Molecular-Field-Enhanced Optical Kerr Effect in Absorbing Liquids

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A large enhancement of the optical Kerr nonlinearity associated with light-induced molecular orientation is observed in a liquid of anisotropic organic molecules when it is doped with a small amount of dye. The effect is ascribed to a photoinduced intermolecular force field, whose orienting action adds to the direct optical field action. The experimental results are in agreement with a model based on such interpretation. The proposed mechanism is in principle very general, and should work in all absorbing liquids made of anisotropic molecules. [S0031-9007(96)01885-6]

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The most effective mechanism for optical Kerr effect in transparent organic liquids at the nanosecond time scale is light-induced molecular orientation [1]. It results from the torque that the optical electric field exerts on the molecules due to their anisotropic polarizability. In absorbing liquids other mechanisms for large nonlinear optical response are present, but they are mostly isotropic. Light-induced molecular orientation is therefore still the main origin of nonlinear birefringence but, as we have found, its nature can be largely modified by light absorption.

We turned a transparent liquid into absorbing by mixing it with small amounts of a dichroic dye. A large enhancement of its nonlinear birefringence was then observed. The enhancement factor was about 20 for dye concentrations of 0.26%. The material chosen for our experiments has a liquid-crystalline nematic mesophase a few degrees below our working temperatures. Pretransitional phenomena [2] thus allowed us to single out the orientational effects from other competing mechanisms, showing that it is indeed light-induced molecular orientation which is enhanced.

A similar increase of the optical nonlinearity had been reported a few years ago for dye-doped liquid crystals in the nematic phase [3], and a model for it has been recently proposed [4]. An analogy between the isotropic liquid and nematic phases is not straightforward, because of the complex collective response characterizing the liquid crystal mesophase. Nevertheless, we developed a model for the orientational nonlinearity of absorbing isotropic liquids, based on the same main idea of Ref. [4], which explains well our experimental results.

According to our picture, the enhanced optical Kerr effect is the result of two processes. The first one is electronic excitation of molecules, induced by light absorption. This process is anisotropic, since its probability is proportional to $\cos^2\theta$, where θ is the angle between the optical electric field and the molecule transition dipole. Therefore, it generates an oriented population of excited molecules and a corresponding hole in the orientational distribution of ground-state molecules. Absorption alone, however, does not change the total orientational distribution of liquid molecules, which remains isotropic. The second process is provided by intermolecular interactions. Each molecule has an average orientational energy $U(\theta)$ which depends on the orientational distribution of the neighbor molecules. In particular, if the latter is isotropic, $U(\theta)$ reduces to a constant. If, however, intermolecular forces depend significantly on the molecular electronic state, then the excited-state and ground-state populations are weighted differently in $U(\theta)$, and an anisotropic mean-field energy is generated. The net photoinduced intermolecular field $U(\theta)$ can then induce, together with the optical field, an enhanced molecular orientation of the whole liquid.

This picture was made quantitative in our model. Here we just briefly sketch our procedure, deferring to another article a more detailed presentation. Consider a mixture of rodlike liquid host molecules and dye molecules, in the presence of a linearly polarized light wave of intensity I and frequency ν. We assume that the dye molecule transition dipole is parallel to its geometrical long axis. If there is one excited state of dye molecules, we must consider three populations, i.e., ground and excited-state dye molecules and host molecules, which will be identified with the index $\alpha = g, e, h$, respectively. The number of molecules per unit volume and solid angle is denoted as $f_\alpha(\theta)$, where θ is the angle between the molecule axis and the optical electric field. We introduce the distribution moments of order l, $Q_\alpha^{(l)} = \int P_l(\cos\theta) f_\alpha(\theta)\, d\Omega$, where $P_l(x)$ is the Legendre polynomial of order l. Of particular significance are the total number densities $Q_\alpha^{(0)}$, and the $l = 2$ moments $Q_\alpha^{(2)}$, since the degree of orientation of a population (order parameter) is measured by the ratio $Q_\alpha^{(2)}/Q_\alpha^{(0)}$. We also denote as $N_d = Q_g^{(0)} + Q_e^{(0)}$ the total dye density and as $N_t = N_d + Q_h^{(0)}$ the total liquid density.

The excitation probability per unit time can be written as $p(\theta) = (3\alpha_0/h\nu N_d) I \cos^2\theta$, where α_0 is the light absorption coefficient, and h is Planck's constant. If τ_e is the excited-state lifetime, the transition rate at a given angle θ is $(\partial f_e/\partial t)_{\rm trans} = -(\partial f_g/\partial t)_{\rm trans} = p f_g - f_e/\tau_e$. Besides the electronic transitions, we must account for the rotational Brownian motion of the molecules and for the rotational drifts induced by intermolecular interactions and external optical field. To this purpose, we use a diffusional approximation with diffusion constants D_α, and a mean-field approximation with the orientational energy $U_\alpha = U_\alpha^{(1)} + U_\alpha^{(2)}$, where $U_\alpha^{(1)}$ is the dielectric polarization energy describing the direct coupling with the optical field and $U_\alpha^{(2)}$ the intermolecular interaction mean-field energy. The first term is given by $U_\alpha^{(1)} = -(\eta_\alpha I/2nc)\cos^2\theta$, where $\eta_\alpha/4\pi$ is the anisotropy of molecular optical polarizability (corrected for local field effects), n is the refractive index, and c the light speed in vacuum. For the second term, we set $U_\alpha^{(2)} = -\frac{1}{2}\sum_{\beta=h,g,e} u_{\alpha\beta}(Q_\beta^{(2)}/N_t)\cos^2\theta$, which is the simplest function of θ compatible with the system $D_{\infty h}$ symmetry. The coefficients $u_{\alpha\beta}$ measure the strength of intermolecular orientational interactions. They depend on the electronic state, and are functions of molecular structures, of density, and of temperature.

Transition, diffusion, and drift rates can be combined into a single set of coupled dynamical equations for the functions $f_\alpha(\theta, t)$, or equivalently for the moments $Q_\alpha^{(l)}(t)$. The link with the experiment is then provided by the expression for the light-induced birefringence $\Delta n(t) = \Delta\epsilon(t)/2n = \sum_\alpha \eta'_\alpha Q_\alpha^{(2)}(t)/2n$ where $\eta'_\alpha/4\pi$ are the (local field corrected) polarizability anisotropies at the wavelength of the light used as probe.

Skipping all intermediate steps, we write down directly the steady-state solution for the birefringence induced by light of constant intensity I, obtained by neglecting the moments $Q_\alpha^{(l)}$ with $l > 2$ and for small N_d/N_t,

$$\Delta n = \frac{1}{2n}(\eta'_e - \eta'_g D_e/D_g) Q_e^{(2)} + \frac{\eta'_h}{2nu_{hh}}\frac{T^*}{T - T^*}\left[\frac{\eta_h N_t}{nc} I + \Delta u Q_e^{(2)}\right], \qquad (1)$$

with $\Delta u = u_{he} - u_{hg} D_e/D_g$ and $T^* = u_{hh} Q_h^{(0)}/15kN_t$, where k is Boltzmann constant and T is the absolute temperature. The dye field $Q_e^{(2)}$ is given by

$$Q_e^{(2)} = \frac{2\alpha_0\tau_d}{5h\nu} I f(I),$$

with

$$f(I) = \left[1 + \left(1 + \frac{11 D_e \tau_d}{7 D_g \tau_e}\right)\frac{I}{I_s} + \left(\frac{27 D_e \tau_d}{35 D_g \tau_e}\right)\left(\frac{I}{I_s}\right)^2\right]^{-1}, \qquad (2)$$

where $\tau_d = (\tau_e^{-1} + 6D_e)^{-1}$ and $I_s = h\nu N_d/\alpha_0\tau_e$.

A brief discussion of Eq. (1) is now in order. The first term is associated with the "trivial" direct contribution of dye molecules to the birefringence of the medium, arising from the different polarizabilities of excited- and ground-state dye molecules, i.e., $\eta'_g \neq \eta'_e$, and/or from the anisotropy in the total dye distribution resulting from the different diffusivities, i.e., $D_e \neq D_g$.

The second term is more interesting, as it gives the contribution to the birefringence associated with the host liquid orientation, induced by the combined action of the optical field and the photoinduced intermolecular interaction field, corresponding, respectively, to the first and second terms in square brackets. They have a common factor $T^*/(T - T^*)$ which diverges for $T \rightarrow T^*$, T^* being the critical temperature at which the isotropic orientational distribution becomes unstable because of intermolecular interactions. In most cases this divergence cannot be really observed, as T^* is far below the transition point to the solid phase. However, for materials having a liquid-crystalline nematic mesophase, T^* is just below the transition temperature T_c from the isotropic to the nematic phase. In this case the $(T - T^*)^{-1}$ power law can be observed [2], and it can be exploited to single out the orientational effects from the direct dye nonlinearity (first term).

The photoinduced intermolecular field depends critically on the material constant Δu. This quantity can be both positive and negative, and its sign and magnitude depend on how different the orientational intermolecular energies u_{he}, u_{hg} and/or the orientational diffusivities D_e, D_g are, in the ground and excited state of dye molecules.

The dimensionless function $f(I)$ in Eq. (2) describes the saturation behavior of the photoinduced intermolecular field. In particular, for $I \ll I_s$, $f(I) \simeq 1$ and the molecular-field effect is proportional to the intensity I. For high intensities $I \gg I_s$ the orientational mean field vanishes because, when complete bleaching of the dye is achieved, excited- and ground-state dye populations are isotropic again. It follows that there is an optimum intensity $I_{\max} = I_s[27/35(D_e/D_g)(\tau_d/\tau_e)]^{-1/2}$ maximizing the molecular-field contribution to the birefringence Δn.

The enhancement ratio between the total orientational Kerr nonlinearity and that arising from the direct optical field only is given by

$$A(I) = 1 + \frac{2}{5}\left(\frac{\Delta u \tau_d}{h}\right)\left(\frac{n\alpha_0\lambda}{\eta_h N_t}\right) f(I), \qquad (3)$$

where λ is light wavelength in vacuum. Typical values for the constants entering Eq. (3) are $\tau_d \sim 1$ ns [5], $\eta_h N_t \sim 1$, and $\Delta u \sim 0.1$ eV, from which we estimate $A(0) \simeq 1 + 10^4(\alpha_0\lambda)$. For visible light and with $\alpha_0 \sim 20\ \mathrm{cm}^{-1}$, the expected enhancement factor is of the order of 10.

Finally, it is worth noting that the same model can be applied with minor changes also to an absorbing pure liquid, instead of a dye-host liquid mixture. A detailed calculation shows that in the nonsaturation limit $I \ll I_s$ Eq. (1) is indeed reproduced provided that all subscripts h are changed into g (or vice versa). The saturation behavior, however, is not the same because in the dye-liquid mixture case we assumed $N_d/N_t \ll 1$, which is no longer valid in the pure liquid case where $N_d = N_t$.

In the experiment, we used the commercial liquid crystal mixture E63 produced by Merck-BDH, doped with the dye 4,5—diamino 2,7—diisopentyl anthraquinone at a concentration of 0.26% w/w. This specific mixture was chosen because it shows a large absorption-induced enhancement of the optical nonlinearity in the nematic phase [3]. At the working wavelength $\lambda = 532$ nm, the mixture has $\alpha_0 = 22\ \text{cm}^{-1}$. The sample was made by sandwiching a 600 μm thick film of liquid between two plane glass substrates. A transparent sample of pure E63 was used as a reference.

In planning the experiment, we had to take into account that saturation sets a limit to the maximum birefringence Δn which can be induced in the medium by the photoinduced molecular field. Moreover, the sample useful thickness is also limited by the penetration length α_0^{-1}. Therefore the maximum optical phase retardation which can be obtained is $\phi_{\max} \sim 2\pi\Delta n_{\max}/\alpha_0\lambda$. Since the contribution to Δn from the photoinduced molecular field is proportional to α_0, the corresponding $\phi_{\max}$ is independent of the absorption coefficient α_0 and of dye concentration. The order of magnitude of $\phi_{\max}$ for our material is estimated to be in the range 10^{-2}–10^{-1} rad.

To measure the nonlinear birefringence, we adopted a pump and probe geometry, with the polarization plane of the probe beam forming an angle of 45° with that of the pump. The birefringence results in a change of the probe polarization, which turns elliptical when propagating through the sample. The probe output-polarization ellipticity is given by the reduced Stokes parameter $s_3 = (I_+ - I_-)/(I_+ + I_-)$, where I_+ and I_- are the right and left circular polarization components. A small phase shift ϕ yields $s_3 = \sin\phi \simeq \phi$ in a plane wave. An additional proportionality factor is introduced because the measurement actually involved an integration over the transverse beam profile. Both pump and probe beams were from a Nd:YAG laser, with a pulse duration of 22 ns. The orientational response time of the liquid was measured in a separate experiment to be in the range 5–10 ns for our working temperatures. Therefore, the pulse length is large enough to approximately achieve steady-state response of the molecular orientation. The pump beam was frequency doubled, to obtain $\lambda = 532$ nm, falling in the absorption band of the dye. The probe beam was left at the fundamental wavelength $\lambda' = 1064$ nm, outside the absorption band, to minimize the direct nonlinear optical effects of dye molecules. The pump beam spot diameter was 270 μm.

We verified that no significant contribution to the signal arose from isotropic effects such as thermal lensing because of imperfect alignment of the setup, by switching the pump polarization plane from +45° to −45° with respect to the probe polarization plane. Then, the isotropic nonlinear effects remain unchanged in the two cases, while the birefringence effects change sign.

All measurements were repeated on the dye-doped sample and on the pure reference sample, varying the pump pulse energy and the sample temperature. The pure sample showed a nonlinear birefringence which we identify with the ordinary orientational Kerr effect. The absorbing sample, instead, showed a larger signal, which we identify with the combined action of the optical field and photoinduced intermolecular field (the direct dye contribution is negligible in our case, as highlighted by the temperature behavior). Figure 1 shows the measured nonlinear phase shift as a function of pump pulse energy, together with our theoretical predictions from Eq. (1). Only one adjustable scale factor was used to fit the data, to account for the proportionality constant between the signal and $\Delta n(I)$. The values for τ_e and D_e in the saturation function $f(I)$ were obtained from time-resolved fluorescence [5], and we assumed $D_g = D_e$. The value of Δu was obtained from Fig. 2. The local temperature increase due to light absorption was also taken into account in the theory. The predicted saturation behavior is clearly observed, including the existence of an optimal pulse energy. The transparent sample showed no saturation, as expected for the investigated intensity range.

The measured enhancement $A(I)$ between the total optical nonlinearity occurring in the absorbing sample and the ordinary optical Kerr effect occurring in the transparent sample as a function of pulse energy is shown in Fig. 2, together with our predictions based on Eq. (3). In the latter, the coefficient Δu was used as an adjustable parameter. The best-fit value is $\Delta u = 0.15 \pm 0.05$ eV, where the uncertainty is mainly due to the estimate of the constant η_h in Eq. (3). For a light intensity $I \ll I_s$, the

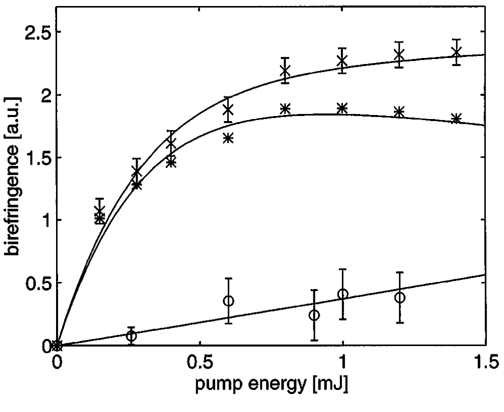

FIG. 1. Measured nonlinear phase shift vs pump pulse energy for the dye-doped sample (crosses), the pure sample (circles), and their difference (stars) yielding the contribution of molecular field only. To compare the pure and doped sample nonlinearities it is convenient to correct the data for the local heating and the intensity decrease due to light absorption in the dyed sample. However, since the dyed sample data are our main results, we preferred to leave them unchanged and to inversely correct the pure sample data. The lines are from a best fit based on Eq. (1).

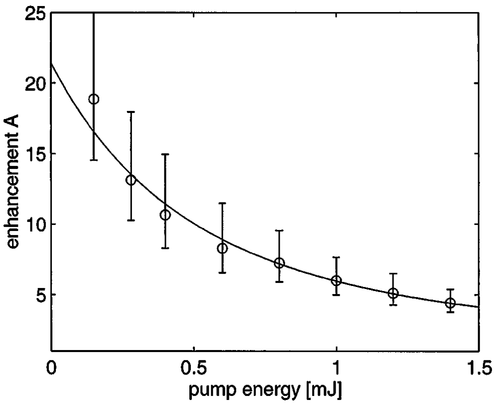

FIG. 2. Enhancement of nonlinearity vs pump pulse energy in the dye-doped sample with respect to the pure transparent sample. Laser heating and absorption losses are taken into account as in the previous figure. Circles: experimental data. Line: best fit based on Eq. (3).

measured enhancement of the nonlinear birefringence was $A(0) = 21$. This value is comparable to the enhancement of 10 observed in the nematic phase for the same dye concentration and pump wavelength [6].

To make sure that we are indeed observing the orientational nonlinearity we investigated the temperature dependence of the effect close to the isotropic-nematic transition point $T_c = 87$ °C. The experimental results are shown in Fig. 3, where the inverse signal is plotted vs temperature. The straight lines are from linear best fit. The pretransitional $(T - T^*)^{-1}$ power law is clearly observed both in the absorbing and transparent sample, showing that the involved degree of freedom is indeed the orientational order parameter. We obtain $T^* = 78$ °C. In the dye-doped sample, the apparent value of T^* is affected by laser-induced heating, and therefore is pulse-energy dependent. We observe a decrease of about 5 K/mJ, consistent with the laser-induced heating estimated from the material thermal constants.

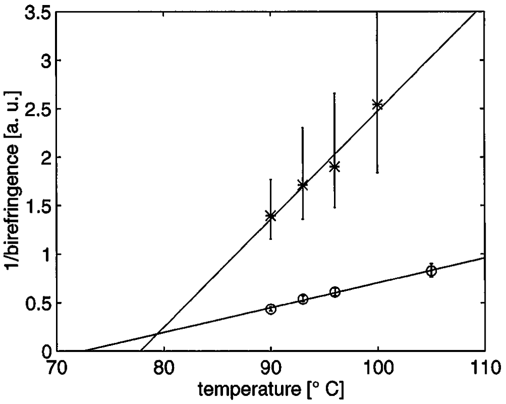

FIG. 3. Inverse nonlinear phase shift vs temperature for the absorbing sample (circles) and the transparent sample (stars). Pump pulse energy is 1 mJ. Straight lines are from a linear best fit.

In conclusion, we observed a large enhancement of the optical Kerr nonlinearity associated with molecular orientation in a dye-doped organic liquid. This is attributed to a photoinduced intermolecular force field which combines with the optical electric field in orienting the molecules. The experimental results are in agreement with the predictions of our model. The mechanism proposed to explain the enhancement is very general, requiring only that liquid molecules be anisotropically light absorbing and that the orientational intermolecular interactions change with the molecule electronic state. From the applicative point of view, the main drawback of this nonlinearity mechanism is light absorption. The ratio between nonlinearity and absorption losses is, however, material dependent, and therefore further research is needed to explore the final limits of this kind of optical nonlinearity.

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[1] Y. R. Shen, *The Principles of Nonlinear Optics* (John Wiley & Sons, New York, 1984), p. 291; R. W. Boyd, *Nonlinear Optics* (Academic Press, Boston, 1992), p. 178.
[2] G. K. L. Wong and Y. R. Shen, Phys. Rev. Lett. **30**, 895 (1973); Phys. Rev. A **10**, 1277 (1974).
[3] I. Jánossy, A. D. Lloyd, and B. S. Wherret, Mol. Cryst. Liq. Cryst. **179**, 1 (1990).
[4] I. Jánossy, Phys. Rev. E **49**, 2957 (1994).
[5] D. Paparo, L. Marrucci, G. Abbate, E. Santamato, P. Bartolini, and R. Torre, Mol. Cryst. Liq. Cryst. **282**, 461 (1996).
[6] D. Paparo, P. Maddalena, G. Abbate, E. Santamato, and I. Jánossy, Mol. Cryst. Liq. Cryst. **251**, 73 (1994).