Braz J Phys (2012) 42:355–359
DOI 10.1007/s13538-012-0107-9

SBF SOCIEDADE BRASILEIRA DE FÍSICA

CONDENSED MATTER

Enhancement of the Nonlinear Optical Absorption of the E7 Liquid Crystal at the Nematic–Isotropic Transition

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Received: 17 April 2012 / Published online: 14 November 2012

Abstract We present an experimental study of the nonlinear optical absorption of the eutectic mixture E7 at the nematic–isotropic phase transition by the Z-scan technique, under continuous-wave excitation at 532 nm. In the nematic region, the effective nonlinear optical coefficient β, which vanishes in the isotropic phase, is negative for the extraordinary beam and positive for an ordinary beam. The parameter S_{NL}, whose definition in terms of the nonlinear absorption coefficient follows the definition of the optical-order parameter in terms of the linear dichroic ratio, behaves like an order parameter with critical exponent 0.22 ± 0.05, in good agreement with the tricritical hypothesis for the nematic–isotropic transition.

Keywords Liquid crystal · Z-Scan · Phase transition

1 Introduction

After numerous theoretical and experimental studies, the nematic–isotropic (N-I) transition in liquid crystals still poses certain controversies and reveals new, interesting facets. For example, although geometrical arguments lead to the conclusion that the nematic⇆isotropic transition is of first order [1], measurements of enthalpy and volume changes at the transition, when compared with experimental results at melting, fully support the scenario of a weak first-order phase transition with strong fluctuations, which may lead to an effective critical behavior and an effective critical exponent [2–6]. Although there are no systematic or conclusive studies on this thermodynamic behavior, a few experimental studies point to the occurrence of tricritical, rather than just critical, effective exponents [7, 8].

Curiously, there is scarce literature on the behavior of the nonlinear optical response of liquid crystals at this phase transition. Recently, we reported on the divergence of the nonlinear optical birefringence Δn_2 in the nematic side of the N-I transition of the thermotropic liquid crystal E7, measured with a continuous-wave (cw) laser at $\lambda = 532$ nm [9]. The critical exponent seems to corroborate the tricritical character of this phase transition. Previously, Li et al. [10] had shown that the optical absorption of a pure sample of 5CB under ms pulses of a $\lambda = 514$-nm cw laser is linear at the nematic side of the N-I transition, i.e., $(\beta_{\parallel,\perp} = 0)$. Although multiphoton absorption processes are usually observed under intense pulsed laser irradiation, there are many reports on the observation of two-photon absorption under irradiation of middle- or low-power cw lasers in highly absorbing dye-doped liquid crystal, as a consequence of a two-photon absorption process [11–14] or due to reorientation of the nematic director [15].

The main purpose of this paper is to report on the observation of nonlinear optical absorption in a planar-oriented sample of the thermotropic liquid crystal E7

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and its enhancement in the neighborhood of the N-I phase transition, under irradiation by a middle-power $\lambda = 532$-nm cw laser. In Section 2, we describe the Z-scan technique, which is used for measuring the nonlinear optical absorption coefficient β. In Section 3, we present the experimental data and discuss the possible mechanisms for the nonlinear absorption observed in our case. Finally, in Section 4, we sum up the conclusions.

2 Experimental Details

The abbreviation E7 stands for a liquid crystal mixture consisting of several types of cyanobiphenyls, mainly 5CB and, in less quantity, triphenyl. It exhibits a nematic phase in the temperature interval from -10 °C up to the transition to the isotropic phase at $T_{\rm NI} = 58$ °C. In this experiment, we used commercial E7 (Merck), without additional purification. The samples were conditioned in a parallel glass cell, separated by 20-μm-thick spacers. The glass plates were coated with polyvinyl alcohol (PVA) and buffed for homogeneous planar alignment of the liquid crystal. The sample was placed in a hot stage (INSTEC) on a computer-controlled translational stage (Newport). The temperature of the sample was controlled with a precision of 0.2 °C between 20 °C and $T_{\rm NI}$.

The Z-scan technique exploits the formation of a lens in a medium by a tightly focused Gaussian-profile laser beam to measure the transmitted intensity of the sample as a function of position along the direction of propagation of the beam (the z-axis) [16]. The magnitude and sign of the nonlinear absorption β can be obtained by means of the open-aperture configuration of the Z-scan technique. A sketch of the experimental setup is shown in Fig. 1. In this setup, the totality of the power at the exit of the sample is measured. Our experimental setup used a cw laser ($\lambda = 532$ nm, Verdi, Coherent), and the power of the laser varied from approximately 30 mW close to the N-I transition up to 100 mW far from the transition. The beam waist at focus was about 26 μm, and an oscilloscope (Tektronics, Standfor) was used for data acquisition. The polarization (**E**) of the laser beam was set either parallel or perpendicular to the nematic director (**n**). For these geometrical configurations, the optical torque is null, i.e., director reorientation is not expected.

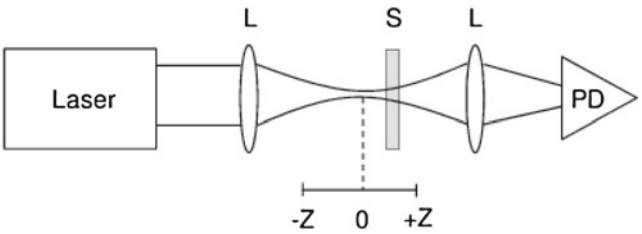

Fig. 1 Sketch of the Z-scan apparatus in the open-aperture configuration: The lens, sample, and photodetector are labeled L, S, and PD, respectively

In systems exhibiting nonlinear absorption, for sufficiently thin samples, and to first-order corrections in the irradiance, the normalized transmittance in the open-aperture (Γ_o) configuration of the Z-scan technique is given by [17]

$$\Gamma_o = 1 - \frac{\Theta}{\left[1 + \left(\frac{z}{z_0}\right)^2\right]}. \tag{1}$$

Here, z_0 is the Rayleigh range of the beam, $\Theta = \beta I_0 L_{ef}/2$, where $L_{ef} = \left[1 - \exp\left(-\alpha_0 L\right)\right]/\alpha_0$ is the effective thickness of the sample, β is the nonlinear optical absorption coefficient, and I_0 is the irradiance at the waist of the laser beam. Although (1) is derived assuming a two-photon absorption process, it can be applied to fit the open-aperture Z-scan curve in any case, assigning to β the meaning of an effective nonlinear optical absorption coefficient.

3 Experimental Results and Discussions

In Fig. 2a, b, we show typical open-aperture Z-scan traces, obtained at $T = 35$ °C (nematic phase) for the two relative orientations of the nematic director and beam polarization, $\mathbf{n} \parallel \mathbf{E}$ and $\mathbf{n} \perp \mathbf{E}$, respectively. The error bars correspond to the standard error of the mean for at least ten measurements in each z-position. As can be seen, for $\mathbf{n} \parallel \mathbf{E}$ the transmittance of the sample increases when approaching the focal point, showing that the nonlinear optical absorption is negative ($\beta < 0$). For $\mathbf{n} \perp \mathbf{E}$, the transmittance decreases as the focal point is approached, which shows that the nonlinear optical absorption is positive ($\beta > 0$). Within the sensitivity of our experimental setup, no nonlinear optical absorption was observed in the isotropic phase ($\beta_{\rm iso} \simeq 0$). We have also checked the nonlinear optical response of the empty glass cell with PVA coating: for the intensities in our experiment, the cell does not show any nonlinear optical response.

In Fig. 3, we show β in the nematic region and in the isotropic phase, for polarization of the incident beam parallel and perpendicular to the director. For each relative orientation of the director and the optical field, the β values resulting from the fittings were rather independent of the laser beam power. For $\mathbf{n} \parallel \mathbf{E}$, the sample displays $\beta < 0$ and, for $\mathbf{n} \perp \mathbf{E}$, the sample dis-

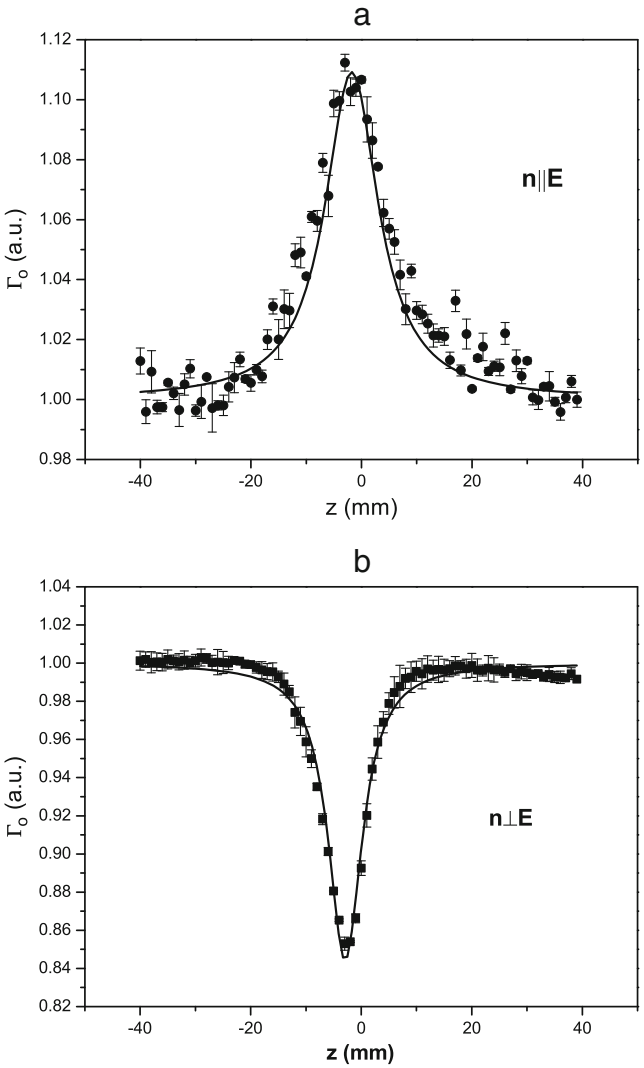

Fig. 2 Typical Z-scan curves in open-aperture configuration at $T = 35$ °C: **a** $\mathbf{n} \parallel \mathbf{E}$ for incident power $P = 3$ mW and **b** $\mathbf{n} \perp \mathbf{E}$ for incident power $P = 40$ mW. *Solid lines* are theoretical fits using (1)

plays $\beta > 0$ over the entire nematic region, i.e., $\beta_{\parallel} < 0$ and $\beta_{\perp} > 0$, with increasing absolute values as the N-I transition temperature is approached from below. It is also clear that the magnitude of $\beta_{\parallel}$ is bigger than that of $\beta_{\perp}$. The fitting of the experimental data with (1) gives an effective nonlinear absorption coefficient β for the nonlinear optical process observed in the E7 liquid crystal of about -10^{-2} and 10^{-3} m/W, for $\beta_{\parallel}$ and $\beta_{\perp}$, respectively.

The origin of the nonlinear optical response in the nematic phase and its enhancement when approaching the N-I transition is not clear yet. The optical absorption of liquid crystals containing saturated and unsaturated phenyl is relevant in the UV spectral region, involving $\pi \rightarrow \pi^*$ electronic transitions, which have negligible absorption in the visible range [18]. As shown by the pioneering work of Chatelain [1, 19], the linear scattering due to fluctuations of the nematic director is strong for small scattering wavevector **q** and weakly dependent on temperature. Measurements of the scattering in a E7 liquid crystal sample showed an approximately constant scattering coefficient over almost all of the nematic range, with a light increase in a temperature interval of about 5 °C in the vicinity of T_{NI} [20]. Linear scattering makes the transmitted power independent of the sample position, leading to a flat response in the normalized transmittance curve in an open-aperture Z-scan measurement.

Another source of many nonresonant stimulated scattering processes, such as stimulated Raman scattering (SRS), stimulated Brillouin scattering (SBS), stimulated orientational scattering (SOS), and stimulated thermal scattering (STS), has been observed in thermotropic liquid crystals under appropriate conditions [21]. Usually, the SRS and SBS processes require long interaction paths (of the order of 1 cm) and very strong lasers [22, 23]. In the case of SOS, the forward orthogonal polarized beam generated by stimulated scattering grows like $I(z) = I_0^{\mathrm{noise}} e^{(G_o I_e - \alpha)z}$, where G_o is the intensity gain factor and α is an effective loss coefficient combining linear absorption and scattering processes. For a 200-μm-thick sample of E7 liquid crystal, the threshold intensity is $\sim 10^3$ W/cm^2[24], comparable to the intensity in our setup for $\mathbf{n} \perp \mathbf{E}$. For a 20-μm-thick sample, therefore, the threshold intensity for an SOS

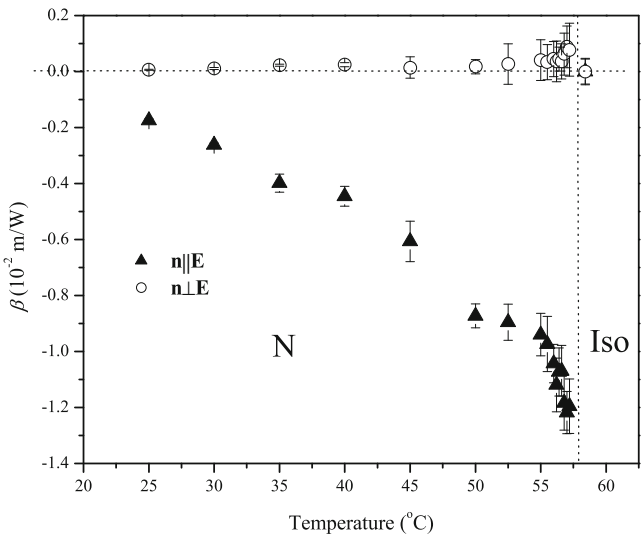

Fig. 3 Nonlinear optical absorption coefficient β as a function of temperature in the nematic range, for both configurations of the nematic director relative to the beam polarization. The *black triangles* and *circles* correspond to $\mathbf{n} \parallel \mathbf{E}$ and $\mathbf{n} \perp \mathbf{E}$, respectively. The *dotted vertical line* indicates the clearing temperature

process is 1 order of magnitude higher. Finally, a highly absorbing medium is necessary to trigger a STS process. In a 150-μm planar-aligned dye-doped sample of 5CB, a STS process is observed when the interaction length is about 1 mm, with oblique incidence and an incident laser power ($\lambda = 514.5$ nm) of ~ 400 mW [25]. Any nonlinear scattering in an open-aperture Z-scan experiment should yield results resembling nonlinear absorption with $\beta > 0$, because along with the dominant forward beam, this process originates a small amount of backscattered radiation for both incident lasers I_0 and I_e ($\mathbf{n} \perp \mathbf{E}$ and $\mathbf{n} \parallel \mathbf{E}$, respectively). Studies of the nonlinear scattering show that it is also nearly temperature independent [26] and inversely proportional to the square of the beam wavelength, i.e., proportional to λ^{-2} [27]. A similar study of a planar-oriented sample of 5CB [10], using the $\lambda = 514.5$-nm line of an argon laser at comparable power, showed no nonlinear optical absorption, either in the nematic phase or close to the N-I transition.

Although the wavelength in our setup lies close to the maximum absorbance of the E7 liquid crystal, two-photon absorption can be ruled out in view of the low laser power. Two-photon absorption with low-power lasers has only been observed in highly absorbing dye-doped liquid crystals, which is not the case here. A more likely source of nonlinear absorption is laser-induced reorientation of absorbing species as seen in a 50-μm-thick homeotropically oriented sample of dye-doped 5CB [15].

An optical field exerts an optical torque proportional to the dieletric anisotropy $\Delta\varepsilon$ [27]. From the balance between the elastic torque and the optical torque, under hard-boundary and small director-reorientation conditions, it can be shown that the maximum reorientation $\theta_{\max}$ for the extraordinary ray is proportional to $\Delta\varepsilon/K_1$, where K_1 is the elastic constant for splay distortion. Since $\Delta\varepsilon \propto S$ and $K_1 \propto S^2$, the maximum reorientation in the nematic phase satisfies $\theta_{\max} \propto S^{-1}$. It follows that $\theta_{\max}$ increases as T approaches T_{NI}. In the case of the ordinary ray, the threshold intensity for director reorientation is proportional do $K_3/\Delta\varepsilon \propto S$ where K_3 is the elastic constant for bend distortion. Hence, the nonlinear absorption observed in the E7 liquid crystal below T_{NI} could be due to the reorientation of absorbing species present in the liquid crystalline matrix along with a reduction of ordering associated with heating that leads to absorption depletion, a reduction expected to be more effective in the case of the extraordinary ray.

In the nematic phase, given the dichroic ratio $R = \alpha_{\parallel}/\alpha_{\perp}$ of the sample, i.e., the ratio between the linear absorbances of radiation with the polarization parallel and perpendicular to director, an optical order parameter $S = (R-1)/(R+2)$ can be defined, provided the transition moment is parallel to the molecular axis [29]. By analogy, we can define a nonlinear dichroic ratio $R_{\mathrm{NL}} = |\beta_{\parallel}/\beta_{\perp}|$ and the parameter $S_{\mathrm{NL}} = (R_{\mathrm{NL}} - 1)/(R_{\mathrm{NL}} + 2)$. Figure 4 displays S_{NL} as a function of T. Clearly, S_{NL} vanishes at the N-I transition and is equals to zero in the isotropic phase.

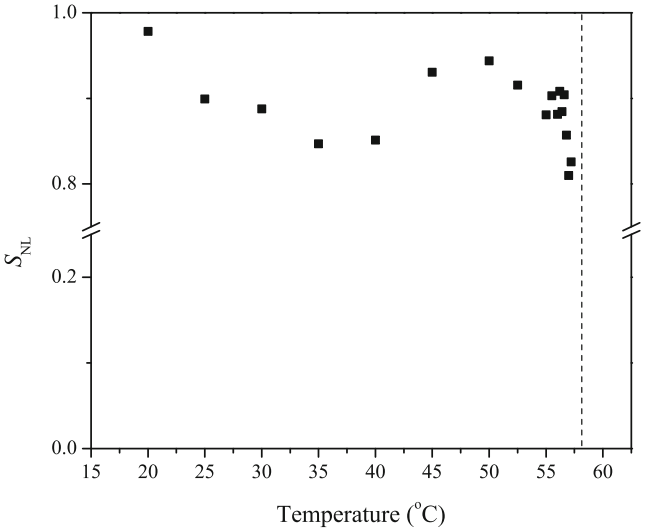

Fig. 4 Coefficient S_{NL} as a function of temperature. The *dashed line* indicates the clearing temperature

Figure 5 displays S_{NL} as a function of the reduced temperature in log scales. Also, shown is a linear fit, close the transition temperature, under the assumption that $S_{\mathrm{NL}} \propto \left(1 - \frac{T}{T^{\dagger}}\right)^{\phi}$, where ϕ is the critical exponent and $T^{\dagger}$ is the temperature of the effective or virtual

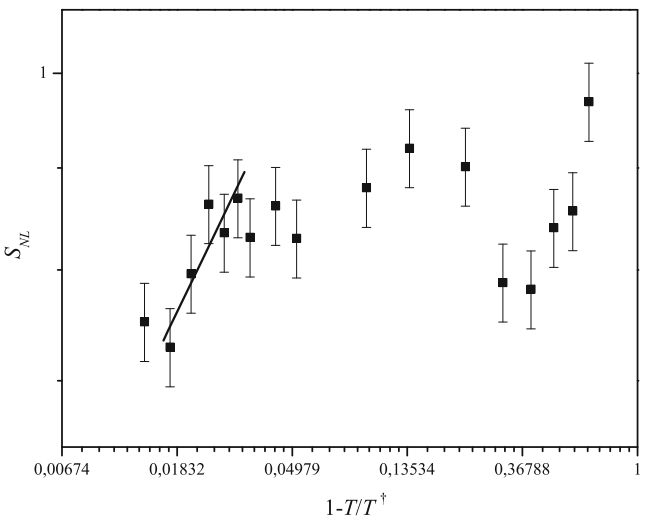

Fig. 5 Log–log plot of the absolute value of S_{NL} as a function of the reduced temperature. The *solid line* represents a typical linear fit to the data closest to the transition temperature

second-order transition seen from below T_{NI}, which is different from the spinodal temperature T^{**}, the absolute limit of the nematic phase upon heating. For a homologous series of liquid crystals, it has been shown that $T^{\dagger} - T_{NI} \simeq 0.2\,^{\circ}\mathrm{C}$ [28], which is of the order of the experimental uncertainty in our measurements. With this being considered and attention paid to the sensitivity of the fitting to the choice of $T^{\dagger}$, we proceeded to vary $T^{\dagger}$ between 58.1 and 58.4 °C. The resulting average critical exponent ϕ was 0.22 ± 0.05, close to the accepted value for the order-parameter critical exponent under the assumption that the N-I transition has a tricritical character.

4 Conclusions

We have investigated the nonlinear optical absorption of an homogeneously oriented sample of liquid crystal E7 in the nematic phase and close to the N-I transition under continuous 532-nm wave excitation. The effective nonlinear optical absorption exhibits opposite character for the two geometrical configurations of the nematic director relative to the polarization of the incident beam, i.e., $\beta_{||} < 0$ and $\beta_{\perp} > 0$. We tentatively ascribe this behavior to the combination of an optical-field-induced reorientation of the nematic director and heating of the sample due to absorbing species in the liquid crystalline matrix. Interestingly, the coefficient S_{NL}, defined from the β values in an analogy to the optical order parameter S defined from the linear optical-absorption coefficients, satisfies an order-parameter power law with critical exponent 0.22 ± 0.05, which points to a N-I transition with a tricritical character.

Acknowledgements This work had received the financial support of the Brazilian agencies CAPES, CNPq, FAPESP, Fundação Araucária, and the Secretaria de Ciência, Tecnologia e Ensino Superior do Governo do Paraná, and this was conducted as part of the research program of the Instituto Nacional de Ciência e Tecnologia de Fluidos Complexos.

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