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Nonlinear Birefringence of Liquid Crystals

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Liquid crystals are promising materials for nonlinear optical devices. In addition to the linear birefringence, liquid crystals possess third order nonlinear susceptibilities associated with a variety of mechanisms. Due to the bulk anisotropy of these materials, the nonlinear refractive index n_2 sensitively depends on the direction of light polarization with respect to the nematic director. We have used the Z-scan method, recently developed by the CREOL group,[1] to determine the nonlinear refractive indices of the pure liquid crystals 5CB and 8CB, and of the mixture E7 in the isotropic and nematic phases, and, in the case of 8CB, in the smectic phase. We have measured the nonlinear refractive indices $n_{2\parallel}$ and $n_{2\perp}$ for light polarized parallel and perpendicular to the director, respectively, using millisecond pulses from a CW Ar^+ laser and nanosecond pulses from a Q-switched Nd:YAG laser. We have also measured the nonlinear absorption. The nonlinear response of our samples on the millisecond timescale is comparable to the 'giant optical nonlinearity' associated with director reorientation, although in our geometry, director reorientation is not expected to occur. On the nanosecond timescale, the nonlinearity is still two orders of magnitude greater than for CS_2. Our results are consistent with the effects of laser heating on the millisecond timescale, but fast nonlinear absorpiton observed on the nanosecond scale suggests that laser heating is not the sole mechanism.

1. INTRODUCTION

The large linear birefringence and dielectric constant anisotropy are well known intrinsic properties of liquid crystals. Much work has been done to investigate their physical origins as well as to explore their potential applications.[2] More recently, the nonlinear optical response of liquid crystals has become the subject of increased study both experimentally[3] and theoretically.[4] Since liquid crystal molecules typically have delocalized π-electronic structures, they are believed to be potential sources of fast and large optical nonlinearities.[5] Due to the bulk anisotropy of these materials, the nonlinear refractive index n_2 and nonlinear absorption coefficient β are expected to depend on the direction of polarization of light with respect to the nematic director $\hat{n}$.

Several techniques have been developed to measure the nonlinear refractive index n_2. These include nonlinear interferometry,[6] wave mixing,[7,8] and beam-distortion measurements.[9] Interferometry and wave mixing are potentially sensitive techniques, but require relatively complex experimental setups and the results give only the magnitude but not the sign of n_2. Beam-distortion measurements, on the

other hand, require precise beam scans followed by complex wave-propagation analyses. We find that the single-beam technique developed by CREOL group,[1] referred to as the Z-scan technique, is ideal because of its simplicity and high sensitivity in measuring both n_2 and β. Z-scan results determine the sign of n_2, and the analysis can be extended to include information regarding the dynamics of the nonlinear processes.[10] The technique is based on the transformation of phase distortion induced by the nonlinear medium to amplitude distortion during beam propagation. Both the sign and magnitude of the nonlinear refractive index as well as the nonlinear absorption coefficient can be measured using this method. The extended Z-scan analysis[10] can also give the time constant of the nonlinear processes.

In this paper, we report our measurements using the Z-scan technique of the third order nonlinear susceptibilities of the pure liquid crystals 5CB and 8CB, and of the mixture E7 using nanosecond pulses from a frequency doubled Nd:YAG laser and milisecond pulses from a CW Ar^+ laser. Both the nonlinear refractive indices and nonlinear absorption coefficients for light polarized parallel (denoted by subscript $\|$) and perpendicular (denoted by subscript $\perp$) to the director have been measured.

2. Z-SCAN TECHNIQUE

The schematic of the Z-scan experimental setup is shown in Figure 1. A Gaussian laser beam is focused at $z = 0$ plane ($z < 0$ correspond to pre-focal and $z > 0$ to post-focal positions), and the transmittance of a nonlinear medium through a finite aperture is measured in the far field as a function of the sample position z. For simplicity, we only consider pure nonlinear refraction; the effects of nonlinear absorption will be included later.

A thin sample, with thickness smaller than the diffraction length of the focused beam, with a positive n_2 can be regarded as a thin converging lens, whose focal length varies with sample position along the z-axis. Starting the scan far from the focal point at large negative values of z, the beam intensity is low and nonlinear effects are negligible. Initially, therefore the transmittance remains relatively constant. As the sample is moved closer to the focus, the beam intensity increases significantly leading to a self-focusing in the sample. This self-focusing with the sample at small negative values of z will cause the beam to broaden at the aperture and hence the measured transmittance is decreased. As the sample is moved through the focal point at $z = 0$ to a post-focal position, the same self-focusing causes the beam to narrow leading to an increase in the transmittance. Consequently a pre-focal minimum (valley) followed by a post-focal maximum (peak) in the transmittance versus sample position curve corresponds to a positive n_2; and conversely a peak followed by a valley is a signature of a negative n_2. The magnitude of n_2 can be evaluated using the following analysis.[1]

For the intensity dependent third order nonlinear refractive process, the refrac-

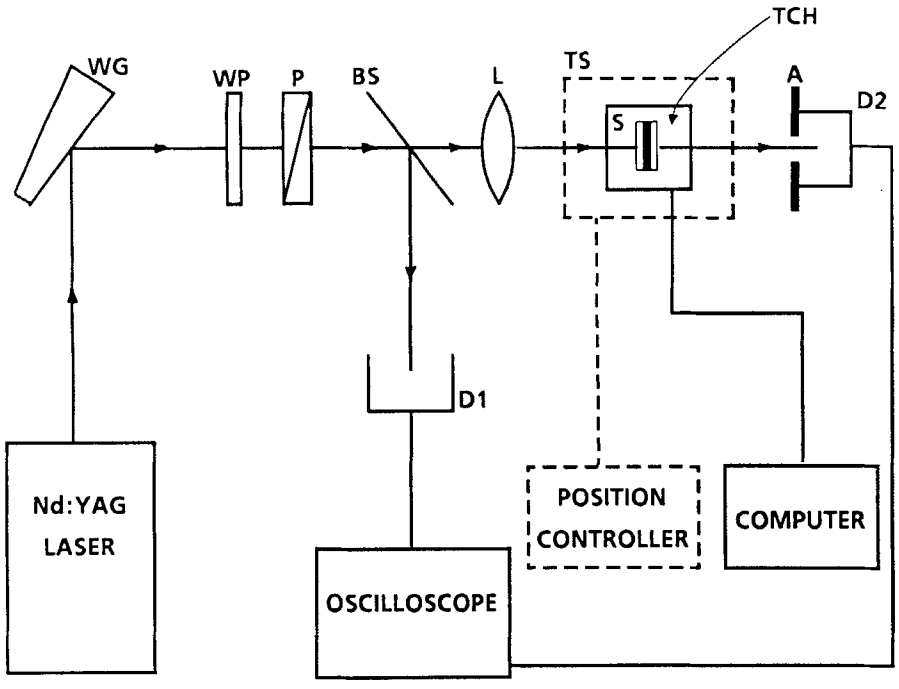

FIGURE 1 Schematic of experimental setup for Z-scan measurements. The abbreviations are: WG, wedged glass; WP, wave plate; P, polarizer; BS, beam splitter; L, lens; TS, translation stage; S, liquid crystal sample; TCH, temperature controlled housing; A, aperture; D1 and D2, photodiode detectors.

tive index can be expressed in terms of the linear refractive index n_0 and the nonlinear indices n_2 or γ

$$n = n_0 + \frac{n_2}{2}|E|^2 = n_0 + \gamma I \tag{1}$$

where E is the peak value of electric field and I is the intensity of the laser beam within the sample. For a Gaussian beam travelling in the $+z$ direction and focused at $z = 0$, E can be written as

$$E(z, r, t) = E_0(t)\frac{w_0}{w(z)}\exp\left[-\frac{r^2}{w^2(z)} - \frac{ikr^2}{2R(z)}\right]e^{i\left(kz-\omega t-\tan^{-1}\frac{z}{z_0}\right)} \tag{2}$$

where $w(z) = w_0(1 + z^2/z_0^2)^{1/2}$ is the laser beam radius at sample position z, $R(z) = z + z_0^2/z$ is the radius of curvature of the wavefront, $z_0 = kw_0^2/2 = \pi w_0^2/\lambda$ is the diffraction length of the focused beam, and k and λ are the wave vector and wave length of the laser beam in free space. $E_0(t)$ denotes the radiation field at the focus $z = 0$ and contains the temporal evelope of the laser pulse. If the sample thickness

L is smaller than diffraction length, the intensity I and the nonlinear phase change $\Delta\phi$ within the sample are given by

$$\frac{d\Delta\phi}{dz'} = \Delta n(I)\,\frac{2\pi}{\lambda} \tag{3a}$$

and

$$\frac{d\,I}{dz'} = -\alpha(I)\,I \tag{3b}$$

where $\alpha(I) = \alpha_0 + \beta I + \ldots$, and α_0 and β are linear and nonlinear absorption coefficients, respectively; z' is the position measured from the entrance surface of the sample. Equation (3) can be solved to give the phase shift and amplitude at the exit surface of the sample. By using Gaussian decomposition,[1] one can get the field distribution and from this the intensity distribution at the aperture. For the purely refractive nonlinear process

$$E_a(z, r, t) = E(z, r = 0, t)e^{-\left(\frac{\alpha L}{2}\right)} \sum_{m=0}^{\infty} \frac{[i\Delta\phi_0(z, t)]^m}{m!}\,\frac{w_{m0}}{w_m} \cdot \exp\left[-\frac{r^2}{w_m^2} - \frac{ikr^2}{2R_m} - i\theta_m\right] \tag{4}$$

where $d = d_0 - z$ is the propagation distance from the sample to aperture, d_0 is the distance between the focus and aperture, and $L_{\text{eff}} = (1 - e^{-\alpha_0 L})/\alpha_0$ is the effective sample thickness. $\Delta\Phi_0(t) = k\,L_{\text{eff}}\,\gamma\,I_0(t)$ is the on-axis phase shift at the focus where $I_0(t)$ is the on-axis intensity at focus, and following Reference 1,

$$\Delta\phi_0(z, t) = \Delta\Phi_0/(1 + z^2/z_0^2), \qquad w_{m0}^2 = \frac{w^2(z)}{2m + 1},$$

$$d_m = \frac{k\,w_{m0}^2}{2}, \qquad g = 1 + d/R(z),$$

$$w_m^2 = w_{m0}^2\left[g^2 + \frac{d^2}{d_m^2}\right], \qquad R_m = d\Big/\left[1 - \frac{g}{g^2 + d^2/d_m^2}\right], \text{ and}$$

$$\theta_m = \tan^{-1}\left[\frac{d}{g\,d_m}\right].$$

It is now straightforward to obtain the transmittance $T(z)$ by integrating the intensity

over the aperture for a given sample position z. In the case of small nonlinear phase shift ($\Delta\Phi_0 < 1$) and small aperture, the expression for the normalized transmittance becomes[10]

$$T_N(z) = 1 + \frac{4x}{(1 + x^2)(9 + x^2)}\Delta\Phi_0 \tag{5}$$

where $x = z/z_0$. Because of its simplicity, this expression is useful for fitting data, and the values of γ and n_2 obtained from fitting the data with this expression agree to better than 1% with those obtained from the full expression in Equation (4) if $\Delta\Phi_0 < 1$. The relative aperture size A (defined as the aperture transmittance in the linear regime) controls the sensitivity, since a large aperture will reduce the variation in $T_N(z)$. Maximum sensitivity is obtained in the limit as $A \to 0$. For an open aperture ($A = 1$) where all light is collected by the detector, beam narrowing and broadening effects are suppressed in the normalized transmittance curve and $T_N(z) = 1$ for all values of z and $\Delta\Phi_0$ if there is no nonlinear absorption.

In the case where nonlinear absorption is taking place simultaneously with nonlinear refraction, the nonlinear absorption coefficient β can be determined from an open aperture Z-scan. The normalized transmittance for a temporally Gaussian pulse is given by[1]

$$T_N(z, A = 1) = \frac{1}{\sqrt{\pi}\, q_0(z, 0)} \int_{-\infty}^{+\infty} \ln[1 + q_0(z, 0)\, e^{-\tau^2}]\, d\tau \tag{6}$$

where $q_0(z,t) = q_0(t)/(1 + z^2/z_0^2)$, and $q_0(t) = \beta I_0(t)(1 - e^{-\alpha_0 L})/\alpha_0$. Once an open aperture Z-scan is performed, the nonlinear absorption coefficient β can be unambiguously determined. With β known, a finite aperture ($A < 1$) Z-scan can be performed to determine the nonlinear refractive index γ or n_2. Detailed calculations show[1] that for a material with $\beta/2k\,|\gamma| \leq 1$, there exists a simple procedure to calculate γ with less than 10% error. The process is simply to divide the finite aperture ($A < 1$) transmittance by the open aperture one ($A = 1$); the new transmittance curve thus obtained can then be used to calculate n_2 as if $\beta = 0$.

3. EXPERIMENT

Samples of the pure liquid crystals 5CB, 8CB, and of the mixture E7 obtained from EMI Chemicals were used without further purification. The liquid crystal was sandwiched between two 25 mm × 38 mm × 0.95 mm glass plates. The plates were coated with polyimide and then buffed to achieve homogeneous (planar) alignment of the liquid crystal with the nematic director in the plane of the glass plates. The plates were separated with mylar spacers such that the thickness of the liquid crystal samples was 25 μm or 120 μm. The experimental setup is shown in Figure 1. We used a seeded frequency doubled Nd:YAG laser with 7 ns pulses

and a CW Ar^+ laser with a shutter providing 10 ms pulses for our measurements. A wave plate and polarizer combination was used to control the pulse energy, which was selected to optimize the Z-scan measurements. The temporal pulse profile was monitored using a fast photodiode D1 and the transmittance after the aperture was measured by photodiode D2. A converging lens (f = 125 mm) was used to focus the Gaussian beam to a beam waist of w_0 = 7.5 μm. The liquid crystal sample was mounted in an Instec temperature controlled housing (TCH) whose temperature was computer controlled. A Daedal translation stage (TS) was used to position the sample with micron resolution.

Figure 2 shows a small aperture (A = 1%) transmittance of a 25 μm thick homogeneously aligned 5CB sample in the $\hat{n}\|E$ geometry using 7 ns laser pulses (λ = 532 nm) with a pulse energy of 24 μJ. The measurements were taken at the fixed temperature T = 25.0°C. The peak-valley configuration of this curve indicates a negative (self-defocusing) nonlinear refractive index n_2, while the strongly suppressed peak and enhanced valley reveal the existence of strong nonlinear absorption. An open aperture and otherwise identical Z-scan was performed for the same sample in order to determine the nonlinear absorption coefficient β.

The results of this open aperture measurement are shown in Figure 3 with open circles. By fitting the data with Equation (6) (the solid curve in the plot) we get β = 3.2×10^{-9} m/W = 3.2×10^2 cm/GW, which is about 50 times larger than that of ZnSe, where β = 5.8 cm/GW. The transmittance obtained by dividing the small aperture transmittance by the open aperture one is shown in Figure 4. Having eliminated the effects of absorption, the transmittance curve thus obtained is now apparently an odd function of z, as expected from Equation (5). The theoretical fit (solid line) to the full expression from Equation 4 gives $\gamma_{\|}$ = -2.4×10^{-16}

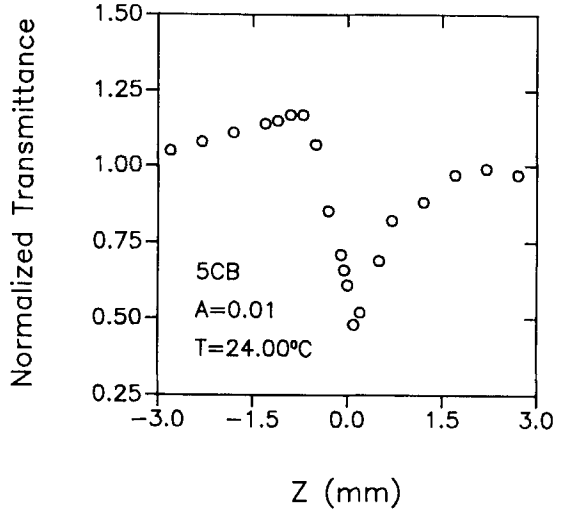

FIGURE 2 Transmittance of a 25 μm thick 5CB sample measured with small aperture (A = 0.01) using 7 ns pulses at λ = 532 nm. The shape of the curve indicates large negative nonlinear refraction together with strong nonlinear absorption.

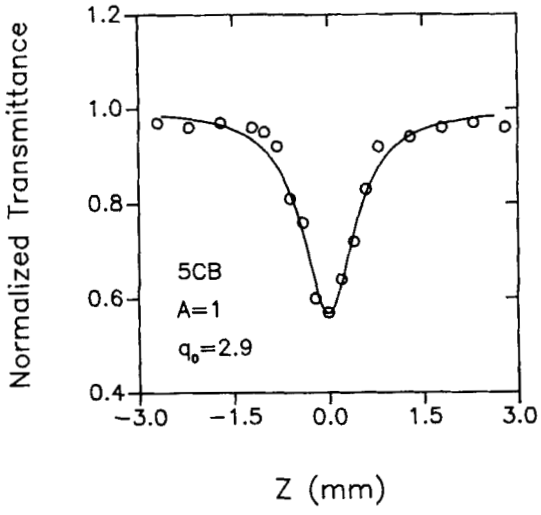

FIGURE 3 Transmittance of the same sample as in Figure 1 measured with open aperture (A = 1) using 7 ns pulses at λ = 532 nm indicating a strong nonlinear absorption. Open circles are the measured data and solid line is the theoretical fit.

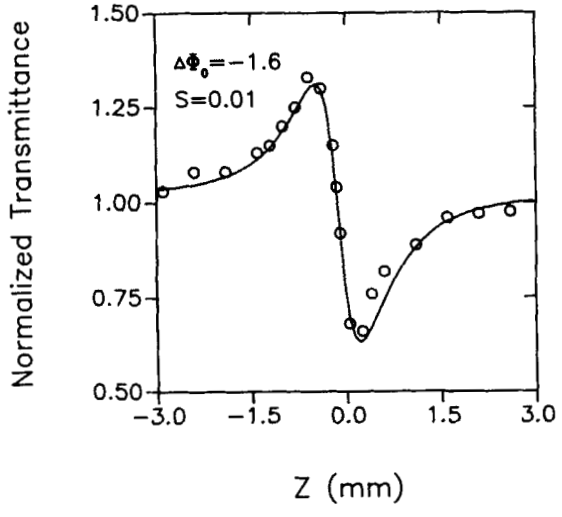

FIGURE 4 Transmittance obtained by dividing the small aperture transmittance data by those obtained with open aperture. Open circles are results of the division, and the solid line is the theoretical fit.

m^2/W or $n_{2\|} = -1.7 \times 10^{-9}$ esu. This is more than two orders of magnitude greater than the intensity dependent refractive index ($n_2 = 1.2 \times 10^{-11}$ esu) of CS_2.

We have also carried out measurements for 120 μm thick 5CB sample and obtained the same value of $n_{2\|}$ as above to within experimental error. In the geometry $\hat{n} \perp E$ under the same conditions we obtained $n_{2\perp} = 2.5 \times 10^{-10}$. Mea-

TABLE I

Nonlinear refractive indices at 24°C

Material	CS_2	5CB	8C	E7
$n_{2\parallel}$ ($\times 10^{-11}$esu)	+1.2	−175	−77	−115
$n_{2\perp}$ ($\times 10^{-11}$esu)	+1.2	+25	+11	+10

* Nd:YAG laser pulses with T_{FWHM} = 6.5 ns at λ = 0.532 μm were used.

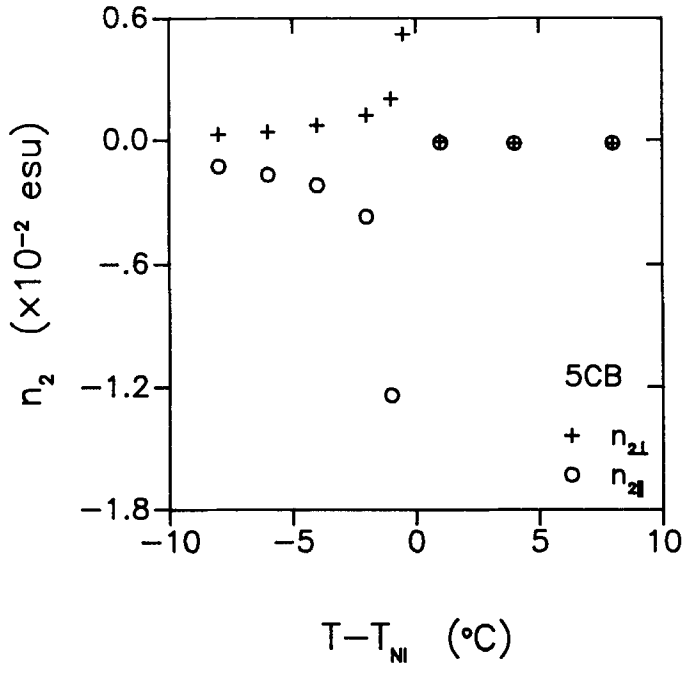

FIGURE 5 The temperature dependence of $n_{2\parallel}$ and $n_{2\perp}$ for the nematic liquid crystal 5CB using 10 ms Ar^+ laser pulses at λ = 514 nm. The nonlinear birefringence diverges as $(T_{NI} - T)^{-1}$.

surements for 120 μm thick 8CB and E7 samples for both geometries have been carried out and the results are summarized in Table I.

In addition to the nanosecond measurements, we have measured the nonlinear refractive indices of 5CB in the nematic and isotropic phases in the millisecond regime as functions of temperature. With the samples mounted as before, using a shutter, 10 ms pulses from a CW Ar^+ laser at λ = 514 nm were used in these measurements. The beam waist was 20 μm, and the power was typically 100 mW. Figure 5 shows the nonlinear refractive indices for both parallel and perpendicular geometries as functions of temperature. Again, strong nonlinear birefringence in the nematic phase was observed with $n_{2\parallel}$ and $n_{2\perp}$ differing not only in magnitude but also in sign. These results are consistent with laser heating of the sample and the consequent reduction of orientational order. If the linear absorption and laser heating of the sample is independent of polarization, then this mechanism gives

$n_{2\parallel} \simeq -2\, n_{2\perp}$. Deviations from this relation in our results are likely due to dichroism of our sample. In the millisecond regime we did not observe nonlinear absorption within the sensitivity of our experiment.

4. DISCUSSION AND CONCLUSIONS

Using the Z-scan technique, we have been able to measure for the first time[11] both nonlinear refractive indices and nonlinear absorption coefficients of the aligned nematic and smectic liquid crystals. Using 10 ms pulses at $\lambda = 514$ nm, we measured positive $n_{2\perp} \simeq +10^{-3}$ esu for light polarization perpendicular to the director which increased rapidly as the nematic-isotropic transition temperature was approached from below. For light polarized parallel to the director, the nonlinear index was negative, with $n_{2\parallel} \approx -2n_{2\perp}$. The average nonlinear index is $\bar{n}_2 = (n_{2\parallel} + 2n_{2\perp})/3 \approx 0$ below the nematic-isotropic transition, while the nonlinear birefringence is strongly temperature dependent, with $\Delta n_2 = n_{2\parallel} - n_{2\perp} \simeq -1.4 \times 10^{-2}\,(T_{NI} - T)^{-1}$ esu-K. The nonlinear absorption at the low intensities used in these measurements was too small to be measured. In our geometry, director reorientation is not expected to occur, since there is no torque on the director due to the optical field for $\hat{n} \parallel E$; and since the threshold for the optical twist transition[12] in the $\hat{n} \perp E$ configuration is well above the intensities used in our experiment. We expect therefore that the observed nonlinearity is predominantly due to laser heating of the sample, which results in changes in the orientational order parameter, density, and the refractive indices. A crude estimate of the thermally induced nonlinearity[13] is consistent with our measured values.

Using 7 ns pulses polarized parallel to the director, we measured $n_{2\parallel} = -1.7 \times 10^{-9}$ esu and $\beta_{\parallel} = 3.2 \times 10^{-9}$ m/W for 5CB while for polarization perpendicular to the director we found $|n_{2\parallel}/n_{2\perp}| = 7$. The mechanisms which give rise to the large nonlinear index for polarization parallel to the director, to the large nonlinear birefringence and to the large nonlinear absorption coefficient anisotropy are not well understood. It is likely that one important contribution is laser heating of the sample. The measured values of the nonlinear indices are six orders of magnitude smaller than the millisecond results, and this is comparable to the expected contribution[13] from slow thermal effects. However, we have also observed strong nonlinear absorption in the nanosecond measurements which must be a result of a fast process since it was not seen in the millisecond experiments. We also suppose that this fast nonlinear absorption is accompanied by a correspondingly fast nonlinear refraction. Our preliminary analysis of the temporal profile of the transmitted pulse indicates that this process is not slower than the nanosecond range. Further work is needed to understand the mechanism responsible for the fast nonlinearity observed with nanosecond pulses.

We have found that the third order nonlinearity in the liquid crystals studied with nanosecond pulses is two orders of magnitude greater than that of CS_2. The large nonlinear refractive index and nonlinear birefringence of these materials may be useful for device applications.

Acknowledgments

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References

1. M. Sheik-bahae, A. A. Said and E. W. Van Stryland, *Opt. Lett.*, **14**, 955 (1989).
2. See, for example, P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1974); L. M. Blinov, *Electro-Optical and Magneto-Optical Properties of Liquid Crystals*, (John Wiley & Sons, New York, 1983).
3. M. J. Soileau, E. W. Van Stryland and S. Guha, *Mol. Cryst. Liq. Cryst.*, **143**, 139 (1987); I. C. Khoo, *Opt. Eng.*, **28**, 1108 (1989).
4. Michael A. Lee, S. Risser, S. Klemm and D. W. Allender, *Mol. Cryst. Liq. Cryst.*, **143**, 131 (1987).
5. S. Risser, S. Klemm, D. W. Allender and Michael A. Lee, *Mol. Cryst. Liq. Cryst.*, **150b**, 631 (1987).
6. M. J. Weber, D. Milam and W. L. Smith, *Opt. Eng.*, **17**, 463 (1978).
7. S. R. Friberg and P. W. Smith, *IEEE J. Quantum Electron.*, QE-23, 2089 (1987).
8. P. A. Madden, F. C. Saunders and A. M. Scott, *IEEE J. Quantum Electron.*, QE-22, 1287 (1986).
9. W. E. Williams, M. J. Soileau and E. W. Van Stryland, *Opt. Comm.*, **50**, 256 (1984).
10. H. J. Yuan, L. Li and P. Palffy-Muhoray (to be published).
11. Preliminary results were reported by H. J. Yuan, L. Li and P. Palffy-Muhoray, *SPIE Proc.*, 1307 (Orlando, 1990).
12. E. Santamato, G. Abbate and P. Maddalena, *Phys. Rev.*, A **36**, 2389 (1987).
13. P. Palffy-Muhoray, in *Liquid Crystals—Applications and Uses*, Ed. B. Bahadur Vol. 1. (World Scientific, Singapore, 1990).