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MOLECULAR KERR RELAXATION THEORY FOR NONDIPOLAR LIQUIDS IN REORIENTING PULSE FIELDS ☆

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The time variations of the difference in refractive index in optical birefringence are calculated for a liquid composed of nondipolar anisotropically polarizable molecules acted on by reorienting pulse fields. The molecular dynamics is based on Sack's equation, taking into account small inertial effects (a modification of the Smoluchowski rotational diffusion equation). The time variations in birefringence are analyzed for rectangular and cosine pulse shapes on the basis of Sack's equation and are plotted for a gaussian pulse on the basis of Smoluchowski's equation. Measurements are proposed of the birefringence component with frequency 4ω related to the square of the electric anisotropy reorientation parameter of the molecules.

1. Introduction

The general molecular theory of electro-optical effects in isotropic dielectrics has long been at the centre of interest. Its various aspects have been dealt with in a number of monographs [1–3].

The relaxation theory of Kerr's effect [4–8] induced in liquids with nondipolar anisotropically polarizable molecules as proposed by us takes small inertial effects into account. The molecular dynamics model assumed will be that of Sack's equation [9] – a modification of Smoluchowski's equation of rotational brownian motions. Sack's equation has been applied by Coffey [10,11] in the theory of dielectric relaxation and Kerr relaxation and, recently, in that of third-order nonlinear electric polarization in liquids [12]. On omission of small inertial effects Sack's model reduces to the Smoluchowski model widely used in the description of dispersion and absorption in both linear [13,14] and nonlinear [15,16] phenomena of molecular optics. Although they do not take into account the intermolecular interactions so highly important in liquids [17], they nonetheless provide a qualitatively correct picture of the rotational relaxation of molecules in a liquid and macromolecules in a solution [18–20].

We consider the rise and decay of birefringence, induced by rectangular and sine pulse electric fields. Moreover, we perform a graphical analysis of the time variations of birefringence induced by a gaussian pulse within the framework of Smoluchowski's model.

In part, our results have been reported in the Proceedings of the Conference on "Ultrafast Phenomena in Spectroscopy '85", held at Reinhardsbrunn, GDR [21].

2. Theory

We consider an isotropic liquid of density ρ composed of N nondipolar noninteracting molecules, having the linear polarizability components $a_{\alpha\beta}$. The liquid is acted on by two electric fields: a weak

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measuring field with the optical frequency $E_1(t) = E_1 \cos \omega t$ and a reorienting field $E_2(t) = E_2 g(t)$ sufficiently strong to induce nonlinear polarization and reorientation in the molecules. $E_2(t)$ is assumed as applied in the Z-direction of laboratory coordinates, whereas the measuring field $E_1(t)$ as directed (i) along the X-axis and (ii) along the Z-axis.

For axially symmetric molecules with optical polarizability components $a_{\parallel}$, $a_{\perp}$ respectively parallel and perpendicular to the axis of symmetry, classical molecular electric birefringence theory predicts [1–4] the difference in light refractive indices, at the two experimental configurations, to amount to

$$\Delta n = n_{\parallel} - n_{\perp} = C(a_{\parallel} - a_{\perp})\langle P_2(\cos \theta_t)\rangle_{\theta_t}. \tag{1}$$

Above, $P_2(\cos \theta_t)$ is a Legendre polynomial of the second order, $\theta_t = \theta(t)$ is the polar angle between the symmetry axis of the molecule and the laboratory Z-axis and, for the Lorentz local field model,

$$C = (2\pi\rho/n)\left[\tfrac{1}{3}(n^2 + 2)\right]^2, \tag{2}$$

where n is the weak-field refractive index.

Statistical averaging (1) is performed with an appropriate model of the molecular dynamics in the medium. The method leading to the solution of Sack's equation, as well as the averaging procedure, are given in the appendix; here, we give but the final result:

$$\Delta n(t) = C(a_{\parallel} - a_{\perp})\left[\pm \tfrac{2}{15} q A_{12}(t) + \tfrac{4}{315} q^2 B_{22}(t) + \ldots\right], \tag{3}$$

where we have introduced the parameter of reorientation of the molecular anisotropy of polarizability in the reorienting field:

$$q = \left(|\alpha_{\parallel} - \alpha_{\perp}|/2kT\right)\left[\tfrac{1}{3}(n^2 + 2)\right]^2 E_2^2, \tag{4}$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizability components of the molecule (parallel and perpendicular to its axis of symmetry) in the presence of the reorienting field, k is Boltzmann's constant, and T the absolute temperature of the liquid. The time dependence of the birefringence is inherent in the relaxation functions $A_{12}(t)$ and $B_{22}(t)$. We shall calculate them further on for rectangular-shaped and cosine reorienting fields.

3. Rise in birefringence for rectangular reorienting pulse

Consider a rectangular pulse, switched on at $t = 0$,

$$g(t) = u(t) = 0, \quad t < 0; \quad g(t) = u(t) = 1, \quad 0 < t; \quad g(t) = u(t) = \tfrac{1}{2}, \quad t = 0, \tag{5}$$

where $u(t)$ is the unit step function. By eqs. (A.10) and (A.11), and with the initial condition $A_{12}(0) = B_{22}(0) = 0$, we obtain the relaxation functions of rise in birefringence in the following form:

$$A_{12}(t) = 1 - \tfrac{1}{2}(1 + \xi/\xi_2)\exp(-t/_{-}\tau_2) - \tfrac{1}{2}(1 - \xi/\xi_2)\exp(-t/_{+}\tau_2), \tag{6}$$

$$\begin{aligned} B_{22}(t) = c_2\{ & {}_{-}\tau_2\left[1 - \exp(-t/_{-}\tau_2)\right] - {}_{+}\tau_2\left[1 - \exp(-t/_{+}\tau_2)\right] \\ & + 2\xi/\xi_2^2\left[\exp(-t/_{-}\tau_2) - \exp(-t/_{+}\tau_2)\right] \\ & - \tfrac{1}{2}(1 + \xi/\xi_2)t\exp(-t/_{-}\tau_2) + \tfrac{1}{2}(1 - \xi/\xi_2)t\exp(-t/_{+}\tau_2)\}. \end{aligned} \tag{7}$$

These formulae involve two modified rotational relaxation times of birefringence ${}_{+}\tau_2$, ${}_{-}\tau_2$, equal to:

$${}_{\pm}\tau_2 = 2/(\xi \pm \xi_2); \quad \xi_2 = \xi(1 - 24kT/I\xi)^{1/2}; \quad c_2 = 6kT/I\xi_2. \tag{8}$$

Thus, the rise in birefringence on applying the pulse (5) at $t = 0$ is dependent on exponential functions with the relaxation times ${}_{+}\tau_2$, ${}_{-}\tau_2$. The nonlinear term related with the square of the molecular reorientation parameter q is moreover dependent on functions that are products of the time t and an exponential $t\exp(-t/{}_{+}\tau_2)$, $t\exp(-t/{}_{-}\tau_2)$, thus $t\exp(-t/{}_{\pm}\tau_2)$. The birefringence increases from the initial value $\Delta n(0) = 0$ up to a steady-state value $\Delta n(\text{s.s.})$ for ${}_{-}\tau_2 \ll t$, equal to

$$\Delta n(\text{s.s.}) = \tfrac{2}{15}C(a_{\parallel} - a_{\perp})\left[\pm q + \tfrac{2}{21}q^2 c_2({}_{-}\tau_2 - {}_{+}\tau_2) + \ldots\right]. \tag{9}$$

The modified birefringence relaxation times ${}_{\pm}\tau_2$ can also be expressed in the approximate form

$${}_{-}\tau_2 \approx \tau_2/(1 + 6\gamma), \quad {}_{+}\tau_2 \approx \left[6\gamma/(1 - 6\gamma)\right]\tau_2, \tag{10}$$

where the results obtained with Sack's equation (A.2) are valid for small inertial effects, i.e. if

$$\gamma = kT/I\xi^2 \ll 1. \tag{11}$$

In (10), τ_2 is the well-known birefringence relaxation time [4–6]

$$\tau_2 = \tfrac{1}{3}\tau_1 = 1/6D = I\xi/6kT, \tag{12}$$

τ_1 is Debye's dipole relaxation time, and D is the coefficient of isotropic rotation diffusion of the molecules. Within the framework of Smoluchowski's rotational diffusion model we make use of the formulae (A.12) and (A.13) corresponding to the assumption of $\gamma = 0$ in eqs. (6), (7). This leads to

$$A_{12}(t;\ \gamma = 0) = 1 - \exp(-t/\tau_2), \tag{13}$$

$$B_{22}(t;\ \gamma = 0) = 1 - (1 - t/\tau_2)\exp(-t/\tau_2), \tag{14}$$

since now ${}_{+}\tau_2 \to 0$, ${}_{-}\tau_2 \to \tau_2$.

On neglecting small inertial effects, the formulae (3), (13), (14) lead to the following expression for the time-rise in birefringence

$$\Delta n(t;\ \gamma = 0) = \tfrac{2}{15}C(a_{\parallel} - a_{\perp})\left\{\pm q\left[1 - \exp(-t/\tau_2)\right] + \tfrac{2}{21}q^2\left[1 - \exp(-t/\tau_2) + (t/\tau_2)\exp(-t/\tau_2)\right]\right\}, \tag{15}$$

whereas the steady-state birefringence is [3]

$$\Delta n(\text{s.s.};\ \gamma = 0) = \tfrac{2}{15}C(a_{\parallel} - a_{\perp})\left(\pm q + \tfrac{2}{21}q^2\right). \tag{16}$$

Fig. 1 shows the normalized birefringence rise function

$$\eta_{\pm}(t) = \frac{\Delta n(t;\ \gamma = 0)}{\Delta n(\text{s.s.};\ \gamma = 0)} = 1 - \frac{1 \mp \frac{2}{21}q(t/\tau_2 - 1)}{1 \pm \frac{2}{21}q}\exp(-t/\tau_2) \tag{17}$$

plotted versus the time t for some values of the polarizability anisotropy reorientation parameter q. One notes that the deviations from exponentiality are insignificant.

4. Rise in birefringence in a cosine reorienting field

We shall now consider the case of a cosine pulse

$$g(t) = \tfrac{1}{2}\left[\exp(-i\omega t) + \exp(i\omega t)\right]u(t). \tag{18}$$

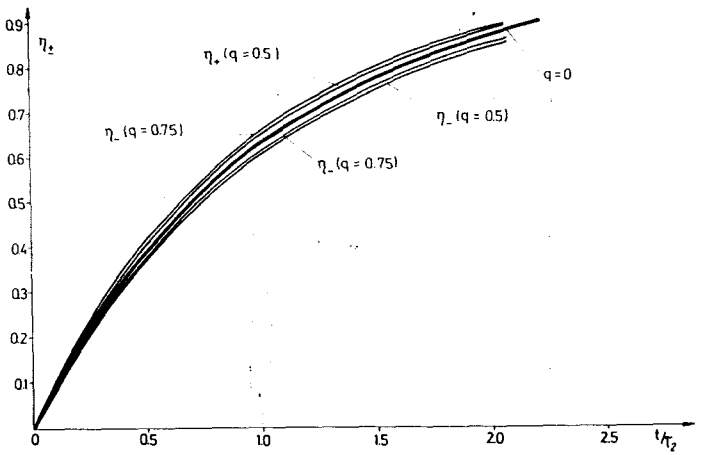

Fig. 1. Time dependence of the normalized Kerr effect rise function $\eta_{\pm}(t)$ for some values of the reorientation parameter q.

With regard to (A.10), (A.11) we obtain the steady-state birefringence relaxation functions A_{12}, B_{22}:

$$A_{12}(\text{s.s.}) = \tfrac{1}{2}c_2\{{}_-\tau_2[1 + r_{-22}(\omega)\cos(2\omega t - \psi_{-22})] - {}_+\tau_2[1 + r_{22}(\omega)\cos(2\omega t - \psi_{22})]\}, \tag{19}$$

$$\begin{aligned} B_{22}(\text{s.s.}) = {} & \tfrac{1}{4}c_2^2\{{}_-\tau_2^2[1 + \tfrac{1}{2}r_{-22}^2(\omega)] - {}_+\tau_2^2[1 + \tfrac{1}{2}r_{22}^2(\omega)] - {}_+\tau_2{}_-\tau_2[r_{22}^2(\omega) + r_{-22}^2(\omega) + 2] \\ & + {}_-\tau_2({}_-\tau_2 - {}_+\tau_2)r_{-22}(\omega)\cos(2\omega t - \psi_{-22}) + {}_+\tau_2({}_+\tau_2 - {}_-\tau_2)r_{22}(\omega)\cos(2\omega t - \psi_{22}) \\ & + 2{}_-\tau_2^2 r_{-22}^2(\omega)\cos(2\omega t - 2\psi_{-22}) + 2{}_+\tau_2^2 r_{22}^2(\omega)\cos(2\omega t - 2\psi_{22}) \\ & + {}_-\tau_2 r_{-24}(\omega)[{}_-\tau_2 r_{-22}(\omega)\cos(4\omega t - \psi_{-24} - \psi_{-22}) \\ & + {}_+\tau_2 r_{22}(\omega)\cos(4\omega t - \psi_{-24} - \psi_{22})] \\ & + {}_+\tau_2 r_{24}(\omega)[{}_+\tau_2 r_{22}(\omega)\cos(4\omega t - \psi_{24} - \psi_{22}) - {}_-\tau_2 r_{-22}(\omega)\cos(4\omega t - \psi_{24} - \psi_{-22})]\}, \end{aligned} \tag{20}$$

where ${}_{\pm}\tau_2$, c_2 are given by eqs. (8).

From eqs. (3), (19), (20) we note that in the steady state of birefringence there appears a component with frequency 4ω related with the squared optical anisotropy of the molecule [6] (beside the components with frequency 0 and 2ω). The birefringence is dependent on the modified dispersion functions

$$r_{\pm 2m}(\omega) = (1 + m^2\omega^2{}_{\pm}\tau_2^2)^{-1/2}, \tag{21}$$

whereas the individual birefringence components oscillate with phase shifts $\psi_{\pm 2m}$ given by

$$\cos\psi_{\pm 2m} = r_{\pm 2m}(\omega), \quad \sin\psi_{\pm 2m} = m\omega_{\pm}\tau_2 r_{\pm 2m}(\omega). \tag{22}$$

Thus, if small inertial effects are taken into account, the steady-state magnitude as well as the dispersion and absorption properties of the birefringence undergo a modification, and the shape of the oscillations becomes dependent on two modified rotational relaxation times, ${}_{\pm}\tau_2$.

Let us now consider the rise in birefringence due to the pulse (18) as described by the Smoluchowski model. By (A.13), (A.14), with the initial conditions $A_{12}(0) = B_{22}(0)$, we get

$$2A_{12}(t;\ \gamma = 0) = 1 - \exp(-t/\tau_2) + r_{22}(\omega)\left[\cos(2\omega t - \psi_{22}) - r_{22}(\omega)\exp(-t/\tau_2)\right], \tag{23}$$

$$\begin{aligned} 4B_{22}(t;\ \gamma = 0) = {} & \left[1 + \tfrac{1}{2}r_{22}^2(\omega)\right]\left[1 - \exp(-t/\tau_2)\right] + r_{22}(\omega)\left[\cos(2\omega t - \psi_{22}) - r_{22}(\omega)\exp(-t/\tau_2)\right] \\ & + r_{22}^2(\omega)\left[\cos(2\omega t - 2\psi_{22}) - r_{22}^2(\omega)\left(1 - 4\omega^2\tau_2^2\right)\exp(-t/\tau_2)\right] \\ & + (2\omega\tau_2)^{-1} r_{22}^2(\omega)\sin 2\omega t \exp(-t/\tau_2) \\ & + \tfrac{1}{2}r_{22}(\omega)r_{24}(\omega)\left[\cos(4\omega t - \psi_{22} - \psi_{24}) - r_{22}(\omega)r_{24}(\omega)\left(1 - 8\omega^2\tau_2^2\right)\exp(-t/\tau_2)\right] \\ & + 2r_{22}^2(t/\tau_2)\exp(-t/\tau_2) \end{aligned} \tag{24}$$

involving the following dispersion factors and shifts in phase:

$$r_{2m}(\omega) = \left(1 + m^2\omega^2\tau_2^2\right)^{-1/2}, \quad \sin\psi_{2m} = m\omega\tau_2 r_{2m}(\omega), \tag{25}$$

well known from the classical theory of nonlinear relaxation processes, related with nonlinear third-order polarization in liquids [15]. The birefringence increases up to a steady state, described by the functions

$$2A_{12}(\text{s.s.};\ \gamma = 0) = 1 + r_{22}(\omega)\cos(2\omega t - \psi_{22}), \tag{26}$$

$$\begin{aligned} 4B_{22}(\text{s.s.};\ \gamma = 0) = {} & 1 + \tfrac{1}{2}r_{22}^2(\omega) + r_{22}(\omega)\cos(2\omega t - \psi_{22}) + r_{22}^2(\omega)\cos(2\omega t - 2\psi_{22}) \\ & + \tfrac{1}{2}r_{22}(\omega)r_{24}(\omega)\cos(4\omega t - \psi_{22} - \psi_{24}). \end{aligned} \tag{27}$$

One notes that, in the steady state, the birefringence term linear in q consists of a frequency-independent part and of a part which oscillates proportionally to $\cos(2\omega t - \psi_{22})$. The term proportional to q^2 is moreover characterized by the presence of a component with the frequency 4ω. Eqs. (26), (27) result directly from (19), (20) on putting $\gamma = 0$.

If reorientation is caused by an optical field, $\omega\tau_2 \approx \infty$, and the relaxation functions of the optical Kerr effect take the form

$$2A_{12}(t;\ \gamma = 0;\ \omega\tau_2 \approx 0) = 4B_{22}(t;\ \gamma = 0;\ \omega\tau_2 \approx 0) = 1 - \exp(-t/\tau_2). \tag{28}$$

Eqs. (26), (27) prove moreover that, in the steady state of birefringence, the 2ω component

$$\begin{aligned} \Delta n^{2\omega}(\text{s.s.};\ \gamma = 0) = {} & \tfrac{2}{15}C(a_\parallel - a_\perp)r_{22}(\omega)\left\{\pm q\cos(2\omega t - \psi_{22})\right. \\ & \left. + \tfrac{1}{21}q^2\left[\cos(2\omega t - \psi_{22}) + r_{22}(\omega)\cos(2\omega t - 2\psi_{22})\right]\right\} \end{aligned} \tag{29}$$

is accompanied by a birefringence component with the frequency 4ω:

$$\Delta n^{4\omega}(\text{s.s.};\ \gamma = 0) = \tfrac{1}{315}C(a_\parallel - a_\perp)q^2 r_{22}(\omega)r_{24}(\omega)\cos(4\omega t - \psi_{22} - \psi_{24}) \tag{30}$$

dependent on the square of the parameter q^2. The time-rise of the 4ω component is described by the formula

$$\begin{aligned} \Delta n^{4\omega}(t;\ \gamma = 0) = {} & \tfrac{1}{315}C(a_\parallel - a_\perp)q^2 r_{22}(\omega)r_{24}(\omega) \\ & \times\left[\cos(4\omega t - \psi_{22} - \psi_{24}) - r_{22}(\omega)r_{24}(\omega)\left(1 - 8\omega^2\tau_2^2\right)\exp(-t/\tau_2)\right]. \end{aligned} \tag{31}$$

Predictably, measurements of the 4ω component can provide information concerning the influence of the square of the reorientation parameter q^2 on the optical birefringence of liquids.

5. Birefringence in a gaussian reorienting field

For the case of a gaussian laser pulse

$$g(t) = \exp\left[-4\ln(2)(t/T_G)^2\right], \tag{32}$$

where T_G is the pulse half-width, eqs. (A.13), (A.14) lead to

$$A_{12}(t;\ \gamma = 0) = \frac{1}{\tau_2}\int_{-\infty}^{t} \exp\left[-4\ln(2)(u/T_G)^2 - (t-u)/\tau_2\right] \mathrm{d}u, \tag{33}$$

$$B_{22}(t;\ \gamma = 0) = \frac{1}{\tau_2^2}\int_{-\infty}^{t} \exp\left[-4\ln(2)(u/T_G)^2 - (t-u)/\tau_2\right] \times \int_{-\infty}^{u} \exp\left[-4\ln(2)(u/T_G)^2 - (u-u_1)/\tau_2\right] \mathrm{d}u_1\, \mathrm{d}u. \tag{34}$$

Eqs. (33) and (34) enable us to calculate numerically the shape of the time variations of the birefringence relaxation functions for different values of the pulse half-width. The results of our calculations are plotted in figs. 2 and 3 showing the shapes of $A_{12}(t;\ \gamma = 0)$ and $B_{22}(t;\ \gamma = 0)$ given by formulae (33) and (34), for values of T_G ranging from $0.6\tau_2$ to $15\tau_2$. The response of the system in its dependence on T_G is well apparent. It differs markedly from the gaussian reorienting pulse shape (32), especially if τ_2 is comparable with T_G or longer. Figs. 2 and 3 moreover show that the characteristic delay of the maximum of the response functions (33), (34) with respect to the stimulating pulse increases with increasing relaxation time. This is due to the presence of memory in the system.

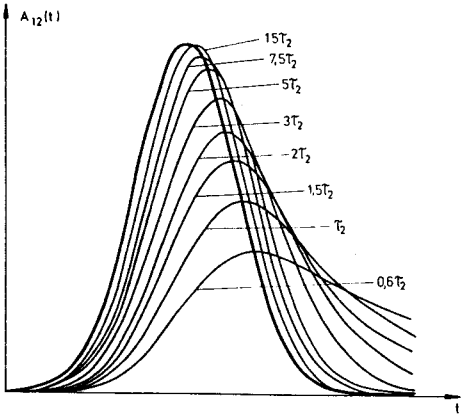

Fig. 2. Time dependence of the Kerr effect relaxational reorientation function $A_{12}(t)$ for some values of the gaussian pulse half-width.

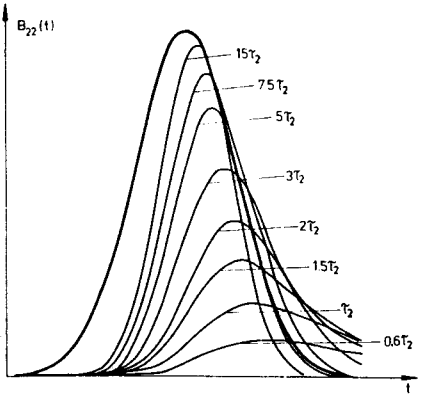

Fig. 3. Time dependence of the Kerr effect relaxational reorientation function $B_{22}(t)$ for some values of the gaussian pulse half-width.

6. Decay of birefringence on removal of the reorienting pulse

One obtains the relaxation function of birefringence decay due to removal of the reorienting pulse $g(t)$ at the moment of time t_0 by putting $g(t) = 0$ in eqs. (A.10)–(A.12). This leads to the equation

$$d^2A/dt^2 + \xi\, dA/dt + (6kT/I)A = 0 \tag{35}$$

for our two relaxation functions $A_{12}(t_0 < t) = B_{22}(t_0 < t) = A(t)$.

For the sake of simplicity, we make the assumption that the pulse was sufficiently long for the liquid to have attained its steady-state birefringence Δn(s.s.), given by the initial conditions

$$A_{12}(\text{s.s.}) = 1, \quad B_{22}(\text{s.s.}) = \alpha_2({}_+\tau_2 - {}_-\tau_2).$$

The solutions of eq. (35) then take the form

$$A_{12}(t_0 < t) = \tfrac{1}{2}(1 + \xi/\xi_2)\exp(-t/{}_-\tau_2) + \tfrac{1}{2}(1 - \xi/\xi_2)\exp(-t/{}_+\tau_2) = 1 - A_{12}(t), \tag{36}$$

$$B_{22}(t_0 < t) = c_2\left[{}_-\tau_2 \exp(-t/{}_-\tau_2) - {}_+\tau_2 \exp(-t/{}_+\tau_2)\right]. \tag{37}$$

The decay is the sum of two exponentials involving the two modified relaxation times ${}_+\tau_2$ and ${}_-\tau_2$. If small inertial effects are neglected, eqs. (36), (37) go over into the well-known result of Benoit [22]:

$$A_{12}(t_0 < t;\ \gamma = 0) = B_{22}(t_0 < t;\ \gamma = 0) = 1 - \exp(-t/\tau_2) \tag{38}$$

for birefringence decay described by a single relaxation time τ_2.

7. Discussion

The above theoretical analyses are especially important in connection with the development of a new technique for producing arbitrarily shaped, high-rate optical pulses [23,24]. This achievement can have an important impact on such diverse fields as optical digital communication, where the optical Kerr effect is a most important one; as well as laser fusion. Until now the precise shape of the pulses was not controllable. The new technique [23,24] allows the pulse shape to be controlled even on the femtosecond time scale. Recently, experimentalists were able to demonstrate the formation of pulse sequences and most recently the creation of a "square" optical pulse [24]. This brings our analyses close to reality for not only gaussian shape but also rectangular or cosinusoidal shapes of the reorienting pulse, as stated above.

Attention should be drawn to the latest work of Evans and co-workers [25,26] on molecular dynamics simulations of rise and decay transients in liquids applying the model of 108 C_2 triatomics interacting with a 3×3 site–site Lennard-Jones potential. In some cases, the results of Evans et al. as well as those of Coffey, Rybarsch and Schröer [27] do not confirm the conventional view on rise and decay transients based on Smoluchowski's model of rotational brownian motions. Thus, e.g., ref. [25], the rise and decay transients of induced birefringence differ essentially from exponentiality and are oscillatory in shape. Similar results have also been obtained in refs. [26,27]. Accordingly, we treat the application of Sack's equation including small inertial effects to the relaxational theory of the Kerr effect leading to rise and decay transients in the form of superpositions of exponentials as a new theoretical approach which can contribute to the explanation of experimental results.

Acknowledgement

We wish to thank the referees for remarks that have led to the present, revised version of our paper.

Appendix

The statistical average in (1) is defined as

$$\langle P_2(\cos\theta)\rangle_{\theta_i} = \int_0^{2\pi} \mathrm{d}\phi \int_0^{\pi} P_2(\cos\theta) f(\theta, t) \sin\theta \, \mathrm{d}\theta, \tag{A.1}$$

where $f(\theta, t)$ is the statistical distribution function searched for, describing the probability of the molecule having the orientation θ at the moment of time t. The function is to be calculated from the Sack equation

$$\frac{1}{\xi}\frac{\partial^2 f}{\partial t^2} + \frac{\partial f}{\partial t} = \frac{kT}{I\xi}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{1}{kT}\left[\frac{\partial u}{\partial\theta}\frac{\partial f}{\partial\theta} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial u}{\partial\theta}\right) f\right]\right\}, \tag{A.2}$$

which is a modification of the Smoluchowski equation for rotational brownian motion of geometrically spherical molecules in liquids. Here, I is the moment of inertia of the molecule, $u = u(\theta, E_{2Z}(t))$ its potential energy in the reorienting field $E_{2Z}(t)$, ξ a friction constant which determines the rate of approach to the equilibrium distribution in velocity space [9], k the Boltzmann constant and T the absolute temperature. Moreover,

$$kT/I\xi = 1/6\tau_2, \tag{A.3}$$

where $\tau_2 = \frac{1}{3}\tau_D$ is the well-known relaxation time of rotational birefringence [4–6], and τ_D Debye's dipole relaxation time [1–3]. We have recourse to the Maxwell–Boltzmann equilibrium distribution function in a static reorienting field:

$$f(\theta, 0) = \exp[-u(\theta, 0)/kT]\left(\int_0^{2\pi}\int_0^{\pi} \exp[-u(\theta, 0)/kT] \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi\right)^{-1}, \tag{A.4}$$

which, on the assumption of a small value $q \ll 1$ of the polarizability anisotropy reorientation parameter, can be written in a satisfactory approximation as a series expansion. The change in potential energy of a dipolar axially symmetric molecule in a reorienting field $E_2(0)$ directed along the Z-axis is:

$$u(\theta, 0) = -\tfrac{1}{6}(\alpha_\parallel + 2\alpha_\perp)E_2^2 - \tfrac{1}{3}(\alpha_\parallel - \alpha_\perp)P_2(\cos\theta)E_2^2, \tag{A.5}$$

and the expansion of (A.4) is of the form:

$$f(\theta, 0) = (1/4\pi)\left\{1 \pm \tfrac{2}{3}qP_2(\cos\theta) + \tfrac{4}{63}q^2\left[P_2(\cos\theta) + \tfrac{9}{5}P_4(\cos\theta)\right]\right\}. \tag{A.6}$$

We thus search for a time-dependent statistical distribution function $f(\theta, t)$ in the following form:

$$f(\theta, t) = (1/4\pi)\left\{1 \pm \tfrac{2}{3}qA_{12}(t)P_2(\cos\theta) + \tfrac{4}{63}q^2\left[B_{22}(t)P_2(\cos\theta) + \tfrac{9}{5}B_{24}(t)P_4(\cos\theta)\right]\right\}, \tag{A.7}$$

whereas

$$u(\theta, t) = -\tfrac{1}{6}(\alpha_\parallel + 2\alpha_\perp)E_2^2 g^2(t) - \tfrac{1}{3}(\alpha_\parallel - \alpha_\perp)P_2(\cos\theta)E_2^2 g^2(t). \tag{A.8}$$

The unknown reorientation functions $A_{12}(t)$, $B_{22}(t)$, $B_{24}(t)$ are determined inserting (A.7) and (A.8) into (A.2), differentiating, and having recourse to the orthogonality properties of Legendre polynomials:

$$\int_0^{\pi} P_i(\cos\theta)P_j(\cos\theta) \sin\theta \, \mathrm{d}\theta = 2\delta_{ij}/(2j+1). \tag{A.9}$$

On equating the terms at the same powers of the expansion parameter q we arrive at the following equations:

$$d^2A_{12}/dt^2 + \xi\, dA_{12}/dt + (6kT/I)A_{12} = (6kT/I)g^2(t), \tag{A.10}$$

$$d^2B_{22}/dt^2 + \xi\, dB_{22}/dt + (6kT/I)B_{22} = (6kT/I)A_{12}(t)g^2(t), \tag{A.11}$$

$$d^2B_{24}/dt^2 + \xi\, dB_{24}/dt + (20kT/I)B_{24} = (20kT/I)A_{12}(t)g^2(t), \tag{A.12}$$

whence we calculate directly the required relaxation functions for different reorienting pulse shapes $g(t)$. It is worth noting that the function $B_{24}(t)$, in an approximation to E_2^4, contributes nothing to the birefringency. On neglecting small inertial effects – this amounts to rejecting the terms in the second derivative in eqs. (A.10)–(A.12) – one arrives at the equations of the Smoluchowski model of rotational brownian motion [6–8]:

$$\tau_2\, dA_{12}/dt + A_{12} = g^2(t), \tag{A.13}$$

$$\tau_2\, dB_{22}/dt + B_{22} = A_{12}g^2(t), \tag{A.14}$$

$$\tau_2\, dB_{24}/dt + B_{24} = A_{12}g^2(t), \quad \tau_4 = 1/20D. \tag{A.15}$$

In fact, eqs. (A.13)–(A.15) are particular cases of the more general equations of Watanabe and Morita [6] for arbitrary values of q.

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