

CHANGES IN RAYLEIGH SCATTERING OF LIGHT CAUSED BY LASER OPTICAL SATURATION

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Rayleigh scattering of a light beam by substances whose molecules, macromolecules or colloid particles are totally aligned in the electric field of an intense laser beam is discussed. Formulas are derived for the nonlinear changes in vertical and horizontal scattered intensity components involving five optical reorientation functions, which are calculated numerically and plotted for arbitrary values of molecular reorientation parameters. These changes are shown to be particularly large in solutions of polymers and colloids, where even total optical saturation is achievable by usual laser technique. The present line of investigation is proposed as a new method of determining the sign and value of the optical anisotropy of macromolecules and colloid particles. It is shown moreover that Krishnan's reciprocity relations are not in general fulfilled by the scattered intensity components in the presence of an intense laser beam, but hold only if the scattering microsystems are axially-symmetric and the laser light oscillations vertical.

1. Introduction

Rayleigh light scattering is subject to more or less considerable changes when the optically anisotropic molecules or macromolecules of the medium are subjected to reorientation by a DC or AC electric field [1-4] or by the electric field of a laser beam [2, 5]. Experimentally, hitherto, changes have been observed in the intensity of light scattered by solutions of polymers and colloids placed in a DC or AC electric field [1, 3, 4]. Recent measurements by Lalanne [6] with the aim of finding and determining nonlinear changes in light scattering by molecular liquids were inconclusive as a result of certain anomalous effects — emergence of the theoretically predicted, induced nonlinearity [2] at sufficiently high laser intensity was preceded by irregular deviations (dispersion of values of usual, linear Rayleigh scattering) probably due to the signalled optical breakdown, rendering the liquid "opaque".

It is our aim here to carry out a detailed, quantitative analysis of the problem in order to determine those conditions in which nonlinear changes in Rayleigh scattering induced by strong laser light can be observed and measured to the best advantage. We shall in particular consider the cases and conditions admitting of optical saturation, meaning total alignment of

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the microsystems (molecules, macromolecules or colloid particles) in the electric field of a laser beam. In molecular liquids, optical saturation cannot generally be achieved in experiment even if the focussed beam of a giant ruby laser is recurred to, because the liquid scatterer undergoes destruction by optical breakdown before saturation sets in. The anisotropy optically induced in molecular liquids is insignificant, and the changes in scattering due to it require more refined and perfected methods for their detection. However, present measuring techniques have proved sufficient for detecting optically induced nonlinear changes in Rayleigh scattering of light in macromolecular and colloidal systems, where a high degree of alignment of the microsystems can easily be obtained.

2. Usual Rayleigh light scattering

Let us consider a system of N rigid noninteracting microsystems (molecules, macromolecules, or colloid particles) immersed in another, isotropic medium of volume V scattering light incident with electric vector $\mathbf{E}^\omega = \mathbf{E}^0 e^{i\omega t}$ oscillating at frequency ω . We assume the linear dimensions $2r$ of the microsystems as small with respect to the light wavelength $\lambda = 2\pi c/\omega$ permitting to restrict considerations to scattering of the electric kind in the dipole approximation (*i.e.* neglecting scattering processes of higher multipole orders related with inhomogeneities of the electric field within the limits of a microsystem). Once we assume moreover that the probe electric field strength \mathbf{E}^ω is small, the dipole moment induced in a microsystem at frequency ω can be expressed as:

$$m_\sigma^\omega = \alpha_{\sigma\tau}^\omega E_\tau^\omega, \quad (1)$$

with $\alpha_{\sigma\tau}^\omega$ denoting the tensor of linear optical polarizability of the microsystem with respect to the frequency ω .

We now introduce the tensor of scattered light intensity [8]:

$$I_{\sigma\tau}^\omega = \frac{\rho}{c^4} \left\langle \frac{d^2 m_\sigma^\omega}{dt^2} \frac{d^2 m_\tau^\omega}{dt^2} \right\rangle_{\Omega, t}, \quad (2)$$

where $\rho = N/V$ is the number density of microsystems and the symbol $\langle \rangle_{\Omega, t}$ stands for averaging over orientations Ω of the microsystems and over the time t of one oscillation period of the optical field.

By Eq. (1), we can rewrite (2) as follows:

$$I_{\sigma\tau}^\omega = \rho \left(\frac{\omega}{c} \right)^4 \langle \alpha_{\sigma\nu}^\omega \alpha_{\tau\varrho}^\omega \rangle_\Omega \langle E_\nu^\omega E_\varrho^\omega \rangle_t. \quad (3)$$

With the aim of further calculations, it is convenient to transform the tensor $\alpha_{\sigma\nu}^\omega$ from laboratory reference axes x, y, z to axes 1, 2, 3 fixed at the centre of the microsystem by means of the transformation formulas:

$$\alpha_{\sigma\nu}^\omega = c_{\sigma\alpha} c_{\nu\gamma} \alpha_{\alpha\gamma}^\omega, \quad (4)$$

where the $c_{\sigma\alpha}$'s are cosines of the angles between axes σ and α belonging to the two reference systems respectively.

Assuming the tensor $a_{\alpha\gamma}^{\omega}$ given in the molecular reference system as constant, the scattering tensor (3) can be written with regard to (4) as follows:

$$I_{\sigma\tau}^{\omega} = a_{\omega}^{-2} a_{\alpha\gamma}^{\omega} a_{\beta\delta}^{\omega} \langle c_{\sigma\alpha} c_{\tau\beta} c_{\nu\gamma} c_{\rho\delta} \rangle_{\Omega} I_{\nu\rho}^{\text{is}}, \quad (5)$$

where we have introduced the tensor of isotropic light scattering:

$$I_{\nu\rho}^{\text{is}} = \rho \left(\frac{\omega}{c} \right)^4 a_{\omega}^2 \langle E_{\nu}^{\omega} E_{\rho}^{\omega} \rangle_t, \quad (6)$$

$a_{\omega} = a_{\alpha\alpha}^{\omega}/3$ denoting the mean polarizability of the isolated microsystem.

In the absence of externally applied fields, we are justified in performing in (5) an unweighted averaging over all possible orientations of the microsystems with respect to the laboratory axes [9]:

$$\begin{aligned} \langle c_{\sigma\alpha} c_{\tau\beta} c_{\nu\gamma} c_{\rho\delta} \rangle_{\Omega} = & \frac{1}{30} \{ (4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}) \delta_{\sigma\tau}\delta_{\nu\rho} + \\ & + (4\delta_{\alpha\gamma}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta}) \delta_{\sigma\nu}\delta_{\tau\rho} + (4\delta_{\alpha\delta}\delta_{\beta\gamma} - \delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\gamma}\delta_{\beta\delta}) \delta_{\sigma\rho}\delta_{\tau\nu} \} \end{aligned} \quad (7)$$

leading finally for optically inactive substances to:

$$I_{\sigma\tau}^{\omega} = I_{\sigma\tau}^{\text{is}} + \frac{1}{5} \kappa_{\omega}^2 (I_{\sigma\tau}^{\text{is}} + 3I_{\nu\rho}^{\text{is}} \delta_{\sigma\tau}), \quad (8)$$

where we have introduced the following optical anisotropy of polarizability:

$$\kappa_{\omega}^2 = \frac{3a_{\alpha\beta}^{\omega} a_{\alpha\beta}^{\omega} - a_{\alpha\alpha}^{\omega} a_{\beta\beta}^{\omega}}{18a_{\alpha\alpha}^{\omega} a_{\beta\beta}^{\omega}}. \quad (9)$$

If the incident light propagates along y and observation is along x , the elements of the scattering tensor for vertical oscillations V (directed along z) and horizontal oscillations H_v (directed along y) are defined as follows:

$$\begin{aligned} V_v &= I_{zz}(zz), & H_v &= I_{yy}(zz), \\ V_h &= I_{zz}(xx), & H_h &= I_{yy}(xx), \end{aligned} \quad (10)$$

where v and h stand for oscillation directions of incident light.

With regard to the preceding definitions, we have by Eq. (8) the well-known relations for usual light scattering by small microsystems [10]:

$$\frac{V_v}{I_{zz}^{\text{is}}} = 1 + \frac{4}{5} \kappa_{\omega}^2, \quad (11)$$

$$\frac{H_v}{I_{zz}^{\text{is}}} = \frac{V_h}{I_{xx}^{\text{is}}} = \frac{H_h}{I_{xx}^{\text{is}}} = \frac{3}{5} \kappa_{\omega}^2. \quad (12)$$

Eq. (12) expresses Krishnan's reciprocity relation.

3. Linear changes in scattered light intensity

We proceed to consider the case when the scattering system is acted on by the light wave of an intense incident laser beam with electric vector $\mathbf{E}^{\omega L} = \mathbf{E}^0 e^{i\omega L t}$ oscillating at frequency ω_L in general not equal to ω . If the field strength $\mathbf{E}^{\omega L}$ is sufficiently large, two processes take place, consisting in: (i) nonlinear electronic polarizability of the microsystems giving rise to multiharmonic light scattering, which we shall not consider here [8], and (ii) reorientation of microsystems in the electric field of the laser wave (intensity I^L), described by the statistical distribution function at thermodynamical equilibrium [8]:

$$f(\Omega, I^L) = \frac{\exp(-\beta \langle u(\Omega, \mathbf{E}^{\omega L}) \rangle_t)}{\int \exp(-\beta \langle u(\Omega, \mathbf{E}^{\omega L}) \rangle_t) d\Omega}, \quad (13)$$

where $\beta = 1/kT$ and the potential energy of a microsystem averaged over one oscillation period of the laser field is:

$$\langle u(\Omega, \mathbf{E}^{\omega L}) \rangle_t = -\frac{1}{2} \alpha_{\sigma\tau}^{\omega L} \langle E_{\sigma}^{\omega L} E_{\tau}^{\omega L} \rangle_t \quad (14)$$

$\alpha_{\sigma\tau}^{\omega L}$ being the polarizability tensor at frequency ω_L .

In the case now under consideration, the unweighted mean value $\langle \rangle_{\Omega}$ in Eqs (3), (5) has to be replaced by the statistical mean value in the presence of laser light of intensity I^L defined as:

$$\langle G \rangle_{\Omega}^{I^L} = \int G(\Omega) f(\Omega, I^L) d\Omega. \quad (15)$$

In this formulation of the problem, computations can be effected to the end on the simplifying assumption that the microsystems have the axial symmetry (thus, with respect to the 3-axis) when the transformation formula (4) reduces to:

$$a_{\sigma\nu} = a(1 - \kappa) \delta_{\sigma\nu} + 3\alpha\kappa c_{\sigma 3} c_{\nu 3}, \quad (16)$$

where we now have:

$$a = \frac{1}{3} (a_{33} + 2a_{11}), \quad \kappa = \frac{a_{33} - a_{11}}{a_{33} + 2a_{11}}. \quad (17)$$

Let the 3-axis of the molecular system subtend the angle ϑ with the laboratory z -axis. We have the directional cosines:

$$\begin{aligned} c_{x3} &= \sin \vartheta \cos \varphi, \\ c_{y3} &= \sin \vartheta \sin \varphi, \\ c_{z3} &= \cos \vartheta, \end{aligned} \quad (18)$$

φ denoting the azimuth.

Clearly, the components (10) are now functions of the laser light intensity I^L which we can express quite generally by the tensor:

$$I_{\sigma\tau}^L = \langle E_{\sigma}^{\omega L} E_{\tau}^{\omega L} \rangle_t. \quad (19)$$

Recurring to Eqs (3) and (15), (18), we now obtain the relative, laser light-induced variations of the components (10) in the form:

$$\delta V_v(I^L) = \frac{V_v(I^L) - V_v}{V_v} = \frac{20\kappa_\omega \Phi(I^L) + 16\kappa_\omega^2 \Psi(I^L)}{5 + 4\kappa_\omega^2}, \quad (20)$$

$$\delta H_v(I^L) = \frac{H_v(I^L) - H_v}{H_v} = -Q_1(I^L), \quad (21)$$

$$\delta V_h(I^L) = \frac{V_h(I^L) - V_h}{V_h} = -Q_2(I^L), \quad (22)$$

$$\delta H_h(I^L) = \frac{H_h(I^L) - H_h}{H_h} = -T(I^L), \quad (23)$$

where the components V_v , H_v , V_h and H_h in the absence of the laser wave are defined by the expressions (11) and (12).

Above, we have introduced the following functions defining reorientation of microsystems in the electric laser field:

$$\Phi(I^L) = \frac{1}{2} \langle 3 \cos^2 \vartheta - 1 \rangle_{\Omega}^{I^L}, \quad (24)$$

$$\Psi(I^L) = \frac{1}{16} \langle 45 \cos^4 \vartheta - 30 \cos^2 \vartheta + 1 \rangle_{\Omega}^{I^L}. \quad (25)$$

$$Q_1(I^L) = \langle 1 - 15 \cos^2 \vartheta \sin^2 \vartheta \sin^2 \varphi \rangle_{\Omega}^{I^L}, \quad (26)$$

$$Q_2(I^L) = \langle 1 - 15 \cos^2 \vartheta \sin^2 \vartheta \cos^2 \varphi \rangle_{\Omega}^{I^L}, \quad (27)$$

$$T(I^L) = \langle 1 - 15 \sin^4 \vartheta \cos^2 \varphi \sin^2 \varphi \rangle_{\Omega}^{I^L}, \quad (28)$$

where the statistical averaging procedure has to be performed in accordance with the definition (15) with the distribution function (13) involving a potential energy of the form:

$$\langle u(\Omega, I^L) \rangle_i = u(0, I^L) - \frac{1}{2} (a_{33}^{\omega L} - a_{11}^{\omega L}) \{ \sin^2 \vartheta (I_{xx}^L \cos^2 \varphi + I_{yy}^L \sin^2 \varphi) + I_{zz}^L \cos^2 \vartheta \} \quad (29)$$

resulting from Eq. (14) with regard to Eqs (16)–(19).

In particular, in the absence of a laser field ($I^L = 0$), when the statistical mean value (15) goes over into the unweighted mean value, we have the following non-vanishing quantities:

$$\langle \cos^{2k} \vartheta \rangle_{\vartheta} = \frac{1}{2k+1},$$

$$\langle \cos^{2k} \varphi \rangle_{\varphi} = \frac{(2k-1)!!}{2^k \cdot k!}, \quad (30)$$

and the reorientation functions (24)–(28) are all seen to vanish quite obviously.

In the case of a not very strong electric field $E^{\omega L}$, reorientation of microsystems is but slight and, with regard to Eqs (13) and (29), is given by the following distribution

function:

$$f(\Omega, I^L) = f(\Omega, 0) \left\{ 1 + \frac{\beta}{2} (a_{33}^{\omega L} - a_{11}^{\omega L}) [\sin^2 \vartheta (I_{xx}^L \cos^2 \varphi + I_{yy}^L \sin^2 \varphi) + I_{zz}^L \cos^2 \vartheta - \frac{1}{3} (I_{xx}^L + I_{yy}^L + I_{zz}^L)] \right\} \quad (31)$$

transforming the reorientation functions (24)–(28) to:

$$\Phi(I^L) = \frac{a_{33}^{\omega L} - a_{11}^{\omega L}}{30 kT} (2I_{zz}^L - I_{xx}^L - I_{yy}^L), \quad (32)$$

$$\Psi(I^L) = \frac{a_{33}^{\omega L} - a_{11}^{\omega L}}{84 kT} (2I_{zz}^L - I_{xx}^L - I_{yy}^L), \quad (33)$$

$$Q_1(I^L) = \frac{a_{33}^{\omega L} - a_{11}^{\omega L}}{21 kT} (2I_{xx}^L - I_{yy}^L - I_{zz}^L), \quad (34)$$

$$Q_2(I^L) = \frac{a_{33}^{\omega L} - a_{11}^{\omega L}}{21 kT} (2I_{yy}^L - I_{zz}^L - I_{xx}^L), \quad (35)$$

$$T(I^L) = \frac{a_{33}^{\omega L} - a_{11}^{\omega L}}{21 kT} (2I_{zz}^L - I_{xx}^L - I_{yy}^L). \quad (36)$$

On inspection of the above derived expressions (20)–(23) one sees that the laser light-induced variations of the respective scattered intensities no longer fulfil Krishnan's reciprocity relations (12) generally. However, if one assumes the vector $\mathbf{E}^{\omega L}$ to oscillate in the z -direction, Eqs (21)–(23) and (26)–(28) lead to the following relation:

$$\delta H_o(I^L) = \delta V_h(I^L) = -\frac{1}{2} \delta H_h^*(I^L) = \frac{a_{33}^{\omega L} - a_{11}^{\omega L}}{21 kT} I_{zz}^L. \quad (37)$$

This relation permits direct determinations of the sign and value of a microsystem's optical anisotropy at the oscillation frequency of the laser light wave [2].

4. Light scattering at optical saturation

We shall now consider the situation which arises when the electric field $\mathbf{E}^{\omega L}$ of the incident laser beam is so large as to cause a considerable degree of orientation of the microsystems or even, in the limiting case, their total alignment. With the aim of simplifying our calculations we assume the field $\mathbf{E}^{\omega L}$ to oscillate in the z -direction, $I_{xx}^L = I_{yy}^L = 0$, and with regard to Eq. (29) the distribution function (13) can be written as:

$$f^{\pm}(\Omega, I^L) = \frac{\exp(\pm a_L \cos^2 \vartheta)}{2\pi \int_0^{\pi} \exp(\pm a_L \cos^2 \vartheta) \sin \vartheta d\vartheta}, \quad (38)$$

where

$$a_L = \frac{|a_{33}^{\omega L} - a_{11}^{\omega L}|}{2kT} I_{zz}^L \quad (39)$$

is a dimensionless, positive reorientation parameter of the axially-symmetric microsystem. In Eq. (38), the sign “+” is for positive anisotropy when $a_{33} > a_{11}$ (prolate molecules, like CS_2) whereas the sign “-” is for negative anisotropy, $a_{33} < a_{11}$ (oblate molecules, such as C_6H_6).

As obvious from (37), the distribution function depends on the angle ϑ only, so that the functions (26)–(28) can in a first step be averaged over all possible values of the azimuth φ , yielding:

$$Q(I^L) = Q_1(I^L) = Q_2(I^L) = \frac{1}{2} \langle 15 \cos^4 \vartheta - 15 \cos^2 \vartheta + 2 \rangle_{\Omega}^{I^L}, \quad (40)$$

$$T(I^L) = \frac{1}{8} \langle 30 \cos^2 \vartheta - 15 \cos^4 \vartheta - 7 \rangle_{\Omega}^{I^L}. \quad (41)$$

With respect to Eqs (15) and (38) the following Langevin functions of even order can be introduced:

$$L_{2k}^{\pm}(a_L) = \frac{\int_0^{\pi} \cos^{2k} \vartheta \exp(\pm a_L \cos^2 \vartheta) \sin \vartheta \, d\vartheta}{\int_0^{\pi} \exp(\pm a_L \cos^2 \vartheta) \sin \vartheta \, d\vartheta}. \quad (42)$$

At not too large values of the reorientation parameter (39) one is justified in expanding the Boltzmann factor in (42) in powers of a_L and, with Eq. (30) taken into account, one obtains:

$$L_{2k}^{\pm}(a_L) = \sum_{n=0}^{\infty} c_n^k (\pm a_L)^n, \quad (43)$$

where the expansion coefficients are of the form:

$$c_n^k = \frac{1}{n! (2n+2k+1)} - \sum_{l=1}^n \frac{c_{n-l}^k}{l! (2l+1)}. \quad (44)$$

To a satisfactory accuracy, Eq. (43) yields:

$$\begin{aligned} L_2^{\pm}(a_L) &= \frac{1}{3} \pm \frac{4a_L}{45} + \frac{8a_L^2}{945} \mp \frac{16a_L^3}{14175} - \dots, \\ L_4^{\pm}(a_L) &= \frac{1}{5} \pm \frac{8a_L}{105} + \frac{16a_L^2}{1575} \mp \frac{32a_L^3}{51975} - \dots, \end{aligned} \quad (45)$$

and the reorientation functions (24), (25), (40) and (41) take the form:

$$\Phi_{\pm}(a_L) = \pm \frac{2a_L}{15} + \frac{4a_L^2}{315} \mp \frac{8a_L^3}{4725} - \dots, \quad (46)$$

$$\Psi_{\pm}(a_L) = \pm \frac{a_L}{21} + \frac{4a_L^2}{315} \pm \frac{4a_L^3}{10395} - \dots, \quad (47)$$

$$Q_{\pm}(a_L) = \mp \frac{2a_L}{21} + \frac{4a_L^2}{315} \pm \frac{8a_L^3}{2079} - \dots, \tag{48}$$

$$T_{\pm}(a_L) = \pm \frac{4a_L}{21} + \frac{4a_L^2}{315} \mp \frac{32a_L^3}{10395} - \dots \tag{49}$$

If the reorientation parameter a_L is equal to or larger than unity (that is, if ——— in accordance to Eq. (34) ——— either the laser intensity I^L is very large or the absolute optical anisotropy $|a_{33}^{oL} - a_{11}^{oL}|$ is considerable), the Langevin functions (42) have to be calculated without expanding the Boltzmann factor. The substitution $t = \sqrt{a_L} \cos \vartheta$ now transforms (42) conveniently to:

$$L_{2k}^{\pm}(a_L) = \frac{\int_{-\sqrt{a_L}}^{\sqrt{a_L}} t^{2k} e^{\pm t^2} dt}{a_L^k \int_{-\sqrt{a_L}}^{\sqrt{a_L}} e^{\pm t^2} dt} \tag{50}$$

and integration *per partes* of the numerator:

$$\int t^{2k} e^{\pm t^2} dt = \pm \frac{1}{2} t^{2k-1} e^{\pm t^2} \mp \frac{2k-1}{2} \int t^{2k-2} e^{\pm t^2} dt \tag{51}$$

leads to the following recurrential formula:

$$L_{2k}^{\pm}(a_L) = \pm \frac{1}{2\sqrt{a_L} I_{\pm}(a_L)} \mp \frac{2k-1}{2a_L} L_{2k-2}^{\pm}(a_L), \tag{52}$$

where $L_0^{\pm} = 1$ and where we have introduced the integrals:

$$I_{\pm}(a_L) = e^{\mp a_L} \int_0^{\sqrt{a_L}} e^{\pm t^2} dt. \tag{53}$$

The reorientation functions (24), (25), (40) and (41) expressed by way of the Langevin functions (42) take the form:

$$\Phi_{\pm}(a_L) = \frac{1}{2} \{3L_2^{\pm}(a_L) - 1\}, \tag{54}$$

$$\Psi_{\pm}(a_L) = \frac{1}{16} \{45 L_4^{\pm}(a_L) - 30 L_2^{\pm}(a_L) + 1\}, \tag{55}$$

$$Q_{\pm}(a_L) = \frac{1}{2} \{15 L_4^{\pm}(a_L) - 15 L_2^{\pm}(a_L) + 2\}, \tag{56}$$

$$T_{\pm}(a_L) = \frac{1}{8} \{30 L_2^{\pm}(a_L) - 15 L_4^{\pm}(a_L) - 7\}, \tag{57}$$

involving, with regard to (52), the Langevin functions:

$$L_2^{\pm}(a_L) = \pm \frac{1}{2\sqrt{a_L} I_{\pm}(a_L)} \mp \frac{1}{2a_L}, \tag{58}$$

$$L_4^{\pm}(a_L) = \pm \frac{1}{2\sqrt{a_L} I_{\pm}(a_L)} \mp \frac{3}{2a_L} L_2^{\pm}(a_L) = \pm \frac{2a_L \mp 3}{4a_L^2 I_{\pm}(a_L)} + \frac{3}{4a_L^2}. \tag{59}$$

Graphs of the Langevin functions (58) and (59) are shown in Fig. 1. The reorientation functions (54)–(57) for positive and negative optical molecular anisotropy are plotted in Figs 2 and 3 respectively. The reorientation function (54) intervenes in the effect of optical birefringence [11, 12] and has been tabulated by O’Konski *et al.* [11] for positive anisotropy and by Shah [13] for negative anisotropy.

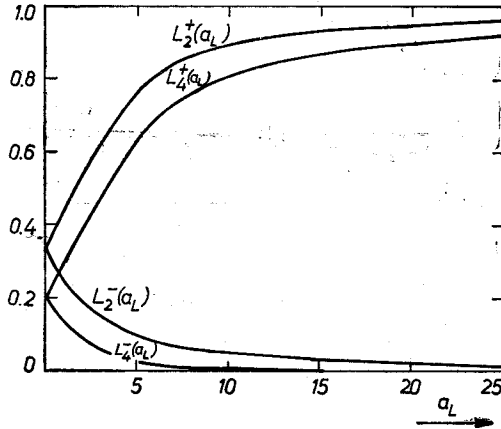


Fig. 1. Graphs of generalized Langevin functions (52) for positive and negative anisotropy (prolate and oblate molecules), respectively

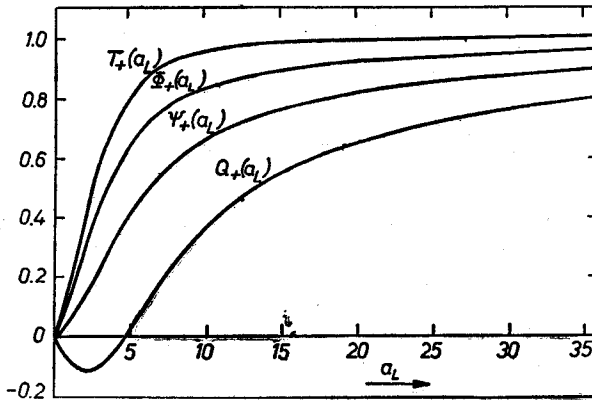


Fig. 2. Graphs of optical reorientation functions (54)–(57) for prolate molecules

Let us consider the limiting case when $a_L \rightarrow \infty$. For prolate microsystems, we now have:

$$L_2^+(\infty) = L_4^+(\infty) = 1, \quad (60)$$

and all reorientation functions (54)–(57) tend to unity:

$$\Phi_+(\infty) = \Psi_+(\infty) = Q_+(\infty) = T_+(\infty) = 1. \quad (61)$$

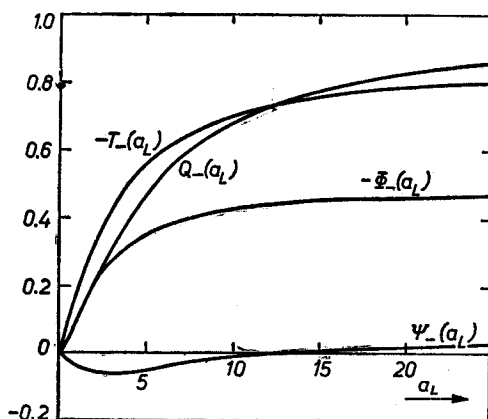


Fig. 3. Graphs of reorientation functions (54)–(57) for oblate molecules

This indeed is the case of optical saturation, when all the microsystems are aligned with their axes of maximal polarizability along the direction of oscillations of the electric field of the intense laser light wave. The variations of scattered components (20)–(23) now achieve their extremal values:

$$\delta V_v^+(\infty) = \frac{20 \kappa_\omega + 16 \kappa_\omega^2}{5 + 4 \kappa_\omega^2}, \quad (62)$$

$$\delta H_v^+(\infty) = \delta V_h^+(\infty) = \delta H_h^+(\infty) = -1. \quad (63)$$

Of particular interest here is the change in vertical component (62) which, for small values of the anisotropy parameter $\kappa_\omega \ll 0.1$ can be written in a good approximation as follows:

$$\delta V_v^+(\infty) = 4\kappa_\omega, \quad (64)$$

and thus yields directly the value of the optical anisotropy of the microsystem.

For the remaining case of oblate microsystems, optical saturation gives a value of

$$L_2^-(\infty) = L_4^-(\infty) = 0 \quad (65)$$

and consequently the reorientation functions (54)–(57) assume their extremal values:

$$\Phi_-(\infty) = -\frac{1}{2}, \quad \Psi_-(\infty) = \frac{1}{16}, \quad Q_-(\infty) = 1, \quad T_-(\infty) = -\frac{7}{8} \quad (66)$$

leading respectively to the following variations of the scattered intensity components (20)–(23):

$$\delta V_v^-(\infty) = \frac{-10 \kappa_\omega + \kappa_\omega^2}{5 + 4 \kappa_\omega^2}, \quad (67)$$

$$\delta H_v^-(\infty) = \delta V_h^-(\infty) = -1, \quad (68)$$

$$\delta H_h^-(\infty) = \frac{7}{8}. \quad (69)$$

For microsystems presenting low anisotropy, we have by Eq. (67):

$$\delta V_{\nu}^{-}(\infty) = -2\kappa_{\omega}. \quad (70)$$

It is thus seen that investigation of the change in components (63), (64), (69), and (70) due to the state of optical saturation permits determinations not only of the value but also of the sign of the anisotropy of the microsystems. By Eqs (11) and (12), studies of usual Rayleigh scattering provide information only regarding the square of the optical molecular anisotropy.

5. Discussion and conclusions

Before proceeding to a discussion of the results derived, we shall consider the case when the scattering molecules undergo alignment under the effect of an AC electric field $\mathbf{E}^{\omega} = \mathbf{E}^0 e^{i\omega t}$ oscillating at frequency ω sufficiently small to orient the permanent molecular dipoles $\boldsymbol{\mu}$ also. Assuming the symmetry axis of a microsystem to subtend the angle ϑ with the direction of the field \mathbf{E}^{ω} acting along z , the statistical distribution function takes the form [8]:

$$f(\Omega, \mathbf{E}^{\omega}) = f(\Omega, 0) \left\{ 1 + \frac{\mu \cos \vartheta}{kT(1+i\omega\tau_D)} E_0 e^{i\omega t} + \frac{\beta}{12} \left(a_{33}^{\omega} - a_{11}^{\omega} + \frac{\mu^2}{kT} \frac{1}{1+i\omega\tau_D} \right) \times \right. \\ \left. \times (3 \cos^2 \vartheta - 1) \left(1 + \frac{e^{i2\omega t}}{1+i2\omega\tau_B} \right) E_0^2 + \dots \right\}, \quad (71)$$

where τ_D is the Debye relaxation time and τ_B — the relaxation time of anisotropy [14] mutually related by the formula $\tau_D = 3\tau_B$.

With regard to Eq. (71), the reorientation functions (24), (25), (40) and (41) become:

$$\Phi(\omega) = \frac{2g^{\omega}}{15}, \quad (72)$$

$$T(\omega) = -2Q(\omega) = 4Y(\omega) = \frac{4}{21} g^{\omega}, \quad (73)$$

the reorientation parameter now being of the form:

$$g^{\omega} = \frac{E_0^2}{4kT} \left[a_{33}^{\omega} - a_{11}^{\omega} + \frac{\mu^2}{kT(1+i\omega\tau_D)} \right] \left(1 + \frac{e^{i2\omega t}}{1+i2\omega\tau_B} \right). \quad (74)$$

In the case of a DC electric field $\omega = 0$, the parameter (74) takes the form:

$$g^0 = \frac{E_{DC}^2}{2kT} \left(a_{33}^0 - a_{11}^0 + \frac{\mu^2}{kT} \right), \quad (75)$$

whereas in that of an electric field of high frequency, when $\omega\tau_D \rightarrow \infty$ and $\omega\tau_B \rightarrow \infty$ simultaneously, we have:

$$g^{\infty} = \frac{a_{33}^{\infty} - a_{11}^{\infty}}{4kT} E_0^2 = \frac{a_{33}^{\infty} - a_{11}^{\infty}}{2kT} I. \quad (76)$$

Thus, as could be expected, at oscillations at optical frequencies the permanent dipoles take no part in the reorientation process and do not affect the scattered light intensity. The sole contribution in this case is that from reorientation of the ellipsoid of electronic polarizability.

In the general case, the parameter (74) is a complex quantity and can be resolved into a real and an imaginary part:

$$\begin{aligned} \operatorname{Re}(g^\omega) = & \frac{E_0^2}{4kT} \left\{ (a_{33}^\omega - a_{11}^\omega) \left(1 + \frac{\cos 2\omega t + 2\omega\tau_B \sin 2\omega t}{1 + 4\omega^2\tau_B^2} \right) + \right. \\ & \left. + \frac{\mu^2}{1 + \omega^2\tau_D^2} \left[1 + \frac{(1 - 2\omega^2\tau_D\tau_B) \cos 2\omega t + \omega(\tau_D + 2\tau_B) \sin 2\omega t}{1 + 4\omega^2\tau_B^2} \right] \right\} \quad (77) \end{aligned}$$

$$\begin{aligned} \operatorname{Im}(g^\omega) = & \frac{E_0^2}{4kT} \left\{ \frac{a_{33}^\omega - a_{11}^\omega}{1 + 4\omega^2\tau_B^2} (2\omega\tau_B \cos 2\omega t - \sin 2\omega t) + \right. \\ & \left. + \frac{\mu^2}{1 + \omega^2\tau_D^2} \left[\omega\tau_D + \frac{\omega(\tau_D + 2\tau_B) \cos 2\omega t - (1 - 2\omega^2\tau_D\tau_B) \sin 2\omega t}{1 + 4\omega^2\tau_B^2} \right] \right\}. \quad (78) \end{aligned}$$

Benoit *et al.* [1] and, recently, Stoylov [3] studied theoretically and experimentally the changes in light scattering by solutions of macromolecules and colloid particles subjected to a DC electric field. Stoylov extended his investigations to the case of electric saturation. Jennings *et al.* [4] performed similar investigations for the case of an AC electric field and studied in particular the component scattered at double frequency 2ω which, as seen from Eqs (77) and (78), accompanies the steady (non-alternating) component. In this connection, the question arises of whether laser technique permits studies of the reorientation effect in disperse systems? In molecular liquids, the relaxation times are known to lie between 10^{-10} and 10^{-13} sec [15] and are thus sufficiently short for reorientation of molecules to occur during a single light pulse of a strong laser having a duration of 10^{-8} to 10^{-10} sec. Since the anisotropy of polarizability of molecules is, at the most, of order 10^{-23} cm³, the reorientation parameter (39) results of order $10^{-10} I_L$ at room temperature. As a consequence of this, with the aim of achieving a value of $\alpha_L = 1$, upward of which optical saturation sets in, one would have to apply a focussed laser beam of intensity $I_L = 10^{10}$ esu in the focus. Regrettably, however, optical breakdown of liquids occurs in electric fields of order 10^6 esu, before optical saturation can take place. Thus, in molecular liquids, only small changes in scattered light intensity of an order of 10^{-3} at the best can be hoped for. Such variations can be observed when recurring to very sensitive measuring procedures.

Conditions for observation are much more favourable in macromolecular and colloidal substances. Thus *e.g.* for aqueous solutions of protein molecules of dimensions 50–700 Å, the relaxation times lie between 10^{-6} and 10^{-8} sec [16], so that reorientation of the microsystems can still take place in the electric field of laser beams of pulse duration exceeding 10^{-6} sec. For these molecules, the reorientation parameter α_L is of the order of $10^{-4} I_L$. Consequently, optical saturation can now be achieved even at an intensity I_L of the order of 10^4 esu requiring the nonfocussed beam of a ruby laser with extended pulse duration.

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