

CLASSICAL THEORY OF NONLINEAR MOLECULAR LIGHT SCATTERING

by

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Summary. The present paper brings a classical theory of the non-linearly scattered light engendered in an isotropic medium by an incident light beam of very great intensity (e. g. a laser beam). The intensity of the scattered light is obtained in the form of the expression $I_n^e = A_n^e I + B_n^e I^2 + \dots$, wherein the coefficient A_n^e accounts for linear Rayleigh scattering, whereas B_n^e characterizes the additional non-linear scattering given rise to by the very intense incident light beam of intensity I . The coefficients A_n^e and B_n^e are derived in general form for an arbitrary isotropic medium and are then discussed for the case of systems consisting of mutually interacting molecules, the latter being isotropic, or anisotropic with a centre of symmetry, or possessing no centre of inversion. From the numerical evaluations of the Rayleigh ratio S and depolarization ratio D , the non-linear variations of these quantities produced by a light beam of intensity amounting to $I=2 \times 10^4$ e.s.u. are shown to be accessible to detection in substances whose molecules are non-dipolar and highly anisotropic (e.g. CS_2) or in dipolar substances consisting of molecules with considerable first hyperpolarizability (e.g. CHCl_3). Investigation of non-linearly scattered light, if experimentally practicable, will allow to obtain direct information concerning the non-linear polarization (hyperpolarizability) of the molecules of various substances.

1. INTRODUCTION

In 1956, Buckingham published a paper [1] in which he proposed a theory of the birefringence induced in isotropic media by a light beam of very high intensity. According to Buckingham, the isotropic medium becomes anisotropic for two reasons. In the first place, owing to interaction between the oscillating electric field of the light beam and the anisotropic molecules of the medium, the latter tend to become oriented with their axis of maximum polarizability perpendicular

to the direction of light propagation, so that the body is now optically birefringent. This, obviously, is birefringence of a kind due to an effect of optical molecular orientation resembling the electric and magnetic orientation introduced by Langevin [2] for explaining the temperature dependence of the Kerr and Cotton-Mouton effects. Secondly, an effect arises consisting in the induction of optical anisotropy within the molecule itself. This is the counterpart of the electric non-linear deformation or hyperpolarizability discussed by Voigt [3], Born [4] and Buckingham and Pople [5] in the theory of the electric birefringence of gases. The effect of non-linear optical (as well as electrical) deformation can appear even in inert gases, since the dipolar moment induced in the atom is given by the expression [5]

$$m = aE + \frac{1}{6} cE^3 + \dots$$

provided the intensity E of the oscillating electric field is sufficiently great. Here a denotes the scalar polarizability and c — the scalar hyperpolarizability characterizing the non-linear deformation of the atom.

Thus, the constant characterizing Buckingham's effect is seen to consist of a term in c accounting for the effect of optical hyperpolarizability and — in the case of anisotropic molecules — of a second term proportional to $a^2\kappa_a^2/kT$ and accounting for the effect of optical molecular orientation (κ_a denotes the anisotropy of the molecule, k — Boltzman's constant and T — the absolute temperature). Clearly, the experimental detection of this effect would require the use of a light beam of very great intensity. Since the publishing of Buckingham's paper, the techniques of constructing high intensity light sources have made enormous progress and the lasers operating at present produce light beams of an intensity that would have seemed inachievable several years ago. At present the detection of the anisotropy induced in a medium by an intense light beam is only a matter of evolving appropriate measuring techniques.

Thus, it is now the moment to proceed to an investigation of molecular light scattering due to a very intense light beam. The point is that the intensity of the scattered light, which commonly is a linear function of the intensity I of the incident light, can in general be a non-linear function of I provided investigation is effected at sufficiently high intensity of the beam. The problem has already been dealt with theoretically for two simple cases, namely for atomic gases and ones consisting of isotropic non-linearly polarizable molecules [6] and for gases possessing axially symmetric and linearly polarizable molecules [7, 8]. In the first case we have non-linear light scattering due solely to the effect of optical hyperpolarizability, whereas in the second case we have scattering due to the effect of optical molecular orientation only.

In the general case, the dipole moment induced in the gas molecule is given

by the following expansion [5]:

$$\mathbf{m} = \mathbf{a} \cdot \mathbf{E} + \frac{1}{2} \mathbf{b} : \mathbf{E}^2 + \frac{1}{6} \mathbf{c} : \mathbf{E}^3 + \dots,$$

where \mathbf{a} is the polarizability tensor of the molecule and \mathbf{b} and \mathbf{c} are the tensors of its hyperpolarizability. The scattered light intensity with oscillations in the direction \mathbf{n} is known to be proportional to the quantity $\overline{(\mathbf{m} \cdot \mathbf{n})^2}$, where the line $\overline{\quad}$ denotes the time-average. In a first approximation it is sufficient to average the quantities $\overline{(\mathbf{m} \cdot \mathbf{n})^2}$ over all possible orientations of the molecule with equal probability. In the result thus obtained, the first term in $a^2 E_0^2$ determines linear Rayleigh scattering (since $I = \frac{1}{2} E_0^2$) while the two remaining terms in $b^2 E_0^4$ and acE_0^4 describe non-linear light scattering as due to the effect of optical hyperpolarizability (the terms containing odd powers of E vanish on averaging with respect to the time). In the case of molecules already possessing optical anisotropy, averaging has to be carried out with the well-known Boltzman factor $\exp \left\{ \frac{-u}{kT} \right\} = 1 - \frac{u}{kT} + \dots$, wherein u is the time-average of the molecule's potential energy, proportional to $a\kappa_a E^2$ in the first approximation [1]. Thus, in addition to the previous terms containing $b^2 E_0^4$ and acE_0^4 , a new term proportional to $(a^3 \kappa_a^3 / kT) E_0^4$ and arising from the effect of optical molecular orientation appears in the expression for non-linear scattering.

The evaluations carried out in the course of the present investigation show that in the case of a gas consisting of strongly anisotropic molecules, such as CS_2 , non-linear light scattering is primarily due to molecular orientation. On the other hand, in the case of molecules presenting a small degree of anisotropy but whose first hyperpolarizability b is large, such as CHCl_3 , the contribution to non-linear light scattering due to the molecular orientation is quite negligible as compared to the very great contribution from hyperpolarizability. In dense media both effects, that of hyperpolarizability and that of molecular orientation, undergo modification by the appropriate parameters of radial and angular molecular correlations. It is also worth noting here that, while investigation of optical birefringence (Buckingham's effect) will lead to the direct determination of the value of the second hyperpolarizability c only, measurement of non-linear light scattering is apt moreover to yield the first hyperpolarizability b of the (e.g. tetrahedral) molecule which is all the more interesting as there is no other method of determining the value of b directly.

In the present paper, from considerations of classical electrodynamics and statistical mechanics, a general theory of non-linear light scattering is developed for the effect such as it can occur in an isotropic medium illuminated with a light beam of very high intensity. The theory is discussed for several special cases and applied for computing the non-linear variations of the Rayleigh coefficient and of the degree of depolarization as due to such illumination.

2. GENERAL THEORY

We shall consider a medium of volume V , macroscopically isotropic in the absence of external forces. Let $\mathbf{E} = \mathbf{E}_0 \cos \omega t$ be the electric field associated with the plane polarized light wave incident on the medium. We assume that the wavelength λ of this light is large with respect to the distance between mutually interacting molecules and, at the same time, that its oscillation frequency ω is far remote from the electronic absorption region.

Let us denote the direction of the oscillations of the electric vector \mathbf{E} in the incident light beam by the unit vector \mathbf{e} and in the scattered light by the unit vector \mathbf{n} . Obviously, \mathbf{n} is perpendicular to the vector \mathbf{R}_0 directed from the centre of V to the point at which the scattered light is observed. We at first assume \mathbf{e} and \mathbf{n} to be oriented quite arbitrarily with respect to the fixed system of reference XYZ located at the centre of the volume V . The n -component of the scattered intensity at a sufficiently great distance R_0 , ($R_0 \gg \lambda$), is given by the equation

$$I_n^e = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \overline{\langle \dot{M}_\alpha \dot{M}_\beta n_\alpha n_\beta \rangle_E}, \quad (1)$$

where M_α is the α -component of the oscillating dipole moment induced in the medium of volume V by the electric field \mathbf{E} of the incident light wave. The brackets $\langle \rangle_E$ in Eq. (1) stand for the statistical average in the presence of the electric field at thermodynamical equilibrium of the system,

$$\langle \Phi \rangle_E = \frac{\int \Phi(\tau, \mathbf{E}) \exp \left\{ -\frac{\overline{U(\tau, \mathbf{E})}}{kT} \right\} d\tau}{\int \exp \left\{ -\frac{\overline{U(\tau, \mathbf{E})}}{kT} \right\} d\tau} \quad (2)$$

with $U(\tau, \mathbf{E})$ denoting the total potential energy of the system at configuration τ in the electric field \mathbf{E} .

In the case of a weak electric field, the dipole moment \mathbf{M} depends on \mathbf{E} linearly. If, however, the field strength is high enough, the medium experiences non-linear polarization in addition to the linear polarization. In this case, the intensity I_n^e of the scattered light must be an even function of the amplitude E_0 :

$$I_n^e = \frac{1}{2} A_n^e E_0^2 + \frac{1}{4} B_n^e E_0^4 + \dots = A_n^e I + B_n^e I^2 + \dots, \quad (3)$$

with $I = \overline{E^2} = \frac{1}{2} E_0^2$ denoting the incident intensity and

$$A_n^e = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\{ \frac{\partial^2}{\partial E_0^2} \overline{\langle \dot{M}_\alpha \dot{M}_\beta n_\alpha n_\beta \rangle_E} \right\}_{E=0},$$

$$B_n^e = \frac{1}{6R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\{ \frac{\partial^4}{\partial E_0^4} \langle \overline{\overline{\overline{\overline{M_\alpha M_\beta n_\alpha n_\beta}}} \rangle}_E \right\}_{E=0}. \quad (4)$$

The first coefficient A_n^e of the expression (3) describes linear Rayleigh scattering and the second coefficient B_n^e — the additional non-linear scattering produced by an intense light beam. By the definition of (2), these coefficients can be written as follows:

$$A_n^e = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\langle \frac{\partial^2 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0} n_\alpha n_\beta e_\gamma e_\delta \right\rangle, \quad (5)$$

$$B_n^e = \frac{1}{6R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\{ \left\langle \left(\frac{\partial^4 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0 \partial E_\epsilon^0 \partial E_\eta^0} - \frac{6}{kT} \frac{\partial^2 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0} \frac{\partial^2 \overline{\overline{\overline{\overline{U}}}}}{\partial E_\epsilon^0 \partial E_\eta^0} \right) n_\alpha n_\beta e_\gamma e_\delta e_\epsilon e_\eta \right\rangle + \frac{6}{kT} \left\langle \frac{\partial^2 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0} n_\alpha n_\beta e_\gamma e_\delta \right\rangle \times \left\langle \frac{\partial^2 \overline{\overline{\overline{\overline{U}}}}}{\partial E_\epsilon^0 \partial E_\eta^0} e_\epsilon e_\eta \right\rangle \right\}, \quad (6)$$

where the brackets $\langle \rangle$ without lower index denote the statistical average at zero electric field, as resulting from (2) for $E=0$.

In the absence of an electric field, all directions of the unit vectors \mathbf{e} and \mathbf{n} with respect to the fixed system of reference have the same probability, so that the products of their components appearing in Eqs. (5) and (6) can be averaged isotropically and we obtain

$$A_n^e = \frac{1}{30R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\langle \frac{\partial^2 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0} \{ 5[1 - (\mathbf{e} \cdot \mathbf{n})^2] \delta_{\alpha\beta} \delta_{\gamma\delta} + [3(\mathbf{e} \cdot \mathbf{n})^2 - 1] \sigma_{\alpha\beta\gamma\delta} \} \right\rangle, \quad (7)$$

$$B_n^e = \frac{1}{1260R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\{ \left\langle \frac{\partial^4 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0 \partial E_\epsilon^0 \partial E_\eta^0} - \frac{6}{kT} \frac{\partial^2 \overline{\overline{\overline{\overline{M_\alpha M_\beta}}}}}{\partial E_\gamma^0 \partial E_\delta^0} \frac{\partial^2 \overline{\overline{\overline{\overline{U}}}}}{\partial E_\epsilon^0 \partial E_\eta^0} \right\rangle \times \right. \\ \left. \times \{ 7[1 - (\mathbf{e} \cdot \mathbf{n})^2] \delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} + [3(\mathbf{e} \cdot \mathbf{n})^2 - 1] \sigma_{\alpha\beta\gamma\delta\epsilon\eta} \} \right\} + \frac{A_n^e}{3kT} \left\langle \frac{\partial^2 \overline{\overline{\overline{\overline{U}}}}}{\partial E_\epsilon^0 \partial E_\eta^0} e_\eta \right\rangle, \quad (8)$$

where we have denoted

$$\sigma_{\alpha\beta\gamma\delta} = \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}, \\ \sigma_{\alpha\beta\gamma\delta\epsilon\eta} = \delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} + \delta_{\alpha\gamma} \sigma_{\delta\epsilon\eta\beta} + \delta_{\alpha\delta} \sigma_{\epsilon\eta\beta\gamma} + \delta_{\alpha\epsilon} \sigma_{\eta\beta\gamma\delta} + \delta_{\alpha\eta} \sigma_{\beta\gamma\delta\epsilon}, \quad (9)$$

and $\delta_{\alpha\beta}$ is the unit tensor with components equalling unity for $\alpha=\beta$ and zero for $\alpha \neq \beta$.

Expansion (3) together with the coefficients (7) and (8) determines the general form of the intensity of the non-linear scattered light in an arbitrary isotropic medium.

We now assume that the polarized light propagates in the Y -axis direction with its electric vector oscillating parallel or perpendicular to the plane of observation (XY -plane). If for simplicity the light scattered is observed along the X -axis, we obtain from Eqs. (7) and (8)

$$A_{||}^{\parallel} = A_{||}^{\perp} = A_{\perp}^{\parallel} = \frac{1}{30R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\langle \frac{\partial^2 \overline{\overline{M}_\alpha \overline{M}_\beta}}{\partial E_\gamma^0 \partial E_\delta^0} (5\delta_{\alpha\beta} \delta_{\gamma\delta} - \sigma_{\alpha\beta\gamma\delta}) \right\rangle, \quad (10)$$

$$A_{\perp}^{\perp} = \frac{1}{9R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\langle \frac{\partial^2 \overline{\overline{M}_\alpha \overline{M}_\beta}}{\partial E_\gamma^0 \partial E_\delta^0} (\sigma_{\alpha\beta\gamma\delta} - 2\delta_{\alpha\beta} \delta_{\gamma\delta}) \right\rangle + \frac{4}{3} A_{||}^{\parallel}, \quad (11)$$

$$B_{||}^{\parallel} = B_{||}^{\perp} = B_{\perp}^{\parallel} = \frac{1}{1260R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\langle \frac{\partial^4 \overline{\overline{M}_\alpha \overline{M}_\beta}}{\partial E_\gamma^0 \partial E_\delta^0 \partial E_\epsilon^0 \partial E_\eta^0} - \frac{6}{kT} \frac{\partial^2 \overline{\overline{M}_\alpha \overline{M}_\beta}}{\partial E_\gamma^0 \partial E_\delta^0} \frac{\partial^2 U}{\partial E_\epsilon^0 \partial E_\eta^0} \right\rangle \left\langle 7\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} - \sigma_{\alpha\beta\gamma\delta\epsilon\eta} \right\rangle + \frac{A_{||}^{\parallel}}{3kT} \left\langle \frac{\partial^2 U}{\partial E_\epsilon^0 \partial E_\eta^0} \right\rangle, \quad (12)$$

$$B_{\perp}^{\perp} = \frac{1}{270R_0^2} \left(\frac{2\pi}{\lambda\omega} \right)^4 \left\langle \frac{\partial^4 \overline{\overline{M}_\alpha \overline{M}_\beta}}{\partial E_\gamma^0 \partial E_\delta^0 \partial E_\epsilon^0 \partial E_\eta^0} - \frac{6}{kT} \frac{\partial^2 \overline{\overline{M}_\alpha \overline{M}_\beta}}{\partial E_\gamma^0 \partial E_\delta^0} \frac{\partial^2 U}{\partial E_\epsilon^0 \partial E_\eta^0} \right\rangle \times \\ \times (\sigma_{\alpha\beta\gamma\delta\epsilon\eta} - 4\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta}) + \frac{8}{3} B_{||}^{\parallel} + \frac{1}{9kT} (3A_{\perp}^{\perp} - 8A_{||}^{\parallel}) \left\langle \frac{\partial^2 U}{\partial E_\epsilon^0 \partial E_\eta^0} \right\rangle, \quad (13)$$

where the lower subscripts $||$ and \perp refer to twice the intensity of the scattered component oscillating parallel or perpendicular to the plane of observation, respectively, and the upper subscripts $||$ and \perp indicate that the electric vector of the incident beam is oscillating parallel or perpendicular to the plane of observation.

From Eqs. (10)–(13) we see that, in general,

$$I_{||}^{\parallel} = I_{||}^{\perp} = I_{\perp}^{\parallel} \neq I_{\perp}^{\perp}.$$

Thus, the Krishnan reciprocal relation is satisfied also in the case of non-linear molecular light scattering.

3. APPLICATION OF THE THEORY TO SPECIAL CASES

If the volume V of the medium contains N molecules of one species, we may expand \mathbf{M} as the sum of the moments of the individual molecules:

$$\mathbf{M} = \sum_{p=1}^N \mathbf{m}^{(p)}, \quad (14)$$

where $\mathbf{m}^{(p)}$ is the dipole moment induced in the p -th molecule by the oscillating electric field \mathbf{E} .

In general, the p -th molecule immersed in the medium is acted on by the effective electric field $\mathbf{E}^{(p)} + \mathbf{F}^{(p)}$, where $\mathbf{F}^{(p)}$ is the electric molecular field existing at the centre of the p -th molecule and produced by the remaining molecules of the medium in the presence of the field \mathbf{E} . On expanding the moment $\mathbf{m}^{(p)}$ in powers of the field $\mathbf{E}^{(p)} + \mathbf{F}^{(p)}$, we obtain for its α -component [9]

$$m_{\alpha}^{(p)} = a_{\alpha\beta}^{(p)}(E_{\beta}^{(p)} + F_{\beta}^{(p)}) + \frac{1}{2} b_{\alpha\beta\gamma}^{(p)}(E_{\beta}^{(p)} + F_{\beta}^{(p)})(E_{\gamma}^{(p)} + F_{\gamma}^{(p)}) + \frac{1}{6} c_{\alpha\beta\gamma\delta}^{(p)}(E_{\beta}^{(p)} + F_{\beta}^{(p)})(E_{\gamma}^{(p)} + F_{\gamma}^{(p)})(E_{\delta}^{(p)} + F_{\delta}^{(p)}) + \dots, \quad (15)$$

where $a_{\alpha\beta}^{(p)}$ is the optical polarizability tensor of the p -th isolated molecule, and $b_{\alpha\beta\gamma}^{(p)}$ and $c_{\alpha\beta\gamma\delta}^{(p)}$ are the tensors of its hyperpolarizability. In the case of optically inactive substances and throughout spectral ranges widely remote from those in which absorption appears, the tensors $a_{\alpha\beta}$, $b_{\alpha\beta\gamma}$ and $c_{\alpha\beta\gamma\delta}$ are symmetric in all suffixes and real.

In a first approximation, the molecular field $\mathbf{F}^{(p)}$ appearing in (15) can be neglected and we have, by Eq. (14),

$$\overline{M_{\alpha} M_{\beta}}^t = \frac{1}{2} \omega^4 \sum_{p=1}^N \sum_{q=1}^N \{ a_{\alpha\gamma}^{(p)} a_{\beta\delta}^{(q)} + b_{\alpha\gamma\epsilon}^{(p)} b_{\beta\delta\eta}^{(q)} E_{\epsilon}^0 E_{\eta}^0 + \frac{1}{8} (a_{\alpha\gamma}^{(p)} c_{\beta\delta\epsilon\eta}^{(q)} + c_{\alpha\gamma\epsilon\eta}^{(p)} a_{\beta\delta}^{(q)}) E_{\epsilon}^0 E_{\eta}^0 + \dots \} E_{\gamma}^0 E_{\delta}^0. \quad (16)$$

To the same approximation, the time-averaged potential energy of the system is (cf. [1]):

$$\overline{U(\tau, E)}^t = U(\tau, 0) - \frac{1}{4} \sum_{p=1}^N \{ a_{\alpha\beta}^{(p)} + \frac{1}{16} c_{\alpha\beta\gamma\delta}^{(p)} E_{\gamma}^0 E_{\delta}^0 + \dots \} E_{\alpha}^0 E_{\beta}^0. \quad (17)$$

1.3 ATOMS AND ISOTROPIC MOLECULES

At first we shall discuss the simpler case of a medium consisting of atoms or isotropic molecules with a centre of inversion, for which we have [9]

$$a_{\alpha\beta} = a\delta_{\alpha\beta}, \quad b_{\alpha\beta\gamma} = 0, \quad c_{\alpha\beta\gamma\delta} = \frac{1}{3} c (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}), \quad (18)$$

where $a = a_{\alpha\alpha}/3$ is the mean polarizability of an isolated molecule and $c = c_{\alpha\alpha\beta\beta}/5$ is its mean hyperpolarizability.

In the present case, by Eqs. (16), (17) and (18), we obtain from Eqs. (10)–(13)

$$A_{||} = A_{\perp}^{\perp} = A_{\perp}^{\parallel} = 0, \quad B_{||} = B_{\perp}^{\perp} = B_{\perp}^{\parallel} = 0, \\ A_{\perp}^{\perp} = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p a_q \right\rangle = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^2 N (1 + G_R), \quad (19)$$

$$B_{\perp}^{\perp} = \frac{1}{2R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p c_q \right\rangle = \frac{1}{2R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a c N (1 + G_R), \quad (20)$$

where the integral parameter [10, 11]

$$G_R = \frac{\rho}{V} \iint \{g^{(2)}(\mathbf{r}_p, \mathbf{r}_q) - g^{(1)}(\mathbf{r}_p) g^{(1)}(\mathbf{r}_q)\} d\mathbf{r}_p d\mathbf{r}_q \quad (21)$$

describes radial correlation of the molecules, $\rho = N/V$ is the molecule number density, while $g^{(1)}(\mathbf{r}_p)$ and $g^{(2)}(\mathbf{r}_p, \mathbf{r}_q)$ are the ordinary and binary correlation functions, respectively.

The parameter G_R may be rewritten in the form [11]

$$G_R = 4\pi\rho \int_0^{\infty} \{g(r_{pq}) - 1\} r_{pq}^2 dr_{pq} = \rho k T \beta_T - 1, \quad (22)$$

where $g(r_{pq})$ is the well-known radial correlation function and β_T — the isothermal compressibility coefficient of the medium.

We shall now take account of the effect of the molecular field \mathbf{F} , which generally exists in a dense medium and is given for isotropically polarizable molecules by the expansion [10]

$$F_{\alpha}^{(p)} = - \sum_{r=1}^N a_r T_{\alpha\beta}^{(pr)} E_{\beta} + \sum_{r=1}^N \sum_{s=1}^N a_r a_s T_{\alpha\beta}^{(pr)} T_{\beta\gamma}^{(rs)} E_{\gamma} - \dots, \quad (23)$$

where the tensor of dipole—dipole interaction is of the form

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha} r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}). \quad (24)$$

Using the molecular field (23), we obtain from Eqs. (10) and (13) in a first approximation

$$A_{\parallel} = \frac{3}{5R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^4 N J_R, \quad (25)$$

$$B_{\parallel} = \frac{27}{70R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^3 c N J_R, \quad (26)$$

with [12]

$$\begin{aligned} J_R &= \frac{1}{6N} \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N \sum_{s=1}^N T_{\alpha\beta}^{(pr)} T_{\alpha\beta}^{(qs)} \right\rangle = \\ &= 2 \frac{\rho}{V} \iint r_{pq}^{-6} g^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q + \dots = 2\rho \int r_{pq}^{-6} g(\mathbf{r}_{pq}) d\mathbf{r}_{pq} \end{aligned} \quad (27)$$

denoting a parameter of radial correlation of the isotropic molecules.

The foregoing discussion proves that in the system of isotropic molecules, when $\mathbf{F} = 0$, only the "Rayleigh components" A_{\perp}^{\perp} and B_{\perp}^{\perp} have non-zero values. However, if $\mathbf{F} \neq 0$, the anisotropic components $A_{\parallel}^{\parallel} = A_{\perp}^{\parallel} = A_{\parallel}^{\perp}$ and $B_{\parallel}^{\parallel} = B_{\perp}^{\parallel} = B_{\parallel}^{\perp}$ are also non-zero.

3.2. ANISOTROPIC MOLECULES WITH A CENTRE OF INVERSION

If the molecules of the medium are optically anisotropic and present a centre of inversion ($b_{\alpha\beta\gamma}=0$), Eqs. (10)–(13) yield, when (16) and (17) are recurred to,

$$A_{||} = \frac{1}{30R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N (3a_{\alpha\beta}^{(p)} a_{\alpha\beta}^{(q)} - a_{\alpha\alpha}^{(p)} a_{\beta\beta}^{(q)}) \right\rangle, \quad (28)$$

$$A_{\perp}^{\pm} = \frac{1}{9R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N a_{\alpha\alpha}^{(p)} a_{\beta\beta}^{(q)} \right\rangle + \frac{4}{3} A_{||}, \quad (29)$$

$$B_{||} = \frac{1}{140R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\{ \left\langle \sum_{p=1}^N \sum_{q=1}^N (3a_{\alpha\beta}^{(p)} c_{\alpha\beta\gamma\gamma}^{(q)} - a_{\alpha\alpha}^{(p)} c_{\beta\beta\gamma\gamma}^{(q)}) \right\rangle + \right. \\ \left. + \frac{2}{9kT} \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N (9a_{\alpha\beta}^{(p)} a_{\gamma\alpha}^{(q)} a_{\beta\gamma}^{(r)} - 9a_{\alpha\beta}^{(p)} a_{\alpha\beta}^{(q)} a_{\gamma\gamma}^{(r)} + 2a_{\alpha\alpha}^{(p)} a_{\beta\beta}^{(q)} a_{\gamma\gamma}^{(r)}) \right\rangle \right\}, \quad (30)$$

$$B_{\perp}^{\pm} = \frac{1}{30R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\{ \left\langle \sum_{p=1}^N \sum_{q=1}^N a_{\alpha\alpha}^{(p)} c_{\beta\beta\gamma\gamma}^{(q)} \right\rangle + \right. \\ \left. + \frac{4}{9kT} \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N (3a_{\alpha\beta}^{(p)} a_{\alpha\beta}^{(q)} - a_{\alpha\alpha}^{(p)} a_{\beta\beta}^{(q)}) a_{\gamma\gamma}^{(r)} \right\rangle \right\} + \frac{8}{3} B_{||}. \quad (31)$$

In particular, the molecules being symmetric about the z-axis, we can express the components of the tensors $a_{\alpha\beta}^{(p)}$ and $c_{\alpha\beta\gamma\delta}^{(p)}$ as follows:

$$a_{\alpha\beta}^{(p)} = a\delta_{\alpha\beta} + a\kappa_a(3k_\alpha^{(p)}k_\beta^{(p)} - \delta_{\alpha\beta}), \\ c_{\alpha\beta\gamma\gamma}^{(p)} = \frac{5}{3}c\delta_{\alpha\beta} + \frac{7}{6}c\kappa_c(3k_\alpha^{(p)}k_\beta^{(p)} - \delta_{\alpha\beta}), \quad (32)$$

wherein $\mathbf{k}^{(p)}$ is the unit vector along the z-axis of the molecular system xyz attached to the centre of molecule p , and [13]

$$a = \frac{1}{3}(a_{zz} + 2a_{xx}), \quad \kappa_a = \frac{a_{zz} - a_{xx}}{3a}, \\ a = \frac{1}{15}(3c_{zzzz} + 12c_{xxxx} + 8c_{xxxx}), \quad \kappa_c = \frac{2}{21c}(3c_{zzzz} + 3c_{xxxx} - 4c_{xxxx}), \quad (33)$$

The parameters κ_a and κ_c defined here describe the anisotropy of polarizability and hyperpolarizability of an axially symmetric molecule. Assuming for simplicity [9] $c_{xxxx} = \frac{1}{6}(c_{zzzz} + c_{xxxx})$, the parameters c and κ_c defined above reduce to [13]

$$c = \frac{1}{3}(c_{zzzz} + 2c_{xxxx}), \quad \kappa_c = \frac{c_{zzzz} - c_{xxxx}}{3c}.$$

With respect to (32), the following result is obtained from Eqs. (28)–(31) for

axially symmetric molecules:

$$A_{||} = \frac{3}{10R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^2 \kappa_a^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 \cos^2 \theta_{pq} - 1) \right\rangle, \quad (34)$$

$$A_{\perp} = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \right\rangle + \frac{4}{3} A_{||}, \quad (35)$$

$$B_{||} = \frac{3}{40R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a \kappa_a \left\{ c \kappa_c \left\langle \sum_{p=1}^N \sum_{q=1}^N (3 \cos^2 \theta_{pq} - 1) \right\rangle + \right. \\ \left. + \frac{81}{14kT} a^2 \kappa_a^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N [9 \cos \theta_{pq} \cos \theta_{qr} \cos \theta_{rp} - 3 (\cos^2 \theta_{pq} + \cos^2 \theta_{qr} + \cos^2 \theta_{rp}) + 2] \right\rangle \right\}, \quad (36)$$

$$B_{\perp} = \frac{1}{2R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a \left\{ c \left\langle \sum_{p=1}^N \sum_{q=1}^N \right\rangle + \right. \\ \left. + \frac{4}{5kT} a^2 \kappa_a^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \sum_{r=1}^N (\cos^2 \theta_{pq} + \cos^2 \theta_{qr} + \cos^2 \theta_{rp} - 1) \right\rangle \right\} + \frac{8}{3} B_{||}, \quad (37)$$

here, θ_{pq} denotes the angle between the axis of symmetry of molecule p and that of molecule q .

On applying classical statistical mechanics, the foregoing expressions can be put in the form

$$A_{||} = \frac{3}{5R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^2 \kappa_a^2 N (1 + J_A), \quad (38)$$

$$A_{\perp} = \frac{1}{R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a^2 N (1 + G_R) + \frac{4}{3} A_{||}, \quad (39)$$

$$B_{||} = \frac{3}{20R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a \kappa_a N \left\{ c \kappa_c (1 + J_A) + \frac{81}{14kT} a^2 \kappa_a^2 (1 + 3J_A + J'_A) \right\}, \quad (40)$$

$$B_{\perp} = \frac{1}{2R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 a N \left\{ c (1 + G_R) + \frac{8}{5kT} a^2 \kappa_a^2 (1 + G_R + 2J_A + J'_A) \right\} + \frac{8}{3} B_{||}. \quad (41)$$

Here, the following integral parameters have been introduced

$$J_A = \frac{\rho}{2V} \iint (3 \cos^2 \theta_{pq} - 1) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (42)$$

$$J'_A = \frac{\rho^2}{2V} \iiint (\cos^2 \theta_{pq} + \cos^2 \theta_{qr} + \cos^2 \theta_{rp} - 1) g^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \quad (43)$$

$$J''_A = \frac{\rho^2}{2V} \iiint \{ 9 \cos \theta_{pq} \cos \theta_{qr} \cos \theta_{rp} - 3 (\cos^2 \theta_{pq} + \cos^2 \theta_{qr} + \cos^2 \theta_{rp}) + 2 \} g^{(3)}(\tau_p, \tau_q, \tau_r) d\tau_p d\tau_q d\tau_r, \quad (44)$$

accounting for the angular correlation of the axially symmetric molecules; $g^{(2)}(\tau_p, \tau_q)$ is the correlation function for pairs of molecules p and q having the configuration τ_p and τ_q (containing the positional and orientational variables \mathbf{r} and ω) and $g^{(3)}(\tau_p, \tau_q, \tau_r)$ — that for triples of molecules p, q and r .

The angular correlation parameter J_A given by (42) appears also in the theory of the Kerr [14, 15] and Cotton-Mouton effects [12, 16]; its value can be determined from those two phenomena.

If the scattering system consists of non-interacting molecules, all correlation parameters (22) and (42)—(44) vanish and Eqs. (34)—(41) hold for perfect gases.

3.3 MOLECULES WITHOUT CENTRE OF INVERSION

We now proceed to the discussion for the case of molecules without a centre of inversion, for which the components of the tensor $b_{\alpha\beta\gamma}$ appearing in Eq. (16) are non-zero. Thus, in addition to Eqs. (30) and (31), we have the following terms:

$${}_b B_{||} = \frac{2}{105R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N (4b_{\alpha\beta\gamma}^{(p)} b_{\alpha\beta\gamma}^{(q)} - b_{\alpha\beta\beta}^{(p)} b_{\alpha\gamma\gamma}^{(q)}) \right\rangle, \quad (45)$$

$${}_b B_{\perp}^{\perp} = \frac{2}{35R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 \left\langle \sum_{p=1}^N \sum_{q=1}^N (2b_{\alpha\beta\gamma}^{(p)} b_{\alpha\beta\gamma}^{(q)} + 3b_{\alpha\beta\beta}^{(p)} b_{\alpha\gamma\gamma}^{(q)}) \right\rangle. \quad (46)$$

For molecules exhibiting the axial symmetry,

$$b_{\alpha\beta\gamma}^{(p)} = b(k_{\alpha}^{(p)}\delta_{\beta\gamma} + k_{\beta}^{(p)}\delta_{\gamma\alpha} + k_{\gamma}^{(p)}\delta_{\alpha\beta} - 2k_{\alpha}^{(p)}k_{\beta}^{(p)}k_{\gamma}^{(p)}) + b\kappa_b \{5k_{\alpha}^{(p)}k_{\beta}^{(p)}k_{\gamma}^{(p)} - (k_{\alpha}^{(p)}\delta_{\beta\gamma} + k_{\beta}^{(p)}\delta_{\gamma\alpha} + k_{\gamma}^{(p)}\delta_{\alpha\beta})\}, \quad (47)$$

so that Eqs. (45) and (46) yield

$${}_b B_{||} = \frac{2}{105R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 b^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \{3(1 + 16\kappa_b - 20\kappa_b^2) \cos \theta_{pq} + 4(2 - 5\kappa_b)^2 \cos^3 \theta_{pq}\} \right\rangle, \quad (48)$$

$${}_b B_{\perp}^{\perp} = \frac{2}{35R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 b^2 \left\langle \sum_{p=1}^N \sum_{q=1}^N \{3(11 + 8\kappa_b - 10\kappa_b^2) \cos \theta_{pq} + 2(2 - 5\kappa_b)^2 \cos^3 \theta_{pq}\} \right\rangle, \quad (49)$$

where

$$b = \frac{1}{3} (b_{zzz} + 2b_{xxz}), \quad \kappa_b = \frac{b_{zzz} - b_{xxz}}{3b} \quad (50)$$

are the mean hyperpolarizability and the anisotropy of hyperpolarizability of an isolated molecule.

In the case of a perfect gas, Eqs. (48) and (49) go over into

$${}_b B_{||} = \frac{2}{105R_0^2} \left(\frac{2\pi}{\lambda} \right)^4 b^2 N (19 - 32\kappa_b + 40\kappa_b^2), \quad (51)$$

$${}_b B_{\perp}^{\perp} = \frac{2}{35R_0^2} \left(\frac{2\pi}{\lambda}\right)^4 b^2 N (41 - 16\kappa_b + 20\kappa_b^2). \quad (52)$$

We shall now discuss the case of molecules possessing the tetrahedral symmetry (e.g. CH₄), for which the tensor components are of the form

$$\begin{aligned} a_{\alpha\beta} &= a\delta_{\alpha\beta}, \\ b_{\alpha\beta\gamma} &= b_{xyz} \{i_{\alpha}(j_{\beta}k_{\gamma} + k_{\beta}j_{\gamma}) + j_{\alpha}(k_{\beta}i_{\gamma} + i_{\beta}k_{\gamma}) + k_{\alpha}(i_{\beta}j_{\gamma} + j_{\beta}i_{\gamma})\}, \\ c_{\alpha\beta\gamma\delta} &= c_{xxxx} \sigma_{\alpha\beta\gamma\delta} + (c_{xxxx} - 3c_{xxxx}) (i_{\alpha}i_{\beta}i_{\gamma}i_{\delta} + j_{\alpha}j_{\beta}j_{\gamma}j_{\delta} + k_{\alpha}k_{\beta}k_{\gamma}k_{\delta}) \end{aligned} \quad (53)$$

and Eqs. (12) and (13) yield, on neglecting the radial and angular correlations,

$$B_{||} = \frac{16}{35R_0^2} \left(\frac{2\pi}{\lambda}\right)^4 b_{xyz}^2 N, \quad (54)$$

$$B_{\perp}^{\perp} = \frac{1}{2R_0^2} \left(\frac{2\pi}{\lambda}\right)^4 \left\{ ac + \frac{48}{35} b_{xyz}^2 \right\} N, \quad (55)$$

where $c = (3/5)(c_{xxxx} + 2c_{xxxx})$ is the mean hyperpolarizability. In this case, $A_{||}^{\perp} = 0$ and A_{\perp}^{\perp} is given by Eq. (19) for $G_R = 0$.

4. NUMERICAL EVALUATIONS AND DISCUSSION

The formulas derived above for the scattering components will now be applied to the aim of calculating appropriate measurable quantities, such as the light scattering constant and depolarization ratio.

We define the light scattering constant S also known as Rayleigh's ratio as follows for the unpolarized incident beam:

$$S = \frac{1}{2} (I_{||}^{\perp} + I_{\perp}^{\perp} + I_{||}^{\perp} + I_{\perp}^{\perp}) \left(\frac{n^2 + 2}{3}\right)^2 \frac{R_0^2}{VI}, \quad (56)$$

where n is the refractive index of a spherical sample.

By Eqs. (3) and (10)–(13), the scattering constant may be expressed in the form

$$S = S_0 + S_1 I + \dots \quad (57)$$

with

$$S_0 = \frac{1}{2} (3A_{||} + A_{\perp}^{\perp}) \left(\frac{n^2 + 2}{3}\right)^2 \frac{R_0^2}{VI}, \quad (58)$$

$$S_1 = \frac{1}{2} (3B_{||} + B_{\perp}^{\perp}) \left(\frac{n^2 + 2}{3}\right)^2 \frac{R_0^2}{VI}. \quad (59)$$

On substituting herein Eqs. (19) and (20) we obtain for a medium consisting of optically isotropic molecules

$$S_0 = \frac{1}{2} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 a^2 \rho (1 + G_R) = \frac{\pi^2 (n^2 - 1)^2}{2\lambda^4} kT\beta_T, \quad (60)$$

$$S_1 = \frac{1}{4} \left(\frac{2\pi}{\lambda} \right)^4 \left(\frac{n^2 + 2}{3} \right)^2 ac\rho (1 + G_R) = \frac{1}{2} \left(\frac{c}{a} \right) S_0^{\text{is}}. \quad (61)$$

Eq. (60) is the Einstein—Smoluchowski—Rocard formula [17], which for $G_R=0$ reduces to the well-known result of Rayleigh for perfect gases.

On rewriting Eq. (57) with Eqs. (60) and (61) in the form

$$\frac{S - S_0^{\text{is}}}{S_0^{\text{is}}} = \frac{1}{2} \left(\frac{c}{a} \right) I, \quad (62)$$

we see that the measurement of the relative change in Rayleigh ratio produced by a strong light beam of intensity I yields directly the value of the hyperpolarizability c of an isotropic molecule.

In the case of tetrahedral molecules, with regard to (54) and (55), Eq. (62) must be replaced by the following formula (in the absence of intermolecular interactions):

$$\frac{S - S_0^{\text{is}}}{S_0^{\text{is}}} = \frac{1}{2} \left\{ \left(\frac{c}{a} \right) + \frac{144}{35} \left(\frac{b_{xyz}}{a} \right)^2 \right\} I. \quad (63)$$

We now proceed to determine the order of magnitude of the change in S for methane, for which we have the following data [5, 9]: $a = 2.4 \times 10^{-24}$ cm³, $b_{xyz} = 0.2 \cdot 10^{-30}$ e.s.u. and $c = 2.6 \cdot 10^{-36}$ e.s.u. Thus, we obtain on the basis of Eq. (63)

$$\frac{S - S_0^{\text{is}}}{S_0^{\text{is}}} = 0.5(1.08 + 0.03) \cdot 10^{-12} I = 10^{-8},$$

for $I = 2 \cdot 10^4$ e.s.u.

When the molecules of the medium are anisotropic and possess the axial symmetry, we find from (58) and (59) with the help of Eqs. (38)–(41)

$$S_0 = \left\{ 1 + \frac{13}{5} \kappa_a^2 \left(\frac{1 + J_A}{1 + G_R} \right) \right\} S_0^{\text{is}}, \quad (64)$$

$$S_1 = S_1^{\text{hyp}} + S_1^{\text{or}}, \quad (65)$$

where

$$S_1^{\text{hyp}} = \frac{1}{2} \left(\frac{c}{a} \right) S_0^{\text{is}} \left\{ 1 + \frac{17}{10} \kappa_a \kappa_c \left(\frac{1 + J_A}{1 + G_R} \right) \right\} \quad (66)$$

denotes the contribution to S_1 resulting from the effect of optical hyperpolarizability and

$$S_1^{\text{or}} = \frac{a\kappa_a^2 S_0^{\text{is}}}{35kT(1 + G_R)} \{ 28(1 + G_R + 2J_A + J'_A) + 17\kappa_a(1 + 3J_A + J''_A) \} \quad (67)$$

— that from the effect of molecular orientation.

For carbon disulphide [13] $a=8.77 \cdot 10^{-24} \text{ cm}^3$, $\kappa_a=0.37$ and $c=56.5 \cdot 10^{-36} \text{ e.s.u.}$, and formulas (64)–(67) yield for $t=20^\circ\text{C}$, if the anisotropy of hyperpolarizability and the correlation of the molecules are neglected,

$$\frac{S-S_0}{S_0}=(2.1+22) \cdot 10^{-12} I=10^{-6}.$$

It will be seen that in the case of CS_2 the important contribution to S arises from the orientational molecular effect.

For molecules without a centre of inversion we have in addition to (65) the following contribution, if Eqs. (51) and (52) are used:

$$S_1^{\text{hyp}}=\frac{24}{35}\left(\frac{b}{a}\right)^2(5-4\kappa_b+5\kappa_b^2)S_0^{\text{is}}. \quad (68)$$

In the case of molecules with very small anisotropy (κ_a , κ_b and $\kappa_c \leq 0.1$), we have by (64)–(67) and (68) in good approximation:

$$\frac{S-S_0}{S_0}=\left\{\frac{1}{2}\left(\frac{c}{a}\right)+\frac{24}{7}\left(\frac{b}{a}\right)^2+\frac{4a\kappa_a^2}{5kT}\right\}I. \quad (69)$$

Using the following data for chloroform [12]: $a=8.23 \cdot 10^{-24} \text{ cm}^3$, $\kappa_a=-0.094$, $b=11.3 \cdot 10^{-29} \text{ e.s.u.}$ and $c=20 \cdot 10^{-36} \text{ e.s.u.}$, we obtain from (69):

$$\frac{S-S_0}{S_0}=(2.3+671.7+1.6) \cdot 10^{-12} I=10^{-5}.$$

We thus see that the effect due to first hyperpolarizability b has an important influence on S ; the two remaining contributions to S play no role in the case of CHCl_3 . In the case of non-polarized incident light the depolarization ratio of the light scattered is defined as

$$D=\frac{I_{||}^{\parallel}+I_{||}^{\perp}}{I_{\perp}^{\parallel}+I_{\perp}^{\perp}}=D_0+D_1 I+\dots, \quad (70)$$

where we have, by Eqs. (10)–(13),

$$D_0=\frac{2A_{||}^{\parallel}}{A_{\perp}^{\parallel}+A_{\perp}^{\perp}}, \quad D_1=\frac{2B_{||}^{\parallel}-(B_{\perp}^{\parallel}+B_{\perp}^{\perp})D_0}{A_{\perp}^{\parallel}+A_{\perp}^{\perp}}. \quad (71)$$

D_0 is the usual depolarization ratio of linearly scattered light, whereas D_1 determines the influence on D due to the light beam of high intensity I .

We confine the discussion of D to the case of systems consisting of isotropic and tetrahedral molecules (for other cases this discussion is similar to the one carried out above for S). On substituting (19), (20), (25) and (26) into Eq. (71), we have in good approximation for systems of isotropic interacting molecules

$$D_0 = \frac{6a^2 J_R}{5(1 + G_R + \dots) + 7a^2 J_R}, \quad (72)$$

$$D_1 = - \frac{35 \left(\frac{c}{a} \right) (1 + G_R + \dots) D_0 + 9(11D_0 - 6) ac J_R}{14 \{ 5(1 + G_R + \dots) + 7a^2 J_R \}}. \quad (73)$$

For carbon tetrachloride at $t=20^\circ\text{C}$ we have [12]: $\rho=6.23 \cdot 10^{21} \text{ cm}^{-3}$, $\beta_T=105 \cdot 10^{-12} \text{ cgs.}$, $1 + G_R=0.026$ (computed from Eq. 22), $D_0=0.06$, $J_R=1.3 \times 10^{43} \text{ cm}^{-6}$, $a=10.5 \cdot 10^{-24} \text{ cm}^3$ and [18] $c=28 \cdot 10^{-36} \text{ e.s.u.}$, whence we have, from the foregoing expressions,

$$\frac{D - D_0}{D_0} = -10.8 \cdot 10^{-12} I = -10^{-7}.$$

Thus, the non-linear change in D is now entirely negligible.

In the case of tetrahedral molecules, we obtain in addition to Eq. (73), by (54) and (55),

$$D_1 = \frac{32}{35} \left(\frac{b_{xyz}}{a} \right)^2. \quad (74)$$

We see that measurements of D_1 can yield directly the value of the first hyperpolarizability of the tetrahedral molecules. A formula analogous to (74) was obtained by Andrews and Buckingham [19] for the effect of a strong static electric field on D .

From the foregoing numerical evaluations we conclude that the non-linear change in S or D , as caused by a light beam of the high intensity of $I=2 \cdot 10^4 \text{ e.s.u.}$, should be accessible to experimental detection only in the case of substances consisting of strongly anisotropic molecules (e.g. CS_2) or molecules without a centre of inversion and possessing a large first hyperpolarizability b (e.g., CHCl_3). In other cases, for obtaining a measurable variation in S or D , it would be necessary to use light of much greater intensity or to evolve a method allowing to measure very small variations of the quantities in question. Finally, it should be stated that even in atomic gases non-linear scattering can be considerable if the light oscillation frequency lies near an eigen-frequency of the electronic oscillators [20].

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