One- and biphotonic reorientational nonlinearities in dye-doped nematic and cholesteric liquid crystals

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This investigation elucidates one- and biphotonic reorientational nonlinearities in dye-doped nematic liquid crystals (DDNLCs) and dye-doped cholesteric liquid crystals (DDCLCs) using the Z-scan technique. Three cases—DDNLCs stimulated by one green beam polarized linearly parallel and perpendicular to the LC director and DDCLCs stimulated by one circularly polarized green beam—are considered without and with simultaneous stimulation by one linearly polarized red beam. Green-beam-induced dye reorientation through trans-cis isomerization and red-beam-induced suppression of dye reorientation by cis-trans back isomerization are responsible for the one- and biphotonic nonlinearities, respectively. The nonlinear refractive indices obtained herein are two orders of magnitude larger than those obtained elsewhere [Fuh et al., Opt. Exp. 13, 10634 (2005)]. The induced biphotonic nonlinearities can be modulated by controlling the intensity of the red beam in different ways due to the difference among the capabilities of the red beam to suppress the reorientation of the dyes and LCs in the three cases. © 2008 American Institute of Physics. [DOI: 10.1063/1.2993751]

I. INTRODUCTION

Dye-doped liquid crystals (LCs) have received substantial interest in the recent decade in the development of optical applications owing to their high birefringence and highly flexible optical controllability via the manipulation of the interaction of LCs with the photoexcited dyes.1–6 In particular, they are known to exhibit large optical nonlinearities, which have been studied extensively,7–15 because of their potential applications to photonics, used as, for example, inexpensive nonlinear optical elements, high-speed optical switching devices, real-time coherent optical signal processors, and photorefractive holographic storage.10,11

Various approaches are employed to measure optical nonlinearity. They include nonlinear interferometry, degenerate four-wave mixing, and beam distortion measurements, known as Z-scan.12–14 Z-scan is a powerful technique and the most simple; it is based on the wave front distortion that is caused by self-focusing or defocusing. It can be used to measure the magnitude and sign of a nonlinear refractive index and/or a nonlinear absorption coefficient. Some works have examined the optical nonlinearity of the dye-doped nematic LCs (DDNLCs) using the Z-scan technique under various conditions, such as in an external field, at different temperatures and using two incident wavelengths (biphotonic method).15–18 In particular, Fuh et al.18 studied optical nonlinearity (optical Kerr effect) in the Dispersed Red 1 (DR1)-DDNLC cell using the Z-scan technique with biphotonic pumping. Such optical nonlinearity can be induced by the pumping of one focused red beam, and the induced nonlinear refractive index (n2) can be modulated by controlling the intensity of a simultaneously illuminating green beam. The obtained n2 was only as low as of the order of 10–6 cm2/W because of the strong thermal effect due to the excitation of DR1-dye. Additionally, until now, few works have investigated the optical nonlinearity that is produced in the dye-doped cholesteric LCs (DDCLCs) and experimentally compared the uses of DDNLCS and DDCLCs. Accordingly, this work elucidates one- and biphotonic nonlinearities not only in DDNLCS but also in DDCLCs using the Z-scan technique. Three cases are considered under one- and biphotonic illuminations—DDNLCs pumped by one green beam with a linear polarization parallel and perpendicular to the LC director, and DDCLCs pumped by one circularly polarized green beam—without and with simultaneous irradiation by one red beam, respectively. Experimental results demonstrate that the mechanisms by which the one- and biphotonic nonlinearities are induced in each case are, respectively, green-beam-induced dye reorientation via trans-cis isomerization and red-beam-induced suppression of dye reorientation by cis-trans back isomerization. The n2 obtained herein is of the order of 10–4 cm2/W, which is two orders of magnitude greater than that obtained in an earlier work.18 The obtained biphotonic nonlinearity can be modulated by modifying the intensity of the red beam in various ways because of the discrepancy among the capabilities of the red beam to sup-

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press the dye and the LC reorientation in the three cases.

II. EXPERIMENTS

The nematic LC, right-handed chiral dopant, and azo dye adopted in this experiment are BL009 ($n_{\parallel}=1.5266$, $\Delta n=0.2915$), CB15 and D2 (all purchased from Aldrich), respectively. The mixing ratios in two homogeneous mixtures of BL009:D2 and BL009:CB15:D2 are, respectively, 99:1 wt % and 85:14:1 wt %. The two homogeneous mixtures are both injected into the empty cells, which are fabricated by combining two indium-tin-oxide (ITO)-coated glass slides that are separated by 38-μm-thick plastic spacers, to form homogeneously aligned DDNLc and planar DDCLC cells. The ITO glass slides in these samples are precoated with polyvinyl alcohol and rubbed in the same direction. The “n” represents the director in the DDNLcs. The helical pitch of the DDCLC cell is confirmed to be ~0.93 μm using an infrared spectrometer, at which the Bragg reflection band of the DDCLC cell is far away from the visible region.

Figure 1 schematically depicts the setup for measuring one- or biphotonic nonlinearity based on DDNLc and DDCLC cells. One incident green pump beam ($E_G$), from an Ar+ laser ($\lambda_G=514.5$ nm), propagates along the $z$ axis through lens $L_1$ (focal length=20 cm) and then passes through the sample. The green beam can be focused by $L_1$ with a beam radius of ~22 μm at the focal point ($z=0$). The polarization state of the green beam can be precontrolled to be linear (parallel or perpendicular to $n$, denoted by $\parallel$ or $\perp n$) or circular. The sample can be moved back or forth along the $z$ axis in the range $|z|\leq 8$ cm. Through the sample, the transmittance of the green beam can be measured as a function of the sample position ($z$) along the $z$ axis using a photodiode ($P$) that is placed behind a diaphragm ($D$) with an aperture with a diameter of 1 mm. Another lens $L_2$ (focal length =5 cm) and a low-pass color filter are installed between the $D$ and the $P$ to collect only the green light. After the optical nonlinear effect of the sample has occurred due to self-focusing or defocusing, the incident green beam wave front can be modified by moving the sample back or forth along the $z$ axis near $z=0$, such that the detected transmittance of the beam may vary with $z$, yielding the so-called $Z$-scan curve. The nonlinear coefficient(s) can be determined from the obtained $Z$-scan curve(s). If required, one red pump beam ($E_R$) that is linearly polarized parallel to $n$, derived from a high power He–Ne laser ($\lambda_R$: 633 nm, power $\leq 35$ mW), is simultaneously focused using a removable lens $L_A$ with a large focal length of 80 cm onto the green-beam-pumped spot of each sample from its rear at an incident angle of ~3° to generate and further modulate the biphotonic nonlinearity. The diameter of the spot of the red beam at the focus is about 100 μm and fully contains the diameter of the green beam on the sample. Three cases are herein considered in investigating the one- and biphotonic nonlinearities: cases (i) and (ii) DDNLc cell pumped by $E_G\parallel n$ and $E_G\perp n$ in DDNLc and circular $E_G$ in DDCLC with fixed $I_G=33$ W/cm$^2$. The $n$, $E_G$, and $I_G$ represent, respectively, the director of the DDNLc, the optical field of the green beam, and its intensity.

III. RESULTS AND DISCUSSION

Figure 2 presents three $Z$-scan curves obtained for cases (i)–(iii) with the intensity of the green beam $I_G=33$ W/cm$^2$ at the focus ($z=0$) for studying the corresponding one-photonic nonlinearities, in which $E_R$ is preblocked. The curves through points plotted as squares ($\blacksquare$), diamonds ($\blacklozenge$), and triangles ($\blacktriangle$) represent the variations in the normalized transmittance with $z$ in cases (i), (ii), and (iii), respectively. The normalized transmittance ($T$) is defined as the ratio of the transmittance detected by $P$ when the sample is placed at $|z|\leq 8$ to that at $z$ sufficiently far from $z=0$ (say, $|z|\geq 8$ cm in Fig. 2) that no nonlinear effect occurs. Each curve in Fig. 2 has a signature of negative refractive nonlinearity, in which self-defocusing occurs, such that the prefocal maximum (peak, $T_p$) is followed by a postfocal minimum (valley, $T_v$). The figure also reveals that the induced refractive nonlinearity in cases (i) and (ii) is the strongest and the weakest, respectively. The mechanism that generates the negative refractive nonlinearity in each case involves the reorientation of the LCs, which is explained in detail as follows. D2-dyes are well known to be stable in the elongated $trans$ form in the dark. The guest–host effect causes the
trans-D2 molecules to align parallel to the long axes of the LC molecules. The probability that a D2 molecule absorbs a photon is proportional to the square of the cosine of the angle between the polarization of the pump beam and the transition dipole moment of the dye.\textsuperscript{19} The transition dipole moment of a D2 molecule is approximately parallel to its long axis. Therefore, the order $\alpha_{(i)}(=1711$ cm$^{-1})>\alpha_{(ii)}(=437$ cm$^{-1})>\alpha_{(iii)}(=304$ cm$^{-1})$ herein is reasonably obtained, where $\alpha_{(i)}$, $\alpha_{(ii)}$, and $\alpha_{(iii)}$ are the linear absorption coefficients of the green beam in cases (i), (ii), and (iii), respectively. Via the absorption process, the D2 molecules in the LC host can undergo the green-beam-induced trans-cis isomerization and tend to reorient themselves and in turn, the LCs perpendicular to the linearly and circularly polarized $E_G$, minimizing the free energy of the DDNLC and DDCLC systems, respectively, in a steady state.\textsuperscript{2,4,19} A higher linear absorption coefficient of the green beam corresponds to a stronger photoinduced LC reorientation effect. Focusing makes the intensity at the center much greater than that at the border in the Gaussian profile of the incident green beam, so an obvious gradient of LC reorientation in the pumped region of the sample may cause refractive nonlinearity. Since $\alpha_{(i)} > \alpha_{(ii)} > \alpha_{(iii)}$, the strength of the LC reorientation effect induced at the center of the pumped region follows the order case (i) > case (ii) > case (iii), yielding the experimental results shown in Fig. 2. The nonlinear refractive index $n_2$ can be determined from the normalized peak-to-valley difference ($\Delta T_{p-v} = T_p - T_v$) for each $Z$-scan curve using the following equation:\textsuperscript{14}

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} \Phi_0 (\text{for}|\Phi_0| \leq \pi),$$

where $S = 1 - \exp(-2r_G^2/w_G^2)$ is the aperture linear transmittance, $r_G$ represents the radius of the aperture of the diaphragm, $w_G$ denotes the beam radius at the diaphragm in the linear regime, and $\Phi_0$ is the on-axis phase shift at the focus. $\Phi_0$ is defined as

$$\Phi_0 = 2\pi n_0 L_{\text{eff}} \lambda_0,$$

where $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$ with $L$ as the sample thickness, $\alpha$ is the linear absorption coefficient of the green beam, and $\lambda_0$ is the wavelength of the green beam in vacuo. The on-axis change in the refractive index at the focus $\Delta n_0$ is related to the nonlinear refractive index $n_2$ according to

$$\Delta n_0 = n_2 l_0,$$

where $l_0$ is the on-axis intensity of the green beam at the focus (that is, $l_0 = I_G$). Substituting $\Delta n_0$ [in Eq. (3)] and $\Phi_0$ [in Eq. (2)] into Eq. (1), and then using the given values of $\alpha$ ($\alpha_{(i)}$, $\alpha_{(ii)}$, and $\alpha_{(iii)}$ for cases (i)–(iii), respectively), $S$ (0.0308, 0.0164, and 0.0198 for cases (i)–(iii), respectively), $\Delta T_{p-v}$ (obtained from the three cases), $L_{\text{eff}}$ (0.00058, 0.00225, and 0.00185 cm in cases (i)–(iii), respectively), $\lambda_0$ (0.514 $\mu$m), and $l_0$ (33 W/cm$^2$) into Eq. (1), yields $n_2$ as approximately $(-8.5 \pm 1.2) \times 10^{-4}$, $(-0.27 \pm 0.02) \times 10^{-4}$, and $(-1.7 \pm 0.2) \times 10^{-4}$ cm$^2$/W in cases (i)–(iii), respectively. The $n_2$ obtained in each case in this experiment is two orders of magnitude greater than those obtained elsewhere,\textsuperscript{18} where the obtained $n_2$ was as low as of

FIG. 3. Variation in peak-to-valley difference associated with normalized transmittance ($\Delta T_{p-v}$) in $Z$-scan curves with $I_G$ (6.7–33 mW/cm$^2$) in cases (i)–(iii) (curves with □, ●, and ○ dots, respectively).
of the green beam by their interaction with the reoriented dyes; therefore, the probe transmission dynamically increases. A higher intensity of the green beam corresponds to a greater amount of trans-cis isomerized dyes and, in turn, a larger angle of reorientation of the LCs, and therefore there becomes a higher transmission. Notably, these experimental data of the nonzero probe transmittances shown in Fig. 4 indicate that the lowest intensity of the green beam used (6.7 W/cm²) is higher than the Freedericksz transition threshold. A second separate experiment measures the temperature at each pumped spot (in the green pumped intensity range of 6.7–33 W/cm²) in the D2-DDNLcs or D2-DDCLCs in either case is ±0.7 °C, in which range the thermal effect can be neglected. Consequently, the experimental results obtained in these two separate experiments show that the mechanism by which the one-photonic nonlinearities are induced herein is the reorientational effect.

To measure the biphotonic nonlinearity in each case, the linear red pump beam (E_R) is turned on to simultaneously pump the cell under the illumination of E_G. Figure 5 plots the variation in the obtained n_2 with the intensity of the red beam I_R=0–83 W/cm² with fixed I_G=33 W/cm² in cases (i)–(iii) that corresponds to curves with ■, ●, and ▲-dots, respectively. This figure presents the modulabilities of the biphotonic nonlinearities in different cases by varying the intensity of the red beam. The mechanism that dominates the generation and the further modulability of the induced biphotonic nonlinearity can be attributed to the suppression of the dye reorientation by the instantaneous red-beam-induced cis-trans back isomerization, which in turn suppresses the dye and thus the LC reorientation. The suppression of reorientation can be understood in detail as follows. Azo dyes typically remain in the trans-state in the dark. The cis-isomers absorb less light in the red region, as indicated by the absorption spectra published in the authors’ earlier work. After the DDNLc or DDLC cell has been stimulated with the green beam, the dyes and thus the LCs can reorient through the trans-cis isomerization. The cis-isomers exhibit new n–π* type active transitions in the red region. With the simultaneous excitation of the red beam, the cis-dyes may promptly return to the trans-state through the cis-trans back isomerization, instantaneously suppressing the reorientation of the dyes and the LCs. The increase in the intensity of the red beam can enhance the suppression effect and thus decrease the reorientation angle of the dyes and the LCs; in turn increasing the probability of the dyes to be re-excited by the green beam and thus decreasing the transmission of the green beam. This matches the experimental results shown in Fig. 6, referring to the Z-scan curves without normalization for I_R=0, 3, 14, 28, 55, and 83 W/cm² (curves with ■, ●, ○, ●, ○, and ▲-dots, respectively) and fixing I_G=33 W/cm² in case (iii). Upon the simultaneous irradiation of the red beam, the un-normalized transmittance throughout the Z-scan curve decays. Experimental results for cases (i) and (ii) (not shown) similar to those shown in Fig. 6 for case (iii) show that the suppression effect of reorientation causes that the decay of the un-normalized transmittance is great, moderate, and small, respectively, for cases (i), (iii), and (ii) at a certain I_R due to the order α(α) > α(α) > α(α). As shown in Fig. 5, the n_2 in case (iii) increases in the low-I_R regime (<28 W/cm²), but decreases in the high-I_R regime (>28 W/cm²). According to Eqs. (1)–(3), the n_2 is proportional to the normalized ∆T_p, which is equal to the un-normalized ∆T_p / T(z=–8 cm). Because of the focus of the
green beam, the red beam with a low-$I_R$ can suppress the dye reorientation more effectively at $z=-8$ cm than at $z=-1$ cm (the position of the peak in the $Z$-scan curve), such that the decay range of the un-normalized transmittance at $z=-8$ cm is larger than that at $z=-1$ cm. These discrepancies of the suppression effects at these two sample positions and in turn the un-normalized $\Delta T_{p,e}/T(z=-8)$ cm (and thus the $n_2$) could be increased with increasing $I_R$ and maximize at $I_R=28$ W/cm$^2$. However, with the continuous increase in $I_R$, the suppression effect can gradually saturate at $z=-8$ cm but effectively increase at $z=-1$ cm, which in turn decreases the un-normalized $\Delta T_{p,e}/T(z=-8)$ cm and thus the $n_2$. Furthermore, the linear absorption coefficients of the red beam under the simultaneous irradiation of the green beam are measured to be 164, 44, and 27 cm$^{-1}$ in cases (i), (ii), and (iii), respectively. The average parallelism between the $E_R$ and the long axes of the dyes and the LCs for case (i) is much larger than that for case (iii). Therefore, the $E_R$’s capability to suppress the dye and the LC reorientations for the former is much better than that for the latter; in turn, the maxima of $n_2$ for case (i) shifts to a low $I_R$, say, 3 W/cm$^2$ (Fig. 5). Moreover, the two factors of the inherent weak green-beam-induced nonlinearity and the small red-beam-induced suppression effect due to the configuration of $E_R \perp n$ can cause that the $n_2$ be almost unchanged with increasing $I_R$ in case (iii), as shown in Fig. 5. To sum up the above explanations, the modulabilities of the biphotonic nonlinearities presented in Fig. 5 are, therefore, reasonable.

It is noted that the thermodiffusion that occurred in a binary system may induce the so-called Soret effect, which explains that the thermal-induced radial temperature gradient possibly promotes a dye concentration gradient in the sample under the illumination of the Gaussian beam. This effect is strongly dependent on some factors, such as the thickness of the sample, the viscosity of the host, and the temperature gradient of the illuminated region. In this work, the second separate experiment described in the former paragraph shows that the thermal effect is insignificant in the formation of the nonlinear effect, which implies that the temperature gradient of the illuminated region in the Gaussian beam is very small. Moreover, the strong interaction between the homogeneously aligned LCs and the dyes and the large viscosity of BL009 (~83 times of that of water at 20 °C) both suppress the thermodiffusion of the dye molecules. From the above considerations, the induced Soret effect is estimated to be negligible in this work.

IV. CONCLUSION

In summary, this work examines the one- and biphotonic nonlinearities in DDNLCs and the DDCLCs using the $Z$-scan method without and with the simultaneous irradiation of one red beam, respectively. Three cases are considered: DDNLCs are illuminated by one green beam with linear polarization parallel and perpendicular to the cell director and DDCLCs are irradiated by one circularly polarized green beam. The dominant causes of the one- and biphotonic nonlinearities are, respectively, the reorientation and the suppression of reorientation by the green-beam-induced trans-cis and the red-beam-induced cis-trans back isomerizations. Additionally, the obtained biphotonic nonlinearity can be modulated by controlling the intensity of the red beam in various ways because of the difference in the red beam’s capabilities to suppress the dye and the LC reorientation among the three cases.

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