

[with a similar equation for $l^{(0)\dagger}(t)$] where ξ' is given by

$$\xi'(\omega') = Z^{-1}B(\omega')[1 - \exp(-\hbar\omega'/kT)],$$

$$B(\omega') = \int_0^\infty dE \rho(E + \hbar\omega') \rho(E) \bar{l}^2(E + \hbar\omega', E) \\ \times \exp(-E/kT). \quad (\text{B7})$$

The Hamiltonian may be written now as

$$H = \frac{1}{2}\hbar\omega\sigma_z + \frac{1}{2}\{l^{(0)}\sigma_+ + l^{(0)\dagger}\sigma_-\} + H_l^{(0)} \quad (\text{B8})$$

in terms of the uncoupled loss field operators. From the equations of motion of the Pauli operators—found from (B8)—one can find the equations (26) and (27).

Dispersion of the Electrically Induced Refractive-Index Anisotropy in Nonpolar Liquids as a Probe of Reaction Kinetics*

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The theory of the dispersion of the refractive-index anisotropy induced in nonpolar fluids by external electric fields is extended to the case of chemically reacting fluids. Explicit expressions for the induced anisotropy are derived for a model nonpolar fluid with (1) no pair correlations, (2) rotational diffusion dynamics, and (3) a simple two-state (or species) chemical equilibrium. Limiting cases of the results are discussed.

I. INTRODUCTION

Nonlinear optical techniques have proved useful for studying the physics of fluids, but as yet few chemical applications have arisen from this work.^{1,2} In this article, we derive relations between chemical reaction rate constants and a phenomenon whose measurement in the high-frequency range has become possible because of the development of nonlinear optics—the dispersion of the refractive-index anisotropy induced in fluids by external electric fields. Of course, measurements of refractive index anisotropies have been routinely performed for many years at low or static frequencies (0 to about 10^6 Hz), but the newer techniques allow the higher end of this range to be extended to optical frequencies.³

In a previous article, general relations for the dispersion of the refractive-index anisotropy of a one-component system have been obtained in terms of molecular rotational correlation functions.³ By suitable arguments, the results were then applied to a dilute solution in the rotational diffusion approximation. In a separate article the effect of chemical reaction

rates on the depolarized light scattering spectrum was calculated in the same approximation.⁴ In the present article, we modify the correlation functions derived for the light-scattering theory and then apply them to the refractive-index calculation.

II. THEORY

It was shown in I that for a nonpolar fluid the difference between the refractive indices induced in directions parallel to the z and x axes, respectively, $n_z - n_x$, by an external electric field of frequency ω_e is related to the fluid density, ρ , the fluid refractive index in the absence of the field, n_0 , and the induced polarization anisotropy, $\langle \pi(\omega, \omega_e) \rangle$, by the relation

$$n_z(\omega, \omega_e) - n_x(\omega, \omega_e) \\ = 2\pi\rho[(n_0^2(\omega) + 2)/n_0(\omega)] \langle \pi(\omega, \omega_e) \rangle. \quad (1)$$

The induced anisotropy may be expressed in terms of the basic correlation function of this article, $\langle A(t)\pi(0) \rangle_0$, by

$$\langle \pi(\omega, \omega_e) \rangle = (2kT)^{-1} \langle A(0)\pi(0) \rangle_0 \\ + (2kT)^{-1} \text{Re} \left\{ \exp 2i\omega_e t \left[\langle A(0)\pi(0) \rangle_0 \right. \right. \\ \left. \left. - 2i\omega_e \int_0^\infty \langle A(0)\pi(t) \rangle_0 \exp(-2i\omega_e t) dt \right] \right\}. \quad (2)$$

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¹ I. L. Fabelinskii, *Molecular Scattering of Light* (Plenum Press, Inc., New York, 1968), Chap. 10.

² R. W. Minck, R. W. Terhune, and C. C. Wang, *Appl. Opt.* **5**, 1595 (1966).

³ R. Pecora, *J. Chem. Phys.* **50**, 2650 (1969), referred to as I in the text. Further references to experimental and previous theoretical work are given in this reference.

⁴ B. J. Berne and R. Pecora, *J. Chem. Phys.* **50**, 783 (1969); **51**, 475 (1969), referred to as II in the text.

The correlation function may, in turn, be expressed in terms of molecular polarizabilities α_{ij} in a laboratory fixed coordinate system and the amplitude of the local field on a molecule, \mathbf{F}_0 ,

$$\langle A(0)\pi(t) \rangle_0 = (2N)^{-1} \left\langle \sum_{i,j=1}^N [\alpha_{zz}^{(i)}(\Omega(t)) - \alpha_{xx}^{(i)}(\Omega(t))] \alpha^{(i)}(\Omega(0)) : \mathbf{F}_0 \mathbf{F}_0 \right\rangle \quad (3)$$

where N is the number of molecules in the fluid, the zero subscript on the brackets denotes an average over an equilibrium ensemble, and $\Omega(t)$ represents the Euler orientation angles of a molecule at time t .

The polarizabilities in the laboratory system above may be expressed in terms of those in a molecule-fixed system by using the transformation law between the spherical components of the polarizability tensor α_n in the two systems.

$$\alpha_n(\Omega) = (8\pi^2/5)^{1/2} \sum_{n'} D_{n,n'}^J(\Omega) \alpha_{n'}, \quad (4)$$

where the $D_{\kappa,m}^J$ are the Wigner rotation matrices and $\Omega = \alpha, \beta, \gamma$ represents the Euler angles through which the laboratory coordinate system must be rotated in order to coincide with the molecule-fixed system⁵ and

$$\begin{aligned} \alpha_{-2} &= \frac{1}{2}(\alpha_{xx} - \alpha_{yy}) - i\alpha_{xy} \\ \alpha_{-1} &= \alpha_{xz} - i\alpha_{zy} \\ \alpha_0 &= 2/6^{1/2} [\alpha_{zz} - \frac{1}{2}(\alpha_{xx} + \alpha_{yy})] \\ \alpha_1 &= -(\alpha_{-1})^* \\ \alpha_2 &= (\alpha_{-2})^*. \end{aligned} \quad (5)$$

The correlation function $\langle A(0)\pi(t) \rangle_0$ was evaluated in II for systems with (1) no correlations between different molecules [terms with $i \neq j = 0$ in Eq. (3)], (2) the rotational motion obeying the rotational diffusion equation. This theory should apply to solutes in a dilute solution whose solvent molecules are optically isotropic. We now extend this theory to the case where, in addition, the molecule may transform between two states with, in general, different polarizabilities and diffusion coefficients. When both the polarizabilities and rotational diffusion coefficients of the two species are equal, the rate constant for the transformation does not, as we show below, affect the dispersion of the refractive index anisotropy.

For the two-state system we obtain by the same reasoning as used in II

$$\langle A(0)\pi(t) \rangle_0 = C^{-1} \sum_{\alpha, \gamma=1}^2 C_\alpha \langle A(0)\pi(t) \rangle_{\gamma\alpha}, \quad (6)$$

where the subscript $\gamma\alpha$ indicates that the average is to be taken with the molecule in the state α at time zero and in the state γ at time t . The equilibrium concentration of species α is $C_\alpha = (N_\alpha/V)$ and the total concentration is $C = [(N_1 + N_2)/V]$. Equation (6) does not yet include the stated assumptions about the absence of pair correlations and the dynamics of rotation and chemical transformation.

To evaluate the average in Eq. (6), we first calculate the distribution function for molecular rotation and chemical transformation using the assumptions stated above. Let $P_\alpha(\Omega, t)$ be the probability that the molecule is in state α with orientation Ω at time t . It was shown in Appendix A of II that $P_\alpha(\Omega, t)$ obeys the coupled differential equations

$$\begin{aligned} [\partial P_1(\Omega, t)/\partial t] &= \theta_1 \nabla_\Omega^2 P_1(\Omega, t) \\ &\quad + k_{12} P_2(\Omega, t) - k_{21} P_1(\Omega, t) \\ [\partial P_2(\Omega, t)/\partial t] &= \theta_2 \nabla_\Omega^2 P_2(\Omega, t) \\ &\quad + k_{21} P_1(\Omega, t) - k_{12} P_2(\Omega, t), \end{aligned} \quad (7)$$

where θ_α is the rotational diffusion coefficient of species α and $k_{\alpha\gamma}$ is the rate constant which describes the disappearance of molecules from the state γ . We emphasize that there is no reference to molecular translational diffusion in Eqs. (7). Although translational diffusion is important in light scattering, it is clear from Eq. (3) that it does not explicitly affect the refractive index anisotropy. We have also assumed for simplicity in Eqs. (7) that the rotational motion is isotropic.

Another important assumption in Eqs. (7) is that when one species is converted into the other it preserves the same orientation in the new state as it had in the old. When this assumption is not valid Eqs. (7) must be modified. We do not treat this case further here.

The functions needed are the solutions of Eqs. (7) subject to the boundary conditions

$$P_{\gamma\alpha}(\Omega, 0) = \delta_{\gamma\alpha} \delta(\Omega - \Omega_0). \quad (8)$$

We see that the solution satisfying this boundary condition may be interpreted as the probability density that a molecule which is in state α with orientation Ω_0 at time 0 is in state α with orientation Ω at time t . $P_{\gamma\alpha}(\Omega, \Omega_0, t)$ may be expanded in terms of Wigner rotation matrices with coefficients independent of the Ω, Ω_0 ,

$$P_{\gamma\alpha}(\Omega, \Omega_0, t) = \sum_{J,K,M} B_{\gamma\alpha}^J(t) D_{KM}^{J*}(\Omega) D_{KM}^J(\Omega_0). \quad (9)$$

Then

$$\begin{aligned} \langle A(0)\pi(t) \rangle_{\gamma\alpha} &= (8\pi^2)^{-1} \int d^3\Omega \int d^3\Omega_0 [\alpha_{zz}(\Omega, \gamma) - \alpha_{xx}(\Omega, \gamma)] \\ &\quad \alpha(\Omega_0, \alpha) : \mathbf{F}_0 \mathbf{F}_0 P_{\gamma\alpha}(\Omega, \Omega_0, t). \end{aligned} \quad (10)$$

⁵ The conventions for the $D_{K,M}^J$ matrices (except for the normalization condition used here) and the Euler angles are those given by K. A. Valiev and I. D. Eskin, Opt. Spektrosk. 12, 758 (1962) [Opt. Spectrosc. 12, 429 (1962)]; and K. A. Valiev, *ibid.* 13, 505 (1962) [13, 282 (1962)].

Solving Eqs. (7) by Laplace transformation, using the expansion Eq. (9), and Eq. (5), we obtain

$$\langle A(0)\pi(t) \rangle_{\gamma\alpha} = (F_0^2/10)[\cos^2\theta - \sin^2\theta \cos^2\phi] \\ \times \sum_n \alpha_n^\gamma(\omega) \alpha_n^{\alpha\gamma}(\omega_e) B_{\gamma\alpha}^{(2)}(t), \quad (11)$$

where θ , ϕ are the polar and azimuthal angles, respectively, describing the orientation of the external field in the laboratory coordinate system and the Laplace transforms of the $B_{\gamma\alpha}^{(2)}(t)$ are given by

$$\tilde{B}_{11}^{(2)}(s) = [(s + 6\theta_2 + k_{12})/\Delta(s)] \\ \tilde{B}_{21}^{(2)}(s) = [k_{21}/\Delta(s)] \\ \tilde{B}_{12}^{(2)}(s) = [k_{12}/\Delta(s)] \\ \tilde{B}_{22}^{(2)}(s) = [(s + 6\theta_1 + k_{21})/\Delta(s)], \quad (12)$$

where

$$\Delta(s) = [s + 6\theta_2 + k_{12}][s + 6\theta_1 + k_{21}] - k_{21}k_{12}.$$

Substituting Eqs. (12), (11), and (6) into Eq. (3) and setting $S = 2i\omega$ gives the induced anisotropy,

$$\langle \pi(\omega, \omega_e) \rangle = (F_0^2/20CkT)[\cos^2\theta - \sin^2\theta \cos^2\phi] \\ \times \left\{ \sum_{\gamma\alpha} \sum_n C_\alpha \alpha_n^\gamma(\omega) \alpha_n^{\alpha*}(\omega_e) \delta_{\gamma\alpha} \right. \\ \left. + \text{Re}\{\exp(2i\omega_e t) [\sum_{\gamma,\alpha} \sum_n C_\alpha \alpha_n^\gamma(\omega) \alpha_n^{\alpha*}(\omega_e) \right. \\ \left. \times (\delta_{\alpha\gamma} - 2i\omega_e B_{\gamma\alpha}^{(2)}(s = 2i\omega))] \} \right\}. \quad (13)$$

The simplest case arises when $\lambda \equiv k_{12} + k_{21} \gg \theta_1, \theta_2$. Equation (13) in this case reduces to the analog of Eq. (57) of I,

$$\langle \pi(\omega, \omega_e) \rangle = \frac{F_0^2}{20CkT} [\cos^2\theta - \sin^2\theta \cos^2\phi] \\ \times \left\{ A + B \frac{\cos(2\omega_e t - \psi_p)}{[(2\omega/\lambda)^2 + 1]^{1/2}} \right\}, \quad \text{for } \omega \gg \theta_1, \theta_2,$$

where

$$A = C_1 \sum_n \alpha_n^{(1)}(\omega) \alpha_n^{(1)*}(\omega_e) + C_2 \sum_n \alpha_n^{(2)}(\omega) \alpha_n^{(2)*}(\omega_e)$$

and

$$B = C_1 \left\{ \sum_n \alpha_n^{(1)}(\omega) \alpha_n^{(1)*}(\omega_e) [1 - (C_1/C)] \right. \\ \left. - \sum_n \alpha_n^{(1)}(\omega) \alpha_n^{(2)*}(\omega_e) (C_2/C) \right\} \\ + C_2 \left\{ \sum_n \alpha_n^{(2)}(\omega) \alpha_n^{(2)*}(\omega_e) [1 - (C_2/C)] \right. \\ \left. - \sum_n \alpha_n^{(2)}(\omega) \alpha_n^{(1)*}(\omega_e) (C_1/C) \right\}. \quad (14)$$

Note that when $\alpha_n^{(1)}(\omega) = \alpha_n^{(2)}(\omega_e)$ and $\alpha_n^{(1)}(\omega_e) = \alpha_n^{(2)}(\omega)$, $B = 0$ and all dispersion effects disappear as we expect on physical grounds.

Equation (3) reduces to Eq. (57) of I when it is assumed that $\theta_1 = \theta_2 \equiv \theta$ and the polarizability anisotropies of the two species are equal, $\alpha_n^{(1)} = \alpha_n^{(2)} \equiv \alpha_n$. In this case the birefringence is, of course, not affected by the chemical rate constant and the system behaves, as far as birefringence is concerned, as one species with diffusion coefficient θ and polarizability anisotropies α_n .

When $\lambda = 0$, Eq. (13) reduces to the equation for the birefringence of two independent species each with its own θ_α and α_n^α . Each of the species contributes to the total anisotropy in proportion to its fractional equilibrium concentration.

III. SUMMARY AND DISCUSSION

Equation (13) when multiplied by the constants in Eq. (1) (setting $\rho = C$) gives the refractive index anisotropy induced by the external electric field. The most serious limitation of this expression is that it applied only to species with no permanent dipole moments or else to frequencies high enough to exclude any molecular orientation by coupling of the electric field to the molecular permanent dipole moments.

The simplest case that still retains rate constant information in the dispersion equation is that in which the reaction rate is much faster than the rotational diffusion rates. This condition is probably difficult to satisfy for small molecules in solution but might be satisfied in certain cases for reactions of macromolecules in solution. Such reactions must, of course, be accompanied by a change in the spherical polarizability components for any refractive index dispersion effects to be observed under the stated conditions.