

# ON THE EFFECT OF A STRONG OSCILLATING ELECTRIC FIELD ON THE REFRACTIVE INDEX OF ISOTROPIC MEDIA

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An arbitrary isotropic medium in an intense optical field is shown to gain optical anisotropy, defined by the tensor of optical permittivity:

$$n_{\sigma\tau}^2 - n^2 \delta_{\sigma\tau} = A \delta_{\sigma\tau} E_0^2 + B(3E_{0\sigma}E_{0\tau} - \delta_{\sigma\tau}E_0^2).$$

The quantities  $A$  and  $B$  are generally even functions of powers of the field amplitude  $E_0$ , with  $A$  accounting for the isotropic properties of the medium related with non-polarization and opticostriction, and  $B$  accounting for the optical anisotropy induced in the medium by the intense optical field. In the quadratic approximation of the theory,  $B$  is field independent and represents a constant of optical birefringence consisting of a term resulting from the effect of nonlinear optical deformation and a term due to that of optical molecular orientation. The constant  $B$  is discussed systematically for cases of gases, liquids and multi-component systems whose molecules are generally anisotropic of arbitrary symmetry or of well defined e.g. spherical and axial symmetry, possessing permanent dipole or quadrupole moments or otherwise. It is moreover shown that the orientational part of  $B$  is strictly related with the anisotropic part of the intensity of Rayleigh light scattering. Also, the relaxational theory of non-linear changes in the complex optical permittivity due to an intense oscillating electric field is reviewed.

## 1. Introduction

Several years before the earliest lasers became operational, a paper by Buckingham (1956) appeared predicting the possibility of inducing optical birefringence in an isotropic medium by means of an intense light beam. It was only quite recently that Paillette (1966) published the first quantitative measurements of optically induced birefringence in several organic liquids subjected to a laser beam (see also earlier attempts by Mayer and Gires 1964). His results point to an important role of the optical anisotropy of the molecules of the dipolar and non-dipolar substances investigated, in accordance with the theoretical predictions of Buckingham (1956). Moreover a similar effect, consisting in intensity-dependent refractive index variations for the two senses of circular polarization of light, was calculated and observed in liquids by Maker *et al.* (1964, 1965).

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In view of these first successful experiments, it is now of the greatest interest to study not only the optical birefringence, but also the non-linear variations in refractive index and particularly their dependence on the oscillation frequency of the applied electric field in the entire range of frequencies *i.e.* both in the Debye and optical dispersion band. The low-frequency problem had already been discussed by Peterlin and Stuart (1943), Frenkel (1946) and Volkenshteyn (1951), who extended Debye's well-known relaxation theory to the case of a strong oscillating electric field. Although in the case of dense media this theory yields but a qualitative description, it nevertheless in a simple manner accounts for the essential mechanism of the phenomenon *i.e.* of the Kerr effect as due to a strong oscillating electric field (see *e.g.* the monograph of Fabyelinskiy 1965 with the papers cited there, Bloembergen and Lallemand 1966, and Kielich 1966).

From the theoretical viewpoint, the fundamental problem of the relaxation theory of nonlinear variations in refractive index consists in calculating the distribution function in the first, second and higher approximations from the kinetic equation of diffusion (Debye 1929, Peterlin and Stuart 1943) or Fokker-Planck equation (Lebowitz and Résibois 1965). In the general case their solution is beset with very great difficulties and can be obtained effectively only in some special cases as *e.g.* for statistically non-interacting and at the same time electrically axially-symmetric but geometrically spherical molecules. In the present paper, the problem is discussed in some detail, and the nonlinear variations of the complex refractive index are calculated. Furthermore, calculations are given of the effect of a very intense optical field on the refractive index of a gas consisting of molecules of arbitrary symmetry. The theory is then extended by classical statistical methods to the case of dense media involving molecular correlations of the radial and angular kinds.

## 2. Molecular relaxational theory

We consider a medium of volume  $V$ , macroscopically isotropic in the absence of external fields, containing  $N$  identical molecules which we assume to be anisotropic in their electromagnetic properties but geometrically spherical. Let two electric fields act simultaneously on the medium: the one,  $\mathbf{E}_1 = \mathbf{E}_{01} e^{i\omega_1 t}$ , oscillating with the time  $t$  at a frequency  $\omega_1$  and playing the part of a measuring field of low strength inducing but linear polarization in the medium, and an intense field  $\mathbf{E}_2 = \mathbf{E}_{02} e^{i\omega_2 t}$  oscillating at frequency  $\omega_2$  of strength sufficient for inducing non-linear polarization. If the medium is sufficiently dense, a molecule is acted on by the local fields  $\mathbf{F}_1$  and  $\mathbf{F}_2$  and the dipole moment induced by  $\mathbf{F}_1$  in the presence of  $\mathbf{F}_2$  is given by the following expansion (to within terms linear in  $\mathbf{F}_1$  and quadratic in  $\mathbf{F}_2$ ):

$$m_{1\alpha} = \left\{ a_{\alpha\beta}^{\omega_1} + b_{\alpha\beta\gamma}^{\omega_1, \omega_2} F_{2\gamma} + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} F_{2\gamma} F_{2\delta} + \dots \right\} F_{1\beta}, \quad (2.1)$$

wherein the tensor  $a_{\alpha\beta}^{\omega_1}$  defines the linear *i.e.* first-order electric polarizability of the molecule which, in general, depends on the frequency  $\omega_1$ . The other tensors in (2.1) define non-linear polarizabilities of the molecule dependent simultaneously on  $\omega_1$  and  $\omega_2$ , with  $b_{\alpha\beta\gamma}^{\omega_1, \omega_2}$  denoting the second-order and  $c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2}$  the third-order electric polarizability tensor due to the strong field  $\mathbf{F}_2$ . The explicit forms of the dependence of these tensors on the frequencies  $\omega_1$  and

$\omega_2$  can be derived either classically or by quantum methods (see, Kielich 1963a, 1965; Butcher 1965 and the papers cited there).

Under the effect of the intense electric field  $\mathbf{F}_2$  the molecules of the medium undergo orientation and their distribution in an elementary body angle is given by the probability  $f(\Omega, \mathbf{E}_2)d\Omega$ . By classical Maxwell-Boltzmann statistics, for the case of a system at thermodynamical equilibrium in the presence of the electric field  $\mathbf{E}_2$  at temperature  $T$ , the statistical distribution function is given as

$$f(\Omega, \mathbf{E}_2) = \frac{\exp\{-\beta u(\Omega, \mathbf{E}_2)\}}{\int \exp\{-\beta u(\Omega, \mathbf{E}_2)\}d\Omega}, \quad (2.2)$$

where  $u(\Omega, \mathbf{E}_2)$  is the potential energy gained by the molecule when acted on by the intense electric field  $\mathbf{F}_2$ , whereas  $\beta = 1/kT$  is a temperature parameter. With accuracy up to the square of the field strength  $\mathbf{F}_2$ , we get the expansion

$$u(\Omega, \mathbf{E}_2) = -\mu_\alpha F_{2\alpha} - \frac{1}{2} a_{\alpha\beta}^{\omega_2} F_{2\alpha} F_{2\beta} - \dots \quad (2.3)$$

with  $\mu_\alpha$  denoting the component of the permanent dipole moment of the molecule, and  $a_{\alpha\beta}^{\omega_2}$ —the tensor of its electric polarizability as induced by the intense field  $\mathbf{F}_2$ .

By (2.2) and (2.3), we obtain the statistical distribution functions of the first and second approximations in the form

$$f^{(1)}(\Omega, \mathbf{E}_2) = \beta f^{(0)} \left\{ \mu_\alpha F_{2\alpha} + \frac{1}{2} (a_{\alpha\beta}^{\omega_2} - a^{\omega_2} \delta_{\alpha\beta}) F_{2\alpha} F_{2\beta} \right\}, \quad (2.4)$$

$$f^{(2)}(\Omega, \mathbf{E}_2) = \frac{1}{6} \beta^2 f^{(0)} (3\mu_\alpha \mu_\beta - \mu^2 \delta_{\alpha\beta}) F_{2\alpha} F_{2\beta}, \quad (2.5)$$

where  $f^{(0)} = \Omega^{-1}$  is the statistical distribution function of the zeroth approximation,  $a^{\omega_2} = a_{\alpha\alpha}^{\omega_2} / 3 = (a_{11}^{\omega_2} + a_{22}^{\omega_2} + a_{33}^{\omega_2}) / 3$  is the mean electric polarizability of the molecule, and  $\delta_{\alpha\beta}$ —the unit tensor.

The distribution function can be determined by the foregoing procedure only if the electric field acting on the molecule is static or slowly time-varying and if well-defined conditions of thermodynamical equilibrium exist. Now, in the case under consideration, the molecule is acted on by an electric field that is time-variable. Consequently, molecular orientation is related with a well-defined relaxation time and depends on the viscosity of the medium. The distribution functions have thus to describe kinetic properties of the medium which depend on the appropriate relaxation times, and can be determined from the following kinetic equation of diffusion (Peterlin and Stuart 1943):

$$\nabla^2 f + \beta \{ (\nabla f) \cdot (\nabla u) + f \nabla^2 u \} = \beta W \frac{\partial f}{\partial t}, \quad (2.6)$$

where  $W$  is a frictional torque.

We shall determine the distribution function from Eq. (2.6) for the simple and particularly interesting case of molecules possessing an axis of symmetry *e.g.* along the principal

3-axis defined by a unit vector  $\mathbf{k}$ . With such molecules, we obtain

$$\mu_\alpha = \mu k_\alpha, \quad a_{\alpha\beta} = a \delta_{\alpha\beta} + (a_{\parallel} - a_{\perp}) \left( k_\alpha k_\beta - \frac{1}{3} \delta_{\alpha\beta} \right), \quad (2.7)$$

so that the time-dependent part of the potential energy (2.3) assumes the form

$$u(\Omega, \mathbf{E}_2)_\pm = -\frac{1}{2} \mu \cos \vartheta_2 F_{02} e^{\pm i\omega_2 t} - \frac{1}{24} [3a^{\omega_2} + (a_{\parallel}^{\omega_2} - a_{\perp}^{\omega_2}) (3 \cos^2 \vartheta_2 - 1)] F_{02}^2 e^{\pm i2\omega_2 t}, \quad (2.8)$$

where  $a_{\parallel}$  and  $a_{\perp}$  are, respectively, the polarizability in the directions parallel and perpendicular to the molecule's symmetry axis, which subtends the angle  $\vartheta_2$  with the direction of the electric field  $\mathbf{F}_2$ .

By Eqs (2.4) and (2.5) the solutions of Eq. (2.6) in the first and second approximations are to be expected to be of the form

$$f_{\pm}^{(1)}(\Omega, \mathbf{E}_2) = \frac{1}{2} \beta f^{(0)} \left\{ \cos \vartheta_2 A_{\pm}^{\pm} F_{02} e^{\pm i\omega_2 t} + \frac{1}{12} (3 \cos^2 \vartheta_2 - 1) [B_{\pm}^{\pm} + B_{\pm}^{\pm} e^{\pm i2\omega_2 t}] F_{02}^2 \right\}, \quad (2.9)$$

$$f_{\pm}^{(2)}(\Omega, \mathbf{E}_2) = \frac{1}{24} \beta^2 f^{(0)} (3 \cos^2 \vartheta_2 - 1) [C_{\pm}^{\pm} + C_{\pm}^{\pm} e^{\pm i2\omega_2 t}] F_{02}^2. \quad (2.10)$$

From the expressions (2.8)–(2.10) it is seen that in the case considered both  $f$  and  $u$  depend only on the angle  $\vartheta_2$ , so that the kinetic equation (2.6) can now be written as follows (Peterlin and Stuart 1943):

$$\frac{1}{\sin \vartheta_2} \frac{\partial}{\partial \vartheta_2} \left\{ \sin \vartheta_2 \left( \frac{\partial f}{\partial \vartheta_2} + \beta f \frac{\partial u}{\partial \vartheta_2} \right) \right\} + \beta \frac{\partial u}{\partial \vartheta_2} \frac{\partial f}{\partial \vartheta_2} = \beta W \frac{\partial f}{\partial t}, \quad (2.11)$$

and we obtain the coefficients  $A$ ,  $B$  and  $C$  of Eqs (2.9) and (2.10) in the form

$$A^{\pm} = \frac{\mu}{1 \pm i\omega_2 \tau_1}, \quad B_{\pm}^{\pm} = a_{\parallel}^{\omega_2} - a_{\perp}^{\omega_2}, \quad B_{\pm}^{\pm} = \frac{a_{\parallel}^{\omega_2} - a_{\perp}^{\omega_2}}{1 \pm i2\omega_2 \tau_2},$$

$$C_{\pm}^{\pm} = \frac{\mu^2}{1 \pm i\omega_2 \tau_1}, \quad C_{\pm}^{\pm} = \frac{\mu^2}{(1 \pm i\omega_2 \tau_1)(1 \pm i2\omega_2 \tau_2)}, \quad (2.12)$$

where

$$\tau_1 = \frac{1}{2} \beta W \quad \text{and} \quad \tau_2 = \frac{1}{6} \beta W \quad (2.13)$$

define the relaxation times during which the molecule undergoes orientation.

Knowing the distribution function we can calculate the mean statistical value of the moment induced in the molecule by the field  $\mathbf{F}_1$  in the presence of the field  $\mathbf{F}_2$  and thus the refractive index presented by the medium of density  $\rho$  in the case under consideration:

$$n^2 - 1 = 4\pi\rho \left\langle \frac{\partial m_{1\alpha}}{\partial E_{1\beta}} e_{1\alpha} e_{1\beta} \right\rangle_{E_2}. \quad (2.14)$$

Here,  $\mathbf{e}_1$  is the unit vector in the direction of the field  $\mathbf{E}_1$  whereas the symbol  $\langle \rangle_{E_2}$  stands for statistical averaging in the case of a system subjected to the effect of the field  $\mathbf{E}_2$ :

$$\langle \Phi \rangle_{E_2} = \int \Phi(\tau, \mathbf{E}_2) f(\Omega, \mathbf{E}_2) d\Omega. \quad (2.15)$$

### 2.1. Linearly polarizable molecules

Assuming, as above, that the molecules are axially symmetric and but linearly polarizable, one can neglect the non-linear terms in the expansion of Eq. (2.1), thus obtaining from (2.14)

$$n^2 - 1 = \frac{4\pi}{3} \rho \left( \frac{\partial F_1}{\partial E_1} \right) \int \{3a^{\omega_1} + (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) (3 \cos^2 \vartheta_1 - 1)\} f(\Omega, \mathbf{E}_2) d\Omega, \quad (2.16)$$

where  $\vartheta_1$  is the angle between the symmetry axis of the molecule and the direction of the field  $\mathbf{F}_1$ .

On substituting into Eq. (2.16) the statistical distribution function

$$f(\Omega, \mathbf{E}_2) = f^{(0)} + f^{(1)} + f^{(2)} + \dots$$

with the values  $f^{(1)}$  and  $f^{(2)}$  given by Eqs (2.9) and (2.10), and on averaging over all possible orientations of the molecules, we obtain the refractive index in the presence of an intense oscillating electric field as follows:

$$\begin{aligned} n_{\pm}^2 - n_1^2 &= \frac{\pi Q}{45} \beta (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) \left( a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1} + \frac{\beta \mu^2}{1 \pm i\omega_2 \tau_1} \right) \times \\ &\times \left\{ 1 + \frac{e^{\pm i2\omega_2 t}}{1 \pm i2\omega_2 \tau_2} \right\} \{3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1\} \left( \frac{\partial F_1}{\partial E_1} \right) F_{02}^2, \end{aligned} \quad (2.17)$$

where

$$n_1^2 - 1 = 4\pi Q \rho a^{\omega_1} \left( \frac{\partial F_1}{\partial E_1} \right) \quad (2.18)$$

is the refractive index of light in the absence of an intense electric field ( $\mathbf{E}_2 = 0$ ).

By (2.17) it is seen that the light refractive index is a complex quantity and can be represented in standard form:

$$n_{\pm}^2 = \text{Re}(n^2) \mp i \text{Im}(n^2) \quad (2.19)$$

the real and imaginary parts being given as follows:

$$\begin{aligned} \text{Re}(n^2 - n_1^2) &= \frac{\pi Q}{45} \beta (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) \left\{ (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) \left[ 1 + \frac{\cos 2\omega_2 t + 2\omega_2 \tau_2 \sin 2\omega_2 t}{1 + 4\omega_2^2 \tau_2^2} \right] + \right. \\ &+ \frac{\beta \mu^2}{1 + \omega_2^2 \tau_1^2} \left[ 1 + \frac{(1 - 2\omega_2^2 \tau_1 \tau_2) \cos 2\omega_2 t + \omega_2 (\tau_1 + 2\tau_2) \sin 2\omega_2 t}{1 + 4\omega_2^2 \tau_2^2} \right] \left. \right\} \times \\ &\times \{3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1\} \left( \frac{\partial F_1}{\partial E_1} \right) F_{02}^2, \end{aligned} \quad (2.20)$$

$$\begin{aligned} \text{Im}(n^2 - n_1^2) = & \frac{\pi Q}{45} \beta (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) \left\{ \frac{a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}}{1 + 4\omega_2^2 \tau_2^2} (2\omega_2 \tau_2 \cos 2\omega_2 t - \sin 2\omega_2 t) + \right. \\ & \left. + \frac{\beta \mu^2}{1 + \omega_2^2 \tau_1^2} \left[ \omega_2 \tau_1 + \frac{\omega_2 (\tau_1 + 2\tau_2) \cos 2\omega_2 t - (1 - 2\omega_2^2 \tau_1 \tau_2) \sin 2\omega_2 t}{1 + 4\omega_2^2 \tau_2^2} \right] \right\} \times \\ & \times \{3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1\} \left( \frac{\partial F_1}{\partial E_1} \right) F_{02}^2. \end{aligned} \quad (2.21)$$

In the special case when the oscillation frequency of the intense field  $\mathbf{F}_2$  tends to zero ( $\omega_2 \rightarrow 0$ ), the imaginary part of (2.21) vanishes whereas the real part assumes the form

$$\begin{aligned} 2\text{Re}(n^2 - n_1^2)_{\omega_2 \rightarrow 0} = & \frac{4\pi Q}{45} \beta (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) (a_{\parallel}^0 - a_{\perp}^0 + \beta \mu^2) \times \\ & \times \{3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1\} \left( \frac{\partial F_1}{\partial E_1} \right) F_2^2 \end{aligned} \quad (2.22)$$

determining the effect of a static intense electric field  $\mathbf{F}_2$  on the refractive index. Obviously, Eq. (2.22) leads immediately to the well-known Langevin-Born formula for the Kerr constant if  $\mathbf{F}_1$  is assumed to be of the Lorentz type:

$$\mathbf{F}_1 = \frac{n_1^2 + 2}{3} \mathbf{E}_1. \quad (2.23)$$

The other extreme case results for infinitely great frequency of oscillations of the field  $\mathbf{F}_2$  ( $\omega_2 \rightarrow \infty$ ) e.g. as in a light wave, when Eq. (2.20) reduces to

$$2\text{Re}(n^2 - n_1^2)_{\omega_2 \rightarrow \infty} = \frac{2\pi Q}{45} \beta (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) (a_{\parallel}^{\infty} - a_{\perp}^{\infty}) \{3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1\} \left( \frac{\partial F_1}{\partial E_1} \right) F_{02}^2. \quad (2.24)$$

For an incident light wave propagating on the direction of the Y-axis of the laboratory reference frame, in calculating the refractive indices for oscillations along the Z-axis and X-axis from Eq. (2.18) one obtains by Eq. (2.23) the following formula:

$$\begin{aligned} (n_z^2 - n_x^2)_{\pm} = & \frac{\pi Q}{15} \beta \left( \frac{n_1^2 + 2}{3} \right)^2 (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) \left\{ a_{\parallel}^{\omega_2} - a_{\perp}^{\omega_2} + \frac{\beta \mu^2}{1 \pm i\omega_2 \tau_1} \right\} \times \\ & \times \left\{ 1 + \frac{e^{\pm i\omega_2 t}}{1 \pm i2\omega_2 \tau_2} \right\} (F_{02z}^2 - F_{02x}^2), \end{aligned} \quad (2.25)$$

which defines the birefringence induced in the medium by an intense oscillating electric field.

In the static case ( $\omega_2 = 0$ ), one obtains (2.25) the Langevin-Born formula, whereas in the optical case ( $\omega\tau \rightarrow \infty$ ) — a formula describing Buckingham's effect:

$$n_z^2 - n_x^2 = \frac{2\pi Q}{15kT} \left( \frac{n_1^2 + 2}{3} \right)^2 (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) (a_{\parallel}^{\omega_2} - a_{\perp}^{\omega_2}) (F_{02z}^2 - F_{02x}^2). \quad (2.26)$$

From what precedes, one sees that the medium becomes optically birefringent owing to the statistical process of orientation of the anisotropic molecules in the intense oscillating electric field of a light wave. One sees moreover that an intense electric field of high frequency (such that  $\omega\tau \rightarrow \infty$ ) does not produce direct orientation of permanent molecular dipoles.

## 2.2. Non-linearly polarizable molecules

If one assumes additionally that the molecules of the medium are not only anisotropic but moreover non-linearly polarizable, the full expansion of (2.1) has to be inserted in Eq. (2.14) leading to

$$n^2 - 1 = 4\pi\varrho \left( \frac{\partial F_1}{\partial E} \right) \left\langle \left\{ a_{\alpha\beta}^{\omega_1} + b_{\alpha\beta\gamma}^{\omega_1, \omega_2} e_{2\gamma} F_2 + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} e_{2\gamma} e_{2\delta} F_2^2 + \dots \right\} e_{1\alpha} e_{1\beta} \right\rangle_{E_1}. \quad (2.27)$$

Assuming as before that the molecules present the axial symmetry, we get in addition to (2.7) for the second-order polarizability tensor (omitting for the time being the term with the polarizability tensor of the third order):

$$b_{\alpha\beta\gamma} = b \delta_{\alpha\beta} k_\gamma + (b_{\parallel} - b_{\perp}) \left( k_\alpha k_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) k_\gamma,$$

where we have introduced the notation

$$b = \frac{1}{3} (b_{\parallel} + 2b_{\perp}), \quad b_{\parallel} = b_{333}, \quad b_{\perp} = b_{113} = b_{223},$$

assuming  $b_{222} = 0$  and  $b_{131} = 0$  (without this assumption, we would be dealing with the case of the point group  $C_{3v}$ ).

With the above assumptions, Eq. (2.27) yields

$$n^2 - n_1^2 = \frac{4\pi}{3} \varrho \left( \frac{\partial F_1}{\partial E_1} \right) \int \{ (a_{\parallel}^{\omega_1} - a_{\perp}^{\omega_1}) (3 \cos^2 \vartheta_1 - 1) + [3b^{\omega_1, \omega_2} + (b_{\parallel}^{\omega_1, \omega_2} - b_{\perp}^{\omega_1, \omega_2}) (3 \cos^2 \vartheta_1 - 1)] F_2 \cos \vartheta_2 \} f(\Omega, \mathbf{E}_2) d\Omega \quad (2.28)$$

whence on substituting (2.9) and averaging over all possible orientations of the molecules we obtain the additional contribution to the variation in refractive index due to second-order non-linear polarization of the molecules:

$$(n^2 - n_1^2)_b = \frac{4\pi}{3} \varrho \beta \left( \frac{\partial F_1}{\partial E_1} \right) \left\{ b^{\omega_1, \omega_2} + \frac{2}{15} [3(e_1 \cdot e_2)^2 - 1] (b_{\parallel}^{\omega_1, \omega_2} - b_{\perp}^{\omega_1, \omega_2}) \right\} \frac{\mu F_2^2}{1 + i\omega_2 \tau_1}. \quad (2.29)$$

The additional birefringence from this formula amounts to

$$(n_x^2 - n_x^2)_b = \frac{8\pi}{15} \varrho \beta \left( \frac{n_1^2 + 2}{3} \right)^2 (b_{\parallel}^{\omega_1, \omega_2} - b_{\perp}^{\omega_1, \omega_2}) \frac{\mu}{1 + i\omega_2 \tau_1} (F_{2x}^2 - F_{2x}^2) \quad (2.30)$$

and vanishes for optical frequencies *i.e.* if  $\omega\tau \rightarrow \infty$ .

We still have to calculate the contribution from the third-order polarizability tensor. We shall perform this for the special case of isotropically polarizable molecules, when

$$\alpha_{\alpha\beta} = a\delta_{\alpha\beta}, \quad \mu_{\alpha} = b_{\alpha\beta\gamma} = 0,$$

$$c_{\alpha\beta\gamma\delta} = c_{\perp}\delta_{\alpha\beta}\delta_{\gamma\delta} + \frac{1}{2}(c_{\parallel} - c_{\perp})(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}), \quad (2.31)$$

where  $c_{\parallel} = c_{3333}$  and  $c_{\perp} = c_{1133}$ . In this case Eq. (2.27) yields the following change in refractive index (*cf.* Kielich and Piekara 1959):

$$n^2 - n_1^2 = 2\pi Q \left( \frac{\partial F_1}{\partial E_1} \right) \{c_{\perp}^{\omega_1, \omega_1} + (\mathbf{e}_1 \cdot \mathbf{e}_2)^2 (c_{\parallel}^{\omega_1, \omega_1} - c_{\perp}^{\omega_1, \omega_1})\} F_2^2, \quad (2.32)$$

and the optical birefringence

$$n_x^2 - n_z^2 = 2\pi Q \left( \frac{n_1^2 + 2}{3} \right)^2 (c_{\parallel}^{\omega_1, \omega_1} - c_{\perp}^{\omega_1, \omega_1}) (F_{2x}^2 - F_{2z}^2). \quad (2.33)$$

Hence we find that optical birefringence can also arise in a medium consisting of isotropic atoms or molecules as a result of the non-linear anisotropy induced in them by the square of an intense electric field. Moreover, the effect occurs both in a static field and in one that oscillates at a high rate. In the static case ( $\omega_2 = 0$ ) Eq. (2.33) defines the well-known Voigt effect, whereas in the optical case — the effect considered by Buckingham (1956).

### 3. Refractive index of a gas in the presence of a very intense optical field

We shall now extend our previous considerations to the case of a gas consisting of molecules of arbitrary symmetry subjected to the effect of a very intense oscillating electric field. We shall assume however, for simplicity, that the oscillation frequency of the field is very high, admitting of time-averaging of the molecular energy appearing in the definition of the distribution function of Eq. (2.2). We shall now extend the expansion of the energy  $u(\Omega, \mathbf{E}_2)$  to include the term proportional to the fourth power of  $F_2$  *i.e.* in place of (2.3) we now write

$$u(\Omega, \mathbf{E}_2) = -\mu_{\alpha} F_{2\alpha} - \frac{1}{2} a_{\alpha\beta}^{\omega_1} F_{2\alpha} F_{2\beta} - \frac{1}{6} b_{\alpha\beta\gamma}^{\omega_1} F_{2\alpha} F_{2\beta} F_{2\gamma} -$$

$$- \frac{1}{24} c_{\alpha\beta\gamma\delta}^{\omega_1} F_{2\alpha} F_{2\beta} F_{2\gamma} F_{2\delta} - \dots \quad (3.1)$$

whence on time-averaging we obtain

$$\overline{u(\Omega, \mathbf{E}_2)} = -\frac{1}{4} a_{\alpha\beta}^{\omega_1} e_{2\alpha} e_{2\beta} F_{02}^2 - \frac{1}{64} c_{\alpha\beta\gamma\delta}^{\omega_1} e_{2\alpha} e_{2\beta} e_{2\gamma} e_{2\delta} F_{02}^4 - \dots \quad (3.2)$$

Inserting this expansion into (2.2) we have the distribution functions of the first and second approximation (retaining only terms proportional to  $F_2^4$ ) in the form

$$f^{(1)}(\Omega, \mathbf{E}_2) = \frac{1}{4} \beta f^{(0)} \left\{ a_{\alpha\beta}^{\omega_1} (e_{2\alpha} e_{2\beta} - \langle e_{2\alpha} e_{2\beta} \rangle_0) F_{02}^2 + \right. \\ \left. + \frac{1}{16} c_{\alpha\beta\gamma\delta}^{\omega_1} (e_{2\alpha} e_{2\beta} e_{2\gamma} e_{2\delta} - \langle e_{2\alpha} e_{2\beta} e_{2\gamma} e_{2\delta} \rangle_0) F_{02}^4 + \dots \right\}, \quad (3.3)$$

$$f^{(2)}(\Omega, \mathbf{E}_2) = \frac{1}{32} \beta^2 f^{(0)} \{ a_{\alpha\beta}^{\omega_1} a_{\gamma\delta}^{\omega_2} (e_{2\alpha} e_{2\beta} e_{2\gamma} e_{2\delta} - \langle e_{2\alpha} e_{2\beta} e_{2\gamma} e_{2\delta} \rangle_0 - \\ - \langle e_{2\alpha} e_{2\beta} \rangle_0 e_{2\gamma} e_{2\delta} - e_{2\alpha} e_{2\beta} \langle e_{2\gamma} e_{2\delta} \rangle_0 + 2 \langle e_{2\alpha} e_{2\beta} \rangle_0 \langle e_{2\gamma} e_{2\delta} \rangle_0) F_{02}^4 + \dots \}, \quad (3.4)$$

where

$$\langle e_{2\alpha} e_{2\beta} e_{2\gamma} \dots \rangle_0 = \int e_{2\alpha} e_{2\beta} e_{2\gamma} \dots f^{(0)} d\Omega$$

denotes averaging over all possible orientations of the molecules with the distribution function of the zeroth approximation  $f^{(0)} = \Omega^{-1}$ , i.e. averaging with equal probability.

In the case now under consideration, the dipole moment induced in a molecule has also to be solved with an accuracy up to  $F_2^4$ ; this leads to the tensor of differential polarizability of the molecule in the presence of a strong optical field in the form (Kielich 1961a)

$$\frac{\partial m_{1\alpha}}{\partial E_{1\chi}} = \left\{ a_{\alpha\beta}^{\omega_1} + b_{\alpha\beta\gamma}^{\omega_1, \omega_2} F_{2\gamma} + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} F_{2\gamma} F_{2\delta} + \right. \\ \left. + \frac{1}{6} d_{\alpha\beta\gamma\delta\epsilon}^{\omega_1, \omega_2} F_{2\gamma} F_{2\delta} F_{2\epsilon} + \frac{1}{24} e_{\alpha\beta\gamma\delta\epsilon\eta}^{\omega_1, \omega_2} F_{2\gamma} F_{2\delta} F_{2\epsilon} F_{2\eta} + \dots \right\} \frac{\partial F_{1\beta}}{\partial E_{1\chi}}. \quad (3.5)$$

In the above expansion two new tensors,  $d_{\alpha\beta\gamma\delta\epsilon}$  and  $e_{\alpha\beta\gamma\delta\epsilon\eta}$ , appear; they define the non-linear polarizability of the fourth and fifth orders, respectively.

On taking the time-average of the expansion (3.5) and inserting in (2.14), we obtain

$$n^2 - 1 = 4\pi Q \left( \frac{\partial F_1}{\partial E_1} \right) \int \left\{ a_{\alpha\beta}^{\omega_1} + \frac{1}{4} c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} e_{2\gamma} e_{2\delta} F_{02}^2 + \right. \\ \left. + \frac{1}{64} e_{\alpha\beta\gamma\delta\epsilon\eta}^{\omega_1, \omega_2} e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} F_{02}^4 + \dots \right\} e_{1\alpha} e_{1\beta} f(\Omega, \mathbf{E}_2) d\Omega. \quad (3.6)$$

On substituting herein the distribution functions (3.3) and (3.4), we can write the following expansion of the refractive index in even powers of the amplitude  $E_{02}$  (Kielich 1961 a):

$$n^2 - n_1^2 = Q_2 E_{02}^2 + Q_4 E_{02}^4 + \dots, \quad (3.7)$$

where the expansion coefficients  $Q_2$  and  $Q_4$  are of the form

$$Q_2 = \pi\rho \left( \frac{\partial F_1}{\partial E_1} \right) \left( \frac{F_2}{E_2} \right)^2 \{ c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} \langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} \rangle_0 + \beta \alpha_{\alpha\beta}^{\omega_1} \alpha_{\gamma\delta}^{\omega_2} (\langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} \rangle_0 - \langle e_{1\alpha} e_{1\beta} \rangle_0 \langle e_{2\gamma} e_{2\delta} \rangle_0) \}, \tag{3.8}$$

$$Q_4 = \frac{\pi\rho}{16} \left( \frac{\partial F_1}{\partial E_1} \right) \left( \frac{F_2}{E_2} \right)^4 \{ e_{\alpha\beta\gamma\delta\epsilon\eta}^{\omega_1, \omega_2} \langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0 + 4\beta [ \alpha_{\alpha\beta}^{\omega_1} c_{\gamma\delta\epsilon\eta}^{\omega_2} (\langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0 - \langle e_{1\alpha} e_{1\beta} \rangle_0 \langle e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0) + c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} \alpha_{\epsilon\eta}^{\omega_2} (\langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0 - \langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} \rangle_0 \langle e_{2\epsilon} e_{2\eta} \rangle_0) ] + 2\beta^2 \alpha_{\alpha\beta}^{\omega_1} \alpha_{\gamma\delta}^{\omega_2} \alpha_{\epsilon\eta}^{\omega_2} (\langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0 - \langle e_{1\alpha} e_{1\beta} \rangle_0 \langle e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0 - \langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} \rangle_0 \langle e_{2\epsilon} e_{2\eta} \rangle_0 - \langle e_{1\alpha} e_{1\beta} e_{2\epsilon} e_{2\eta} \rangle_0 \langle e_{2\gamma} e_{2\delta} \rangle_0 + 2 \langle e_{1\alpha} e_{1\beta} \rangle_0 \langle e_{2\gamma} e_{2\delta} \rangle_0 \langle e_{2\epsilon} e_{2\eta} \rangle_0) \}. \tag{3.9}$$

Since in the absence of fields all directions of the unit vectors  $\mathbf{e}_1$  and  $\mathbf{e}_2$  with regard to the axes of the laboratory reference frame are equally probable, we have (Kielich 1961b, 1963b).

$$\begin{aligned} \langle e_{1\alpha} e_{1\beta} \rangle_0 &= \frac{1}{3} \delta_{\alpha\beta}, & \langle e_{2\gamma} e_{2\delta} \rangle_0 &= \frac{1}{3} \delta_{\gamma\delta}, & \langle e_{1\alpha} e_{2\gamma} \rangle_0 &= \frac{1}{3} (\mathbf{e}_1 \cdot \mathbf{e}_2) \delta_{\alpha\gamma}, \\ \langle e_{2\alpha} e_{2\beta} e_{2\gamma} e_{2\delta} \rangle_0 &= \frac{1}{15} \sigma_{\alpha\beta\gamma\delta}, \\ \langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} \rangle_0 &= \frac{1}{90} \{ 10 \delta_{\alpha\beta} \delta_{\gamma\delta} + [3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1] \chi_{\alpha\beta\gamma\delta} \}, \\ \langle e_{1\alpha} e_{1\beta} e_{2\gamma} e_{2\delta} e_{2\epsilon} e_{2\eta} \rangle_0 &= \frac{1}{630} \{ 14 \delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} + [3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1] \chi_{\alpha\beta\gamma\delta\epsilon\eta} \}, \end{aligned} \tag{3.10}$$

where we have used the notation:

$$\begin{aligned} \sigma_{\alpha\beta\gamma\delta} &= \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}, \\ \chi_{\alpha\beta\gamma\delta} &= 3\delta_{\alpha\gamma} \delta_{\beta\delta} + 3\delta_{\alpha\delta} \delta_{\beta\gamma} - 2\delta_{\alpha\beta} \delta_{\gamma\delta} = 3\sigma_{\alpha\beta\gamma\delta} - 5\delta_{\alpha\beta} \delta_{\gamma\delta}, \\ \chi_{\alpha\beta\gamma\delta\epsilon\eta} &= 3\delta_{\alpha\gamma} \sigma_{\delta\epsilon\eta\beta} + 3\delta_{\alpha\delta} \sigma_{\epsilon\eta\beta\gamma} + 3\delta_{\alpha\epsilon} \sigma_{\eta\beta\gamma\delta} + 3\delta_{\alpha\eta} \sigma_{\beta\gamma\delta\epsilon} - 4\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta}. \end{aligned} \tag{3.11}$$

By (3.10), the coefficients (3.8) and (3.9) can be transformed as follows:

$$Q_2 = \frac{1}{2} \left( \frac{\partial F_1}{\partial E_1} \right) \left( \frac{F_2}{E_2} \right)^2 \{ A_2 + [3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1] B_2 \}, \tag{3.12}$$

$$Q_4 = \frac{1}{2} \left( \frac{\partial F_1}{\partial E_1} \right) \left( \frac{F_2}{E_2} \right)^4 \{ A_4 + [3(\mathbf{e}_1 \cdot \mathbf{e}_2)^2 - 1] B_4 \}, \tag{3.13}$$

where we have introduced the constants:

$$A_2 = \frac{2\pi}{9} \rho c_{\alpha\alpha\beta\beta}^{\omega_1, \omega_2}, \quad (3.14)$$

$$B_2 = \frac{\pi\rho}{45} (c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} + \beta a_{\alpha\beta}^{\omega_1} a_{\gamma\delta}^{\omega_2}) \chi_{\alpha\beta\gamma\delta}, \quad (3.15)$$

$$A_4 = \frac{\pi\rho}{1080} (3e_{\alpha\beta\gamma\delta\epsilon\eta}^{\omega_1, \omega_2} \sigma_{\gamma\delta\epsilon\eta} + 4\beta c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} a_{\epsilon\eta}^{\omega_2} \chi_{\gamma\delta\epsilon\eta}) \delta_{\alpha\beta}, \quad (3.16)$$

$$B_4 = \frac{\pi\rho}{15120} \{3e_{\alpha\beta\gamma\delta\epsilon\eta}^{\omega_1, \omega_2} \chi_{\alpha\beta\gamma\delta\epsilon\eta} + 4\beta c_{\alpha\beta\gamma\delta}^{\omega_1, \omega_2} a_{\epsilon\eta}^{\omega_2} (3\chi_{\alpha\beta\gamma\delta\epsilon\eta} - 7\chi_{\alpha\beta\gamma\delta} \delta_{\epsilon\eta}) + 12\beta a_{\alpha\beta}^{\omega_1} c_{\gamma\delta\epsilon\eta}^{\omega_2} \chi_{\alpha\beta\gamma\delta\epsilon\eta} + 2\beta^2 a_{\alpha\beta}^{\omega_1} a_{\gamma\delta}^{\omega_2} a_{\epsilon\eta}^{\omega_2} (3\chi_{\alpha\beta\gamma\delta\epsilon\eta} - 7\chi_{\alpha\beta\gamma\delta} \delta_{\epsilon\eta} - 7\chi_{\alpha\beta\epsilon\eta} \delta_{\gamma\delta})\}. \quad (3.17)$$

The constants  $A_2$  and  $A_4$  define non-linear changes in refractive index of an isotropic nature, whereas  $B_2$  and  $B_4$  define the anisotropy induced in the medium by a strong optical field. The expressions (3.14)–(3.17) hold for non-dense media of arbitrarily symmetric molecules.

From Eqs (3.7), (3.12) and (3.13), we derive the birefringence induced in the medium as follows:

$$n_z^2 - n_x^2 = \frac{1}{6} (n_1^2 + 2)^2 (B_2 + B_4 F_{02}^2 + \dots) (F_{02z}^2 - F_{02x}^2). \quad (3.18)$$

We now proceed to apply the constants (3.14)–(3.17) to some particular molecular symmetries. We shall begin by a discussion of the constants  $A_2$  and  $B_2$ . For convenience, the latter will be resolved into a part defining the effect of non-linear optical deformation:

$$B_2^{\text{def}} = \frac{\pi\rho}{45} (3c_{\alpha\beta\alpha\beta}^{\omega_1, \omega_2} + 3c_{\alpha\beta\beta\alpha}^{\omega_1, \omega_2} - 2c_{\alpha\alpha\beta\beta}^{\omega_1, \omega_2}) \quad (3.19)$$

and a part defining the effect of optical molecular orientation:

$$B_2^{\text{or}} = \frac{\pi\rho}{45kT} (3a_{\alpha\beta}^{\omega_1} a_{\alpha\beta}^{\omega_2} + 3a_{\alpha\beta}^{\omega_1} a_{\beta\alpha}^{\omega_2} - 2a_{\alpha\alpha}^{\omega_1} a_{\beta\beta}^{\omega_2}). \quad (3.20)$$

For molecules having symmetry of the point groups  $C_{6h}$  (thus *e. g.*  $C_6Cl_6$ ) and  $D_{6h}$  (*e. g.*  $C_6H_6$ ) we obtain

$$\begin{aligned} a_{\alpha\beta} &= a_{11} \delta_{\alpha\beta} + (a_{33} - a_{11}) k_\alpha k_\beta, \\ c_{\alpha\beta\gamma\delta} &= (c_{1111} - c_{1133} - c_{3311} - 4c_{1313} + c_{3333}) k_\alpha k_\beta k_\gamma k_\delta + \\ &+ c_{1122} (\delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\beta} k_\gamma k_\delta - k_\alpha k_\beta \delta_{\gamma\delta}) + c_{1133} \delta_{\alpha\beta} k_\gamma k_\delta + \\ &+ c_{3311} k_\alpha k_\beta \delta_{\gamma\delta} + \frac{1}{2} (c_{1111} - c_{1122}) (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) + \\ &+ \frac{1}{2} (2c_{1313} - c_{1111} + c_{1122}) (\delta_{\alpha\gamma} k_\beta k_\delta + \delta_{\alpha\delta} k_\beta k_\gamma + k_\alpha k_\gamma \delta_{\beta\delta} + k_\alpha k_\delta \delta_{\beta\gamma}), \end{aligned} \quad (3.21)$$

and the expressions of Eqs (3.14), (3.19) and (3.20) become

$$A_2 = \frac{2\pi}{9} \varrho (2c_{1111} + 2c_{1122} + 2c_{1133} + 2c_{3311} + c_{3333})^{\omega_1, \omega_2}, \quad (3.22)$$

$$B_2^{\text{def}} = \frac{2\pi}{45} \varrho (7c_{1111} - 5c_{1122} - 2c_{1133} - 2c_{3311} + 12c_{1313} + 2c_{3333})^{\omega_1, \omega_2}, \quad (3.23)$$

$$B_2^{\text{or}} = \frac{4\pi\varrho}{45kT} (a_{33}^{\omega_1} - a_{11}^{\omega_1}) (a_{33}^{\omega_2} - a_{11}^{\omega_2}). \quad (3.24)$$

The above expressions hold moreover for a vast class of various linear molecules (*e. g.*  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , and so forth) belonging to the point group  $D_{\infty h}$ .

In particular, for the spherical symmetry we have also  $a_{11} = a_{33}$ ,  $c_{3333} = c_{1111}$ ,  $c_{1122} = c_{1133} = c_{3311}$ ,  $2c_{1313} = c_{3333} - c_{1133}$  and Eqs (3.22)–(3.24) reduce to

$$A_2 = \frac{2\pi}{3} \varrho (c_{3333}^{\omega_1, \omega_2} + 2c_{1133}^{\omega_1, \omega_2}), \quad (3.25)$$

$$B_2^{\text{def}} = \frac{2\pi}{3} \varrho (c_{3333}^{\omega_1, \omega_2} - c_{1133}^{\omega_1, \omega_2}), \quad (3.26)$$

$$B_2^{\text{or}} = 0. \quad (3.27)$$

Hence, as it was to be expected, in a gas of isotropically polarizable molecules the effect of optical molecular orientation does not appear, but only isotropic deformation.

In the case of anisotropic molecules linearly polarizable in all three directions of the principal axes, the constant (3.20) can be written as follows:

$$B_2^{\text{or}} = \frac{2\pi\varrho}{45kT} \{ (a_{11}^{\omega_1} - a_{22}^{\omega_1}) (a_{11}^{\omega_2} - a_{22}^{\omega_2}) + (a_{22}^{\omega_1} - a_{33}^{\omega_1}) (a_{22}^{\omega_2} - a_{33}^{\omega_2}) + (a_{33}^{\omega_1} - a_{11}^{\omega_1}) (a_{33}^{\omega_2} - a_{11}^{\omega_2}) \}, \quad (3.28)$$

whence for axially-symmetric molecules one obtains immediately (3.24).

We shall at first apply the constants (3.16) and (3.17) to systems having the spherical symmetry, for which in addition to (2.31) we have (Kielich 1961a)

$$e_{\alpha\beta\gamma\delta\epsilon\eta} = \frac{1}{3} e_{113333} \delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta} + \frac{1}{36} (e_{333333} - e_{113333}) (\chi_{\alpha\beta\gamma\delta\epsilon\eta} + 4\delta_{\alpha\beta} \sigma_{\gamma\delta\epsilon\eta}). \quad (3.29)$$

This yields

$$A_4^{\text{def}} = \frac{\pi\varrho}{24} (e_{333333}^{\omega_1, \omega_2} + 2e_{113333}^{\omega_1, \omega_2}), \quad (3.30)$$

$$B_4^{\text{def}} = \frac{\pi\varrho}{24} (e_{333333}^{\omega_1, \omega_2} - e_{113333}^{\omega_1, \omega_2}). \quad (3.31)$$

Thus, in the present case, the only effect is that of non-linear optical deformation.

Assuming for simplicity that the molecules are linearly polarizable and axially-symmetric, the constant (3.17) reduces to

$$B_4^{\text{or}} = \frac{2\pi\varrho}{945k^2T^2} (a_{33}^{\omega_1} - a_{11}^{\omega_1}) (a_{33}^{\omega_2} - a_{11}^{\omega_2})^2. \quad (3.32)$$

#### 4. General theory for a dense medium

Let us consider a dense medium, isotropic in the absence of external fields. As previously, we assume that two light waves are incident on the medium in arbitrary directions, conveying respectively the electric fields  $\mathbf{E}_1 = \mathbf{E}_{01} \cos \omega_1 t$  and  $\mathbf{E}_2 = \mathbf{E}_{02} \cos \omega_2 t$ . We assume moreover that the wavelength of either light beam is strongly in excess of the intermolecular distances, and that their oscillation frequencies  $\omega_1$  and  $\omega_2$  lie outside the regions of electron absorption of the substance of which the medium consists, with  $\omega_2$  sufficiently large to admit of time-averaging of the effect due to the field  $\mathbf{E}_2$  but sufficiently low for the molecules to follow the field.

For generality of the results, we shall now proceed by a semi-macroscopic approach of the theory. We consider a spherical, macroscopic sample of volume  $V$  within the medium in which the field  $\mathbf{E}_1$  induces polarization given by the vector  $\mathbf{P}_1$ . Under the effect of the strong optical field  $\mathbf{E}_2$ , the medium becomes anisotropic, its optical properties being given by the permittivity tensor

$$n_{\sigma\tau}^2 - \delta_{\sigma\tau} = 4\pi \frac{\overline{\partial P_{1\sigma}}}{\partial E_{1\tau}^M}, \quad (4.1)$$

where  $\mathbf{E}_1^M$  is the mean macroscopic field strength existing in the medium, and the indices  $\sigma$  and  $\tau$  relate to the axes  $X$ ,  $Y$  and  $Z$  of the laboratory reference frame attached to the centre of the sphere.

Since the polarization vector  $\mathbf{P}_1$  is defined by the ratio of the dipole moment  $\mathbf{M}_1$  and the volume  $V$  of the sphere, we have

$$\frac{\partial P_{1\sigma}}{\partial E_{1\tau}^M} = \frac{1}{V} \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \right\rangle_{\mathbf{E}_2}, \quad (4.2)$$

once we assume that the volume  $V$  does not depend on the weak optical field  $\mathbf{E}_1$  and the relation between  $\mathbf{M}_1$  and  $\mathbf{E}_1$  is linear.

At present, in Eq. (4.2) the mean statistical value  $\langle \rangle_{\mathbf{E}_2}$  in the presence of the intense field  $\mathbf{E}_2$  is defined as follows:

$$\left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \right\rangle_{\mathbf{E}_2} = \frac{\int \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \exp \{-\beta \overline{U(\tau, \mathbf{E}_2)}\} d\tau}{\int \exp \{-\beta \overline{U(\tau, \mathbf{E}_2)}\} d\tau}, \quad (4.3)$$

where  $U(\tau, \mathbf{E}_2)$  is the total potential energy of the whole system at configuration  $\tau$  under the effect of the field  $\mathbf{E}_2$ .

We assume that the sphere when acted on by the strong field  $\mathbf{E}_2$  changes its volume  $V$  only, without undergoing a change in shape, and that this change is an even function of  $\mathbf{E}_2$ ,

$$V(\mathbf{E}_2) = V(0) + \frac{1}{2} \left( \frac{\partial^2 V}{\partial E_2^2} \right)_0 E_2^2 + \frac{1}{24} \left( \frac{\partial^4 V}{\partial E_2^4} \right)_0 E_2^4 + \dots \quad (4.4)$$

We have thus taken into account the effect of optico-striction, which in quadratic approximation, by analogy with electrostriction, can be expressed as follows:

$$\frac{1}{2} \left( \frac{\partial^2 V}{\partial E_2^2} \right)_0 = -\frac{1}{8\pi} \left\{ \frac{\partial}{\partial p} [(n^2-1)V] \right\}_T = -\frac{V}{8\pi} \left\{ \left( \frac{\partial n^2}{\partial p} \right)_T - (n^2-1) \beta_T \right\} \quad (4.5)$$

with  $p$  denoting the pressure and  $\beta_T$  the isothermal compressibility of the medium.

On expanding (4.2) in a power series in  $\mathbf{E}_2$  we obtain from (4.1) by (4.4) (for the sake of simplicity, we shall restrict our calculations henceforth to terms quadratic in the field  $\mathbf{E}_2$ )

$$n_{\sigma\tau}^2 - n_{1\sigma\tau}^2 = Q_{\sigma\tau}^V + Q_{\sigma\tau}^P, \quad (4.6)$$

where

$$n_{1\sigma\tau}^2 - \delta_{\sigma\tau} = \frac{4\pi}{V} \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \right\rangle \quad (4.7)$$

is the tensor of optical permittivity of the medium in the absence of an intense optical field ( $\mathbf{E}_2 = 0$ ).

In (4.6) the tensors

$$Q_{\sigma\tau}^P = \frac{2\pi}{V} \left\{ \frac{\partial^2}{\partial E_{2\nu} \partial E_{2\epsilon}} \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \right\rangle_{E_1} \right\} \overline{E_{2\nu} E_{2\epsilon}^t}, \quad (4.8)$$

$$Q_{\sigma\tau}^V = -\frac{2\pi}{V^2} \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \right\rangle \left( \frac{\partial^2 V}{\partial E_2^2} \right)_0 \overline{E_2^t} \quad (4.9)$$

describe the effects arising from the changes in polarizability and volume of the sphere, respectively, due to the strong optical field  $\mathbf{E}_2$ .

By the definition of (4.3) the tensor (4.8) can be expressed as follows

$$Q_{\sigma\tau}^P = \frac{2\pi}{V} \left\{ \left\langle \frac{\partial^3 M_{1\sigma}}{\partial E_{1\tau}^M \partial E_{2\nu} \partial E_{2\epsilon}} \right\rangle - \beta \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \frac{\partial^2 U}{\partial E_{2\nu} \partial E_{2\epsilon}} \right\rangle + \beta \left\langle \frac{\partial M_{1\sigma}}{\partial E_{1\tau}^M} \right\rangle \left\langle \frac{\partial^2 U}{\partial E_{2\nu} \partial E_{2\epsilon}} \right\rangle \right\} \overline{E_{2\nu} E_{2\epsilon}^t}. \quad (4.10)$$

On averaging (4.9) and (4.10) over all directions of the vectors  $\mathbf{e}_1$  and  $\mathbf{e}_2$  with respect to the laboratory frame, we obtain from (4.6)

$$n_{\sigma\tau}^2 - n_{1\sigma\tau}^2 = A_2 \frac{\partial E_{1\sigma}}{\partial E_{1\tau}^M} \overline{E_2^t} + B_2 \left( 3 \frac{\partial E_{1\nu}}{\partial E_{1\tau}^M} \overline{E_{2\sigma} E_{2\nu}^t} - \frac{\partial E_{1\sigma}}{\partial E_{1\tau}^M} \overline{E_2^t} \right), \quad (4.11)$$

$$A_2 = \frac{2\pi}{9V} \left\langle \frac{\partial^3 M_{1\alpha}}{\partial E_{1\alpha} \partial E_{2\beta} \partial E_{2\beta}} \right\rangle - \frac{2\pi}{3V^2} \left\langle \frac{\partial M_{1\alpha}}{\partial E_{1\alpha}} \right\rangle \left\{ \frac{\partial}{\partial p} (\chi^\circ V) \right\}_T - \frac{2\pi}{9V} \beta \left\{ \left\langle \frac{\partial M_{1\alpha}}{\partial E_{1\alpha}} \frac{\partial^2 U}{\partial E_{2\beta} \partial E_{2\beta}} \right\rangle - \left\langle \frac{\partial M_{1\alpha}}{\partial E_{1\alpha}} \right\rangle \left\langle \frac{\partial^2 U}{\partial E_{2\beta} \partial E_{2\beta}} \right\rangle \right\}, \quad (4.12)$$

$$B_2 = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \frac{\partial^3 M_{1\alpha}}{\partial E_{1\beta} \partial E_{2\gamma} \partial E_{2\delta}} \right\rangle - \beta \frac{\partial M_{1\alpha}}{\partial E_{1\beta}} \frac{\partial^2 U}{\partial E_{2\gamma} \partial E_{2\delta}} \right\}. \quad (4.13)$$

Eqs (4.11)–(4.13) define the non-linear variation of the optical permeability tensor as produced by a strong optical field in an arbitrary dense isotropic medium. The constant (4.12) defining isotropic changes in refractive index is seen to consist of a term defining the non-linear variation of the moment  $\mathbf{M}_1$ , a temperature-dependent term related with fluctuations of the linear polarization of the medium, and a term related with the change in volume due to the strong optical field (optico-striction).

Assuming now for convenience that the spherical sample is not within the medium but in vacuum, the expression

$$M_{2\sigma} = - \frac{\partial U}{\partial E_{2\sigma}} \quad (4.14)$$

represents the dipole moment induced in the sphere by the strong field  $\mathbf{E}_2$ .

If we assume moreover that the relationship between  $\mathbf{E}_1$  and  $\mathbf{E}_1^M$  is isotropic *i. e.* that

$$\frac{\partial E_{1\sigma}}{\partial E_{1\tau}^M} = \frac{n_1^2 + 2}{3} \delta_{\sigma\tau},$$

we can write Eq. (4.11) as follows:

$$n_{\sigma\tau}^2 - n_1^2 \delta_{\sigma\tau} = \left( \frac{n_1^2 + 2}{3} \right) \{ A_2 \delta_{\sigma\tau} \overline{E_{2z}^2} + B_2 (3 \overline{E_{2\sigma} E_{2\tau}} - \delta_{\sigma\tau} \overline{E_{2z}^2}) \} \quad (4.15)$$

whence on calculating the components  $n_{zz}^2$  and  $n_{xx}^2$  we obtain the optical birefringence:

$$n_{zz}^2 - n_{xx}^2 = \frac{1}{3} (n_1^2 + 2)^2 B_2 (\overline{E_{2z}^2} - \overline{E_{2x}^2}), \quad (4.16)$$

where the optical birefringence constant is defined as

$$B_2 = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \frac{\partial^3 M_{1\alpha}}{\partial E_{1\beta} \partial E_{2\gamma} \partial E_{2\delta}} + \beta \frac{\partial M_{1\alpha}}{\partial E_{1\beta}} \frac{\partial M_{2\gamma}}{\partial E_{2\delta}} \right\rangle. \quad (4.17)$$

Denoting by  $\mathbf{x}$ ,  $\mathbf{y}$ ,  $\mathbf{z}$  unit vectors in the directions of  $X$ ,  $Y$ ,  $Z$ , we can write

$$\mathbf{E}_2 = \mathbf{x} E_{2x} + \mathbf{y} E_{2y} + \mathbf{z} E_{2z} = \{ \mathbf{x} \sin \vartheta \cos \varphi + \mathbf{y} \sin \vartheta \sin \varphi + \mathbf{z} \cos \vartheta \} E_2, \quad (4.18)$$

and the quantity appearing in Eq. (4.16) is

$$\overline{E_{2z}^2} - \overline{E_{2x}^2} = g \overline{E_2^2} = \frac{1}{2} g E_{02}^2, \quad (4.19)$$

where

$$g = \cos^2 \vartheta - \sin^2 \vartheta \cos^2 \varphi \quad (4.20)$$

is a quantity defining the value and sign of the optical birefringence.

If in particular the wave propagates in the direction of the  $Y$ -axis *i. e.* if the vector  $\mathbf{E}_2$  oscillates in the  $XZ$ -plane ( $\varphi = 0$ ), we have according to the direction of polarization of the wave

$$g = \cos^2 \vartheta - \sin^2 \vartheta = \begin{cases} 1 & \text{for } \vartheta = 0^\circ, \\ 0 & \text{for } \vartheta = 45^\circ, \\ -1 & \text{for } \vartheta = 90^\circ. \end{cases}$$

If the wave is not polarized and propagates along the  $Y$ -axis, birefringence vanishes since the functions  $\cos^2 \vartheta$  and  $\sin^2 \vartheta$  when averaged over all values of the angle  $\vartheta$  in the plane perpendicular to the direction of propagation of the wave yield  $1/2$  and  $g = \overline{\cos^2 \vartheta - \sin^2 \vartheta} = 0$ ; similarly,  $g = \pm 1/2$  according to whether the non-polarized wave propagates in the direction of the  $Z$ - or  $X$ -axis.

### 5. Application of the theory to special cases

We shall now discuss the semi-macroscopic theory proposed in the preceding Section with relation to the microscopic structure of the medium involving molecular interactions of the radial and angular kinds.

In the microscopic picture, the dipole moments  $\mathbf{M}_1$  and  $\mathbf{M}_2$  of the volume  $V$  containing  $N$  identical molecules can be expressed as follows:

$$M_{1\sigma} = \sum_{p=1}^N m_{1\sigma}^{(p)}, \quad M_{2\nu} = \sum_{q=1}^N m_{2\nu}^{(q)}, \quad (5.1)$$

where  $m_{1\sigma}^{(p)}$  and  $m_{2\nu}^{(q)}$  are, respectively, dipole moment components of the  $p$ -th and  $q$ -th molecules of the medium acted on by the fields  $\mathbf{E}_1$  and  $\mathbf{E}_2$ .

On substituting (5.1) into Eq. (4.17), we get the optical birefringence constant in molecular form:

$$B_2 = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \sum_{p=1}^N \frac{\partial^3 m_{1\alpha}^{(p)}}{\partial E_{1\beta} \partial E_{2\gamma} \partial E_{2\delta}} + \beta \sum_{p=1}^N \sum_{q=1}^N \frac{\partial m_{1\alpha}^{(p)}}{\partial E_{1\beta}} \frac{\partial m_{2\gamma}^{(q)}}{\partial E_{2\delta}} \right\rangle. \quad (5.2)$$

Generally, in a condensed system such as a compressed gas or a liquid, even in the absence of external fields, a molecular field  $\mathbf{F}_0$  exists owing to the presence of permanent or induced molecular moments (dipoles, quadrupoles, *etc.*). In the presence of external fields  $\mathbf{E}_1$ ,  $\mathbf{E}_2$ , the molecular field  $\mathbf{F}_0$  undergoes a change as a result of polarization of the medium, and has to be replaced by molecular fields  $\mathbf{F}_1$  and  $\mathbf{F}_2$  which, in general, are functions of  $\mathbf{E}_1$  and  $\mathbf{E}_2$ . Hence, in a condensed medium, each (*e. g.* the  $p$ -th) molecule is acted on, in addition to the external fields  $\mathbf{E}_1$  and  $\mathbf{E}_2$ , by the molecular fields  $\mathbf{F}_1^{(p)}$  and  $\mathbf{F}_2^{(p)}$ ; conse-

quently, the moments  $\mathbf{m}_1^{(p)}$  and  $\mathbf{m}_2^{(p)}$  are now functions of the effective fields  $\mathbf{E}_1 + \mathbf{F}_1^{(p)}$  and  $\mathbf{E}_2 + \mathbf{F}_2^{(p)}$ , so that we have the expansions (Kielich 1960, 1963c)

$$m_{1\alpha}^{(p)} = \{a_{\alpha\beta}^{(p)} + b_{\alpha\beta\gamma}^{(p)}(E_{2\gamma} + F_{2\gamma}^{(p)}) + \frac{1}{2} c_{\alpha\beta\gamma\delta}^{(p)}(E_{2\gamma} + F_{2\gamma}^{(p)})(E_{2\delta} + F_{2\delta}^{(p)}) + \dots\} (E_{1\beta} + F_{1\beta}^{(p)}), \quad (5.3)$$

$$m_{2\gamma}^{(q)} = \alpha_{\gamma\delta}^{(q)}(E_{2\delta} + F_{2\delta}^{(q)}) + \frac{1}{2} \beta_{\gamma\delta\epsilon}^{(q)}(E_{2\delta} + F_{2\delta}^{(q)})(E_{2\epsilon} + F_{2\epsilon}^{(q)}) + \dots \quad (5.4)$$

The molecular fields appearing in these expansions can be expressed as follows with an accuracy to within interaction of the dipole type (Kielich 1960):

$$F_{k\alpha}^{(p)} = - \sum_{\substack{q=1 \\ q \neq 2}}^N T_{\alpha\beta}^{(pq)} (\mu_{\beta}^{(q)} + m_{k\beta}^{(q)}), \quad k = 1 \text{ or } 2. \quad (5.5)$$

Here, the tensor

$$T_{\alpha\beta}^{(pq)} = -r_{pq}^{-5} (3r_{pq\alpha}r_{pq\beta} - r_{pq}^2 \delta_{\alpha\beta}) \quad (5.6)$$

characterizes dipole type interaction between molecules  $p$  and  $q$  distant by  $r_{pq}$ .

In certain cases, in a first approximation, we can neglect the molecular fields in (5.3) and (5.4), and the birefringence constant (5.2) becomes

$$B_2 = \frac{\pi}{45V} \chi_{\alpha\beta\gamma\delta} \langle \sum_{p=1}^N c_{\alpha\beta\gamma\delta}^{(p)} + \beta \sum_{p=1}^N \sum_{q=1}^N a_{\alpha\beta}^{(p)} \alpha_{\gamma\delta}^{(q)} \rangle, \quad (5.7)$$

or, by methods of classical statistical mechanics,

$$B_2 = B_2^{\text{def}} + B_2^{\text{or}}, \quad (5.8)$$

where the deformational term  $B_2^{\text{def}}$  is given by Eq. (3.19) whereas the orientational term by the formula

$$B_2^{\text{or}} = \frac{\pi Q}{45} \beta \chi_{\alpha\beta\gamma\delta} \left\{ a_{\alpha\beta} \alpha_{\gamma\delta} + \frac{Q}{V} \iint a_{\alpha\beta}^{(p)} \alpha_{\gamma\delta}^{(q)} g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \right\}; \quad (5.9)$$

$g^{(2)}(\tau_p, \tau_q)$  is a binary correlation function of the molecules  $p$  and  $q$  having the configurations  $\tau_p$  and  $\tau_q$ .

In the special case of axially symmetric molecules, Eq. (5.9) reduces to the form (cf. Buckingham 1956)

$$B_2^{\text{or}} = \frac{4\pi Q}{45kT} (a_{33} - a_{11}) (\alpha_{33} - \alpha_{11}) (1 + JA), \quad (5.10)$$

where (Kielich 1962)

$$JA = \frac{Q}{2V} \iint (3 \cos^2 \theta_{pq} - 1) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \quad (5.11)$$

is an integral parameter determining pairwise molecular correlations of the angular kind.

We shall now take into account the effect of the molecular fields on the orientational birefringence constant (their effect on the deformational term is relatively insignificant) which, with regard to the general expression (5.2) and the expansions (5.3) and (5.4), is of the form

$$B_2^{\text{or}} = \frac{\pi\beta}{45V} \chi_{\alpha\beta\gamma\delta} \left\langle \sum_{p=1}^N \sum_{q=1}^N \{a_{\alpha\beta}^{(p)} + b_{\alpha\beta\eta}^{(p)} F_{0\eta}^{(p)} + \dots\} \times \right. \\ \left. \times \{ \alpha_{\gamma\lambda}^{(q)} + \beta_{\gamma\lambda\mu}^{(q)} F_{0\mu}^{(q)} + \dots \} \left\{ \delta_{\epsilon\beta} + \frac{\partial F_{1\epsilon}^{(p)}}{\partial E_{1\beta}} \right\} \left\{ \delta_{\lambda\delta} + \frac{\partial F_{2\lambda}^{(q)}}{\partial E_{2\delta}} \right\} \right\rangle. \quad (5.12)$$

In particular, on applying this expression to isotropically polarizable molecules, one obtains the optical birefringence constant

$$B_2^{\text{or}} = \frac{2\pi\beta}{45V} \left\langle \sum_{p=1}^N \sum_{q=1}^N a_p \alpha_q \left\{ 3 \frac{\partial F_{1\alpha}^{(p)}}{\partial E_{1\beta}} \frac{\partial F_{2\alpha}^{(q)}}{\partial E_{2\beta}} - \frac{\partial F_{1\alpha}^{(p)}}{\partial E_{1\alpha}} \frac{\partial F_{2\beta}^{(q)}}{\partial E_{2\beta}} \right\} \right\rangle, \quad (5.13)$$

which in general is non-zero if molecular fields of induced dipoles are present in the medium.

By (5.3) and (5.5), we have for isotropically polarizable molecules

$$\frac{\partial F_{1\alpha}^{(p)}}{\partial E_{1\beta}} = - \sum_{\substack{r=1 \\ r \neq p}}^N a_r T_{\alpha\beta}^{(pr)} + \sum_{\substack{r=1 \\ r \neq p}}^N \sum_{\substack{s=1 \\ s \neq r}}^N a_r a_s T_{\alpha\gamma}^{(pr)} T_{\gamma\beta}^{(rs)} - \dots, \quad (5.14)$$

and similarly for the field  $F_2$  on replacing the polarizability  $a$  by  $\alpha$ .

On restricting further calculations to pairwise correlations only, the constant (5.13) reduces with regard to (5.14) to the form

$$B_2^{\text{or}} = \frac{4\pi Q}{5kT} a^2 \alpha^2 J_R, \quad (5.15)$$

where

$$J_R = 2 \frac{Q}{V} \iint \bar{r}_{pq}^{-6} g^{(2)}(\mathbf{r}_p, \mathbf{r}_q) d\mathbf{r}_p d\mathbf{r}_q \quad (5.16)$$

is an integral parameter defining radial correlations of isotropically polarizable molecules (Kielich 1962).

The result of Eq. (5.13) or its special case (5.15) signifies that, even in fluids consisting of linearly and isotropically polarizable molecules, owing to interaction between induced dipolar moments, birefringence of the orientational kind can appear in the medium. Clearly, we have in mind the effect of orientation of assemblages consisting of atoms or spherical molecules, coupled by means of radial forces. We have seen (Eqs (2.25)–(3.27)) that in a medium of noninteracting atoms or spherical molecules only birefringence due to non-linear deformation can arise, since the isolated atoms and molecules do not undergo orientation in an electric field. However, as seen from Eqs (5.15) and (5.16), it suffices that the medium be sufficiently dense to give rise to pairwise radially coupled assemblages, and the

latter will behave at a given instant like anisotropic elements which become oriented by the electric field. This leads to weak birefringence of the medium dependent rather strongly on the temperature.

Similarly, Eq. (5.12) can be used for calculating the effect of molecular fields on the birefringence of liquids of molecules that are dipolar, quadrupolar and so forth. In particular, if the molecules are dipolar and present the axial symmetry, Eq. (5.12) with the molecular field of Eq. (5.5) leads to

$$B_2 = \text{gas} B_2^{\text{or}} \left\{ 1 + J_A + \mu \left( \frac{b_{333} - b_{113}}{\alpha_{33} - \alpha_{11}} + \frac{\beta_{333} - \beta_{113}}{a_{33} - a_{11}} \right) J'_A + \dots \right\}, \quad (5.17)$$

where

$$\text{gas} B_2^{\text{or}} = \frac{4\pi Q}{45kT} (a_{33} - a_{11}) (\alpha_{33} - \alpha_{11}), \quad (5.18)$$

$$J'_A = \frac{Q}{2V} \iint (3 \cos^2 \theta_{pq} + 1) (3 \cos \theta_p \cos \theta_q - \cos \theta_{pq}) \tau_{pq}^3 g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q, \quad (5.19)$$

and the parameter  $J_A$  is given by (5.11).

Thus, although the permanent electric dipoles play no part with regard to direct orientation in an electric field, their presence nevertheless affects the optical birefringence of the liquid indirectly. This effect is of a double nature: In the first place, it comes to play by way of the correlation functions implicate in the parameters (5.11) and (5.19), and secondly through nonlinear polarizability of the molecules due to the molecular field of permanent dipoles. In other words, participation of the permanent electric dipoles in optical birefringence is only possible owing to the existence of intermolecular interactions.

Similarly, one can calculate the contribution to optical birefringence from electric moments, both permanent and induced, of higher orders. Albeit, if one wants to obtain results that are well-adapted for numerical evaluations, it is useful to recur to Onsager's model in calculating the molecular fields (see, Kielich 1962, 1966).

In concluding the present section, we will still give the birefringence constant for multi-component systems which, by Eqs (5.1)–(5.4), can be resolved into a deformational and an orientational part, thus:

$$\begin{aligned} B_2^{\text{def}} &= \frac{\pi Q}{45} \sum_i x_i^2 (3c_{\alpha\beta\alpha\beta}^{(i)} + 3c_{\alpha\beta\beta\alpha}^{(i)} - 2c_{\alpha\alpha\beta\beta}^{(i)}), \quad (5.20) \\ B_2^{\text{or}} &= \frac{\pi Q}{45} \beta \left\{ \sum_i x_i (3a_{\alpha\beta}^{(i)} \alpha_{\alpha\beta}^{(i)} + 3a_{\alpha\beta}^{(i)} \alpha_{\beta\alpha}^{(i)} - 2a_{\alpha\alpha}^{(i)} \alpha_{\beta\beta}^{(i)}) + \right. \\ &\quad \left. + \sum_{ij} x_i x_j \frac{Q}{V} \iint \chi_{\alpha\beta\gamma\delta} \alpha_{\alpha\beta}^{(pi)} \alpha_{\gamma\delta}^{(qj)} g_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \right\}, \quad (5.21) \end{aligned}$$

where the tensors  $\alpha_{\alpha\beta}^{(i)}$ ,  $\alpha_{\alpha\beta}^{(i)}$  and  $c_{\alpha\beta\gamma\delta}^{(i)}$  have their previous physical meaning but now refer to a molecule of the  $i$ -th species, and  $x_i = N_i/N$  is the mole fraction of the  $i$ -th component of the mixture.

6. Relation between optical birefringence and anisotropic light scattering

We will now show that the orientational part of the birefringence constant is related strictly with anisotropic molecular light scattering.

Let us assume here for simplicity that the volume  $V$  of the sphere under consideration is small as compared with the wavelength of the light wave whose electric field strength  $\mathbf{E} = \mathbf{E}_0 \cos \omega t$  is weak, producing only linear polarization in the medium. We thus have by assumption:

$$M_\sigma = \left( \frac{\partial M_\sigma}{\partial E_\nu} \right)_0 E_\nu. \quad (6.1)$$

Let us consider the intensity tensor of scattered light  $I_{\sigma\tau}$ , which we define here as follows ( $\Delta$  stands for a fluctuation):

$$I_{\sigma\tau} = \frac{1}{c^4 V} \langle \Delta \overline{\overline{M_\sigma}} \Delta \overline{\overline{M_\tau}} \rangle_E, \quad (6.2)$$

or by (6.1) for linear scattering as follows:

$$I_{\sigma\tau} = \frac{1}{V} \left( \frac{\omega}{c} \right)^4 \left\{ \left\langle \frac{\partial M_\sigma}{\partial E_\nu} \frac{\partial M_\tau}{\partial E_\nu} \right\rangle - \left\langle \frac{\partial M_\sigma}{\partial E_\nu} \right\rangle \left\langle \frac{\partial M_\tau}{\partial E_\nu} \right\rangle \right\} \overline{E_\nu E_\nu^t}. \quad (6.3)$$

For the case of an isotropic medium, we have to perform averageing, obtaining finally (for comparison, see Kielich 1964)

$$I_{\sigma\tau} = R_{\text{is}} \overline{E_\sigma E_\tau^t} + R_{\text{anis}} (3 \delta_{\sigma\tau} \overline{E^2}^t + \overline{E_\sigma E_\tau^t}), \quad (6.4)$$

where

$$R_{\text{is}} = \frac{1}{9V} \left( \frac{\omega}{c} \right)^4 \left\{ \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} \frac{\partial M_\beta}{\partial E_\beta} \right\rangle - \left\langle \frac{\partial M_\alpha}{\partial E_\alpha} \right\rangle \left\langle \frac{\partial M_\beta}{\partial E_\beta} \right\rangle \right\} \quad (6.5)$$

is a constant defining fluctuational scattering of light of an isotropic nature, whereas

$$R_{\text{anis}} = \frac{1}{90V} \left( \frac{\omega}{c} \right)^4 \left\langle 3 \frac{\partial M_\alpha}{\partial E_\beta} \frac{\partial M_\alpha}{\partial E_\beta} - \frac{\partial M_\alpha}{\partial E_\alpha} \frac{\partial M_\beta}{\partial E_\beta} \right\rangle \quad (6.6)$$

is a constant determining anisotropic light scattering in the medium.

Returning now to the optical birefringence constant in the form of Eq. (4.17) and considering only its temperature-dependent part, and assuming that  $\mathbf{E}_1 = \mathbf{E}_2 = \mathbf{E}$  (i.e. that a single intense light beam propagates in the medium), we can write

$$B_2^{\text{or}} = \frac{2\pi\beta}{45V} \left\langle 3 \frac{\partial M_\alpha}{\partial E_\beta} \frac{\partial M_\alpha}{\partial E_\beta} - \frac{\partial M_\alpha}{\partial E_\alpha} \frac{\partial M_\beta}{\partial E_\beta} \right\rangle. \quad (6.7)$$

On comparing Eqs (6.6) and (6.7), we obtain the relation

$$B_2^{\text{or}} = \frac{4\pi}{kT} \left( \frac{c}{\omega} \right)^4 R_{\text{anis}} \quad (6.8)$$

between the orientational birefringence constant and anisotropic light scattering constant.

If the effect of the molecular fields in the medium can be neglected, the isotropic and anisotropic scattering constants (6.5) and (6.6) can be expressed thus (Kielich 1960):

$$R_{\text{is}} = \left(\frac{\omega}{c}\right)^4 \alpha^2 \varrho \left\{ 1 + \frac{\varrho}{V} \iint [g^{(2)}(r_p, r_q) - g^{(1)}(r_p)g^{(1)}(r_q)] dr_p dr_q \right\}, \quad (6.9)$$

$$R_{\text{anis}} = \frac{1}{90} \left(\frac{\omega}{c}\right)^4 \varrho \left\{ 3\alpha_{\alpha\beta} \alpha_{\alpha\beta} - \alpha_{\alpha\alpha} \alpha_{\beta\beta} + \right. \\ \left. + \frac{\varrho}{V} \iint (3\alpha_{\alpha\beta}^{(p)} \alpha_{\alpha\beta}^{(q)} - \alpha_{\alpha\alpha}^{(p)} \alpha_{\beta\beta}^{(q)}) g^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q \right\}. \quad (6.10)$$

From the general expression of Eq. (6.4), one can calculate various experimentally measurable quantities, thus the Rayleigh ratio  $R$ , depolarization rate  $D$ , and others. If experiment involves a non-polarized beam propagating along the  $Y$ -axis and observation is along the  $X$ -axis, then by (6.4) the tensor components of the intensity of scattered light with oscillations along the  $Y$ - and  $Z$ -axis are

$$I_{yy} = 3R_{\text{anis}} (\overline{E_x^{2f}} + \overline{E_z^{2f}}), \quad (6.11)$$

$$I_{zz} = R_{\text{is}} \overline{E_z^{2f}} + R_{\text{anis}} (3\overline{E_x^{2f}} + 4\overline{E_z^{2f}}). \quad (6.12)$$

Since in this case  $\overline{E_x^{2f}} = \overline{E_z^{2f}} = 1/2\overline{E^{2f}}$ , we obtain

$$R = \frac{I_{yy} + I_{zz}}{\overline{E^{2f}}} = \frac{1}{2} (R_{\text{is}} + 13R_{\text{anis}}), \quad (6.13)$$

$$D = \frac{I_{yy}}{I_{zz}} = \frac{6R_{\text{anis}}}{R_{\text{is}} + 7R_{\text{anis}}}. \quad (6.14)$$

Similarly, one could calculate from equation (6.4)  $R$  and  $D$  for other conditions of observation of scattered light (see, Kielich 1960, 1964).

## 7. Discussion and conclusions

We have proposed a semi-macroscopic theory of non-linear changes in light refractive index induced in an arbitrary isotropic medium by an optical field of high intensity. These changes are shown to be described in a quadratic approximation by two constants  $A_2$  and  $B_2$  which express the molecular structure and thermodynamical state of the medium, as well as its changes, in the presence of the optical field. The constant  $A_2$  defines changes of an isotropic nature which are related, firstly, with non-linear polarization of the medium, secondly, with fluctuations of its linear polarization and, thirdly, with its opticostriction. The anisotropic optical properties of the medium are characterized by the constant  $B_2$ , which defines the amount of optical birefringence induced in it by the intense optical field.

The birefringence constant  $B_2$  as defined by the general equation (4.17) is discussed for several molecular models. In the special case of rarefied atomic gases or of ones consisting of spherical molecules, the optical birefringence is induced solely by non-linear polarization

of the third order. This effect does not depend directly on the temperature (Eq. (3.26)). In the dense state, it is shown to be accompanied by an effect which depends directly on the temperature and arises by orientation of momentary assemblages of radially coupled atoms or spherical molecules (Eq. (5.15)). The respective correlations are described by a parameter (5.16) which appeared *i.a.* in an earlier expression for the depolarization ratio (Kielich 1960):

$$D = \frac{6\alpha^2 J_R}{5\rho k T \beta_T + 7\alpha^2 J_R}, \quad (7.1)$$

where  $\beta_T$  is the isothermal compressibility coefficient of the medium.

In gases of optically anisotropic molecules, optical birefringence is induced simultaneously by the effect of non-linear optical deformation (3.19) and that of optical molecular orientation (3.20). The problem of whether these two effects are numerically of the same order, or whether one of them predominates, will have to be solved in each particular case with regard to the internal structure of the molecules. Indeed, this will depend on whether a molecule is more susceptible to non-linear deformation in an intense optical field, or whether it is more easily oriented by the latter. The answer is readily supplied by measurements of the optical birefringence as a function of the temperature.

Investigation along these lines will provide us with valuable information concerning the anisotropy of both the linear and non-linear optical polarizability of isolated molecules.

In dense substances, such as liquids, both these effects are affected by intermolecular interaction. The effect of molecular orientation depends particularly strongly on molecular correlations; in the case of axially symmetric molecules and in a first approximation of the theory, it depends on the supplementary parameter of angular correlations (5.11). In the same approximation of the theory, an identical parameter appears in the formula

$$D = \frac{6(\alpha_{33} - \alpha_{11})^2 (1 + J_A)}{45\rho \alpha^2 k T \beta_T + 7(\alpha_{33} - \alpha_{11})^2 (1 + J_A)}. \quad (7.2)$$

In the case when the dependence of the polarizability on the light wavelength is negligible, Eqs (5.10) and (7.2) lead to the relationship

$$B_2^{\text{or}} = 4\pi\rho^2 \alpha^2 \beta_T \frac{D}{6 - 7D}, \quad (7.3)$$

which permits to calculate the optical birefringence constant if the depolarization ratio  $D$  of the substance is known experimentally.

Higher approximations of the theory show that in very dense media the coefficient  $B_2^{\text{orient}}$  is affected (in addition to the angular correlations of Eq. (5.11)) by the existing strong molecular fields, particularly in substances of dipolar or quadrupolar molecules. These molecular fields not only affect the linear polarizability of the molecules but, primarily, are able to give rise to non-linear polarizability of the latter in the absence of external electric fields. Consequently, although the permanent molecular dipoles or quadrupoles do not undergo orientation in the optical field directly, they nevertheless are subject to orientation indirectly owing to the presence of mutual molecular correlations of various kinds.

The theory proposed is easily extended to the case of multi-component systems, for which the birefringence constant can be written formally in the form of the following expansion in a power series in the molar fractions:

$$B_2 = \sum_i x_i B_2^{(i)} + \sum_{ij} x_i x_j B_2^{(ij)} + \dots, \quad (7.4)$$

where, by (5.20) and (5.21), we have

$$B_2^{\text{or}} = \frac{\pi \rho}{45} \{3c_{\alpha\beta\alpha\beta}^{(i)} + 3c_{\alpha\beta\beta\alpha}^{(i)} - 2c_{\alpha\alpha\beta\beta}^{(i)} + \beta(3a_{\alpha\beta}^{(i)}\alpha_{\alpha\beta}^{(i)} + 3a_{\alpha\beta}^{(i)}\alpha_{\beta\alpha}^{(i)} - 2a_{\alpha\alpha}^{(i)}\alpha_{\beta\beta}^{(i)})\}, \quad (7.5)$$

$$B_2^{(ij)} = \frac{\pi \rho^2}{45V} \beta \iint \{3a_{\alpha\beta}^{(pi)}\alpha_{\alpha\beta}^{(qj)} + 3a_{\alpha\beta}^{(pi)}\alpha_{\beta\alpha}^{(qj)} - 2a_{\alpha\alpha}^{(pi)}\alpha_{\beta\beta}^{(qj)}\} \mathcal{E}_{ij}^{(2)}(\tau_p, \tau_q) d\tau_p d\tau_q. \quad (7.6)$$

Hence,  $B_2$  is seen to be an additive constant only in the case of a perfect mixture in which no molecular correlations occur. In condensed multi-component systems (mixtures of compressed gases, liquid solutions, etc.) where in addition to correlations between the molecules of one component a role has to be attributed to correlations between molecules of the various components of the system, the constant  $B_2$  is no longer an additive quantity. Thus, investigation of deviations of  $B_2$  from additivity can yield direct information on the molecular structure of a system and on the nature and magnitude of the intermolecular forces active between the molecules of the various components. This is all the more easier as similar parameters of molecular correlations occur also in the theory of molecular light scattering (Kielich 1960) and of the Cotton-Mouton (Kielich 1962) and Kerr (Kielich 1963c) effects. Especially interesting information can be gained in the case of compressed gas mixtures for which the bimolecular correlations function of Eq. (7.6) can be expressed as follows:

$$\Omega^2 \mathcal{E}_{ij}^{(2)}(\tau_p, \tau_q) = \exp\{-\beta u_{ij}(\tau_p, \tau_q)\} \{1 + O(\rho)\}. \quad (7.7)$$

Introducing herein the potential energy of mutual interaction of two molecules  $u_{ij}(\tau_p, \tau_q)$  in the form defined for the molecular model under consideration, one can compute the constant (7.6) numerically (see, Kielich 1966).

The relaxational theory of orientation of anisotropic or dipolar molecules in an oscillating, strong electric field, as presented at the outset in an elementary approach, will have to be generalized, on the one hand, to the case of statistical intermolecular correlations, and on the other to that of electronic dispersion, to an extent permitting *i.a.* to investigate birefringence within appropriate resonance bands where the effects can be expected to attain their maximal values.

Finally, one would like to stress once more that for various reasons it would appear most useful to study experimentally not only the induced optical birefringence, but also the non-linear changes in refractive index induced by an intense laser beam. In the general case, they are given by the equation

$$n_{\sigma\tau}^2 - n_0^2 \delta_{\sigma\tau} = A \delta_{\sigma\tau} E_0^2 + B(3E_{0\sigma} E_{0\tau} - \delta_{\sigma\tau} E_0^2), \quad (7.8)$$

which results from Eqs (3.7) and (4.15) with  $n_1 = n_0$  denoting the refractive index in the absence of the light beam and

$$\begin{aligned} A &= \left( \frac{n_0^2 + 2}{6} \right) (A_2 + A_4 E_0^2 + \dots), \\ B &= \left( \frac{n_0^2 + 2}{6} \right) (B_2 + B_4 E_0^2 + \dots), \end{aligned} \quad (7.9)$$

— constants which are even functions of the amplitude  $E_0 = E_{0z}$  of the strong optical field.

If in particular we assume the strong beam to be polarized with electric oscillations along the  $Z$ -axis, (7.8) yields for the optical permittivity tensor components

$$\begin{aligned} n_{xx}^2 &= n_{yy}^2 = n_0^2 + (A - B) E_{0z}^2, \\ n_{zz}^2 &= n_0^2 + (A + 2B) E_{0z}^2, \end{aligned} \quad (7.10)$$

and the optical birefringence

$$n_{zz}^2 - n_{xx}^2 = n_{zz}^2 - n_{yy}^2 = 3B E_{0z}^2. \quad (7.11)$$

In the case when the strong beam is not polarized and propagates along the  $Y$ -axis, Eq. (7.8) leads to the absolute values of variations

$$\begin{aligned} n_{yy}^2 - n_0^2 &= (A - B) E_0^2, \\ n_{xx}^2 - n_0^2 &= n_{zz}^2 - n_0^2 = \frac{1}{2} (2A + B) E_0^2, \end{aligned} \quad (7.12)$$

and to the birefringence

$$n_{zz}^2 - n_{xx}^2 = 0, \quad n_{zz}^2 - n_{yy}^2 = \frac{3}{2} B E_0^2. \quad (7.13)$$

It is thus seen from Eq. (7.10) or (7.12) that the absolute changes in refractive index measured in a given direction are related not only with the induced optical anisotropy but moreover, in general, with the changes in volume of the medium due to the effect of the strong optical field *i.e.* with the opticostriction implicate in the constant  $A$ . On the other hand, from Eqs (7.11) and (7.13) we see that the differential changes in refractive index are related only with the anisotropy induced in the medium, as defined by the constant  $B$ . Hence by measuring the absolute non-linear changes in refractive index in a given substance and, separately, its optical birefringence, we can use Eqs (7.10)—(7.13) to determine numerically the constant  $A$ , thus determining its opticostriction.

By Eqs (7.10) and (7.12), we obtain for the relative changes in refractive index in the case of a polarized light beam

$$\frac{n_{zz}^2 - n_0^2}{n_{xx}^2 - n_0^2} = \frac{n_{zz}^2 - n_0^2}{n_{yy}^2 - n_0^2} = \frac{A + 2B}{A - B}, \quad (7.14)$$

and in that of a non-polarized beam

$$\frac{n_{zz}^2 - n_0^2}{n_{yy}^2 - n_0^2} = \frac{n_{xx}^2 - n_0^2}{n_{yy}^2 - n_0^2} = \frac{2A + B}{2(A - B)}. \quad (7.15)$$

In particular, restricting theoretical considerations to the effect of molecular orientation, i.e. if  $B = B^{\text{orient}}$  and  $A = 0$ , the relation (7.14) yields  $-2$  (in agreement with Langevin's well-known theory of the Kerr effect), whereas (7.15) yields a value of  $-1/2$ . In the other extreme case assuming that only non-linear deformation is present, we have  $2A^{\text{def}} = 5B^{\text{def}}$  and (7.14) yields a value of  $3$  (in conformity with Voigt's theory), whereas Eq. (7.15) yields  $2$ . It would be of the greatest interest to verify these relationships experimentally.

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