde structure.

The molecular axis is assumed to be along C=C-C bonds which is a valid assumption. The molecular axis makes an angle $\theta = 0°$ with all except C-H bonds with which it makes an angle $\theta = 90°$. Hence according to Subramhanyam's procedure for this molecule

$$\bar{C} = (12.31)\cos 0 + 0.97\cos 0 + 2.90\cos 0 + 0.97\cos 0 + 2.292\cos 0$$

$$= 19.442 * 10^{-24} \ cm^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.3)$$

$$\bar{A} = (6.35 + 0.97 + 2.90 + 0.97 + 2.292)\sin\theta$$

$$+ 3(0.6)\sin 90 = 1.80 * 10^{-24} cm^3 \quad \ldots\ldots\ldots\ldots\ldots (5.4)$$

Hence, $\bar{C} - \bar{A} = 17.642 * 10^{-24} cm^3$.

The applied static field employed E_c in our investigation is 40000 volts/cm. We have evaluated Δb values at the outset for the 3 liquids and have tabulated the results in **Table 5.2** below.

TABLE 5.2: Δb values.

LIQUID	$(\bar{C}-\bar{A})^*$	$\Delta = (\bar{C}-\bar{A})E_c^2/kT$
Methyl-chroride	4.90042	0.094694
Ethyl-alcohol	4.150	0.080193
Cinnamaldehyde	17.642	0.3409

* in units of $10^{-24}cm^3$.

5.2. Calculations of dipole moments

Using the value of ρ determined experimentally and calculated values of Δb, we calculated the dipole moment for each of the three liquids using equation (4.1) and have the tabulated results in Table 5.3 below.

TABLE 5.3: Dipole moments. E_c = 20000volts.

COMPOUND	ρ^* $\pm 10^{-5}$	$(3a^2 + 6\Delta b)$	a	μ^{**} $\pm 10^{-5}$
Methylchroride	0.9729	0.5691	0.0176635	1.8282
Ethylalcohol	0.97707	0.48153	0.010197	1.15252
Cinnamaldehyde	0.8578	0.29862	0.65	57.96

* The average of ten trials
** in units of Debye.

5.3. Discussion.

i). Methyl-chloride and Ethyl-alcohol.

The theoretical value of the dipole moments of Methylchloride and Ethyl alcohol are respectively 1.872 Debye and 1.102 Debye [32]. On comparing these with values obtained by us the discrepancy in the case of Methyl chloride is about 2.5 per cent and in the case of Ethyl alcohol it is about 4 per cent.

The agreement is therefore excellent, the slight discrepancy may be ascribed to the fact that the intensity of incident laser radiation is 5mw only. If a source of higher intensitry could be employed then the depolarization ratio ρ could be estimated to a greater accuray and discrepancy is expected to be even less. Further, it may be pointed out that the accuracy also depends on the calculation of Δb which essentially depends on the $(\bar{C}-\bar{A})$.

According to Subramhanyam et al [3,4] the additivity of bond polarizability technique to calculate $(\bar{C}-\bar{A})$ is very reliable and yields accurate values provided the size of the molecule is not very big and the molecule does not involve double bonds. This is exactly the situation in the case of Methyl-chloride and Ethyl-alcohol, the discrepancy cannot be ascribed to any inaccuracy in the calculation of Δb. It may therefore be concluded that our investigation yields an accurate method for the calculation of dipole moments of molecules of small size and involving no double bonds. But the success of the method i.e the accuracy of the claculated values mostly depends on how accurately we detect and

measure the ratio of intensities of the scattered components.

A Laser source of a power equal to at least 50mw and a Photomultiplier Tube (PMT) as detector will go a long way in enhancing the reliabilitry of our technique in the estimation of dipole moment and optical anisotropy.

2). Cinnamaldehyde

The dipole moment calculated by us in this case is widely different from the value reported in standard tables (For example see Bottcher, S.L or Wells, A. F [30, 31]). The value reported in literature is 12.33 Debye whereas the value obtained by us is 57.96 Debye as can be seen from the Table 5.3.
This very large discrepancy in the case of cinnamaldehyde therefore prompts us to re-examine the procedure we have used for the estimation of Δb.

It must be realized that cinnamaldehyde is not a molecule of small size. Further it involves a benzene ring and alternative single and double bonds in its molecular structure (see figure 5.2)

Subramhanyam et al [25, 26] have suggested a modified procedure for the calculation of $(\bar{C}-\bar{A})$ in the case of such molecules particularly the liquid crystalline molecules. They use the double bond values throughout owing to conjugation of the bonds and also amply justify this drastic assumption of theirs. They also assume that the contribution of C-H bonds to $\bar{C}-\bar{A}$ in the case such

molecules owing to rotational isomerisation [26] is the isotropic polarizability value of the bond.

Suppose we extend this procedure of theirs to the case of cinnamaldehyde the numerical values of both $\bar{C}$ and $\bar{A}$ will differ from what we have obtained as per (5.3) and (5.4). The modified values of $\bar{C}$ and $\bar{A}$ are given by

$$\bar{C} = \{[12.31 + 3(2.90) + 2.92]\cos 0 + 3 \times 0.673]\} \times 10^{-24} cm^3$$

$$= 25.321 \times 10^{-24} cm^3$$

and, $\bar{A} = 0$, since angle of scattring is zero.

$\bar{C}-\bar{A}$ hence turns out to be $25.321 \times 10^{-24} cm^3$ instead of 17.642 as given in table 5.2. If this modified value is used. Δb turns out to be 0.489295 instead of 0.3409 given in Table 5.2. With this value of Δb the dipole moment turns to be 13.42 Debye, which value is very close agreement with the reported value of 12.33 Debye.

Even though with a solitary example of cinnamaldehyde it is difficult to conclude that the method adopted by us to calculate Δb in this case is apt, we can make a general statement that the discrepancy in the calculated values of dipole moment in the case of molecules like Cinnamaldehyde cannot be ascribed to error in the calculation of 'ρ' the depolarization ratio.

So we may again conclude that our method could be employed even in the case of molecules with big size and involving double bonds. Provided we estimate Δb accurately.

5.4 Recommendations for further investigations.

1. At the outset we recommend that to be absolutely sure of the accurancy it is very desirable to employ sources having a power of atleast 50mw and a Photomultiplier Tube (PMT) for detection of the scattered light.

2. Instead of estimating Δb values for the molecules by a separate procedure and using the same for determining a and hence the dipole moment, we recommend that the experimental investigation is made more elaborate and determine both a^2 and Δb from our technique only by solving simultaneous equations.

3. The method could be extended for the investigation of optical anisotropy and dipole moment of liquid crystals. However, for reasons already described we cannot apply external electric field in a direction perpendicular to the incident electric field and perpendicular to plane of incidence. In this case the direction of applied field should be along the direction of incidence or along the direction of scattering.

4. Both with aview to investigate liquid crystals and calculate the ratio of scattering intensities in case II (Applied electric field along the incident direction) and case III (Applied electric field along scattered light). It is highly desirable to work out the design and the form of Chamber as well as copper plates to be

used in these cases.

If the above recommendations are realized practically the method developed by us will eventually turn out to be an excellent tool for the determination of optical anisotropy as well as dipole moment of both the molecules of small size and those of big sizes involving double bonds including the liquid crystalline molecules.

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