Optical-Field-Induced Ordering in the Isotropic Phase of a Nematic Liquid Crystal

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We have shown by measuring the field-induced refractive index that molecular ordering in the isotropic phase of *p*-methoxy benzylidene *p*-*n*-butylaniline (MBBA) can be induced by an intense laser field. We have also measured directly the ordering relaxation time as a function of temperature. The results are compared with the predictions of the Landau–de Gennes model.

The linear optical properties of liquid crystalline materials have been the subject of extensive investigation recently. The nonlinear optical properties of the same materials, however, have not yet received much attention. In this paper, we report the first measurements on the optical-field-induced refractive index for a nematic substance in its isotropic phase. Ordering in the molecular orientation induced by the optical field is essentially responsible for this nonlinear refractive index. Field-induced ordering in the isotropic phase of a nematic system has been previously observed with an applied dc electric or magnetic field,[1-3] but the same effect obtained with an optical field has never been reported before. Using a Q-switched laser pulse, we have also been able to measure directly the relaxation time for the variation of the orientational order. Our results agree well with de Gennes's prediction.[4]

The present work was motivated by the idea that, because of the strong molecular anisotropy, a relatively weak laser field might be sufficient to induce an appreciable ordering in the isotropic phase of a liquid crystalline material. The resultant field-induced refractive index should increase strongly as the temperature approaches the isotropic-mesomorphic phase transition.[4] For our case, we can write the free energy per unit volume for the isotropic phase as

$$F = F_0 + \tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha}^* - \tfrac{1}{2}\chi_{\alpha\beta}E_\alpha^* E_\beta, \qquad (1)$$

$$A = a(T - T^*), \quad \chi_{\alpha\beta} = \bar{\chi}\delta_{\alpha\beta} + \tfrac{2}{3}\delta\chi_{\alpha\beta}(Q_{\alpha\beta}, T),$$

where E_α is the field component along $\hat{\alpha}$, $Q_{\alpha\beta}$ is the tensorial order parameter, a and T^* are constants, and $\delta\chi_{\alpha\beta}$ is the anisotropy in the susceptibility $\chi_{\alpha\beta}$ induced by the ordering $Q_{\alpha\beta}$ at the temperature T. We have neglected in the above expression terms of higher powers of $Q_{\alpha\beta}$ and terms describing the spatial variation of $Q_{\alpha\beta}$. The steady-state value of $Q_{\alpha\beta}$ induced by the field can then be obtained by minimization of F. For a given field, since the induced $Q_{\alpha\beta}$ is usually small such that $\delta\chi_{\alpha\beta} = \Delta\chi Q_{\alpha\beta}$, where $\Delta\chi \equiv \partial\chi_{\alpha\beta}/\partial Q_{\alpha\beta}$, both $Q_{\alpha\beta}$ and $\delta\chi_{\alpha\beta}$ should be proportional to $(T - T^*)^{-1}$.

However, if a short optical pulse is used to induce ordering, the ordering parameter may not be able to respond instantaneously. Then, the transient response of the order parameter is governed by the equation[4]

$$\nu\,\partial Q_{\alpha\beta}/\partial t + AQ_{\alpha\beta} = f_{\alpha\beta}(t), \qquad (2)$$

$$f_{\alpha\beta} = \Delta\chi(3E_\alpha^* E_\beta - |E|^2\delta_{\alpha\beta})/9,$$

where ν is a viscosity coefficient. The solution of the above equation is

$$Q_{\alpha\beta}(t) = (1/\nu)e^{-t/\tau}\int_{-\infty}^{t} f_{\alpha\beta}(t')e^{t'/\tau}\,dt', \qquad (3)$$

where $\tau = \nu/A = \nu/a(T - T^*)$ is the relaxation time. It is seen from Eq. (3) that long after the input pulse is over, $Q_{\alpha\beta}$ should decay as $\exp(-t/\tau)$. For an input laser pulse with a Gaussian pulse shape, $f_{\alpha\beta}(t) = C_{\alpha\beta}\exp(-b^2t^2)$, we have

$$Q_{\alpha\beta}(t) = (C_{\alpha\beta}/b\nu)\exp(-t/\tau)\exp(1/4b^2\tau^2) \times\{1 + \mathrm{erf}[bt - (2b\tau)^{-1}]\} \qquad (4)$$

which varies as $\exp(-t/\tau)$ when $bt \gg 1$.

We can find $Q_{\alpha\beta}(t)$ by measuring the field-induced $\Delta\chi_{\alpha\beta}(t)$. For example, we can measure the birefringence $\chi_{\alpha\alpha} - \chi_{\beta\beta} = \Delta\chi Q_{\alpha\alpha}$ induced by a laser field linearly polarized along $\hat{\alpha}$. We have actually performed such measurements. We used the typical setup for measurements of optical Kerr constants.[5] A finite $Q_{\alpha\alpha}$ was first induced by a Q-switched ruby laser pulse 10 nsec long, and its subsequent variation was probed by a cw He-Ne laser beam.[6] Results were obtained for MBBA at various temperatures in the isotropic phase. In every case, we obtained a perfect

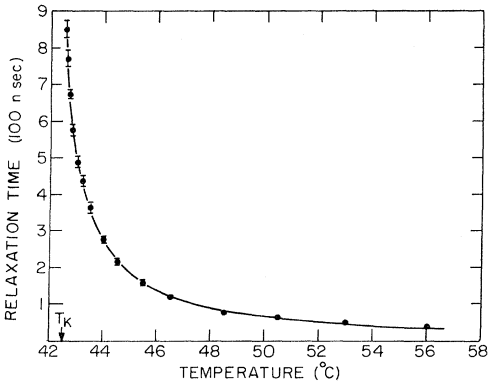

FIG. 1. Relaxation time τ of the order parameter as a function of temperature. The solid curve is the theoretical curve obtained for $\tau = \nu/a(T - T^*)$ with $T^* = 314.7$°K and $\nu = \nu_0 \exp(2800\text{°K}/T)$. The dots are the experimental data points.

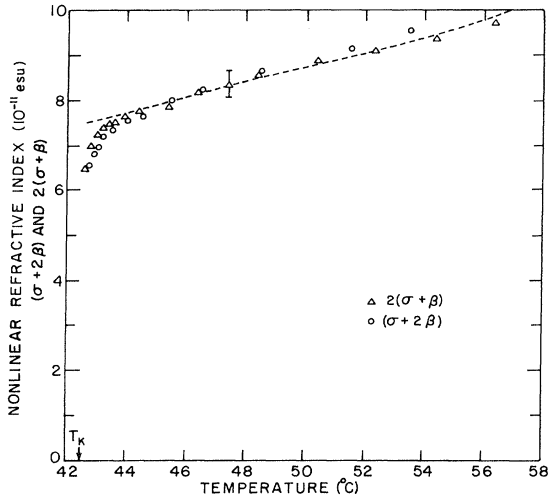

FIG. 2. Nonlinear refractive indices $2(\sigma+\beta)$ and $\sigma + 2\beta$ as a function of temperature. The dashed curve is a theoretical curve obtained from Eq. (4) by assuming $\nu = \nu_0 \exp(2800\text{°K}/T)$ and $\Delta\chi$ a constant.

exponential tail for $Q_{\alpha\alpha}(t)$ from which we calculated the relaxation time τ. In Fig. 1, we present the experimental data τ as a function of T. They agree very well with the theoretical expression $\tau = \nu/a(T - T^*)$ of de Gennes[4] if we assume $\nu = \nu_0 \exp(W/T)$ with $W = 2800$°K as suggested by Stinson and Litster[3] and $T^* = 314.7$°K. The clearing temperature of our material is $T_K = 315.5$°K. The relaxation time varies from ~40 nsec at temperatures far above the phase transition to >800 nsec near the transition. These results are in good agreement with those obtained from light scattering by Stinson and Litster.[3] However, we believe our measurements are more straightforward and accurate.

In general the field-induced $\Delta\chi_{\alpha\beta}$ should also include a part due to field-induced deformation of the electronic cloud around molecules (the electronic contribution to the third-order nonlinearity). According to Owyoung, Hellwarth, and George, the optical Kerr constant $B = (\omega/cn)[(\Delta\chi_{\alpha\alpha} - \Delta\chi_{\beta\beta})/|E_\alpha|^2]$ can be written as $B = (\omega/cn)(\sigma+\beta)$, where σ and β are, respectively, the electronic and the nuclear contributions to the nonlinear refractive index. The nuclear part includes molecular reorientation and redistribution by the field. On the other hand, by measuring the field-induced rotation of the elliptical polarization of a laser pulse,[7] one can obtain the quantity $D = (\omega/cn)(\sigma + 2\beta)$. If the electronic contribution is negligible, then one should have $2B = D$. This is what we would expect for liquid crystalline materials since in this case molecular reorientation should dominate because of the strong molecular anisotropy.[8] In order to show that this is indeed the case, we have conducted separate experiments to measure the optical Kerr constant and the field-induced rotation of the polarization ellipse. Our experimental setups were similar to those used by others.[5,9] The quantities were measured at the time when $|E_\alpha|^2$ reached its peak value. The results, after the correction of scattering loss in the medium,[10] are plotted in Fig. 2 as $2Bcn/\omega$ and Dcn/ω versus T. It is seen in Fig. 2 that the two sets of data obtained from two different experiments agree very well. This therefore indicates $\sigma \ll \beta$, i.e., the electronic contribution to the nonlinear refractive index is indeed negligible.

Thus, knowing that the field-induced molecular ordering is responsible for the observed field-induced refractive index, we can write

$$2B = D = (\omega/cn)\Delta\chi Q_{\alpha\alpha}/|E_\alpha|^2.$$

By approximating our input laser pulse by a Gaussian pulse, we can find from Eq. (4) $Q_{\alpha\alpha}(0)$, and hence B and D, as a function of T. The theoretical curve thus obtained with $\nu = \nu_0 \exp(W/T)$ and $\tau(T)$ in Fig. 1 is also shown in Fig. 2. It agrees well with the experimental data for $T - T_K \gtrsim 1$°K. Presumably, for $T - T_K < 1$°K, the higher-order terms neglected in the free energy F of Eq. (1) may become important[11] or the mean-field theory may break down. Our results remained unchanged when the laser intensity was varied from 0.3 MW/cm^2 to 1 MW/cm^2. This indicates that up to 1 MW/cm^2, the induced order-

ing does not depend nonlinearly on the field intensity.

Schadt and Helfrich[1] have recently found in their measurements on the dc Kerr effect a steady-state response of $(\Delta n/E^2) \propto (T - T^*)^{-\gamma}$ with $\gamma < 1$. The difference between their work and our work is in the driving term of Eq. (2). For polar molecules, the permanent dipoles on the molecules may contribute dominantly to the dc Kerr constant but not at all to the optical Kerr constant.[21] Using a laser pulse to induce ordering, we also have the advantage of avoiding complication due to induced current flow in the medium which would happen if a low-frequency ac field were used to induce ordering.

As shown in Fig. 2, the optical Kerr constant of MBBA is unusually large. In comparison with CS_2, we found $B(\text{MBBA})/B(CS_2) = 10$ at 326°K. One would therefore expect to find self-focusing of the laser beam in such a medium at a relatively low power.[13] Quantitiative study of how self-focusing varies as a function of temperature is presently in progress. We should point out that because of the large nonlinearity, a liquid crystalline material can have potential applications in nonlinear optical devices.

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Balmer-Line Anomalies in a Turbulent Plasma

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Resonance effects between orthogonal components of dynamic and quasistatic electric fields within a turbulent hydrogen plasma are shown to produce satellites on the H_β profile. The splitting on H_α, H_β, H_γ, and H_δ profiles indicates that the quasistatic field strength is 0.9×10^7 V/m. By using a helium tracer, comparison of a forbidden transition with its satellites indicates that the dynamic field (at the plasma frequency) is 1.3×10^7 V/m.

Dynamic and quasistatic electric fields are known to exist simultaneously in turbulent plasmas. The high-frequency fields are due to electronic plasma oscillations and the low-frequency fields to ion-acoustic turbulence. The influence of these local fields has been noted on the 6632-Å (2^1P-3^1P) He I forbidden transition and its satellites.[1-4]

In hydrogen, the low-frequency or quasistatic field can produce a splitting of the Balmer series lines and superimpose the resultant components on the usual Balmer series profiles, Stark broadened by electron collisions. The splitting of these spectral lines is connected with the accidental degeneracy in hydrogen whereby terms of the same n but a different l have almost the same