

RELAXATION OF THE OPTICAL KERR EFFECT OF ANISOTROPIC MOLECULES IN MIXED LIQUIDS *

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The relaxation time of the Kerr effect of nitrobenzene and *m*-nitrotoluene in various mixtures with carbon tetrachloride and various alcohols was determined by measuring the kinetics of the Kerr effect using picosecond laser techniques. These measurements yield information on the rotational motion of molecules in liquids. The relaxation time data are interpreted in terms of an effective local viscosity effect, pair correlation, and coupling of rotational motion with shear modes.

The knowledge of the internal motions of the molecules in liquids, such as the rotational motion, is indispensable for the full understanding of the physics of the liquid state. A variety of experimental techniques can be used to probe the dynamics of molecular motions. Dielectric relaxation [1], microwave absorption [2], infrared [3] and Raman [4] spectroscopy, nuclear [5] and electronic [6] spin relaxation, depolarization of fluorescence [7], and depolarized Rayleigh wing scattering [8], and neutron scattering [9] have all been employed to study the molecular motions in liquids. Recently, picosecond laser techniques have become available for directly measuring the time dependence of the Kerr effect in pure organic liquids [10], and of the dichroism of dye solutions [11]. Almost all of the above mentioned experiments measure the relaxation phenomena of the change of the dielectric or paramagnetic property of matter. The relaxation times may vary depending upon the rank of the observed polarizability (or susceptibility) tensor, and upon the detail of the rotational brownian motion in liquids [12].

In this paper we report the direct measurement of the relaxation times of the optical Kerr effects of

nitrobenzene and *m*-nitrotoluene in mixed liquids by measuring the kinetics of the optical Kerr effect using picosecond laser pulses. In these anisotropic molecules, the relaxation of the Kerr effect is primarily due to the molecular reorientational motion and its coupling with the collective mode of motion in the liquid, such as the angular momentum correlation and shear modes. The contribution to the optical Kerr effect due to electronic cloud distortion or the librational motion of the molecules is either too small or too fast to be resolved with longer than picosecond pulses. In this experiment the relaxation times are measured as functions of concentration and viscosity of the solution. By varying the concentration of the Kerr-active solute in the solution, we are able to deduce the effect of *pair correlation* in liquids. By appropriately choosing the viscosity of the solution, we found that the relevant parameter to describe the viscosity dependence of the relaxation time in mixed liquids is an *effective local viscosity*, which is essentially the bulk viscosity excluding the contribution from solvent molecules. Comparing the results of this experiment and those from light scattering with the data obtained from dielectric relaxation experiment, our data supports the conclusion that the characteristic angular step of the rotation by a small molecule in ordinary liquids is in such a size that neither rotation by simple diffusion

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through small angles nor rotation by a singularly large jump is an adequate picture in describing the rotational motion. The observation of a doublet in the depolarized Rayleigh wing scattering in anisotropic molecules confirmed the existence of the coupling of the molecular rotational motion to the shear motion [13]. In this experiment the relaxation time is observed to be shorter than those obtained from the line width measurements in depolarized Rayleigh wing scattering. This difference can be attributed to the combined effect of rotational motion and shear relaxation in the Kerr effect measurement.

The experimental apparatus for measuring the relaxation time of the Kerr effect has been previously reported [10, 14]. It consists of a mode-locked Nd:glass laser, a potassium dihydrogen phosphate second harmonic generating crystal, and a Kerr gate (1 cm sample cuvette situated between crossed polarizers). Two laser beams are used in the experiment. An intense 1.06 μm pulse with ≈ 8 ps duration is used to induce the Kerr birefringence in the sample solution. The birefringence is caused by partially orienting the anisotropic molecules in the liquid through the interaction of the optical electric field of the laser pulse with the polarizability of the molecules. A second harmonic 0.53 μm pulse with ≈ 6 ps duration, variably delayed with respect to the 1.06 μm exciting pulse, is used to probe the time evolution of the induced transitory birefringence in the sample solution. The intensity profile formed in this manner is a convolution in time of the 1.06 μm pulse, 0.53 μm pulse, and the induced birefringence. The light intensity passing through the Kerr gate is [10]

$$I(\tau) = \int_{-\infty}^{\infty} I_{0.53}(t - \tau) \sin^2 \frac{1}{2} \delta\Phi(t) dt \quad (1)$$

and

$$\delta\Phi(t) = (2\pi l n_{2B} / \lambda \tau_K) \int_{-\infty}^t \overline{E_{1.06}^2}(t') e^{-(t-t')/\tau_K} dt',$$

where $I_{0.53}$ is the intensity profile of the 0.53 μm beam, $\overline{E_{1.06}^2}$ is the time-averaged electric field squared of the 1.06 μm beam in the liquid and $\delta\Phi$ is the phase shift between the parallel and perpendicular components of the 0.53 μm beam after passing through a distance l in the Kerr cell, n_{2B} is the Kerr constant,

and τ_K is the Kerr relaxation time. The relaxation time can be extracted from the measured intensity profile by deconvolution. In the deconvolution an exponential time profile for the laser is assumed.

In the experiment we have studied the relaxation times of nitrobenzene and *m*-nitrotoluene. Carbon tetrachloride and alcohols (*n*-propyl and *n*-decyl) were used as solvents. Carbon tetrachloride, a nonpolar and spherical molecule, is essentially non-Kerr-active. The alcohols, whose Kerr effect was determined to be less than one hundredth of that of nitrobenzene and *m*-nitrotoluene, were chosen for providing the variation of solution viscosity.

As the solute concentration is decreased, the peak intensity of the 0.53 μm light was observed to decrease quadratically. This, expected from eq. (1) for $\delta\Phi \ll 1$, limits the minimum solute concentration to about 20% in the experiment. All experiments were performed at room temperature at $23 \pm 2^\circ\text{C}$. The measured relaxation times of nitrobenzene and *m*-nitrotoluene are plotted as a function of mole fraction in the solution in figs. 1–4. The bulk viscosity of these mixtures is measured, and also plotted on the correspondent graphs. The salient feature of the data presented in these figures is that the relaxation time *decreases* with decreasing concentration, *even with increasing solution viscosity* (in particular, see fig. 4).

Debye's classical theory of dielectric relaxation [15] is generally applicable to single particle rotational relaxation in pure polar liquids. The relaxation time is shown to be proportional to the viscosity of the liquid as

$$\tau = (4\pi a^3 / kT) \eta, \quad (2)$$

where a is the molecular radius of a spherical molecule, T is the temperature, and k is the Boltzmann constant. In reality, liquid molecules hardly behave as single particles. In solution one further finds that the viscosity dependence appearing in eq. (2) is not followed by the relaxation time [16]. This is simply because the viscosity experienced by a solute molecule is not the bulk viscosity. Applying the concept of a mutual viscosity between the solute and the solvent molecules, Hill [17] has successfully shown that the relaxation time of a series of polar molecules in very dilute solution is directly proportional to the mutual viscosity. A general phenomenological expression for the rotational relaxation time of a solute

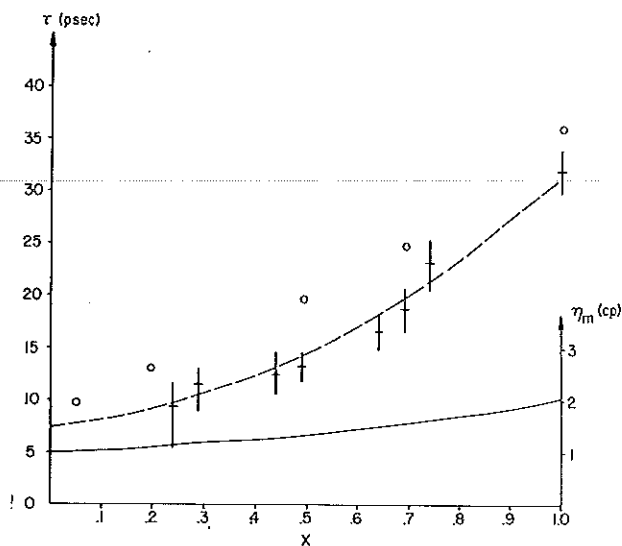


Fig. 1. Kerr relaxation time of nitrobenzene as function of mole fraction in carbon tetrachloride. The crosses are data points; the dash curve is calculated from $\tau = 6.1[(1 + 1.55x) \times x\eta_B + (1 - x)\eta_{AB}]$; the solid curve is the measured viscosity of the mixtures; and the circles are obtained from Alms et al. light scattering data [19].

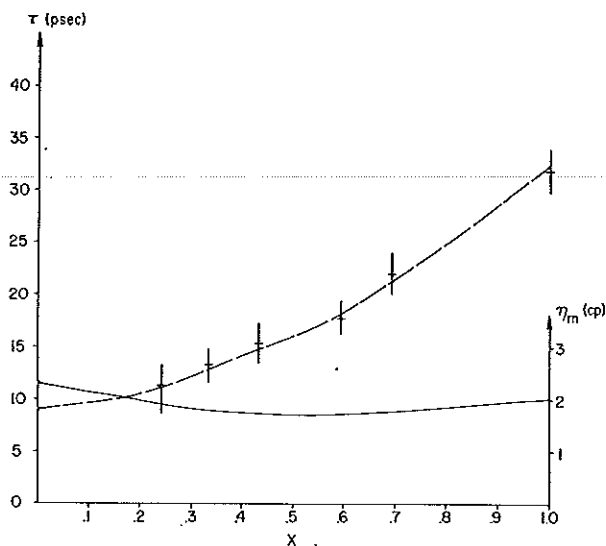


Fig. 2. Kerr relaxation time of nitrobenzene as function of mole fraction in *n*-propanol. The crosses are data points; the dash curve is calculated from $\tau = 7.3[(1 + 1.2x)x\eta_B + (1 - x)\eta_{AB}]$; and the solid curve is the measured viscosity of the mixtures.

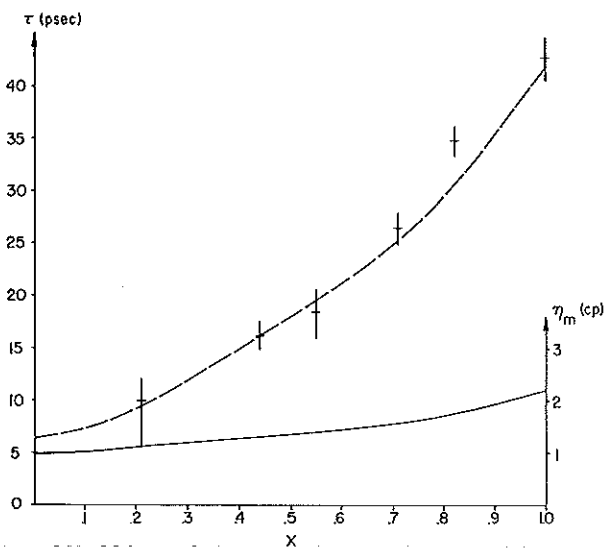


Fig. 3. Kerr relaxation time of *m*-nitrotoluene as function of mole fraction in carbon tetrachloride. The crosses are data points; the dash curve is calculated from $\tau = 6.9[(1 + 1.64x) \times x\eta_B + (1 - x)\eta_{AB}]$; and the solid curve is the measured viscosity of the mixtures.

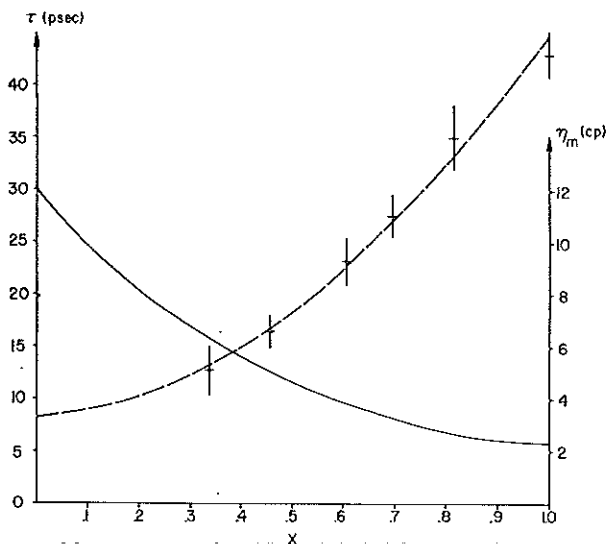


Fig. 4. Kerr relaxation time of *m*-nitrotoluene as function of mole fraction in *n*-decanol. The crosses are data points; the dash curve is calculated from $\tau = 5.5[(1 + 2.56x)x\eta_B + (1 - x)\eta_{AB}]$; and the solid curve is the measured viscosity of the mixtures.

molecule in a binary liquid can be expressed as

$$\tau = c_1(a_B)f(x)\eta_B x + c_2(a_{AB})\eta_{AB}(1-x), \quad (3)$$

where x denotes the molar concentration of the solute B component in the solution, η_B is the viscosity of the solute B molecules in pure liquid, η_{AB} is the mutual viscosity between the solute B and the solvent A molecules. The expressions $c_1(a_B)$ and $c_2(a_{AB})$ account for the variation in molecular sizes in solution, and are dependent on the details of the collisional process. (A special form of c 's has been calculated by Hill [17].) The expression $f(x)$ is specifically inserted here to account for the pair correlative effect among the solute molecules. To the first order, f can be represented as $(1 + \lambda x)$ [18]. As the solute concentration x reduces to zero, the correlation term f clearly approaches one. Eq. (3) can now be written as

$$\tau = C[(1 + \lambda x)x\eta_B + G(1-x)\eta_{AB}], \quad (4)$$

in which $G = c_2/c_1$, is a number not far from one, depending on the sizes of the molecules and the correlation between dissimilar molecules, and C and λ are two parameters which can be numerically determined by measuring τ as function of x . The parameter C is a measure of the rate of change of the relaxation time with respect to the viscosity at a given temperature. The parameter λ is a measure of correlation among solute molecules.

From the measured values of the viscosity as a function of x , the mutual viscosity η_{AB} can be calculated from the expression

$$\eta_m = (x^2/a_m)\eta_B a_B + [2x(1-x)/a_m]\eta_{AB} a_{AB} + [(1-x)^2/a_m]\eta_A a_A, \quad (5)$$

where the subscript m denotes mixture, and the η 's and a 's are viscosities, and intermolecular distances (calculated from $a = M/\rho N_0$ where M = molecular weight, ρ = density, N_0 = Avogadro number). The mutual viscosity η_{AB} at $23 \pm 2^\circ\text{C}$ is determined to be 1.20 for nitrobenzene and carbon tetrachloride, 1.26 for nitrobenzene and *n*-propanol, 0.9 for *m*-nitrotoluene and carbon tetrachloride, and 1.50 for *m*-nitrotoluene and *n*-decanol. The η_{AB} value for nitrobenzene and carbon tetrachloride is in excellent agreement with the value quoted in Hill's paper [17].

The correlation parameter λ and the constant C can now be determined from the data in figs. 1-4 according to eq. (4). The results are: for nitrobenzene $\lambda = 1.55$ and 1.2 , and $C = 6.1$ and 7.3 ps/cP in carbon tetrachloride and *n*-propanol, respectively; and for *m*-nitrotoluene, $\lambda = 1.64$ and 2.56 , and $C = 6.9$ and 5.5 ps/cP, in carbon tetrachloride and *n*-decanol, respectively. In the data reduction, $G = 1$ is assumed. It should be emphasized here that the empirical approach employed in this paper to relate the viscosity and correlation with the relaxation time differs from the other method [19,20] by: (1) employing an effective local viscosity $\eta_{\text{eff}} \propto x\eta_B + (1-x)\eta_{AB}$ for a given solute molecule, instead of the measured viscosity; and (2) the correlation term is only attached to the η_B term in η_{eff} . This formulation has enabled us to interpret the data uniformly, including those of *m*-nitrotoluene in *n*-decanol. Evidently, the relaxation time of *m*-nitrotoluene in *n*-decanol is not simply proportional to the measured viscosity.

In fig. 1, the data obtained from a depolarized Rayleigh wing scattering experiment by Alms et al. [19] is plotted along with the result of this experiment. Aside from the fact that the light scattering data is about 10-40% higher than the Kerr effect data, the significance of which we shall discuss later, it is gratifying that both results have a similar dependence on x . The light scattering data were reduced by Alms et al. [19] according to the relation

$$\tau \propto [(1 + \lambda x)/(1 + gx)](c\eta_m + \tau_0).$$

The data can also be fitted and successfully interpreted by eq. (4).

The rotational motion of a liquid molecule can be visualized as an oscillatory librational motion about an equilibrium position disrupted by a quick angular displacement caused by collisions. It is this latter part of the molecular motion, the brownian rotational motion, for which this experiment and other light scattering or absorption experiments intend to explain. The usual approach to the brownian motion problem is that of the random walk method. It is well known that the random walk problem is reduced to a diffusion problem, provided the time interval during which the total displacement has taken place is sufficiently long [21]. For small molecules such as nitrobenzene and *m*-nitrotoluene, the rotational step can become relatively large so that the diffusional ap-

proach is inadequate. It would therefore be of interest if experimental evidence can be obtained to explain the nature of the characteristic rotational step in liquid. In a general approach to the problem of the theory of the rotational brownian motion, Ivanov [12] has shown that the relaxation time of the measured quantity depends on the rank (K) of the related polarizability tensor. When diffusion is applicable, the relaxation time for a spherical molecule is

$$\tau_K = \tau_0 [K(K+1)]^{-1}, \quad (6)$$

where τ_0 is the time interval during which the molecule stays in the local equilibrium position. In the case of a large angular step, since each large step causes complete randomization, the relaxation time should be independent of the rank. In this experiment according to the theory of the optical Kerr effect of an anisotropic molecule [22], the rank of the related polarizability tensor is $K = 2$, which is the same as that used for light scattering experiments (Rayleigh and Raman); and for absorption experiments (dielectric relaxation, microwave and infrared absorption) the rank is $K = 1$. Using the relaxation time data obtained from the dielectric relaxation measurement $\tau = 48$ ps [23], from the Rayleigh scattering measurement $\tau = 36$ ps [19] or 39 ps [20], and from the Kerr effect $\tau = 32$ ps for nitrobenzene, the calculated ratios are $\tau_1/\tau_{2,K} \approx 1.5$ and $\tau_1/\tau_{2,ls} \approx 1.3$ where the subscripts K and ls denote the Kerr effect and light scattering measurements, respectively. We shall discuss the significance of the difference between $\tau_{2,K}$ and $\tau_{2,ls}$ later. In an analysis for various aromatic liquids [24], $\tau_1/\tau_{2,ls}$ has also been shown to be between 1.1 to 1.5. Therefore the analysis of experimental data suggests that the rotational motion of small molecules (molecular weight $\lesssim 100$), in liquid of modest viscosity ($1 \leq \eta \leq 5$), is not likely describable by diffusion through small angular jumping steps [$\tau_1/\tau_2 = 3$ following eq. (6)], nor by large jumping steps ($\tau_1 \approx \tau_2$). Rather, the rotational motion is probably characterized either by jumps of intermediate size, or more likely by a distribution of the jump angles.

Returning to the interesting result that $\tau_{2,K}$ is smaller than $\tau_{2,ls}$ by about 10–40% it should be emphasized that this fact is evidenced not only from the result measured in this experiment (in nitrobenzene, in *m*-nitrotoluene, $\tau_{2,ls} \approx 50$ ps at 26°C

[20], and in the mixed liquids for all x for nitrobenzene) but also from the results obtained by other laboratories [10,25]. We believe this reduction of Kerr relaxation time is due to the coupling of the reorientational motion to the shear mode relaxation. The spectra of depolarized Rayleigh wing scattering liquid [13] have been successfully interpreted as the difference of two Lorentzians, one with a broad width Γ due to molecular rotational motion, and the other with a narrower width Γ_s due to the coupling with the dissipative shear mode [26]. The Fourier transform of this line shape is correspondingly $e^{-\Gamma t} - R e^{-\Gamma_s t}$ where R is in the order of 0.1 for nitrobenzene [27]. The time dependence of the light intensity passing through the Kerr gate for times greater than the laser pulse width is proportional to $(e^{-\Gamma t} - R e^{-\Gamma_s t})^2$ which can be approximated by an effective decay as $(e^{-\Gamma_K t})^2$ for $t < 3/\Gamma$. Γ_K is roughly 15% larger than Γ , using $\Gamma \approx \Gamma_{ls}$, and $\Gamma_s \approx \Gamma/14$ from the light scattering data of nitrobenzene [27]. This reduction of relaxation time is indeed observed in this experiment. If a signal to noise ratio better than 10^3 is attained, the details of the Kerr relaxation which should have a dip and a long tail at a time greater than $t > 3/\Gamma$ should be observable.

In summary, we have measured the Kerr relaxation time of nitrobenzene and *m*-nitrotoluene in mixed liquids by observing the kinetics of the picosecond laser pulse induced Kerr effect. The relaxation time data are interpreted in terms of an effective viscosity of the mixed liquid and the effect of pair correlation. From the dependence of the relaxation time on the rank of the polarizability tensor, the experimental result has provided new evidence in the understanding of the nature of the rotational motion in liquid. The difference in relaxation times measured by light scattering and Kerr gate experiments is discussed in terms of the coupling of rotational motion to the shear mode in the liquid.

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