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Photoinduced reorientation of nematic liquid crystals doped with an azo dye: A dynamic and steady-state study of reorientation and loss of liquid crystal order

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We compare photoinduced reorientation of homeotropic and planar aligned nematic liquid crystal 4-pentyl-4-cyanobiphenyl (5CB) doped with trace amounts of azo-dye disperse orange 3 (DO3) by studying the optical nonlinearities of the sample. Theoretical and experimental analyses confirm the proposal that the *trans* and *cis* isomers can be treated as independent contributors to the enhancement factor. Dynamic measurements indicate three contributions to photoinduced optical nonlinearities, two of which are isotropic and a third corresponding director reorientation. We also measure a large negative enhancement factor for the *trans* isomer and a positive enhancement factor for the *cis* isomer, consistent with previous measurements. The latter indicates that the mean field for the *cis* isomer is very small. Planar aligned samples demonstrate zenithal gliding whereas homeotropic samples do not. In addition, steady-state and dynamic measurements indicate loss of liquid crystal order associated with absorption as well as possible out-of-plane reorientation.

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I. INTRODUCTION

The effect of dyes on the photoinduced orientation or reorientation of liquid crystals has generated much interest and is well documented in the literature. Initially reported by Jánossy, Lloyd, and Wherrett [1], it was found that small amounts of anthraquinone dye were capable of reducing the optical Freédericksz transition by more than two orders of magnitude. Since that time, many studies have been conducted with various dyes to try and characterize this effect and understand its origins. It has become clear from this work that the dye induced enhancement, also referred to as the *Jánossy effect*, comes from a balance between the intermolecular forces and the diffusive forces between the dye and the liquid crystal host [2–4]. A *fluctuating friction* motor model has been proposed elaborating how diffusive forces might be responsible for reorientation [5]. Kreuzer *et al.* [6] provide evidence of reduced rotational mobility for excited state anthraquinone dyes resulting from an excited state reinforcement of intermolecular hydrogen bonding. They argue that when the solvent molecule size is the same order of magnitude as the solute molecular size, a hydrodynamic model describing diffusion is no longer valid. In this case, hydrogen bonding and charge transfer complexes may well impact rotational mobility. More recently, Truong *et al.* [7] studied the dynamics of the interaction between the anthraquinone dye and the liquid crystal in the isotropic phase and report that rotational diffusion is decreased upon excitation of the dye. They note that the rotational diffusion coefficient can be approximated by an Arrhenius-type expression, in which the “activation” energy is determined by the guest host interaction.

Azo dyes provide an additional complication because of the photoinduced *trans-cis* isomerization. Jánossy and Szabados [8,9] proposed that the enhancement for azo dyes can be represented by the weighted sum of the individual enhancements of the two states, *cis* and *trans*. The relative strength of each state, *cis* or *trans*, is determined by the fraction of dye, X, in the *cis* state (the fraction in the *trans* state being $1-X$). The fraction of dye in the *cis* state is determined by the relative intensity of the incident light, and is represented by a saturation equation. The authors used this model to explain why the enhancement by the dye can switch signs, as has been observed by others [10,11]. Taking advantage of the fact that one can determine the saturation fraction and intensity from nonlinear absorption experiments [12], Becchi *et al.* [13] demonstrated this effect by showing the change in sign of the enhancement factor as the incident light intensity increased. Finally, Galstian *et al.* [14,15] have looked at the impact of out-of-plane reorientation for azo dyes. In these studies, they also consider the loss of liquid crystal order from the interaction between the dye and the liquid crystal host.

The Becchi *et al.* [13] results also show the presence of an additional enhancement effect indicating a surface realignment (gliding) of the director [13]. Such an effect had been previously proposed by Lucchetti *et al.* [16]. Petrossian and Residori also observed such an effect with ionic surfactants for homeotropically aligned samples [17]. Joly *et al.* [18] were able to show, that, in fact, zenithal gliding of the easy axis can occur on polyimide surfaces like those used by Becchi *et al.* [13].

In this paper we continue these investigations, comparing planar aligned samples with homeotropic samples. In particular, we examine the liquid crystal dynamics during reorientation and consider the relative impact of dye-induced loss of order on the reorientation process. In Sec. II, we present the model, based on diffusion equations. The orientational distribution of the dye, in its various states, and the liquid crystal are represented by a superposition of spherical harmonic functions. Prior analyses using such a superposition have typically been applied to photoinduced anisotropy in dyed liquid crystals above the clearing point. In this paper, we will look specifically at photoinduced reorientation in the nematic state, following up on the original work of Jánossy [2]. The result will be an expression from which we can derive an analytic form for the enhancement factor. In Sec. III we describe the experiment and in Sec. IV we present our results within the context of the model. General conclusions are discussed in Sec. V.

II. THEORY

In this section, we describe the effects of photoexcitation and *cis-trans* isomerization on the orientation distribution of the dye in the nematic sample. The interaction between the dye and the liquid crystal is responsible for the photoinduced reorientation.

Consider a dye-liquid crystal system with the director initially aligned along the z axis. Light incident at an angle Θ_n to the normal will excite the dye molecules, altering the distribution of ground and excited state molecules around the z axis. Following the methods of Jánossy [2] and of Marrucci *et al.* [3,4], we consider the orientation distribution of the dye, or the liquid crystal, to be given by a superposition of the spherical harmonic functions, $Y_{l,m}(\theta,\phi)$,

$$f_i(\theta,\phi,t) = \frac{1}{4\pi}\sum_{l=0,2,4,\ldots}\sum_{m\leq l}(2l+1)\left(\frac{l-|m|}{l+|m|}\right)Y_{l,m}(\theta,\phi)Q_i^{l,m}(t), \tag{1}$$

where the index i corresponds to the *trans* (t), *cis* (c) or excited (e) state of the dye and $Q_i^{l,m}$ are the moments of the distribution. For the liquid crystal host, the index h is used. If the reorientation angle is in the xz plane and is small, then the only terms of importance for this analysis are $Y_{0,0}$, $Y_{2,0}$, and $Y_{2,1}$. This expansion can thus be simplified as

$$f_i(\theta,\phi,t) = \frac{1}{4\pi}\left(N_i(t) + 5Q_i^{2,0}(t)P_2^0(\cos\theta) + \frac{5}{3}Q_i^{2,1}(t)P_2^1(\cos\theta)\cos\phi\right), \tag{2}$$

where the zeroth moments, N_i, correspond to the number density of each species i, $P_l^m(x)$ are the associated Legendre polynomials, and $Q_i^{2,-1}=Q_i^{2,1}$. For simplicity, we will use the same formalism as Truong *et al.* [7] and eliminate the superscript 2 in the second moments, $Q_i^{2,0}\rightarrow Q_i^0$ and $Q_i^{2,1}\rightarrow Q_i^1$. For those studies involving photoinduced anisotropy, it was enough to keep the $l,m=2,0$ term. In our case, however, it is necessary to include the $l,m=2,1$ term to allow for reorientation of the director.

The second moments, Q_i^m are related to the order parameter via

$$S_i = \frac{1}{N_i}\sqrt{(Q_i^0)^2 + (Q_i^1)^2}. \tag{3}$$

The Legendre polynomial $P_2^0(\cos\theta)$ is symmetric around the z axis, whereas $P_2^1(\cos\theta)\cos\phi$ is antisymmetric through the yz plane. As already mentioned, it is this latter antisymmetric contribution that is responsible for the enhancement of director reorientation in the liquid crystal. In the absence of an incident pump beam, Q_i^1 are zero. In addition, for small reorientation angles, any changes in Q_i^0 are related to the change in the order of species i, hence impact the liquid crystal order.

Dynamic equations for N_i, and Q_i^m, can be determined from the standard diffusion equation,

$$\frac{\partial}{\partial t}f_i(\theta,\phi,t) - D_i\bar{\nabla}^2 f_i(\theta,\phi,t) - \frac{D_i}{kT}\bar{\nabla}\cdot(f_i\bar{\nabla}U_i) = W_i, \tag{4}$$

where D_i is the rotational diffusion coefficient for species i, and $\bar{\nabla}$ is given by the angular part of the ∇ operator. Using the mean-field approximation, the potential is given by the Maier-Saupe expression [19],

$$U_i = -\frac{1}{3}u_i S_h P_2^0(\cos\theta), \tag{5}$$

where u_i is the orientational interaction energy between the liquid crystal and the host molecules and S_h is the liquid crystal order parameter. The factor of $1/3$ is to maintain consistency with Refs. [4] and [7]. The source-sink term, W_i, on the right-hand side of Eq. (5) is given by

$$W_t = -p_t(\cos\theta)f_t + \frac{F_t}{\tau_t}f_e + \frac{1-F_t}{\tau_t}\frac{N_e}{4\pi} + \frac{F_{c\rightarrow t}}{\tau_{c\rightarrow t}}f_c + \frac{1-F_{c\rightarrow t}}{\tau_{c\rightarrow t}}\frac{N_c}{4\pi},$$

$$W_c = -p_c(\cos\theta)f_c + \frac{F_c}{\tau_c}f_e + \frac{1-F_c}{\tau_c}\frac{N_e}{4\pi} - \frac{1}{\tau_{c\rightarrow t}}f_c,$$

$$W_e = p_t(\cos\theta)f_t + p_c(\cos\theta)f_c - \left(\frac{1}{\tau_t}+\frac{1}{\tau_c}\right)f_e,$$

where

$$p_i(x) = \frac{3\alpha_i}{h\nu N_D}I\left(P_2^0(x)\cos^2\Theta + \frac{2}{3}P_2^1(x)\cos\phi\sin\Theta\cos\Theta + \frac{1}{6}P_2^2(x)(1+\cos 2\phi\sin^2\Theta)\right),$$

α_i is the linear absorption coefficient, and N_D is the total number density of the dye, h is Planck's constant, and I and ν are the intensity and frequency and of the incident light, respectively. The angle Θ is the angle the optical field makes with the z axis. For a planar aligned sample, $\Theta=\Theta_n$. For a homeotropic sample, $\Theta=\Theta_n+\pi/2$. Following Truong, Xu, and Shen [7], the constants F_t, F_c, and $F_{c\rightarrow t}$ correspond to the fraction of molecules preserving their orientation when relaxing from the excited state to the *trans* state, to the *cis* state, or from the *cis* state to the *trans* state, respectively. These have the effect of increasing the relaxation times for those respective expressions.

Equation (4) is a mean-field equation that does not include local effects. Jánossy [2] has pointed out that such a model does not include any detail of molecular structure. In general, diffusion equations, such as the one above, are valid when spatial variations are smooth [20]. On the other hand, if the process of diffusion is considered to be the result of site hopping, rather than that of a random walk, then, as pointed out by Truong *et al.* [7], Eq. (4) may be interpreted in the manner of Kreuzer *et al.* [6]. It is sometimes the case that a diffusion equation must be substituted by a generalized diffusion equation that includes a convolution integral with a frequency dependent diffusion coefficient. This is especially true for barrier crossing problems, where lower in magnitude high frequency diffusion coefficients are more significant. However, for the problem at hand, such is not relevant and we will consider Eq. (4) as adequate for our studies.

Equation (4) can be reduced to a set of dynamic equations for each N_i and Q_i^m,

$$\frac{dN_t}{dt} = -\frac{\alpha_t I}{h\nu N_D}[(3\cos^2\Theta - 1)Q_t^0 + 2\sin\Theta\cos\Theta Q_t^1] + \frac{1}{\tau_t}N_e + \frac{1}{\tau_{c\to t}}N_c, \tag{6a}$$

$$\frac{dN_c}{dt} + \frac{1}{\tau_{c\to t}}N_c = -\frac{\alpha_c I}{h\nu N_D}[(3\cos^2\Theta - 1)Q_c^0 + 2\sin\Theta\cos\Theta Q_c^1] + \frac{1}{\tau_c}N_e, \tag{6b}$$

$$\frac{dN_e}{dt} + \left(\frac{1}{\tau_t} + \frac{1}{\tau_c}\right)N_e = \frac{\alpha_t I}{h\nu N_D}[(3\cos^2\Theta - 1)Q_t^0 + 2\sin\Theta\cos\Theta Q_t^1] + \frac{\alpha_c I}{h\nu N_D}[(3\cos^2\Theta - 1)Q_c^0 + 2\sin\Theta\cos\Theta Q_c^1], \tag{6c}$$

$$\frac{dQ_t^0}{dt} + \left[6D_t\left(1 - \frac{1}{21}\frac{u_t}{kT}S_h\right) + \frac{\alpha_t I}{7h\nu N_D}(6\cos^2\Theta + 5)\right]Q_t^0 = \left(\frac{2}{5}D_t\frac{u_t}{kT}S_h - \frac{1}{5}\frac{\alpha_t I}{h\nu N_D}(3\cos^2\Theta - 1)\right)N_t - \frac{2}{7}\frac{\alpha_t I}{h\nu N_D}\sin\Theta\cos\Theta Q_t^1 + \frac{F_t}{\tau_t}Q_e^0 + \frac{F_{c\to t}}{\tau_{c\to t}}Q_c^0, \tag{7a}$$

$$\frac{dQ_c^0}{dt} + \left[6D_c\left(1 - \frac{1}{21}\frac{u_c}{kT}S_h\right) + \frac{1}{\tau_{c\to t}} + \frac{\alpha_c I}{7h\nu N_D}(6\cos^2\Theta + 5)\right]Q_c^0 = \left(\frac{2}{5}D_c\frac{u_c}{kT}S_h - \frac{1}{5}\frac{\alpha_c I}{h\nu N_D}(3\cos^2\Theta - 1)\right)N_c - \frac{2}{7}\frac{\alpha_c I}{h\nu N_D}\sin\Theta\cos\Theta Q_c^1 + \frac{F_c}{\tau_c}Q_e^0, \tag{7b}$$

$$\frac{dQ_e^0}{dt} + \left[6D_e\left(1 - \frac{1}{21}\frac{u_e}{kT}S_h\right) + \left(\frac{1}{\tau_t} + \frac{1}{\tau_c}\right)\right]Q_e^0 = \frac{\alpha_t I}{h\nu N_D}\left(\frac{1}{5}(3\cos^2\Theta - 1)N_t + \frac{1}{7}(6\cos^2\Theta + 5)Q_t^0 + \frac{2}{7}\sin\Theta\cos\Theta Q_t^1\right) + \frac{\alpha_c I}{h\nu N_D}\left(\frac{1}{5}(3\cos^2\Theta - 1)N_c + \frac{1}{7}(6\cos^2\Theta + 5)Q_c^0 + \frac{2}{7}\sin\Theta\cos\Theta Q_c^1\right) + \frac{2}{5}D_e\frac{u_e}{kT}S_h N_e, \tag{7c}$$

$$\frac{dQ_t^1}{dt} + \left[6D_t\left(1 - \frac{1}{42}\frac{u_t}{kT}S_h\right) + \frac{3\alpha_t I}{7h\nu N_D}(\cos^2\Theta + 2)\right]Q_t^1 = -\frac{6}{5}\frac{\alpha_t I}{h\nu N_D}\sin\Theta\cos\Theta N_t - \frac{6}{7}\frac{\alpha_t I}{h\nu N_D}\sin\Theta\cos\Theta Q_t^0 + \frac{F_t}{\tau_t}Q_e^1 + \frac{F_{c\to t}}{\tau_{c\to t}}Q_c^1, \tag{8a}$$

$$\frac{dQ_c^1}{dt} + \left[6D_c\left(1 - \frac{1}{42}\frac{u_c}{kT}S_h\right) + \frac{1}{\tau_{c\to t}} + \frac{3\alpha_c I}{7h\nu N_D}(\cos^2\Theta + 2)\right]Q_c^1 = -\frac{6}{5}\frac{\alpha_c I}{h\nu N_D}\sin\Theta\cos\Theta N_c - \frac{6}{7}\frac{\alpha_c I}{h\nu N_D}\sin\Theta\cos\Theta Q_c^0 + \frac{F_c}{\tau_c}Q_e^1, \tag{8b}$$

$$\frac{dQ_e^1}{dt} + \left[6D_e\left(1 - \frac{1}{42}\frac{u_e}{kT}S_h\right) + \left(\frac{1}{\tau_t} + \frac{1}{\tau_c}\right)\right]Q_e^1 = \frac{3\alpha_t I}{h\nu N_D}\left(\frac{2}{5}\sin\Theta\cos\Theta N_t + \frac{2}{7}\sin\Theta\cos\Theta Q_t^0 + \frac{1}{7}(\cos^2\Theta + 2)Q_t^1\right) + \frac{3\alpha_c I}{h\nu N_D}\left(\frac{2}{5}\sin\Theta\cos\Theta N_c + \frac{2}{7}\sin\Theta\cos\Theta Q_c^0 + \frac{1}{7}(\cos^2\Theta + 2)Q_c^1\right). \tag{8c}$$

With Eqs. (6)–(8), we can describe the impact of the dye on director reorientation. Assuming that photoexcitation is short, we get five time constants; three associated with reorientation through the dynamics of both Q_i^0 and Q_i^1;

$$\tau_{Qt} \approx \frac{1}{6D_t}, \quad \tau_{Qc} \approx \frac{1}{6D_c + \frac{1}{\tau_{c\to t}}}, \quad \tau_{Qe} \approx \frac{1}{6D_e + \left(\frac{1}{\tau_t} + \frac{1}{\tau_c}\right)},$$

and two associated with isomerization and through the dynamics of Q_i^0 and N_i; $\tau_{c\to t}$ and $\tau_e = \frac{1}{(1/\tau_c)+(1/\tau_t)}$. Truong *et al.* [7] have shown that, in general, the time dependence of the moments of the liquid crystal orientation distribution, Q_h^m, are given by

$$Q_h^m(t) = Q_h^m(\text{pure}) + \frac{C_m}{\tau_m}\int_{-\infty}^{t}[u_tQ_t^m(t') + u_cQ_c^m(t') + u_eQ_e^m(t')]e^{-[(t-t')/\tau_m]}dt', \tag{9}$$

where τ_m is the relaxation time for mode m, C_m is the strength of that mode, and $Q_h^m(\text{pure})$ is the moment of the orientation for the undoped liquid crystal. For electronic relaxation time τ_e much smaller than $\tau_{c\to t}$ and τ_m, Eq. (9) for Q_h^0 and Q_h^1 can be simplified to

$$Q_h^0(t) = Q_h^0(\text{pure}) + C_0[u_tQ_t^0(\infty) + u_cQ_c^0(\infty) + u_eQ_e^0(\infty)] \times\left(1 + \frac{\tau_{c\to t}}{\tau_0 - \tau_{c\to t}}e^{-t/\tau_{c\to t}} - \frac{\tau_0}{\tau_0 - \tau_{c\to t}}e^{-t/\tau_0}\right) \tag{10a}$$

and

$$Q_h^1(t) = C_1[u_tQ_t^1(\infty) + u_cQ_c^1(\infty) + u_eQ_e^1(\infty)](1 - e^{-t/\tau_1}), \tag{10b}$$

respectively, where $Q_h^1(\text{pure})=0$. Because τ_0 and τ_1 are both associated with $l=2$, it is reasonable that they are equal to each other and are associated with a liquid crystal orientational relaxation time, τ, as described by Truong *et al.* [7].

Substituting, Eqs. (6)–(8) into Eq. (10b) results in the photoinduced enhancement of director reorientation, characterized by moment Q_h^1 at steady state,

$$\begin{aligned} Q_h^1(\text{enhanced}) &= C_1(u_tQ_t^1 + u_cQ_c^1 + u_eQ_e^1) \\ &\approx \frac{2}{5}C_1u_e\tau_{Qe}\frac{\alpha_t I}{h\nu}(3\sin\Theta\cos\Theta) \\ &\quad\times\Bigg[\Bigg(1 - \frac{u_t\tau_{Qt}}{u_e\tau_{Qe}} + F_t\frac{u_t\tau_{Qt}}{u_e\tau_t} + F_c\frac{u_c\tau_{Qc}}{u_e\tau_c} \\ &\quad + F_cF_{c\to t}\frac{u_t\tau_{Qt}\tau_{Qc}}{u_e\tau_c\tau_{c\to t}}\Bigg)(1-X) \\ &\quad + R\Bigg(1 - \frac{u_c\tau_{Qc}}{u_e\tau_{Qe}} + F_t\frac{u_t\tau_{Qt}}{u_e\tau_t} + F_c\frac{u_c\tau_{Qc}}{u_e\tau_c} \\ &\quad + F_cF_{c\to t}\frac{u_t\tau_{Qt}\tau_{Qc}}{u_e\tau_c\tau_{c\to t}} - F_{c\to t}\frac{u_t\tau_{Qt}\tau_{Qc}}{u_e\tau_{Qe}\tau_{c\to t}}\Bigg)X\Bigg], \end{aligned} \tag{11}$$

where $R=\alpha_c/\alpha_t$, and X is the faction of dye molecules in the *cis* state. This equation is consistent with a previous derivation [8] showing that the *cis* fraction $X=\frac{X_{\text{sat}}I/I_{\text{sat}}}{1+I/I_{\text{sat}}}$, where X_{sat} is the saturation fraction of dye molecules in the *cis* state, and I_{sat} is saturation intensity. X_{sat} and I_{sat} are dependent on polarization of the incident light and the angle Θ [9]. The steady state value for Q_h^1 determines the Jánossy effect enhancement factor, η, viz.,

$$\eta = \frac{Q_h^1(\text{dyed})}{Q_h^1(\text{pure})}. \tag{12}$$

Combining Eqs. (11) and (12) gives an expression for the enhancement factor,

$$\eta = \eta_t(1-X) + \eta_cX = \eta_t + X(\eta_c - \eta_t). \tag{13}$$

The *trans* and *cis* enhancement factors are determined from Eq. (11) to be

$$\eta_t \approx \frac{6}{5}\frac{\alpha_t}{h\nu}u_e\tau_{Qe}\left(\frac{cn_e\varepsilon_0}{\Delta\varepsilon N_h}\right)\left(1 - \frac{u_t\tau_{Qt}}{u_e\tau_{Qe}} + F_t\frac{u_t\tau_{Qt}}{u_e\tau_t} + F_c\frac{u_c\tau_{Qc}}{u_e\tau_c}\right), \tag{14a}$$

$$\eta_c \approx R\frac{6}{5}\frac{\alpha_t}{h\nu}u_e\tau_{Qe}\left(\frac{cn_e\varepsilon_0}{\Delta\varepsilon N_h}\right)\left(1 - \frac{u_c\tau_{Qc}}{u_e\tau_{Qe}} + F_t\frac{u_t\tau_{Qt}}{u_e\tau_t} + F_c\frac{u_c\tau_{Qc}}{u_e\tau_c}\right). \tag{14b}$$

Equations (13) and (14) support the Jánossy and Szabados experimentally verified proposal [8] that the *trans* and *cis* states can be treated separately, having independent contributions to the photoinduced reorientation [9]. These expressions are also consistent with those derived by Marucci *et al.* [4] for the enhancement of director orientation in the isotropic phase. Clearly, a balance between the dye-host interaction energies and the rotational friction encountered by the dye molecules can determine the sign of the enhancement factor.

For small reorientation angles, the order of the liquid crystal is described by the moment Q_h^0, i.e., $S_h=Q_h^0/N_h$. Substitution of Eqs. (6)–(8) into Eq. (10a) shows that the contribution of the dye to Q_h^0 is proportional to the enhancement factor,

$$\begin{aligned} Q_h^0(\text{enhanced}) &= Q_h^0(t) - C_0u_tQ_t^0(0) \\ &= C_0(u_tQ_t^0 + u_cQ_c^0 + u_eQ_e^0) \\ &\approx \frac{2}{15}C_0u_e\tau_{Qe}\frac{\alpha_t I}{h\nu}\left(\frac{3\cos^2\Theta - 1}{2}\right) \\ &\quad\times\Bigg[\Bigg(1 - \frac{u_t\tau_{Qt}}{u_e\tau_{Qe}} + F_t\frac{u_t\tau_{Qt}}{u_e\tau_t} + F_c\frac{u_c\tau_{Qc}}{u_e\tau_c}\Bigg)(1-X) \\ &\quad + R\Bigg(1 - \frac{u_c\tau_{Qc}}{u_e\tau_{Qe}} + F_t\frac{u_t\tau_{Qt}}{u_e\tau_t} + F_c\frac{u_c\tau_{Qc}}{u_e\tau_c}\Bigg)X\Bigg] \\ &\approx \frac{1}{3}C_0I\left(\frac{3\cos^2\Theta - 1}{2}\right)\eta. \end{aligned} \tag{15}$$

As is described in the next two sections, the effects of dye photoexcitation on the liquid crystal through changes in Q_h^0 and Q_h^1 are determined by measurement of the enhancement factor and the change in order of the liquid crystal sample.

III. EXPERIMENT

The liquid crystal 5CB (4-pentyl-4-cyanobiphenyl) was doped with the *azo*-dye Disperse Orange 3 (DO3) at 0.5% by weight. Samples were prepared with planar alignment and with homeotropic alignment. Planar aligned cells were prepared by spin coating cleaned glass slides with polyimide, which were subsequently rubbed. Homeotropic samples were prepared by treating cleaned glass surfaces with surfactant. Spacers were used to maintain a 50 μm cell thickness. Samples were observed under a crossed-polarized microscope to insure alignment and uniformity.

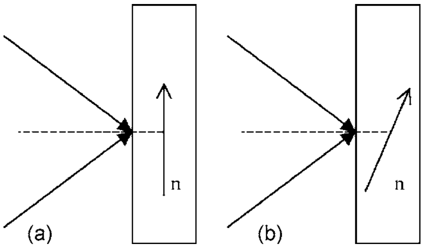

FIG. 1. (a) Bisector of angle between probes is normal to the nematic director, n. Both probes see the same phase shift between the o and e rays. (b) Director, n, is rotated. The top probe sees an increase in the phase shift between the o and e rays, while the bottom probe sees a decrease.

The experiments were designed to measure both the change in the birefringence of the sample and the reorientation enhancement by studying the optical nonlinearities of the samples. To study the effects of photoexcitation of *azo* dye on the liquid crystal, consider two probe laser beams incident on the sample at an angle whose bisector is either parallel or perpendicular to the nematic director *prior* to dye excitation by a pump beam, as shown in Fig. 1(a). The only contribution to the orientational distribution of the liquid crystal is Q_h^0, as Q_h^1 is zero. Measurement of the phase shift between the ordinary (o) and extraordinary (e) components of the probes demonstrate the same shift for each. If, upon photoexcitation of the dye, the second moment, Q_h^0 decreases, then the phase shift between the o and e ray will also decrease. Such a decrease can result from a loss of birefringence due to a loss of nematic order, or from reorientation. If there were director reorientation, the second moment Q_h^1 would then become nonzero. The phase shift between the o and the e rays would increase for one probe and decrease for the other, as shown in Fig. 1(b). Combining the effects of Q_h^0 with those of Q_h^1, we see that each probe sees a different phase shift between the o and the e probes. By comparing the two probes, the effects from the changes in Q_h^1 can be separated from the effects in changes in Q_h^0. The average of the shifts subtracts out the effect of Q_h^1, while one-half the difference of the shifts subtracts out the effects of Q_h^0. As previously shown [13], the latter allows for calculation of the enhancement factor, η.

The experiment is similar to that of Becchi *et al.* [13], with some important modifications. The experimental setup is shown in Fig. 2. The sample was in a temperature controlled sample holder and aligned so that the nematic director was horizontal. The pump beam from an Ar^+ laser tuned to 488 nm was directed to the sample at an angle of 35° to the normal. The laser was horizontally polarized so that reorientation could be facilitated without a Freédericksz threshold. The pump intensity was adjusted by rotating a polarizer placed in between the half-wave plate and the pump polarizer. The probe laser consisted of a HeNe laser, $\lambda_{\mathrm{pr}} = 633$ nm. The beam was split into two probes, 1 and 2, each polarized at 45° to the horizontal. Each probe beam entered the sample at an angle of 45° to the normal and perpendicular to each other. Because of refraction, inside the sample the probe beams were at a smaller angle to the normal, approximately 26°. Care was made to be sure that there was good probe overlap so that each probe beam interrogated the same part of the liquid crystal. The probe beam diameters were significantly smaller than the pump beam diameter and were centered on the pump beam in the liquid crystal sample. The phase shift between the extraordinary (e) and ordinary (o) rays of each probe were measured using a photoelastic modulator (PEM), just as was done in Ref. [13]. A liquid crystal birefringent compensator was used to set the initial phase shift coming into the PEM to zero by adjusting the voltage to the compensator. The sample was aligned such that in the absence of the pump, both probes had the same phase shift. Such alignment accounted for any pretilt in the sample. The output from the detector was sent to a lock-in amplifier, with the time constant set to 1 ms. The output from the lock-in was tested for temporal response and it was found that it was accurate for times less than 10 ms.

At each pump intensity, the phase shift between the e and o rays was measured in time as it grew and as it decayed. With the pump on, the shift was also measured at steady state. All runs were done at 25 °C.

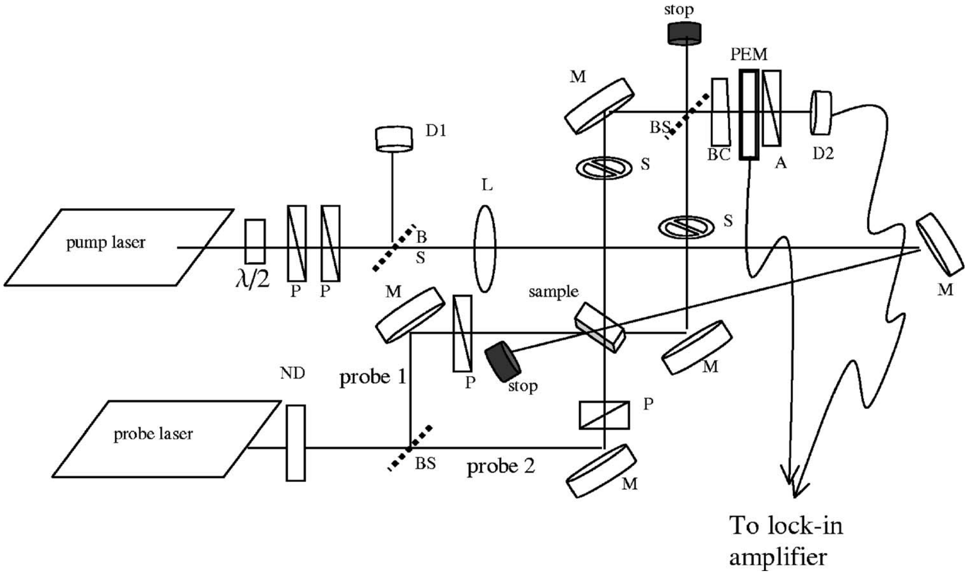

FIG. 2. Experimental setup: P, polarizer; $\lambda/2$, half-wave plate; BS, beam splitter; $D1$, pump input detector; $D2$, signal detector; L, lens; ND, neutral density filter; PEM, photoelastic modulator; M, mirror; S, shutter; BC, birefringent compensator; A, analyzer.

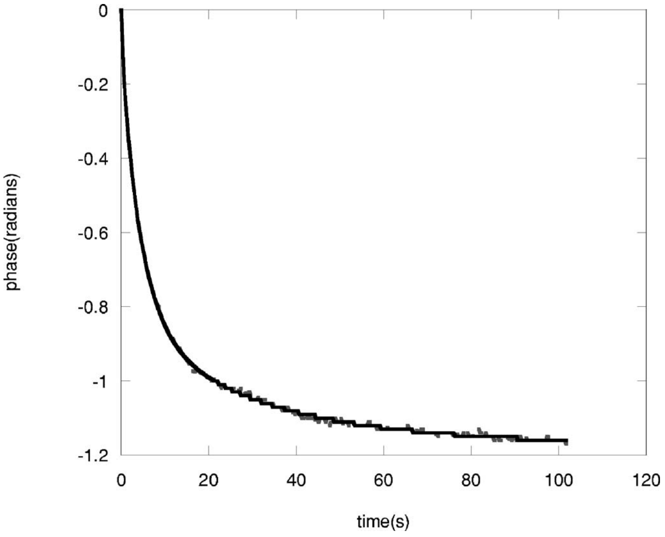

FIG. 3. Phase shift for probe 1 versus time. Solid line is a fit to a triple exponential.

IV. RESULTS AND DISCUSSION

Figures 3 and 4 show the time dependence of the phase shift for the two probe beams for the homeotropic alignment. As already explained, changes in Q_h^0 result in the same shift for each probe in the same direction; whereas changes in Q_h^1, result in the shifts for the two probes having opposite sign. From these figures it is clear that that there are three different contributions to the photoinduced process. While probe 1 monotonically decreases, probe 2 decreases, then increases, and finally decreases as the liquid crystal comes to steady state. Both curves were fit to triple exponentials. Within experimental error, the response times were the same and independent of pump intensity. The three response times were determined to be $\tau_\alpha=0.7\pm0.4$ s, $\tau_\beta=5\pm1$ s, and $\tau_\gamma=31\pm1$ s, respectively.

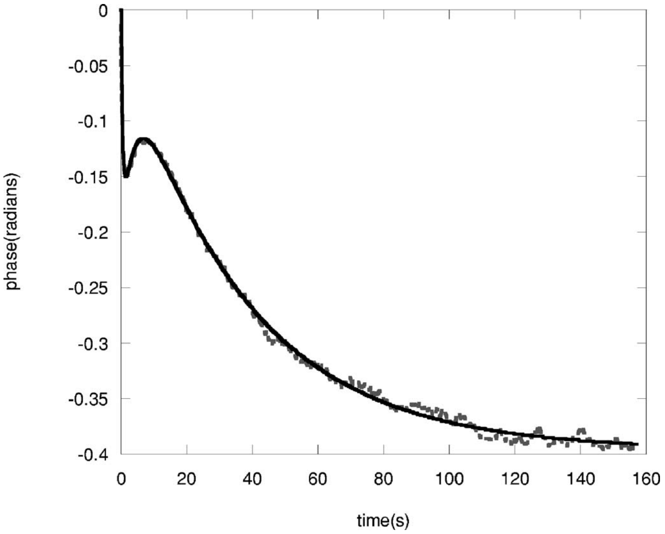

FIG. 4. Phase shift for probe 2 versus time. Solid line is a fit to a triple exponential.

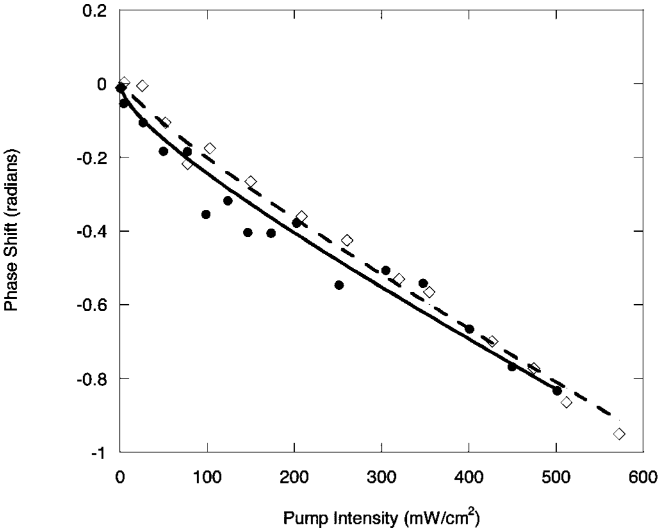

FIG. 5. Phase shift difference between two probe beams versus intensity. Solid circles, planar alignment. Open diamonds, homeotropic alignment.

These results show that all *three* time constants, τ_α, τ_β, and τ_γ, are associated with changes in the $m=0$ mode, Q_h^0, whereas the relaxation of the $m=1$ mode, Q_h^1, only involves the single time constant, τ_β. From Eq. (10a), it is very likely that the time constant τ_α (=0.7±0.4 s), which is only associated with the $m=0$ mode, corresponds to the *cis* to *trans* isomerization, i.e., $\tau_\alpha=\tau_{c\rightarrow t}$. This is consistent with the results of previous measurements which put that time between 500 and 700 ms [12]. Because the second time constant, τ_β, is associated with shifts of opposite sign for the two probes, it must be associated with director reorientation. It is therefore likely that τ_β (=5±1 s) corresponds to $\tau_0=\tau_1=\tau$. The third time constant, τ_γ, is associated only with the dynamics of the $m=0$ mode. Yet, it is not found in the model. However, we do expect Q_h^0 to decrease from thermal effects as well as a general loss of order, simply from the absorption of light by the dye. Another possibility is a relaxation of the $m=0$ mode to a second $m=1$ mode, $P_2^1(\cos\theta)\sin\phi$, not included in the model. This mode would correspond to out-of-plane reorientation, as proposed by Galstian *et al.* [14]. The current experiments cannot distinguish between the different possibilities.

At steady state, the differences in the change in the phase shift, $\Delta\Phi=(\delta\Phi_{\text{probe }1}-\delta\Phi_{\text{probe }2})$, between the e and o rays are shown for both the planar and homeotropic samples, respectively, in Fig. 5. This phase difference between the two probes, in the linear approximation, is

$$\Delta\Phi = 2\frac{2\pi n_e(\beta_{\text{pr}})}{\lambda_{\text{pr}}}\frac{(n_e^2-n_o^2)}{(n_o^2\cos^2\beta_{\text{pr}}+n_e^2\sin^2\beta_{\text{pr}})}\sin\beta_{\text{pr}}\int_0^L\delta(z)dz. \tag{16}$$

This expression is slightly different from that of Marucci *et al.* [21] in that it accounts for the fact that the probe beams do not have normal incidence. In Eq. (16), $\delta(z)$ is reorientation angle of the director. As shown by Becchi *et al.* [13], at very low pump intensities there appears to be an additional mechanism causing light-induced director reorientation, or zenithal gliding. Here we have assumed that this extra nonlinearity follows a standard saturation curve. The phase shift would therefore be

$$\delta = \delta_{\text{bulk}} + \delta_0 \frac{I/I_{\text{sat},\delta}}{1 + I/I_{\text{sat},\delta}}, \tag{17}$$

where δ_{bulk} is the phase shift originating from a bulk mechanism discussed earlier, and δ_0 is the "high intensity" phase shift due to this additional mechanism. In the linear approximation, δ_{bulk} can be found from

$$K_1 d^2 \delta/dz^2 = -\frac{\eta + (n_e^2 - n_o^2)}{2n_o^2 c} \sin 2\Theta I(z), \tag{18}$$

where η is the dye-induced enhancement factor given by Eq. (13).

When the enhancement factor, η, is independent of intensity and δ_0 is zero, Eqs. (17) and (18) can be integrated analytically resulting in a measured phase shift linear with intensity. This would be the case if either the *cis* enhancement factor was equal to the *trans* enhancement factor, $\eta_c = \eta_t$, or if there was no *trans* to *cis* isomerization upon photoexcitation. In spite of the linear appearance of the phase shift with intensity shown in Fig. 5, nonlinear absorption measurements for DO3 in 5CB, using previously developed methods [12], rule out the latter, giving a saturation intensity of 12.7 mW/cm^2 and a saturation fraction of 0.6.

To determine the *trans* and *cis* enhancement factors, the same methods as Becchi *et al.* [13] were used. Equation (13), with measured values for the saturation fraction and saturation intensity, was substituted into Eq. (18). Then, with the boundary conditions $\delta(0) = \delta(L) = 0$, η_t, and η_c were adjusted until numerical integration of Eqs. (16) and (18) agreed with the experimental results, as determined by minimization of χ^2. Since the effects of zenithal gliding are included in the fits, the enhancement factors should be independent of whether the sample is planar or homeotropic. One advantage of measuring the enhancement for the two geometries is that we should be able to force the two fits to give the same enhancement factors, making the results less ambiguous. The fits are shown in Fig. 5 by the solid and dashed lines for the planar and homeotropic samples, respectively. They were also corrected for the fact that the intensity of the light incident on the dye molecules must be corrected for refraction. Clearly there is satisfactory agreement between the theoretical curves and the measured points with the mean deviation more-or-less corresponding to experimental error.

The first result noticed was that, as expected, the enhancement factor is independent of whether the liquid crystal is planar or homeotropic. Our fits show that the *trans* enhancement factor, η_t, is negative and equal to -1550 for the homeotropic sample and equal to -1560 for the planar sample. Our results also show that the *cis* enhancement factor, η_c, is positive and equal to 620. This is consistent with other studies that have also shown η_c to be positive.

For these samples, we measured α_t to be about 1170 cm^{-1} (for extraordinarily polarized light). Estimating u_e/kT to be about 3, and τ_{Qe} to be about 8×10^{-10} s, with $\eta_t = -1550$, we get $u_t \tau_{Qt}/u_e \tau_{De} \approx 1.7$. With $\eta_c = 620$, we find that $u_c \tau_{Qc}/u_e \tau_{Qe}$ is negligible. Both of these results are quite reasonable. For anthraquinones, it was argued that the ratio $u_g \tau_{Qg}/u_e \tau_{Qe}$ is essentially the ratio of excited to ground state diffusion coefficients [6], where subscript g corresponds to the ground state. This was based on the fact that the shape of anthraquinone does not change upon photoexcitation; hence the mean field does not have any significant change as well. This argument, however, cannot be made with *azo* dyes, as the shape of the molecule does change with photoexcitation. Therefore the mean fields, u_t, u_c, and u_e are expected to be different. Yet, the role of diffusive forces through its impact on a particular species lifetime, i.e., τ_{Qt} and τ_{Qe}, is still critical to the enhancement effect. The longer the time that a particular species $i = t$, c, or e is in the Q_i^1 mode, the more impact that particular species has on the reorientation process. Local interactions, such as the formation of charge transfer complexes, can contribute to this effect, and clearly need to be studied in more detail. Without any additional information about the mean fields or the intermolecular interactions, it is very difficult to separate out the contribution to enhancement from differences in mean field and differences in rotational diffusion through local interactions. On the other hand, the negligible ratio, $u_c \tau_{Qc}/u_e \tau_{Qe}$, does tell us that the mean field for the *cis* isomer is very small. In general, a positive enhancement factor tells us that $u_c \tau_{Qc}$ is smaller than $u_e \tau_{Qe}$. Since the order parameter for the *cis* isomer is small ($S \approx 0.1$), the molecule is relatively free to rotate within the liquid crystal matrix. Therefore u_c must be small compared with kT.

Our fits also indicate while for the planar sample there is some zenithal gliding, with $\delta_0 = -0.0017$ radians (about 0.1°), for the homeotropic sample there is no apparent zenithal gliding. While this is quite small, it is significant enough to see a difference between the two curves. Others have also seen evidence of zenithal gliding of liquid crystal on rubbed polyimide surfaces. We are currently investigating whether this is a photoinduced effect.

Since changes in Q_h^0 impact the change in the birefringence of the liquid crystal, the average shift for the two samples corresponds to the change in Q_h^0 as well as to out-of-plane reorientation. These average shifts are shown in Fig. 6. These results indicate that the change in birefringence is significantly different for the homeotropic versus the planar alignment, with a ratio as high as 11.

Equation (15) shows that the contribution of the dye to Q_h^0 is determined by the angle that the optical field makes with the director, Θ. It is proportional to $\frac{1}{2}(3\cos^2\theta - 1)$, as well as to the enhancement factor and the intensity. As the angle Θ is increased, the magnitude of the change in order becomes smaller. At $\Theta > 55°$, this contribution to the order changes sign. In addition, the liquid crystalline order will increase or decrease with the intensity depending on which dye state has a stronger interaction with the liquid crystal. This is all independent of any other effects such as thermal effects.

Because of refraction, the angle Θ is smaller for the homeotropic alignment. Since the change in birefringence is

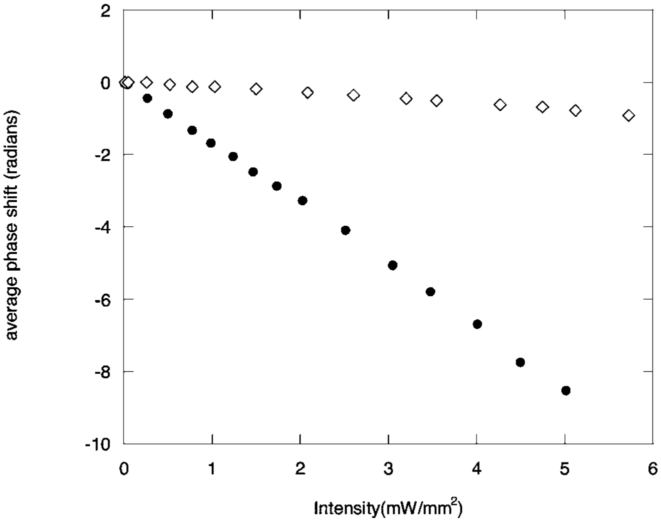

FIG. 6. Average phase shift for two probes versus intensity. Solid circles, planar alignment. Open diamonds, homeotropic alignment.

proportional to the change in Q_h^0, that change, then, should be smaller for the homeotropic sample, as we have observed. This indicates that the order parameter does not change by very much with intensity for this sample. Calculations suggest, however, that the ratio of the average phase shift between the planar and homeotropic alignments should only be between 3 and 4. Yet, as already stated, for our measurements that ratio is approximately 11. On the other hand, our dynamic measurements indicate an additional contribution to the loss of birefringence, thermal effects, for example. Consider that the absorption of light by the dye goes as $\cos^2 \Theta$. Accounting for refraction, the absorption ratio for the dye between the two alignments should be 6.8. This suggests that an additional loss of birefringence could be due to absorption, which would be the case for thermal effects. This combination, then, would explain the experimental results. Finally, we plan on future measurements to investigate the possibility of out-of-plane reorientation.

V. CONCLUSIONS

The most important results here show that for dyes which undergo *trans-cis* isomerization, the enhancement factor can be treated as the weighted sum of the individual enhancement factors, as proposed by Jánossy and Szabados [8], and that the individual enhancement factors result from a balance between the interaction energies of the dye and the host mediated by the rotational friction encountered by the dye molecules, as proposed by Marucci *et al.* [3]. The *trans* isomer shows a large negative enhancement, consistent with previous results and indicating that this enhancement is due to a combination of mean-field and local-field effects. The *cis* isomer, on the other hand, shows a positive enhancement, indicating that the mean field is very small. This is supported by the small *cis* dye order parameter, indicating that the mean field for the *cis* isomer is less than kT. In addition, we observe that the interaction of the dye with the liquid crystal host will necessarily have an effect on the order of the host.

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