Laser Beam-induced Non-linear Effects in Optically Active Media*

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A general equation is proposed for the dynamical electric permittivity tensor, taking into account, besides frequency dispersion, spatial dispersion describing the linear and non-linear optical activities of the medium. It permits one to determine the symmetry relations and value of the optical Kerr effect, a generalised Havelock relation, and the non-linear change in optical rotation angle for arbitrary conditions of observation. Simple examples are adduced to give a microscopic interpretation of the results derived, rendering apparent the basic mechanisms (fluctuations of density, non-linear changes in the optical polarisability tensor and gyration tensor, molecular reorientation, and various radial and angular correlations) leading to induced optical non-linearities. Measurements of non-linear changes in optical rotation angle are shown to be promising in solutions of polymers or colloids, and will permit, *inter alia*, direct determinations of the anisotropy of gyration properties of molecules. macromolecules and colloid particles.

1. Introduction
In linear optics [1, 2], the light source was a classical one, causing only linear polarisation of matter, whereas non-linear variations were caused by a DC electric or magnetic field (Kerr effect, Cotton-Mouton effect [3]). Thus, the light beam was confined to the role of measuring agent (detector) not affecting the properties of the material system. Earlier ideas tending to predict that light, if sufficiently intense, might cause non-linear optical [4], electric or magnetic [5] changes in matter had to remain within the realm of pure theory until the coming of laser technique. Nowadays, experiments making apparent non-linear changes in refractive index are performed in two ways: an intense ruby laser beam inducing the optical Kerr effect is applied in addition to a weak measuring beam [6, 7], or a single intense circularly polarised beam inducing a rotation of the polarisation ellipse is resorted to [8-10]. These phenomena, together with various other new optical effects, constitute the field of non-linear optics [11].

At present, non-linear optics deals not only with dispersion of frequency [12] but moreover with spatial dispersion [11-14]. Particular attention is being given to optically active media [15], in which harmonic generation [15-19] and non-linear optical rotation [20-22] are studied.

It is our aim here to give a strict, quantitative discussion of non-linear variations in refractive index caused in optically active media by strong laser light. In particular, the diagonal and non-diagonal components of the electric permittivity tensor are shown to describe, respectively, the optically induced birefringence and the non-linear change in rotation angle. A discussion is given for some special cases.

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2. Fundamentals

Consider an electromagnetic wave with electric vector $\mathbf{E}^\omega$ and magnetic vector $\mathbf{H}^\omega$ oscillating at frequency ω to be incident on an arbitrary medium, in which it induces electric polarisation $\mathbf{P}^e$ and magnetic polarisation $\mathbf{P}^m$. In the general case, one has the following equations for the tensors of electric and magnetic permittivities:

$$(\epsilon_{\sigma\tau}{}^\omega - \delta_{\sigma\tau})\, E_\tau{}^\omega = 4\pi\, P_\sigma{}^e\,(\omega) \tag{1}$$

$$(\mu_{\sigma\tau}{}^\omega - \delta_{\sigma\tau})\, H_\tau{}^\omega = 4\pi\, P_\sigma{}^m\,(\omega) \tag{2}$$

$\delta_{\sigma\tau}$ denoting the unit Kronecker tensor.

The polarisation vectors $\mathbf{P}^e$ and $\mathbf{P}^m$ comprise in general dipolar, quadrupolar and higher contributions, which can be written as follows [14]:

$$P_\sigma{}^e = D_\sigma{}^e - \frac{1}{3}\,\nabla_\tau\, Q_{\sigma\tau}{}^e + \dots \tag{3}$$

$$P_\sigma{}^m = D_\sigma{}^m - \frac{1}{3}\,\nabla_\tau\, Q_{\sigma\tau}{}^m + \dots \tag{4}$$

$D_\sigma{}^e$ and $D_\sigma{}^m$ being respectively components of the electric and magnetic dipole polarisation vectors, and $Q_{\sigma\tau}{}^e$ and $Q_{\sigma\tau}{}^m$ components of the electric and magnetic quadrupolar polarisation tensors; ∇ is the derivation operator.

The direction of propagation of the electromagnetic wave is given by its wave vector $\mathbf{k}$. Provided the intensity of the wave (the squares of the amplitudes of $\mathbf{E}^\omega$ and $\mathbf{H}^\omega$) is not excessive, one is justified in writing the following linear relations:

$$D_\sigma{}^e = \chi_{\sigma\tau}{}^{ee}\,(\omega, \mathbf{k})\, E_\tau{}^\omega + \chi_{\sigma\tau}{}^{em}\,(\omega, \mathbf{k})\, H_\tau{}^\omega \tag{5}$$

$$D_\sigma{}^m = \chi_{\sigma\tau}{}^{mm}\,(\omega, \mathbf{k})\, H_\tau{}^\omega + \chi_{\sigma\tau}{}^{me}\,(\omega, \mathbf{k})\, E_\tau{}^\omega \tag{6}$$

where $\chi_{\sigma\tau}{}^{ee}$ and $\chi_{\sigma\tau}{}^{mm}$ are respectively tensors of the purely electric and magnetic susceptibility of the medium, and $\chi_{\sigma\tau}{}^{em}$ and $\chi_{\sigma\tau}{}^{me}$ are tensors of its cross electro-magnetic and magneto-electric susceptibilities.

Similar relations can also be written for the components of the quadrupolar polarisation tensors:

$$Q_{\sigma\tau}{}^e = \chi_{\sigma\tau\nu}{}^{ee}\,(\omega, \mathbf{k})\, E_\nu{}^\omega + \chi_{\sigma\tau\nu}{}^{em}\,(\omega, \mathbf{k})\, H_\nu{}^\omega \tag{7}$$

$$Q_{\sigma\tau}{}^m = \chi_{\sigma\tau\nu}{}^{mm}\,(\omega, \mathbf{k})\, H_\nu{}^\omega + \chi_{\sigma\tau\nu}{}^{me}\,(\omega, \mathbf{k})\, E_\nu{}^\omega \tag{8}$$

$\chi_{\sigma\tau\nu}{}^{ee}$ and $\chi_{\sigma\tau\nu}{}^{mm}$ denoting respectively the tensors of electric (or, more pointedly, electro-electric) quadrupolar susceptibility and magnetic quadrupolar susceptibility of the medium, whereas $\chi_{\sigma\tau\nu}{}^{em}$ and $\chi_{\sigma\tau\nu}{}^{me}$ are tensors of its electro-magnetic and its magneto-electric susceptibility.

All susceptibility tensors occurring in equations 5-8 are dependent on frequency dispersion (according to ω) as well as on spatial dispersion (i.e. dispersion according to the wave vector $\mathbf{k}$). Assuming spatial dispersion as small, one can write the dipolar and quadrupolar electric susceptibility tensors thus [14]:

$$\chi_{\sigma\tau}{}^{ee}\,(\omega, \mathbf{k}) = \chi_{\sigma\tau}{}^{ee}\,(\omega) + i\,\chi_{\sigma\tau\nu}{}^{ee}\,(\omega)\, k_\nu + \chi_{\sigma\tau\nu\rho}{}^{ee}\,(\omega)\, k_\nu k_\rho + \dots \tag{9}$$

$$\chi_{\sigma\tau\nu}{}^{ee}\,(\omega, \mathbf{k}) = \chi_{\sigma\tau\nu}{}^{ee}\,(\omega) + i\,\chi_{\sigma\tau\nu\rho}{}^{ee}\,(\omega)\, k_\rho + \dots \tag{10}$$

Above, the tensor $\chi_{\sigma\tau}{}^{ee}(\omega)$ describes only frequency dispersion of the refractive index, the tensor $\chi_{\sigma\tau\nu}{}^{ee}(\omega)$ frequency dispersion of natural optical activity, whereas the tensor $\chi_{\sigma\tau\nu\rho}{}^{ee}(\omega)$ describes the optical activity which can appear in bodies with inversion symmetry.

In this paper, we shall deal with such variations in the tensors (9) and (10) as can be caused

by intense laser light oscillating at a frequency ω_L distinct from the frequency ω of the probe light.

In a quadratic approximation, the non-linear change in refractive index induced by strong laser light can be written as:

$$\Delta \chi_{\sigma\tau}{}^{ee}(\omega, \omega_L) = \frac{1}{2} \chi_{\sigma\tau\nu\rho}{}^{ee}(\omega, \omega_L) \langle E_\nu{}^{\omega_L} E_\rho{}^{\omega_L} \rangle_t \qquad (11)$$

whereas the non-linear change in optical activity induced in the same conditions is:

$$\Delta \chi_{\sigma\tau\nu}{}^{ee}(\omega, \omega_L) = \frac{1}{2} \chi_{\sigma\tau\nu\rho\lambda}{}^{ee}(\omega, \omega_L) \langle E_\rho{}^{\omega_L} E_\lambda{}^{\omega_L} \rangle_t \qquad (12)$$

The symbol $\langle \ \rangle_t$ stands for time-averaging over a period of oscillations of the electric field E^{ω_L}.

The non-linear variations in the phenomenological form of equations 11 and 12 are valid for arbitrary non-dissipative media, isotropic as well as anisotropic. However, we shall restrict the present discussion to isotropic media using classical statistical methods; this will enable us to relate the optically induced non-linearities to the microstructure of matter.

3. Non-linear Refractivity

We consider a homogeneous medium of volume V, isotropic in the absence of externally applied fields. The electric polarisation vector component is now:

$$D_\sigma{}^e = \frac{1}{V} \langle A_{\sigma\tau}{}^\omega \rangle_{\mathbf{E}^{\omega_L}} E_{v\tau}{}^\omega \qquad (13)$$

where $A_{\sigma\tau}{}^\omega$ is the electric polarisability tensor of the medium at frequency ω. For an isotropic medium, this tensor can be averaged statistically in accordance with the definition:

$$\langle A_{\sigma\tau}{}^\omega \rangle_{\mathbf{E}^{\omega_L}} = \int A_{\sigma\tau}{}^\omega(\Gamma, \mathbf{E}^{\omega_L}) f(\Gamma, \mathbf{E}^{\omega_L}) \, d\Gamma \qquad (14)$$

$f(\Gamma, \mathbf{E}^{\omega_L})$ denoting the statistical distribution function for the system at thermodynamical equilibrium in the electric field $\mathbf{E}^{\omega_L}$. Integration in the right-hand term of equation 14 extends over all possible configurational variables Γ. Γ describes the positions and orientations of the microsystems of the material (see section 5).

In the presence of a strong electric field, the material becomes anisotropic. As a consequence, the electric field in vacuum $\mathbf{E}_v{}^\omega$ is now related with the macroscopic field $\mathbf{E}^\omega$ existing within the medium (conceived in the shape of a spherical sample) as follows:

$$3E_{v\sigma}{}^\omega = (\epsilon_{\sigma\tau}{}^\omega + 2\delta_{\sigma\tau}) E_\tau{}^\omega \qquad (15)$$

The same is true for an electric field oscillating at laser frequency ω_L.

In accordance with the phenomenological equation 11, the electric polarisability tensor $A_{\sigma\tau}{}^\omega$ of the medium acted on by the electric field of an intense laser beam undergoes the following non-linear variation:

$$A_{\sigma\tau}{}^\omega(\Gamma, \mathbf{E}^{\omega_L}) = A_{\sigma\tau}{}^\omega + \frac{1}{2} C_{\sigma\tau\nu\rho}{}^{\omega,\omega_L} \langle E_{v\nu}{}^{\omega_L} E_{v\rho}{}^{\omega_L} \rangle_t \qquad (16)$$

where $C_{\sigma\tau\nu\rho}{}^{\omega,\omega_L}$ is the tensor of non-linear polarisability of the medium at frequencies ω and ω_L.

In the quadratic approximation considered here, the perturbed statistical distribution function at thermodynamical equilibrium and temperature T can be written as follows:

$$f(\Gamma, \mathbf{E}^{\omega_L}) = f(\Gamma, 0) \left\{ 1 + \frac{1}{2kT} (A_{\nu\rho}{}^{\omega_L} - \langle A_{\nu\rho}{}^{\omega_L} \rangle) \langle E_{v\nu}{}^{\omega_L} E_{v\rho}{}^{\omega_L} \rangle_t \right\} \qquad (17)$$

the symbol $\langle \ \rangle$ standing for statistical averaging with the non-perturbed distribution $f(\Gamma, 0)$ in the absence of an external field.

On inserting equations 14, 16 and 17 into equation 13 and on averaging over all possible

directions of the electric fields with regard to laboratory reference axes, we obtain:

$$4\pi \, D_\sigma{}^e = 3R_{LL} \, E_{v\sigma}{}^\omega + \{(B_{is}{}^{\omega,\,\omega_L} - B_1{}^{\omega,\,\omega_L}) \, \delta_{\sigma\tau} \, \delta_{v\rho}$$

$$+ \, 3B_2{}^{\omega,\,\omega_L} \, \delta_{\sigma v} \, \delta_{\tau\rho} + 3B_3{}^{\omega,\,\omega_L} \, \delta_{\sigma\rho} \, \delta_{\tau v}\} \, E_{v\tau}{}^\omega \, \langle E_{vv}{}^{\omega_L} \, E_{v\rho}{}^{\omega_L} \rangle_t \tag{18}$$

where

$$R_{LL}{}^\omega = \frac{4\pi}{9V} \langle A_{\alpha\alpha}{}^\omega \rangle \tag{19}$$

is the optical refractivity in the absence of a laser beam (Lorentz-Lorenz function), and

$$B_{is}{}^{\omega,\,\omega_L} = \frac{2\pi}{9V} \left\{ \langle C_{\alpha\alpha\beta\beta}{}^{\omega,\,\omega_L} \rangle + \frac{1}{kT} \langle \Delta \, A_{\alpha\alpha}{}^\omega \, \Delta \, A_{\beta\beta}{}^{\omega_L} \rangle \right\} \tag{20}$$

defines a non-linear change in refractivity of the isotropic kind. This latter variation is seen to consist of a part not directly dependent on temperature, stemming from the mean non-linear polarisability of the medium, and of a temperature-dependent part related to the fluctuations $\Delta \, A_{\alpha\alpha}{}^\omega = A_{\alpha\alpha}{}^\omega - \langle A_{\alpha\alpha}{}^\omega \rangle$ and $\Delta \, A_{\beta\beta}{}^{\omega_L} = A_{\beta\beta}{}^{\omega_L} - \langle A_{\beta\beta}{}^{\omega_L} \rangle$ of its mean linear polarisabilities. The remaining three constants in equation 18 define anisotropic variations in refractivity of the form:

$$B_i{}^{\omega,\,\omega_L} = \frac{\pi}{45V} \sigma_{\alpha\beta\gamma\delta}{}^{(i)} \langle C_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L} + \frac{1}{kT} A_{\alpha\beta}{}^\omega \, A_{\gamma\delta}{}^{\omega_L} \rangle \tag{21}$$

where we have, for $i = 1, 2, 3$:

$$\sigma_{\alpha\beta\gamma\delta}{}^{(1)} = 3\delta_{\alpha\gamma} \, \delta_{\beta\delta} + 3\delta_{\alpha\delta} \, \delta_{\beta\gamma} - 2\delta_{\alpha\beta} \, \delta_{\gamma\delta} \tag{22}$$

$$\sigma_{\alpha\beta\gamma\delta}{}^{(2)} = 4\delta_{\alpha\gamma} \, \delta_{\beta\delta} - \delta_{\alpha\delta} \, \delta_{\beta\gamma} - \delta_{\alpha\beta} \, \delta_{\gamma\delta} \tag{23}$$

$$\sigma_{\alpha\beta\gamma\delta}{}^{(3)} = 4\delta_{\alpha\delta} \, \delta_{\beta\gamma} - \delta_{\alpha\beta} \, \delta_{\gamma\delta} - \delta_{\alpha\gamma} \, \delta_{\beta\delta} \tag{24}$$

Inserting equation 18 in the fundamental equation 1 and having regard to equation 15 we obtain the variation in electric permittivity tensor as follows:

$$\epsilon_{\sigma\lambda}{}^\omega - \delta_{\sigma\lambda} = \left\{ R_{LL} \, \delta_{\sigma\tau} + \left[\frac{1}{3} (B_{is}{}^{\omega,\,\omega_L} - B_1{}^{\omega,\,\omega_L}) \, \delta_{\sigma\tau} \, \delta_{v\rho} \right. \right.$$

$$\left. \left. + \, B_2{}^{\omega,\,\omega_L} \, \delta_{\sigma v} \, \delta_{\tau\rho} + B_3{}^{\omega,\,\omega_L} \, \delta_{\sigma\rho} \, \delta_{\tau v} \right] \langle E_{vv}{}^{\omega_L} \, E_{v\rho}{}^{\omega_L} \rangle_t \right\} (\epsilon_{\tau\lambda}{}^\omega + 2\delta_{\tau\lambda}) \tag{25}$$

Let the probe light propagate along the z-axis. The preceding equation now yields the diagonal components of the permittivity tensor in directions perpendicular to propagation as follows:

$$\frac{\epsilon_{xx}{}^\omega - 1}{\epsilon_{xx}{}^\omega + 2} = R_{LL} + \frac{1}{3} \left[B_{is}{}^{\omega,\,\omega_L} \langle E_{v\sigma}{}^{\omega_L} \, E_{v\sigma}{}^{\omega_L} \rangle_t + B_1{}^{\omega,\,\omega_L} \langle 3E_{vx}{}^{\omega_L} \, E_{vx}{}^{\omega_L} - E_{v\sigma}{}^{\omega_L} E_{v\sigma}{}^{\omega_L} \rangle_t \right] \tag{26}$$

$$\frac{\epsilon_{yy}{}^\omega - 1}{\epsilon_{yy}{}^\omega + 2} = R_{LL} + \frac{1}{3} \left[B_{is}{}^{\omega,\,\omega_L} \langle E_{v\sigma}{}^{\omega_L} \, E_{v\sigma}{}^{\omega_L} \rangle_t + B_1{}^{\omega,\,\omega_L} \langle 3E_{vy}{}^{\omega_L} \, E_{vy}{}^{\omega_L} - E_{v\sigma}{}^{\omega_L} E_{v\sigma}{}^{\omega_L} \rangle_t \right] \tag{27}$$

since, as is immediately obvious from equations 21-24, the following symmetry relations hold for the isotropic body:

$$B_1{}^{\omega,\,\omega_L} = B_2{}^{\omega,\,\omega_L} + B_3{}^{\omega,\,\omega_L} \tag{28}$$

From equations 26 and 27, with a satisfactory approximation, we obtain the following expression for the birefringence induced at frequency ω by laser light of frequency ω_L:

$$n_\parallel - n_\perp = \lambda \, B_\lambda{}^{\omega_L} \langle E_x{}^{\omega_L} \, E_x{}^{\omega_L} - E_y{}^{\omega_L} \, E_y{}^{\omega_I} \rangle_t \tag{29}$$

where we have introduced the optical birefringence constant $B_\lambda{}^{\omega_L}$ measured in experiments and defined as:

$$B_\lambda{}^{\omega_L} = \frac{3}{2n\lambda}\left(\frac{n^2+2}{3}\right)^2\left(\frac{n_L{}^2+2}{3}\right)^2 B_1{}^{\omega,\,\omega_L} \tag{30}$$

with $n_\parallel = \sqrt{\epsilon_{xx}{}^\omega}$, $n_\perp = \sqrt{\epsilon_{yy}{}^\omega}$, with n and n_L standing for the refractive index respectively for the probe and laser light wavelengths.

From what has been said, one sees that birefringence can be induced only by plane polarised light (e.g. polarised along the x- or y-axis). Unpolarised laser light propagating along the propagation direction of the probe light is unable to induce optical birefringence.

For intense light polarised with electric oscillations along the x-axis, one gets from equations 26 and 27 a formula which, in approximation, is a generalised Havelock relation:*

$$\frac{n_\parallel - n}{n_\perp - n} = \frac{B_{is}{}^{\omega,\,\omega_L} + 2B_1{}^{\omega,\,\omega_L}}{B_{is}{}^{\omega,\,\omega_L} - B_1{}^{\omega,\,\omega_L}} \tag{31}$$

In optically inactive substances $A_{\alpha\beta}{}^\omega = A_{\beta\alpha}{}^\omega$, $A_{\alpha\beta}{}^{\omega_L} = A_{\beta\alpha}{}^{\omega_L}$, $C_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L} = C_{\beta\alpha\delta\gamma}{}^{\omega,\,\omega_L}$, and the constants from equations 21-24 are moreover related as follows:

$$B_1{}^{\omega,\,\omega_L} = 2B_2{}^{\omega,\,\omega_L} = 2B_3{}^{\omega,\,\omega_L} \tag{32}$$

Equation 25 now reduces to the earlier form published [23]:

$$\epsilon_{\sigma\lambda}{}^\omega - \delta_{\sigma\lambda} = \left\{R_{LL}\,\delta_{\sigma\tau} + \frac{1}{6}\Big[2B_{is}{}^{\omega,\,\omega_L}\,\delta_{\sigma\tau}\,\delta_{\nu\rho} + B_1{}^{\omega,\,\omega_L}(3\delta_{\sigma\nu}\,\delta_{\tau\rho}\right.$$
$$\left. + 3\delta_{\sigma\rho}\,\delta_{\tau\nu} - 2\delta_{\sigma\tau}\,\delta_{\nu\rho})\Big]\langle E_{\nu\nu}{}^{\omega_L}\,E_{\nu\rho}{}^{\omega_L}\rangle_t\right\}(\epsilon_{\tau\lambda}{}^\omega + 2\delta_{\tau\lambda}) \tag{33}$$

where the anisotropy constant is:

$$B_1{}^{\omega,\,\omega_L} = \frac{2\pi}{45V}\langle 3C_{\alpha\beta\alpha\beta}{}^{\omega,\,\omega_L} - C_{\alpha\alpha\beta\beta}{}^{\omega,\,\omega_L} + \frac{1}{kT}(3A_{\alpha\beta}{}^\omega\,A_{\alpha\beta}{}^{\omega_L} - A_{\alpha\alpha}{}^\omega\,A_{\beta\beta}{}^{\omega_L})\rangle \tag{34}$$

4. Non-linear Optical Activity

The contribution to the electric dipolar polarisation accounting for linear spatial dispersion (the second term of the expansion (9)) can now be written as follows:

$$D_\sigma{}^e = \frac{1}{V}\langle B_{\sigma\tau\nu}{}^\omega\rangle_E{}^{\omega_L}\,E_{\nu\tau}{}^\omega\,S_\nu \tag{35}$$

S being a unit vector in the direction of propagation of the probe light.

The third-rank tensor $B_{\sigma\tau\nu}{}^\omega$ of electric polarisability of the medium at frequency ω describing its natural optical activity can be written as:

$$B_{\sigma\tau\rho}{}^\omega = -i\epsilon_{\sigma\tau\nu}\,G_{\nu\rho}{}^\omega \tag{36}$$

$G_{\nu\rho}{}^\omega$ denoting Born's [1] gyration tensor, and $\epsilon_{\sigma\tau\nu}$ denoting the unit antisymmetric tensor of rank three (the Levi-Cività pseudotensor).

Inserting equation 36 in equation 35 we have

$$D_\sigma{}^e = -\frac{i}{V}\epsilon_{\sigma\tau\nu}\langle G_{\nu\rho}{}^\omega\rangle_E{}^{\omega_L}\,E_{\nu\tau}{}^\omega\,S_\rho \tag{37}$$

In the absence of strong laser light, this yields the dipolar polarisation component in the form:

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*Cited after Langevin [3] as T. H. Havelock, *Proc. Roy. Soc.* 77 (1906) 170; 80 (1908) 28; these publications were unavailable to this author.

$$D_\sigma{}^e = -\frac{i}{3V}\,\epsilon_{\sigma\tau\nu}\,\langle G_{\alpha\alpha}{}^\omega\rangle\,E_{\nu\tau}{}^\omega\,S_\nu \tag{38}$$

and, by equations 1 and 15, the electric permittivity tensor:

$$\epsilon_{\sigma\tau}{}^\omega - \delta_{\sigma\tau} = -\frac{4\pi i}{9V}\,\langle G_{\alpha\alpha}{}^\omega\rangle\,\epsilon_{\sigma\nu\rho}(\epsilon_{\nu\tau}{}^\omega + 2\delta_{\nu\tau})\,S_\rho \tag{39}$$

For light propagating along the z-axis, we have the following non-zero components:

$$\frac{\epsilon_{xy}{}^\omega}{\epsilon_{yy}{}^\omega + 2} = -\frac{\epsilon_{yx}{}^\omega}{\epsilon_{xx}{}^\omega + 2} = -\frac{4\pi i}{9V}\,\langle G_{\alpha\alpha}{}^\omega\rangle = -i\,R_0{}^\omega \tag{40}$$

the constant $R_0{}^\omega$ describing optical rotation in the absence of the field E^{ω_L}.

The angle of optical rotation per unit length of the medium is

$$\theta = \frac{\pi}{\lambda}\,(n_- - n_+) \tag{41}$$

where n^- and n^+ are the indices of refraction for left and right circularly polarised light with amplitudes

$$E_\mp = (E_x \mp i\,E_y)/\sqrt{2} \tag{41a}$$

For the case of diamagnetic isotropic bodies we have approximately [1, 2]

$$n_\pm = n \mp \frac{i\,\epsilon_{xy}{}^\omega}{2n} \tag{42}$$

whence with regard to equations 40 and 41 we get the angle of optical rotation at zero laser intensity:

$$\theta_0 = \frac{4\pi^2}{3\lambda V}\left(\frac{n^2+2}{3n}\right)\langle G_{\alpha\alpha}{}^\omega\rangle = \frac{\pi(n^2+2)}{n\lambda}\,R_0{}^\omega \tag{43}$$

Hence for special cases we come to the well-known results of Born [1] and other [2, 24-26], who took into account also molecular redistribution.

In the presence of strong laser light, by equation 12 the gyration tensor is subject to the following variation:

$$G_{\sigma\tau}{}^\omega(\Gamma, \mathbf{E}^{\omega_L}) = G_{\sigma\tau}{}^\omega + \frac{1}{2}\,D_{\sigma\tau\nu\rho}{}^{\omega,\,\omega_L}\,\langle E_{\nu\nu}{}^{\omega_L}\,E_{\nu\rho}{}^{\omega_L}\rangle_t \tag{44}$$

Above, $D_{\sigma\tau\nu\rho}{}^{\omega,\,\omega_L}$ is a tensor of non-linear gyration for frequencies ω and ω_L, and describes the direct influence of the field $\mathbf{E}^{\omega_L}$ on the optical activity of the medium.

On insertion of the expansion (44) into equation 37 and with regard to the distribution function (17), we derive the following result for the case of an isotropic body:

$$4\pi\,D_\sigma{}^e = -i\epsilon_{\sigma\tau\nu}\,\{3R_0{}^\omega\,\delta_{\nu\rho} + [(R_{is}{}^{\omega,\,\omega_L} - R_1{}^{\omega,\,\omega_L})\,\delta_{\nu\rho}\,\delta_{\lambda\mu}$$
$$+ 3R_2{}^{\omega,\,\omega_L}\,\delta_{\nu\lambda}\,\delta_{\rho\mu} + 3R_3{}^{\omega,\,\omega_L}\,\delta_{\nu\mu}\,\delta_{\rho\lambda}]\,\langle E_{\nu\lambda}{}^{\omega_L}\,E_{\nu\mu}{}^{\omega_L}\rangle_t\}\,E_{\nu\tau}{}^\omega\,S_\rho \tag{45}$$

where the constant $R_0{}^\omega$ defining the natural optical rotation is given by equation 40, whereas the constant

$$R_{is}{}^{\omega,\,\omega_L} = \frac{2\pi}{9V}\left\{\langle D_{\alpha\alpha\beta\beta}{}^{\omega,\,\omega_L}\rangle + \frac{1}{kT}\langle\Delta G_{\alpha\alpha}{}^\omega\,\Delta A_{\beta\beta}{}^{\omega_L}\rangle\right\} \tag{46}$$

defines the isotropic variation in optical rotation. The other constants appearing in equation 45 are of the form:

$$R_i{}^{\omega,\,\omega_L} = \frac{\pi}{45V}\,\sigma_{\alpha\beta\gamma\delta}{}^{(i)}\,\langle D_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L} + \frac{1}{kT}\,G_{\alpha\beta}{}^\omega\,A_{\gamma\delta}{}^{\omega_L}\rangle \tag{47}$$

with $i = 1, 2, 3$, and define optical rotation variations of an anisotropic nature. The tensors $\sigma_{\alpha\beta\gamma\delta}^{(i)}$ are given by equations 22-24.

On insertion of the polarisation (45) together with equation 15 into equation 1, one comes to the following variation of the non-diagonal electric permittivity tensor components:

$$\epsilon_{\sigma\chi}^{\vec{\omega}} - \delta_{\sigma\chi} = - i\epsilon_{\sigma\tau\nu} S_\rho \left\{ R_0^\omega \delta_{\nu\rho} + \left[\frac{1}{3} (R_{is}^{\omega,\,\omega_L} - R_1^{\omega,\,\omega_L}) \delta_{\nu\rho} \delta_{\lambda\mu} \right.\right.$$

$$\left.\left. + R_2^{\omega,\,\omega_L} \delta_{\nu\lambda} \delta_{\rho\mu} + R_3^{\omega,\,\omega_L} \delta_{\nu\mu} \delta_{\rho\lambda} \right] \langle E_{v\lambda}^{\omega_L} E_{v\mu}^{\omega_L} \rangle_t \right\} (\epsilon_{\tau\chi}^{\vec{\omega}} + 2\delta_{\tau\chi}) \qquad (48)$$

Hence, for the probe light propagating in the z-direction, we get the following non-zero non-diagonal components:

$$\frac{\epsilon_{xy}^\omega}{\epsilon_{yy}^\omega + 2} = - \frac{\epsilon_{yx}^\omega}{\epsilon_{xx}^\omega + 2} = - \frac{i}{3} \left\{ 3R_0^\omega + R_{is}^{\omega,\,\omega_L} \langle E_{v\sigma}^{\omega_L} E_{v\sigma}^{\omega_L} \rangle_t \right.$$

$$\left. + R_1^{\omega,\,\omega_L} \langle 3E_{vz}^{\omega_L} E_{vz}^{\omega_L} - E_{v\sigma}^{\omega_L} E_{v\sigma}^{\omega_L} \rangle_t \right\} \qquad (49)$$

because in this case too a symmetry relation similar to that of equation 28 holds:

$$R_1^{\omega,\,\omega_L} = R_2^{\omega,\,\omega_L} + R_3^{\omega,\,\omega_L} \qquad (50)$$

With regard to the definition (41) as well as the relation (42), we find the non-linear variation of the angle of optical rotation:

$$\theta = \theta_0 + \theta_2^{is} \langle E_\sigma^{\omega_L} E_\sigma^{\omega_L} \rangle_t + \theta_2^{anis} \langle 3E_z^{\omega_L} E_z^{\omega_L} - E_\sigma^{\omega_L} E_\sigma^{\omega_L} \rangle_t \qquad (51)$$

where θ_0 is defined by equation 43, whereas the quantities defining the isotropic and anisotropic changes in optical rotation are respectively of the form:

$$\theta_2^{is} = \frac{\pi}{\lambda} \left(\frac{n^2 + 2}{3n}\right) \left(\frac{n_L^2 + 2}{3}\right)^2 R_{is}^{\omega,\,\omega_L} \qquad (52)$$

$$\theta_2^{anis} = \frac{\pi}{\lambda} \left(\frac{n^2 + 2}{3n}\right) \left(\frac{n_L^2 + 2}{3}\right)^2 R_1^{\omega,\,\omega_L} \qquad (53)$$

In particular assuming the laser beam to propagate in the same direction as the probe light (along the z-axis), we have by equation 51 for the change in rotation angle:

$$\theta - \theta_0 = (\theta_2^{is} - \theta_2^{anis}) \langle E_x^{\omega_L} E_x^{\omega_L} + E_y^{\omega_L} E_y^{\omega_L} \rangle_t \qquad (54)$$

In the case of laser light polarised with electric vector $\mathbf{E}^{\omega_L}$ oscillating parallel to the z-axis, we obtain by equation 51 a variation

$$\theta - \theta_0 = (\theta_2^{is} + 2\theta_2^{anis}) \langle E_z^{\omega_L} E_z^{\omega_L} \rangle_t \qquad (55)$$

In the case of laser light circularly polarised with amplitudes defined as equation 41a, we obtain, with regard to equation 54:

$$\theta - \theta_0 = \frac{1}{2} \left(\theta_2^{is} - \theta_2^{anis} \right) \left(|E_+^{\omega_L}|^2 + |E_-^{\omega_L}|^2 \right) \qquad (54a)$$

One thus notes that a variation of the angle of rotation can result by using laser light irrespective of whether it is unpolarised, plane polarised, or circularly polarised.

5. Application to Special Cases

The constants from equations 20, 21, 46 and 47 derived above are valid for arbitrary isotropic bodies. We shall now apply them to the case when the volume V contains N identical microsystems (molecules, macromolecules or colloid particles). Thus:

$$B_{is}{}^{\omega,\,\omega_L} = \frac{2\pi}{9V}\left\{\left\langle\sum_{p=1}^{N} c_{\alpha\alpha\beta\beta}{}^{\omega,\,\omega_L\,(p)}\right\rangle + \frac{1}{kT}\left\langle \varDelta\sum_{p=1}^{N} a_{\alpha\alpha}{}^{\omega(p)}\varDelta\sum_{q=1}^{N} a_{\beta\beta}{}^{\omega_L\,(q)}\right\rangle\right\} \quad (56)$$

$$B_{i}{}^{\omega,\,\omega_L} = \frac{\pi}{45V}\,\sigma_{\alpha\beta\gamma\delta}{}^{(i)}\left\{\left\langle\sum_{p=1}^{N} c_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L\,(p)}\right\rangle + \frac{1}{kT}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N} a_{\alpha\beta}{}^{\omega(p)}a_{\gamma\delta}{}^{\omega_L\,(q)}\right\rangle\right\} \quad (57)$$

$$R_{is}{}^{\omega,\,\omega_L} = \frac{2\pi}{9V}\left\{\left\langle\sum_{p=1}^{N} d_{\alpha\beta\beta}{}^{,\,\omega_L\,(p)}\right\rangle + \frac{1}{kT}\left\langle \varDelta\sum_{p=1}^{N} g_{\alpha\alpha}{}^{\omega(p)}\varDelta\sum_{q=1}^{N} a_{\beta\beta}{}^{\omega_L\,(q)}\right\rangle\right\} \quad (58)$$

$$R_{i}{}^{\omega,\,\omega_L} = \frac{\pi}{45V}\,\sigma_{\alpha\beta\gamma\delta}{}^{(i)}\left\{\left\langle\sum_{p=1}^{N} d_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L\,(p)}\right\rangle + \frac{1}{kT}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N} g_{\alpha\beta}{}^{\omega(p)}a_{\gamma\delta}{}^{\omega_L\,(q)}\right\rangle\right\} \quad (59)$$

Above, $a_{\alpha\beta}{}^{\omega(p)}$ is the polarisability tensor of the p-th microsystem immersed in the medium, whereas the tensor $c_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L\,(p)}$ describes the non-linear variation of its polarisability due to the strong electric field of the laser beam. Likewise, the gyration tensor $g_{\alpha\beta}{}^{\omega(p)}$ and that of non-linear gyration $d_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L\,(p)}$ describe the relevant properties of the p-th microsystem within the medium.

5.1. Isotropic Constants
We begin with the isotropic constants (56) and (58) which, on neglecting terms in non-linear polarisabilities as well as the influence of molecular redistribution on the linear polarisabilities, reduce to:

$$B_{is}{}^{\omega,\,\omega_L} = \frac{2\pi}{VkT}\,a^{\omega}a^{\omega_L}\langle(\varDelta N)^2\rangle \quad (60)$$

$$R_{is}{}^{\omega,\,\omega_L} = \frac{2\pi}{VkT}\,g^{\omega}a^{\omega_L}\langle(\varDelta N)^2\rangle \quad (61)$$

Here, $a^{\omega} = a_{\alpha\alpha}{}^{\omega}/3$ and $a^{\omega_L} = a_{\alpha\alpha}{}^{\omega_L}/3$ are mean polarisabilities of the microsystem, respectively at frequency ω and ω_L, to be had approximatively from the well-known Lorentz-Lorenz formula:

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}\,\rho\,a \quad (62)$$

with $\rho = N/V$ the number density of microsystems in the medium. In the same approximation, the molecular rotatory parameter $g^{\omega} = g_{\alpha\alpha}{}^{\omega}/3$ (the mean value of the gyration tensor) occurs in Born's formula [1, 2]:

$$\theta_0 = \frac{4\pi^2}{\lambda}\left(\frac{n^2+2}{3n}\right)\rho g^{\omega} \quad (63)$$

obviously resulting from equation 43.

Equations 60 and 61 involve the mean square fluctuation of the number of microsystems, a quantity given in statistical mechanics [27] as:

$$\langle(\varDelta N)^2\rangle = N + \rho^2\iint\left\{g^{(2)}(\mathbf{r}_p,\mathbf{r}_q) - g^{(1)}(\mathbf{r}_p)\,g^{(1)}(\mathbf{r}_q)\right\}d\mathbf{r}_p\,d\mathbf{r}_q \quad (64)$$

where $g^{(1)}(\mathbf{r}_p)$ is the ordinary correlation function of molecules at position $\mathbf{r}_p$, whereas $g^{(2)}(\mathbf{r}_p,\mathbf{r}_q)$ is the binary correlation function for microsystems at positions $\mathbf{r}_p$ and $\mathbf{r}_q$.

For the purpose of our calculations, it is preferable to use, instead of the statistical form (equation 64), the following thermodynamical form originally derived by Smoluchowski in his theory of fluctuations [28]:

$$\langle (\Delta N)^2 \rangle = V \rho^2 kT \beta_T \tag{65}$$

with β_T —— the isothermal compressibility coefficient of the medium.

Returning now to equations 62, 63 and 65, we can re-write the constants from equations 60 and 61 in a form more convenient for numerical calculations:

$$B_{is}{}^{\omega,\,\omega_L} = \frac{9\beta_T}{8\pi} \left(\frac{n^2 - 1}{n^2 + 2} \right) \left(\frac{n_L{}^2 - 1}{n^2{}_L + 2} \right) \tag{66}$$

$$R_{is}{}^{\omega,\,\omega_L} = \frac{9\beta_T}{8\pi^2} \left(\frac{n\lambda}{n^2 + 2} \right) \left(\frac{n_L{}^2 - 1}{n_L{}^2 + 2} \right) \theta_0{}^{\omega} \tag{67}$$

Keeping in mind that, by equations 26 and 27, the isotropic variation in electric permittivity is defined as $\Delta \epsilon^{is} = \epsilon_2{}^{is} \langle E_\sigma{}^{\omega_L} E_\sigma{}^{\omega_L} \rangle_t$ with:

$$\epsilon_2{}^{is} = \left(\frac{n^2 + 2}{3} \right)^2 \left(\frac{n_L{}^2 + 2}{3} \right)^2 B_{is}{}^{\omega,\,\omega_L} \tag{68}$$

we obtain with regard to equation 66 the following result:

$$\epsilon_2{}^{is} = \frac{\beta_T}{8\pi} \left(n^2 - 1 \right) \left(\frac{n^2 + 2}{3} \right) \left(n_L{}^2 - 1 \right) \left(\frac{n_L{}^2 + 2}{3} \right) \tag{69}$$

accounting for the electrostrictive contribution to non-linear variations of the refractive index [29, 30].

In a similar manner, inserting equation 67 into equation 52 one obtains the following expression for the isotropic change in optical rotation:

$$\theta_2{}^{is} = \frac{\beta_T}{8\pi} \theta_0{}^{\omega} (n_L{}^2 - 1) \left(\frac{n_L{}^2 + 2}{3} \right) \tag{70}$$

5.2. Anisotropic Constants

We have seen that the optical birefringence (29) induced in the medium by intense laser light is, in accordance with equation 30, fully defined by the constant $B_1{}^{\omega,\,\omega_L}$ alone. From equations 22 and 57 and by classical statistical mechanics [27], this constant can be put in the form:

$$B_1{}^{\omega,\,\omega_L} = \frac{\pi\rho}{45} \left\{ 3c_{\alpha\beta\alpha\beta}{}^{\omega,\,\omega_L} + 3c_{\alpha\beta\beta\alpha}{}^{\omega,\,\omega_L} - 2c_{\alpha\alpha\beta\beta}{}^{\omega,\,\omega_L} \right.$$
$$+ \frac{1}{kT} \left(3a_{\alpha\beta}{}^{\omega} a_{\alpha\beta}{}^{\omega_L} + 3a_{\alpha\beta}{}^{\omega} a_{\beta\alpha}{}^{\omega_L} - 2a_{\alpha\alpha}{}^{\omega} a_{\beta\beta}{}^{\omega_L} \right)$$
$$\left. + \frac{\rho^2}{VkT} \iint \sigma_{\alpha\beta\gamma\delta}{}^{(1)} a_{\alpha\beta}{}^{\omega(p)} a_{\gamma\delta}{}^{\omega_L(q)} g^{(2)}(\Gamma_p, \Gamma_q) d\Gamma_p d\Gamma_q \right\} \tag{71}$$

where $g^{(2)}(\Gamma_p, \Gamma_q)$ is the binary correlation function of microsystems p and q at configurations Γ_p and Γ_q (the configurational coordinates contain the positional variables $\mathbf{r}$ and orientational variables Ω of the microsystems).

The first term of equation 71 defines birefringence due to non-linear polarisability of the microsystems. The second term depends directly on temperature and results from reorientation of anisotropic microsystems in the electric field of the laser light [4]. In addition to these two, which describe the optical birefringence in gaseous or highly dilute media, equation 71 contains a third term which is of significance in condensed media, where it accounts for various molecular correlations of the radial as well as of the angular kinds. A discussion of the roles of these various correlations in optically inactive substances is to be found elsewhere [23, 30-33]. Here, we adduce only the result which is obtained for axially symmetrical microsystems when the

83

term in non-linear electronic polarisability is omitted (in certain cases, such terms cannot be neglected, as shown in references 23 and 34-36):

$$B_1{}^{\omega,\,\omega_L} = \frac{4\pi\rho}{45kT}(a_{33}{}^{\omega} - a_{11}{}^{\omega})(a_{33}{}^{\omega_L} - a_{11}{}^{\omega_L})(1 + J_A) \tag{72}$$

Above [31]:

$$J_A = \frac{\rho}{2V}\iint(3\cos^2\theta_{pq} - 1)\,g^{(2)}(\Gamma_p,\Gamma_q)\,d\Gamma_p\,d\Gamma_q \tag{73}$$

is a parameter of correlations of the angular kind between microsystems whose symmetry axes subtend an angle θ_{pq}.

Moreover, from equations 51 and 53, one notes that the anisotropic change in angle of rotation is fully described by a single constant $R_1{}^{\omega,\,\omega_L}$. Similarly to equation 71, we may write it out, obtaining:

$$R_1{}^{\omega,\,\omega_L} = \frac{\pi\rho}{45}\left\{3d_{\alpha\beta\alpha\beta}{}^{\omega,\,\omega_L} + 3d_{\alpha\beta\beta\alpha}{}^{\omega,\,\omega_L} - 2d_{\alpha\alpha\beta\beta}{}^{\omega,\,\omega_L}\right.$$

$$+ \frac{1}{kT}(3g_{\alpha\beta}{}^{\omega}a_{\alpha\beta}{}^{\omega_L} + 3g_{\alpha\beta}{}^{\omega}a_{\beta\alpha}{}^{\omega_L} - 2g_{\alpha\alpha}{}^{\omega}a_{\beta\beta}{}^{\omega_L})$$

$$\left. + \frac{\rho^2}{VkT}\iint\sigma_{\alpha\beta\gamma\delta}{}^{(1)}g_{\alpha\beta}{}^{\omega(p)}a_{\gamma\delta}{}^{\omega_L(q)}g^{(2)}(\Gamma_p,\Gamma_q)\,d\Gamma_p\,d\Gamma_q\right\} \tag{74}$$

The symmetry properties of the gyration tensor $g_{\alpha\beta}$ are such as to nullify all its components in the case of molecules possessing a centre of symmetry and a plane of symmetry (e.g. molecules of the point groups O_h, T_d, T_h, D_{6h}, D_{3h}, C_{6v}, C_{3v}, etc.).

For groups T and O we have $g_{11} = g_{22} = g_{33} = g$ and $a_{11} = a_{22} = a_{33} = a$, which can be summarised by writing:

$$g_{\alpha\beta}{}^{\omega} = g^{\omega}\,\delta_{\alpha\beta}, a_{\alpha\beta}{}^{\omega_L} = a^{\omega_L}\,\delta_{\alpha\beta}$$

$$d_{\alpha\beta\gamma\delta}{}^{\omega,\,\omega_L} = d_1{}^{\omega,\,\omega_L}\,\delta_{\alpha\beta}\,\delta_{\gamma\delta} + d_2{}^{\omega,\,\omega_L}(\delta_{\alpha\gamma}\,\delta_{\beta\delta} + \delta_{\alpha\delta}\,\delta_{\beta\gamma}) + d_3{}^{\omega,\,\omega_L}(\delta_{\alpha\gamma}\,\delta_{\beta\delta} - \delta_{\alpha\delta}\,\delta_{\beta\gamma}).$$

In the case here under consideration, linear rotation is given by equation 63 whereas the non-linear change in rotation angle reduces to the simple form:

$$R_1{}^{\omega,\,\omega_L} = \frac{4\pi}{3}\rho\,d_2{}^{\omega,\,\omega_L} \tag{75}$$

showing it to be due to non-linear gyration alone, since there is no orientation of molecules with isotropic polarisability in the absence of molecular redistribution [23, 31].

In the case of strongly anisotropic molecules and not excessively high temperatures one is justified in omitting in equation 74 the term in non-linear gyration, which in general is numerically small as compared with the temperature-dependent term resulting from molecular reorientation, e.g. for the point group D_2 the diagonal tensor components $g_{\alpha\beta}$ and $a_{\alpha\beta}$ are non-zero, so that:

$$R_1{}^{\omega,\,\omega_L} = \frac{2\pi\rho}{45kT}\left\{(g_{11}{}^{\omega} - g_{22}{}^{\omega})(a_{11}{}^{\omega_L} - a_{22}{}^{\omega_L}) + (g_{22}{}^{\omega} - g_{33}{}^{\omega})(a_{22}{}^{\omega_L} - a_{33}{}^{\omega_L})\right.$$

$$+ (g_{33}{}^{\omega} - g_{11}{}^{\omega})(a_{33}{}^{\omega_L} - a_{11}{}^{\omega_L})$$

$$\left. + \frac{\rho}{V}\sum_{s,t=1}^{3}g_{ss}{}^{\omega}a_{tt}{}^{\omega_L}\iint(3\cos^2\theta_{pq}{}^{(st)} - 1)\,g^{(2)}(\Gamma_p,\Gamma_q)\,d\Gamma_p\,d\Gamma_q\right\} \tag{76}$$

$\theta_{pq}{}^{(st)}$ denoting the angle between the principal axis s of molecule p and the axis t of molecule q.

In particular, for the point groups C_3, D_3, C_4, D_4, C_6, D_6 we have $g_{11} = g_{22} \neq g_{33}$ and $a_{11} = a_{22} \neq a_{33}$, and equation 76 reduces to:

$$R_1{}^{\omega,\,\omega_L} = \frac{4\pi\rho}{45kT}\,(g_{33}{}^{\omega} - g_{11}{}^{\omega})\,(a_{33}{}^{\omega_L} - a_{11}{}^{\omega_L})\,(1 + J_A) \tag{77}$$

If, for simplicity, one neglects molecular angular correlations in the temperature-dependent term of equation 74, one has explicitly for the point group C_1 (e.g. secondary butyl alcohol):

$$R_1{}^{\omega,\,\omega_L} = \frac{2\pi\rho}{45kT}\left\{(g_{11}{}^{\omega} - g_{22}{}^{\omega})\,(a_{11}{}^{\omega_L} - a_{22}{}^{\omega_L}) + (g_{22}{}^{\omega} - g_{33}{}^{\omega})\,(a_{22}{}^{\omega_L} - a_{33}{}^{\omega_L})\right.$$

$$\left. + (g_{33}{}^{\omega} - g_{11}{}^{\omega})\,(a_{33}{}^{\omega_L} - a_{11}{}^{\omega_L}) + 6(g_{12}{}^{\omega} a_{12}{}^{\omega_L} + g_{23}{}^{\omega} a_{23}{}^{\omega_L} + g_{31}{}^{\omega} a_{31}{}^{\omega_L})\right\} \tag{78}$$

This expression is equally applicable to the point group C_2 (e.g. H_2O_2) where, however, one has to write $g_{23} = g_{31} = 0$.

Considering only optical reorientation of microsystems in the two effects of optical birefringence and non-linear optical activity, one obtains with regard to equations 72 and 77 the following relation:

$$\frac{R_1{}^{\omega,\,\omega_L}}{B_1{}^{\omega,\,\omega_L}} = \frac{g_{33}{}^{\omega} - g_{11}{}^{\omega}}{a_{33}{}^{\omega} - a_{11}{}^{\omega}} \tag{79}$$

permitting one to determine the ratio of the anisotropy of the gyration tensor and the anisotropy of the optical polarisability tensor. Denoting by r the linear dimensions of a microsystem, the ratio (79) is found to be of order r/λ. For molecules, this amounts to 10^{-4} at $\lambda \simeq 5000$ Å, but can be 100 or 1000 times more for macromolecules or colloid particles.

6. Discussion and Final Remarks

Both optically induced birefringence and non-linear optical activity have been shown to be accessible to a description within the framework of a uniform statistical theory which, in this general form, does not require postulation of any special model assumptions regarding the structure of microsystems or their mutual correlations. The theory can be written completely to give the explicit dependence on frequency in relation to electronic dispersion [11-14, 37, 38], molecular relaxation dispersion [31, 39, 40], as well as spatial dispersion [11, 12] comprising electric and magnetic multipoles of higher orders [13, 14, 41]. Contributions to refractivity, not considered here, from the magnetic permittivity tensor (2) can be calculated as done elsewhere for the case of static magnetic permittivity [42]. A quantum-mechanical formulation of the preceding theory can be given [13, 38]; it can also be extended by methods of quantum field theory [22].

Experiments performed hitherto on different liquids [6-10] have confirmed the theoretical results, taking into consideration various molecular correlations [23, 30-33]. Lately, papers aimed at checking Havelock's relation (31) have appeared; certain of these measurements [43] point to a decisive role of molecular reorientation, when in accordance with equation 31 the result has to be -2, whereas other measurements [44] appear to favour non-linear optical polarisability, when Havelock's relation yields $+3$. The decision seems to hinge on considerations of the role of electrostriction (appearing in the constant B_{is}) as well as of that of the electrocaloric effect [45]. Equation 70, too, points to a role of electrostriction in the isotropic variation of the rotation angle. Thus, be it only for this reason, the mechanism leading to variations in rotation angle is somewhat different from that of optical birefringence which, with regard to equation 29, does not depend on electrostriction. On the other hand, electrostriction intervenes in Havelock's relation (31) and in measurements of absolute variations in refractivity ("retard absolu") [43-46].

The decision as to which of the three mechanisms: electrostriction, non-linear electronic polarisability, or molecular reorientation, plays the chief part in any given case may be expected to come from measurements of optical Kerr effect and non-linear optical activity as

85

functions of temperature. Helpful information might be gleaned from a study of these effects in solutions, as functions of concentration, since variations related to non-linear polarisability have to be additive whereas variations due to optical reorientation exhibit considerable deviations from additivity as a result of various molecular correlations [23, 31]. One has yet another way of studying these non-linear effects by determining their frequency dependence, which is different for each of the mechanisms under consideration, especially near regions of non-linear absorption. Another possibility of direct assessments of the effect of non-linear polarisability suggests itself with regard to a recent paper by Brewer [47], namely by recurring to strong light pulses of a duration of 10^{-12} sec for causing induced non-linearities. Reorientation cannot take place in so short a time, at least in a wide variety of molecular liquids. Obviously, in solutions of polymers or colloid particles, where relaxation times amount to 10^{-6} to 10^{-8} sec, such separation between non-linear polarisability and the reorientation effect may be feasible by use of the now generally applied lasers yielding pulses of nanosecond duration.

Regarding the possibilities of making observations of non-linear changes in optical activity, equation 70 together with equations 30, 53, and 79 leads to the following relative variations of the isotropic and anisotropic components, respectively:

$$\frac{\theta_2{}^{ts}}{\theta_0{}^{\omega}} = \frac{\beta_T}{8\pi}(n_L{}^2 - 1)\left(\frac{n_L{}^2 + 2}{3}\right) \tag{80}$$

$$\frac{\theta_2{}^{anis}}{\theta_0{}^{\omega}} = \frac{n\lambda}{2\pi\rho}\left(\frac{3}{n^2+2}\right)^2\left(\frac{g_{33}{}^{\omega} - g_{11}{}^{\omega}}{3g^{\omega}}\right)\frac{B_\lambda{}^{\omega_L}}{a_{33}{}^{\omega} - a_{11}{}^{\omega}} \tag{81}$$

Since in most liquids [48] β_T is of the order of 10^{-10} dyne/cm², the relative isotropic variation in rotation angle (80) is of an order of 10^{-12} times the laser light intensity. The numerical evaluation of the anisotropic variation (81) is rendered somewhat more difficult because of a lack of relevant data. In molecular liquids [48] $\rho \simeq 6 \times 10^{21}$/cm³, $a_{33} - a_{11} \simeq 5 \times 10^{-24}$ cm³, [7] $B_\lambda \simeq 10^{-7}$ cgs. For d-secondary butylalcohol, the mean molecular rotatory parameter $g = 6 \times 10^{-29}$ cm³ at $\lambda = 5893$ Å [24]. Hence the ratio (81) is also of the order of $\geqslant 10^{-12}$. Clearly, observations of such variations will require the focused beam of a giant ruby laser with electric field strength of order 10^6 to 10^5 e.s.u. Much larger effects (10^2 to 10^6 times larger) can be expected in solutions of macromolecules and colloid particles [49, 50], where a non-focused ruby laser beam should prove sufficient.

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