VOLUME 93, NUMBER 11 PHYSICAL REVIEW LETTERS week ending 10 SEPTEMBER 2004

Nonlinear Refraction in Photoinduced Isotropic State of Liquid Crystalline Azobenzenes

N. Tabiryan, U. Hrozhyk, and S. Serak

Beam Engineering for Advanced Measurements Company, 686 Formosa Avenue, Winter Park, Florida 32789, USA

(Received 22 March 2004; published 9 September 2004)

The photoinduced isotropic state of liquid crystalline azobenzenes exhibits one of the strongest nonlinear optical refraction known for isotropic materials. The optical nonlinearity of these materials is large in a wide band of the visible spectrum and is accompanied with high, over 90%, transmission for red wavelengths.

DOI: 10.1103/PhysRevLett.93.113901 PACS numbers: 42.70.Df, 42.70.Gi, 42.65.Jx, 61.30.–v

Liquid crystals (LCs) provide unprecedented capabilities for modulating optical radiation (see, e.g., [1,2]) and are characterized by ultrahigh constants of nonlinear refraction, $n_2 \sim 10^{-4} - 1\ \mathrm{cm}^2/\mathrm{W}$ and $\delta n \sim 0.3$ ($\delta n = n_2 I_0$ is the change in the effective refractive index of LC induced by a light beam of peak intensity I_0) [3].

These large constants of nonlinear refraction result from optically induced collective reorientation of LC molecules. The torque acting on the LC orientation is present for a particular component of light beam polarization and requires special geometrical conditions for its realization [4]. Isotropic materials, including the isotropic phase of LCs, are free from these disadvantages; however, no fundamental processes of light-matter interaction have been known so far that would make isotropic materials comparable to LC mesophases in their light modulating capability [5–7].

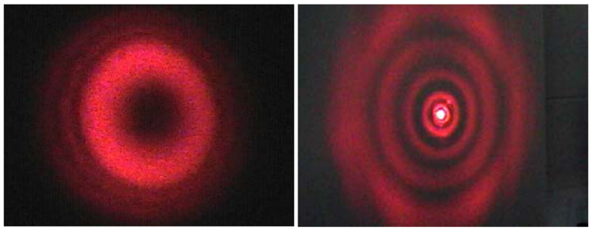
Critical enhancement of the optically induced Kerr effect in the vicinity of isotropic-nematic phase transition places LCs among the materials with the highest optical nonlinearity even in the isotropic phase [8–10], which, however, is still about 8 orders of magnitude smaller compared to mesophases [9–11].

In the present Letter, we show that the constants of nonlinear refraction of photoinduced isotropic (PI) phase of azobenzene LCs are comparable to that of LC mesophases. Typical patterns of self-phase modulation of a He-Ne laser beam remarkable by the fact that they are obtained in 10–20 μm isotropic materials at 10 μW–1 mW power levels of radiation are shown in Fig. 1.

The basic process of obtaining the PI state of an azo LC consists in subjecting it to radiation in the blue-green region of wavelengths; *trans-cis* photoisomerization of azobenzene molecules reduces the order parameter of azo LCs thus driving them into their isotropic phase upon accumulation of a critical concentration of the nonmesogenic *cis* form of azo molecules [12–14]. In thermally induced isotropic (TI) phase, azo LCs consist of *trans* molecules only whereas the PI state of azo LCs is a mixture of *trans* with substantial concentration of the *cis* form of molecules. With decreasing temperature, the TI phase relaxes back to the mesophase following temperature relaxation process (typically, within milliseconds). The PI state of azo LCs can last over tens of hours since dark relaxation is governed by the lifetime of *cis* isomers at fixed temperature.

Figure 2 demonstrates this circumstance for two azo LCs: 8721 and 1007 which are mixtures of compounds of homologous series of asymmetrically 4, 4′-disubstituted azobenzenes (BEAM Co.). The phase transition temperatures for these materials are monotropic smectic $A <$ 28 °C $<$ nematic $<$ 73.5 °C $<$ isotropic for azo LC 8721; and crystal $<$ 17.5 °C $<$ nematic $<$ 52 °C $<$ isotropic for azo LC 1007.

The lifetime of cis-isomers for azo LCs under discussion were measured in the following procedure. The LC-cells were illuminated by a UV radiation ($\lambda = 365$ nm), and the temperature of the nematic-isotropic phase transition T_c was determined at several time intervals. UV exposure decreases T_c by over 50° and 30° for LC 8721 and 1007, respectively. The material was kept at room temperature in-between measurements. T_c was determined in a quick procedure of heating (or cooling) the material over the phase transition point. Since the heating procedure lasted one to 5 min (depending on required temperature increase) and was therefore much shorter



(a) (b)

FIG. 1 (color online). Self-phase modulation patterns in the photoinduced isotropic state of an azo LC for a laser beam of $\lambda = 633$ nm wavelength: (a) 20 μm-thick azo LC 1205 in a beam of 42 μW power focused by a lens of 35 mm focal length; (b) 10 μm-thick azo LC in a beam of 1.75 mW power focused by a lens of 75 mm focal length.

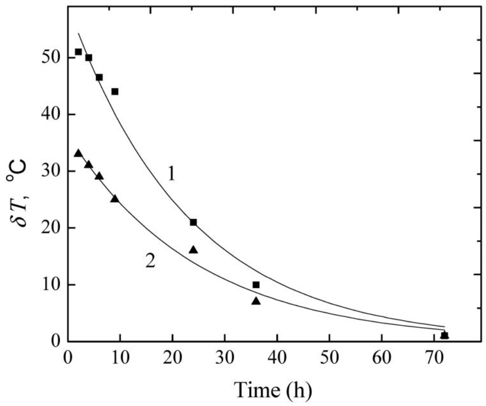


FIG. 2. Spontaneous (dark) relaxation dynamics of photoinduced isotropic phases of 4, 4′-disubstituted azobenzene compositions characterized by the change in the isotropic-nematic phase transition temperature, $\delta T = T_{iso}^{trans} - T_{iso}^{cis}$, due to changing concentration of *cis* isomers: (1) azo LC 8721; (2) azo LC 1007.

than the many hours of relaxation time, it was reasonable to assume that the measurement process did not distort appreciably the obtained data points. The fact that a single exponential function fits well the experimental data points for each LC is in favor of this argument.

Such a metastability results from a small energy barrier ΔU that separates the excited *cis* form of azo molecules from thermodynamically stable *trans* form [15]. Thus even a low power radiation can be expected to be highly efficient in inducing *cis-to-trans* photoisomerization resulting in high optical nonlinearity due to variation of the refractive index of the material with varying ratio of *trans/cis* isomers.

In our experiments, a 20 μm-thick layer of azo LC 1205 (crystal $< 8\,^{\circ}\mathrm{C} <$ nematic $< 59\,^{\circ}\mathrm{C} <$ isotropic) was transformed into its isotropic state by exposing it to UV irradiation of 365 nm wavelength for different periods of time. The transmission of the material was about 92% at $\lambda = 633$ nm and 46% for $\lambda = 532$ nm before UV exposure. The index of nonlinear refraction was measured both for the red and green wavelengths using the well-known *z*-scan technique [16].

The constant of nonlinear refraction n_2, as seen in Fig. 3(a), increases with increasing UV-exposure time, hence with increasing *cis* content of the material. "Gigantic" values of n_2 exceeding 10^{-4} cm^2/W and 10^{-2} cm^2/W for the wavelengths $\lambda = 633$ nm and $\lambda = 532$ nm, correspondingly, were obtained with UV-exposure time of about 30 min. One of the unusual features of the mechanism of the optical nonlinearity under discussion was the increase of n_2 with increasing radius of the laser beam acting on the material [Fig. 3(b)]. The response time decreases with increasing power of radiation reaching $\tau \sim 100$ ms for $P = 250$ μW at $\lambda = 633$ nm and for $P = 3$ μW at $\lambda = 532$ nm (Fig. 4).

The discussion below allows gaining an insight into the mechanism of light interaction with the PI state of azo LCs. Let us proceed from the following expression for the dielectric constant ε of the mixture of *trans* and *cis* isomers [17]: $\varepsilon = \varepsilon_{cis}N_{cis} + \varepsilon_{trans}N_{trans}$, where N_{cis} and N_{trans} are the fractions of the *cis* and *trans* isomers; ε_{cis} and ε_{trans} are the respective dielectric constants at the optical frequency.

Changing concentration of *trans* and *cis* isomers due to photoisomerization may lead to changes in the refractive index of the mixture due to concentration dependence of both the dielectric properties of the LC as well as its order parameter Q:

$$\begin{aligned}\delta\varepsilon &= \varepsilon_{trans}\delta N_{trans} + \varepsilon_{cis}\delta N_{cis} + \frac{\partial\varepsilon}{\partial Q}\delta Q(N_{cis})\\ &= (\varepsilon_{cis} - \varepsilon_{trans})\delta N_{cis} + \frac{\partial\varepsilon}{\partial Q}\delta Q(N_{cis}),\end{aligned} \tag{1}$$

where we took into account that $\delta N_{trans}(\mathbf{r}) = -\delta N_{cis}(\mathbf{r})$.

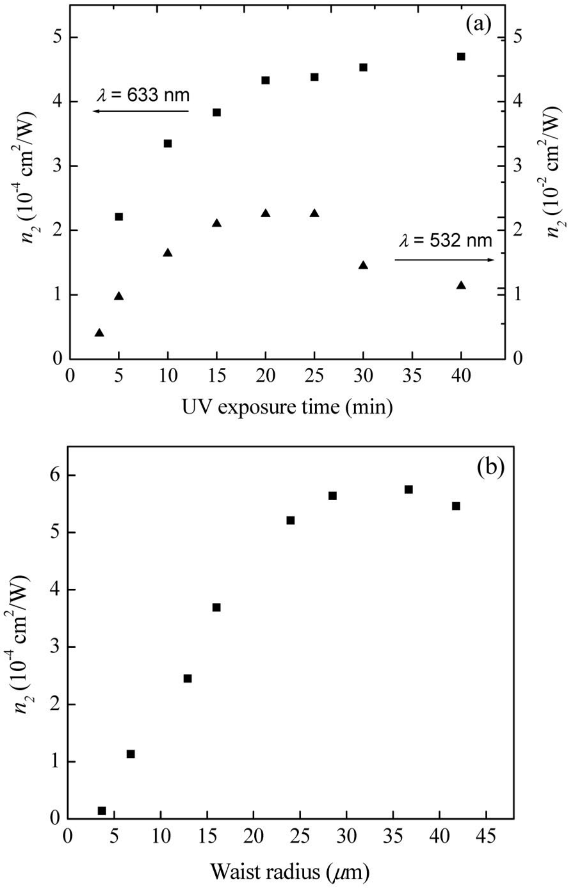


FIG. 3. The constant of nonlinear refraction of azo LC 1205 as a function of (a) the UV-exposure time at the wavelengths $\lambda = 633$ and $\lambda = 532$ nm, and (b) the waist radius of a red laser beam. The power of the laser beam in these measurements was 20 μW and 280 nW for the wavelengths $\lambda = 633$ nm and $\lambda = 532$ nm, correspondingly.

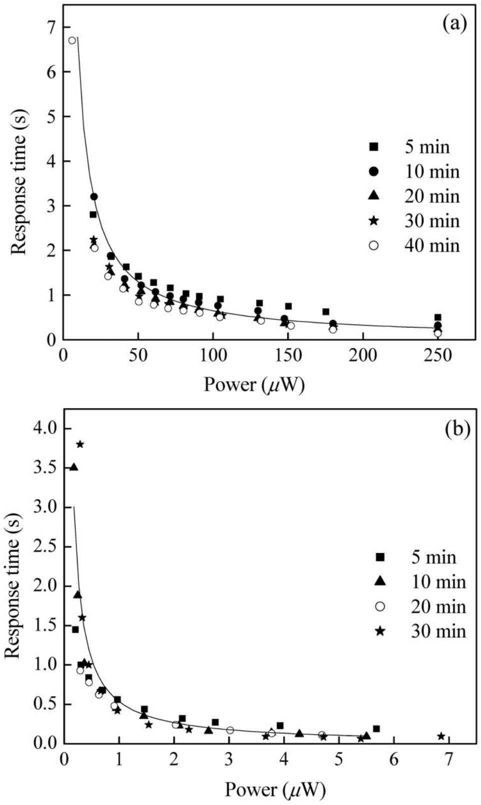


FIG. 4. The response time vs laser beam power for (a) $\lambda = 633$ nm and (b) $\lambda = 532$ nm and different UV-exposure times.

The concentration of *cis* isomers in UV-exposed materials is considerably larger than the critical concentration of photoinduced nematic-isotorpic phase transition. Thus, the order parameter of LC can be considered to be practically zero and to stay unaffected by small changes of the concentration of *cis* molecules. Consequently, the change in the dielectric constant can be evaluated by the expression $\delta\varepsilon = (\varepsilon_{cis} - \varepsilon_{trans})\delta N_{cis}$.

The modulation of concentration of *cis* isomers due to the influence of a laser beam can be described by Eq. (2) below,

$$\frac{\partial N_{cis}}{\partial t} = -\frac{N_{cis}}{\tau_T} - \beta N_{cis} I + D\nabla^2 N_{cis}, \qquad (2)$$

which takes into account the following processes: thermal (dark) relaxation of *cis* isomers into their thermodynamically stable *trans* form characterized by the relaxation time constant τ_T; light-induced *cis-to-trans* photoisomerization proportional to the light intensity I and characterized by the constant β; and diffusion characterized by the diffusion constant D. In Eq. (2), ∇^2 is the Laplace operator.

The quantity βI determines the rate of light-induced relaxation of *cis* isomers which, even for microwatt power incident beams, proved to be much larger than the rate of thermal relaxation: $\beta I \gg 1/\tau_T$. Thus, we will simplify the discussion by omitting the term in Eq. (2) that describes the processes of dark relaxation. Taking into account also the cylindrical symmetry of the problem in a Gaussian laser beam $I(r) = I_0 \exp(-r^2/w^2)$, w is the waist radius of the beam, one can integrate Eq. (2) to yield

$$N_{cis}(r) - N_{cis}(0) = N_{cis}^0 \frac{\beta I_0 w^2}{4D}\left[\ln\left(\frac{r^2}{w^2}\right) + Ei\left(1, \frac{r^2}{w^2}\right) + \gamma\right], \qquad (3)$$

where Ei is the exponential integral function, and $\gamma = 0.577\ldots$ is the Euler's number.

Equation (3) shows that the concentration of *cis* molecules reaches minimum at the axis of the beam and increases with distance proportional to r^2. Assuming that the concentration of *cis* isomers does not change appreciably at the periphery of the cell, far from the region of localization of the laser beam influence, we can evaluate the modulation of *cis* molecules on the axis of the beam simply as $\delta N_{cis} = N_{cis}^0 - N_{cis}(\tau \gg t_P) = N_{cis}(r = 0)$–$N_{cis}(r = R)$, where R is the size of the LC cell and τ_P is the characteristic time scale of photoinduced processes, $\tau_P = 1/\beta I$. Thus

$$\delta N_{cis} = N_{cis}^0 \frac{\beta I_0 w^2}{4D}\left[\ln\left(\frac{R^2}{w^2}\right) + Ei\left(1, \frac{R^2}{w^2}\right) + \gamma\right]. \qquad (4)$$

The size of the laser beam in the focus where the LC cell is positioned in our experiments is of the order of $w = 10$ μm, which is much smaller than the size of the cell $R = 1$ cm. The uncertainty of choosing a value for R is not substantial since the dependence of δN_{cis} on R is of logarithmic nature; the difference between the values of δN_{cis} for $R/w = 1000$ and $R/w = 100\,000$ is less than a factor of 1.7.

Thus, the constant of nonlinear refraction n_2 defined by the expression $\delta n = n_2 I_0$, can be evaluated to be of the order of

$$n_2 = (n_{trans} - n_{cis}) N_{cis}^0 \frac{\beta w^2}{D}. \qquad (5)$$

In obtaining Eq. (5), we took into account the relationship $\delta n = \delta\varepsilon/2n$. The Eq. (5) for the constant of nonlinear refraction conveys the major features specific to the mechanism of optical nonlinearity under discussion: n_2 increases with increasing concentration of *cis* isomers (increasing UV-exposure time) and with increasing beam waist radius [Figs. 3(a) and 3(b)]. Note that the obtained expression does not take into account changes in the absorption spectra of the materials that accompany trans-cis photoisomerization [14]. The effect of such an increase for large UV-exposure times is revealed in decreasing constant of nonlinear refraction for the green wavelength seen in Fig. 3(a).

In order to make numerical evaluation of n_2, we independently measured the refractive indices n_{trans} and n_{cis} of the LC in *trans* and in *cis* states, the constant β, and the diffusion coefficient D of *cis* isomers. The refractive index of the *trans* phase was obtained by measuring the principal values of the refractive indices of the nematic phase of LC with the *trans* state of molecules at the wavelength $\lambda = 633$ nm and at room temperature: $n_{\|} = 1.796$, $n_{\perp} = 1.589$. Thus, $n_{trans} = (n_{\|} + 2n_{\perp})/3 = 1.658$. Measurement of the refractive index in the TI phase of the azo LC could also provide the value of n_{trans}, however, at an elevated temperature. The refractive index of the *cis* state of molecules was obtained to be equal to $n_{cis} = 1.631$ after exposing the material to UV radiation for three hours and verifying that the visible spectrum of the material is no more changing with the illumination time. By that we assume that the concentration of *cis* molecules reaches values close to 100% due to the slowness of thermal relaxation processes compared to photoinduced transformations [18].

The diffusion constant, $D = 3.7 \times 10^{-7}$ cm^2/s, was measured directly by registering the dynamics of recording of diffraction gratings in the material using interfering laser beams ($\lambda = 532$ nm) [19].

Since β determines the response time of the photoinduced processes, $\tau_P = 1/\beta I$, it was measured by fitting the results of a series of experiments where the response time was measured as a function of the intensity of the laser beam (Fig. 4). The value of β was more than 1 order of magnitude larger for a green laser beam ($\lambda = 532$ nm) compared to a red beam ($\lambda = 633$ nm): $\beta_{\mathrm{Green}} = 1.92$ cm^2/J and $\beta_{\mathrm{Red}} = 0.044$ cm^2/J.

The beam waist radius was measured directly using the peak-to-valley distance of the z-scan curves for the lens of $f = 35$ mm focal length: $w = 7.8$ μm for $\lambda = 633$ nm, and $w = 5.1$ μm for $\lambda = 532$ nm [20]. Thus, the evaluated magnitude of n_2 is of the order of $n_2 \sim 10^{-4}$ cm^2/W for the red wavelength, and $n_2 \sim 10^{-2}$ cm^2/W for the green wavelength in good accord with the experimentally measured values.

Thus, we presented here the basic features of optically controlled transformations in the thermodynamically metastable state of azo LC materials. UV-exposure time and the spatial localization of the laser beam turned to be key factors that have an influence on the ultimate magnitude of the constant of nonlinear refraction. The principles underlying this nonlinearity may be generalized to lead to a new class of highly transparent material systems that possess large optical nonlinearity in an isotropic state. Many hours of lifetime of the PI phase of azo LCs used in our experiments makes them highly practical for applications.

The authors are grateful to T. Bunning for initiating and encouraging these studies. Extensive discussions with D. Evans, I. C. Khoo, A. Klosterman, and M. Saleh provided vital feedback in the course of the work supported by Contract No. F33615-03-C-5444.

[1] *Novel Optical Materials and Applications*, edited by I.-C. Khoo, F. Simoni, and C. Umeton (John Wiley & Sons, New York, 1997).
[2] *Liquid Crystals for Optics*, edited by S. D. Jacobs, SPIE Milestone Series Vol. MS 46 (SPIE–International Society for Optical Engineering, Bellingham, WA, 1992).
[3] I.-C. Khoo *et al.*, Mol. Cryst. Liq. Cryst. **358**, 1 (2001).
[4] N. V. Tabiryan, B. Ya. Zel'dovich, and A. V. Sukhov, Mol. Cryst. Liq. Cryst. **136**, 1 (1986).
[5] K. Clays, S. V. Elshocht, and A. Persoons, Opt. Lett. **25**, 1391 (2000).
[6] B. Jean-Jean *et al.*, Phys. Rev. A **39**, 5268 (1989).
[7] G. T. Reed, Nature (London) **427**, 595 (2004).
[8] G. K. L. Wong, and Y. R. Shen, Phys. Rev. Lett. **30**, 895 (1973).
[9] R. Muenster, M. Jarasch, X. Zhuang, and Y. R. Shen, Phys. Rev. Lett. **78**, 42 (1997).
[10] D. Paparo *et al.*, Phys. Rev. Lett. **78**, 38 (1997).
[11] T. V. Truong, L. Xu, and Y. R. Shen, Phys. Rev. Lett. **90**, 193902 (2003).
[12] T. Ikeda, and O. Tsutsumi, Science **268**, 1873 (1995).
[13] V. Grozhik *et al.*, Mol. Cryst. Liq. Cryst. **320**, 433 (1998).
[14] N. Tabiryan, S. Serak, and V. Grozhik, J. Opt. Soc. Am. B **20**, 538 (2003).
[15] P. M. Hogan, A. R. Tajbakhsh, and E. M. Terentjev, Phys. Rev. E **65**, 041720 (2002).
[16] M. Sheik-Bahae *et al.*, Proc. SPIE Int. Soc. Opt. Eng. **1148**, 41 (1989).
[17] L. D. Landau, E. M. Lifshiz, and L. P. Pitaevskii, *Electrodynamics of Continuous Media* (Pergamon Press, Oxford, 1984).
[18] H. Rau, in *Photochromism: Molecules and Systems*, edited by H. Dürr and H. Bouas-Laurent (Elsevier, Amsterdam, 1990).
[19] H. J. Eichler, P. Günter, and D. W. Pohl, *Laser-Induced Dynamic Gratings* (Springer-Verlag, Berlin, 1986).
[20] N. V. Tabiryan, V. Jonnalagadda, M. Mora, and S. R. Nersisyan, Proc. SPIE Int. Soc. Opt. Eng. **4932**, 656 (2003).