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Orienting influence of femtosecond laser pulses on nematic liquid crystals has been studied. We have shown experimentally that in both a nematic liquid crystal doped with anthraquinone dye D4 and nematic matrix "mixture A" (consisting of azoxy-molecules) the efficiency of the liquid-crystal director reorientation under the influence of femtosecond pulses is less than for continuous wave radiation. The mechanism responsible for this difference is associated with light-induced variation of the anchoring conditions.

Keywords: liquid crystals; nonlinear optics; self-action effects

INTRODUCTION

In ordinary liquids consisting of anisotropic molecules, the molecular reorientation may lead to sufficiently large changes of the refractive index Δn. Such reorientation may occur under the action of an

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external electromagnetic field. The time response for the reorientation is about 10 picoseconds [1] and, therefore, in the case of interaction of nano- and subnanosecond pulses with these media the molecular reorientation is the main mechanism of the refractive-index charges. For the liquid-crystal media, the Δn value may be higher because liquid crystals have extremely high nonlinear susceptibility to external optical fields [2,3]. The time response for the reorientation is in the range of milliseconds and even seconds.

Orientation optical nonlinearity of nematic liquid crystals (NLC) is typically nine orders of magnitude higher than the Kerr nonlinearity of ordinary liquids [2]. In Ref. 3 all the characteristic features of the Fréedericksz transition were observed under continuous-wave (CW) radiation. The orienting influence of CW radiation on transparent NLC appears as a direct influence of the electric field of the light wave upon the molecular dipoles induced by the same field. In dye-doped NLC the induced director reorientation is the effect of intermolecular interaction resulting from the absorption of light quanta by dye molecules [4,5]. The NLC director reorientation is named positive if the director is rotated toward the light field and negative in the opposite case. For the transparent NLC the rotation is always positive; for the light-absorbing NLC both signs of the reorientation are possible.

The light-induced director reorientation and all the characteristic features of the Fréedericksz transition in NLC were also observed in Refs. 6 and 7 for the interaction of NLC with the pulsed radiation. Many authors [8–11] note that NLC interacts with pulsed-laser radiation in a more complicated way than the CW radiation. For instance, there is a threshold with respect to the pulse intensity but not to the average light power [9]. Moreover, the director reorientation exhibits a delay under the influence of picosecond pulses [10,11]. The presence of inertia of the director reorientation displays the fact that the reorientation is not related to the direct orienting action of the light field. The results obtained for the picosecond pulses were explained by the influence of the light-induced stresses, variations in the density, and the hydrodynamic flows on the NLC director.

The subject of particular interest is the study of the interaction of femtosecond pulses with NLC. In this case, the pulse duration is comparable or less than the characteristic time of the director inertia that is related to the fundamental NLC parameter: momentum of the liquid-crystal director inertia [7,11,12]. The orientation effects have to be taken into account while using the femtosecond pulses for the investigation of electronic nonlinearities of liquid crystals [13], because even a small director reorientation changes the refraction

index and thus affects the fulfillment of phase-matching conditions. At the same time, even for transparent NLC the manifestation of enhanced orientational phenomena caused by the multiphoton nonlinear optical phenomena (e.g., two-photon absorption) could be expected under the strong fields of femtosecond pulses.

The first experimental results on orientating interaction of femtosecond pulses with NLC were reported in Refs. 14 and 15. In Ref. 14 the light-induced director reorientation in the field of femtosecond pulses was employed to produce a helical structure providing the synchronous third-harmonic generation. The first quantitative study of the femtosecond-light-induced director reorientation was reported in our previous communication [15]. It was found that the interaction of the succession of femtosecond pulses with a transparent nematic matrix is of orientational nature. The nonlinear response of NLC to the femtosecond radiation was close to the response to CW radiation, if average power of the pulsed light beam equaled that the CW beam.

In this article we investigate the orientating interaction of femtosecond light radiation with a number of NLC samples of both pure and dye-doped nematic matrices. The preliminary results were reported in Ref. 16.

EXPERIMENTAL

Samples and Experimental Setup

The samples used throughout the experiments described here are homeotropically aligned NLC. We used a pure E63 matrix, the matrix E63 doped with a small amount of anthraquinone dye D4 (0.15 wt%), and the "mixture A" matrix, consisting of azoxycompounds. Matrix E63 is a mixture of biphenyls and phenylcyclohexanes [17]. The exact composition of "mixture A" is given in Ref. 18. According to the earlier studies, the system E63 + D4 possesses a nonlinear response of the orientational origin because of the change of the intermolecular forces at one-photon light absorption [19]. The "mixture A" possesses the optical nonlinearity of the same origin even without dye dopants [20].

Figure 1 shows the absorption spectra of matrix E63 doped with anthraquinone dye D4. The structural formula of the dye is shown in the inset to the figure. The maximum of the absorption spectra of D4 dye corresponds to the wavelength of 650 nm.

Samples have been prepared between chromium stearyl chloride–coated glass plates, treated to produce homeotropic alignment of NLC. The inner sides of the glasses were coated by a conducting SnO_2 layer, which allowed us to apply an electric field to the samples.

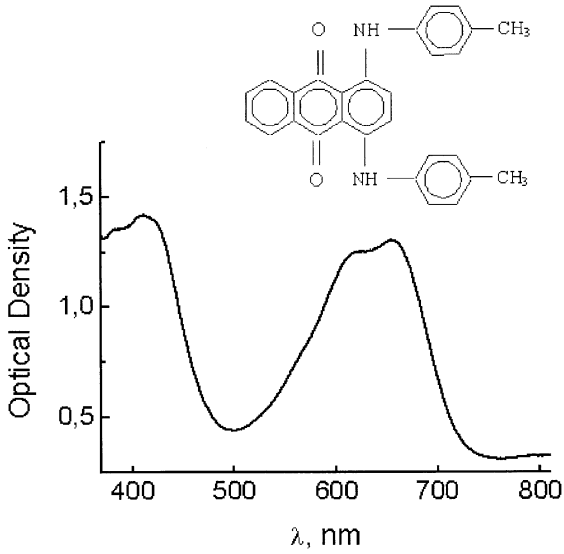

FIGURE 1 Structural formula of anthraquinone dye D4 and absorption spectra of matrix E63 doped with 0.15 wt% of D4.

The thickness of all samples was determined by mylar spacers and equaled 100 μm.

Figure 2 illustrates the experimental setup. The laser beam used for the experiments was the output of the Kerr-lens mode-locked Ti-sapphire laser, which produces 100-fs pulses in the range from 767 to 780 nm with the spectral width of 11 nm and the repetition rate of 100 MHz. The beam was focused with an achromatic lens (L, focal length $f = 20$ cm) into the NLC sample. The beam waist was 100 μm in diameter. The maximum average power at focus was 250 mW, which corresponded to a peak intensity of 300 MW/cm^2. The aberration rings in the cross section of the beam passed through the liquid-crystal sample were observed on a screen placed normally to the beam axis at the 260-mm distance from the sample and then recorded by the 16-bit 2048 × 2048 back-tuned Princeton Instruments VersArray 2048B CCD detector.

Two Glan prisms (Gp1 and Gp2) were used to ensure a linear polarization of the beam incident on the sample and change its power. Double Fresnel rhomb (DFR) provided the linear p-polarization direction (the polarization in the plane of incidence). We were able to carefully change and control the angle of the light incidence on the sample.

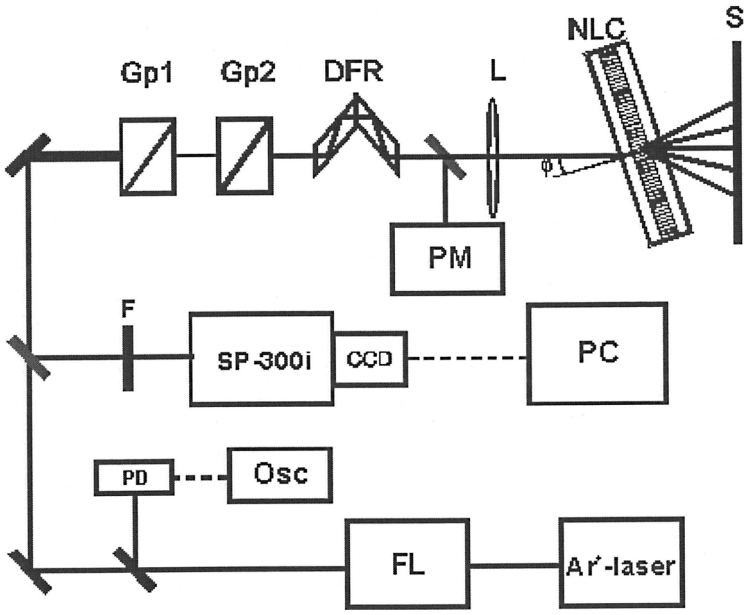

FIGURE 2 Experimental setup: (Ar^+ laser): argon-ion pumping laser; (FL): femtosecond Ti: sapphire laser, (Gp1 and Gp2): polarizing Glan prisms, (DFR): double Fresnel rhomb, (L): lens, (NLC): NLC sample, (S): screen, (PD): avalanche photodiode, (Osc): digital oscilloscope, (F): glass filter, (CCD): digital CCD system, (PC): personal computer, and (PM): power meter.

Experimental Method

The light-induced director reorientation was studied using a light-beam self-action phenomenon [21–23]. Passing through a NCL, the laser beam produces director reorientation that is nonuniform across the beam cross section. The reorientation changes the refractive index and produces a nonlinear lens in the sample that, in turn, affects the light beam. For the sufficiently large change of the refractive index, the far-field divergence of the transmitted beam increases drastically and an aberration pattern—a system of rings—is formed in the beam cross section. The number of the rings N is in a simple way related to the nonlinear phase shift S_{NL}:

$$N = \frac{S_{\mathrm{NL}}}{2\pi} \tag{1}$$

The sign of the light-induced refractive index (i.e., the sense of the director rotation) can be determined from the character of

aberration-pattern transformation at a rather small (of the order of the beam waist radius) and rapid displacement of the crystal across the light-beam propagation direction [24]. If the crystal is shifted upward, the intensity increase of the upper part of aberration pattern (and a related intensity decrease of the lower part) corresponds to self-focusing. The opposite character of the aberration-pattern intensity transformation indicates the self-defocusing. Thus, the observation of the aberration pattern allows one to determine the sense and the angle of the director reorientation.

We carried out the experiments with femtosecond or CW laser beam. Most experiments involved an oblique incidence of the p-polarized beam on NLC, in which case the threshold-free director reorientation is ensured.

EXPERIMENTAL RESULTS

Several experiments were carried out.

In the first series we showed that the interaction of NLC director and femtosecond pulses is of orientating origin. Here, the p-polarized femtosecond radiation fell upon the E63 NLC sample and a dynamical interference pattern was observed on the screen. Within the time interval of about 1 s an aberration pattern consisting of well-defined, concentric, alternating dark and bright rings appeared. In some time upon the beginning of irradiation $T_{\text{est}} \sim 5$–10 s (dependent on the beam power), the steady-state number of the aberration rings N was established. The N value depended in the light-beam power and the light-wave propagation direction.

On an abrupt (by the factor of 5) decrease of the light-beam power, the aberration pattern collapsed to the center during the relaxation time $T_{\text{rel}} \sim 5$ s. Following a rapid increasing of the power up to its initial value, the pattern was restored during a time interval than T_{rel}. In cases of the other two NLC samples—E63 doped with D4 and "mixture A"—we observed similar scenarios. These properties indicate the orientational nature of the light-induced refractive index. If the light-beam self-action had been of thermal nature, that is, the refractive index had been changed because of the NLC heating, the times T_{est} and T_{rel} would be no more than $\sim 10^{-2}$ s [20].

The orientational nature of the phenomenon is also confirmed by the fact that for pure and dye-doped E63 matrices, the picture observed disappears completely under a rather low ac voltage $U \sim 10$ V. "Mixture A" has a negative low-frequency dielectric anisotropy and the external electric field does not suppress the director reorientation.

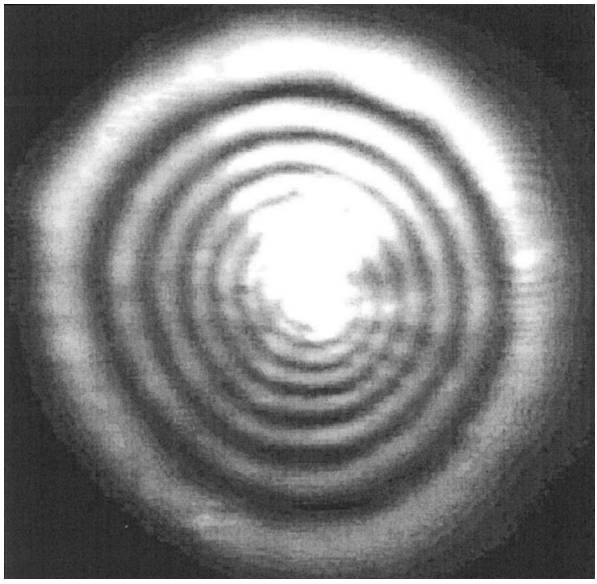

FIGURE 3 Typical form of the aberrational pattern obtained after small (of the order of the beam waist radius) and rapid shift of the E63 nematic LC sample upward (self-focusing case).

To determine the sign of self-action, the NLC sample was shifted upward across the light beam. We observed the intensity increasing in the upper part of the aberration pattern and the decreasing in the lower part. As was explained previously, this indicates the self-focusing of radiation. A typical pattern observed for pure E63 matrix is shown in Fig. 3. The reestablishment of the initial symmetrical form of the aberration pattern occurred in several seconds, which again confirms the orientational mechanism of the nonlinearity.

Another series of experiments was carried out to compare the influence of the femtosecond-pulse succession and the CW radiation on the NLC samples. We measured the corresponding dependencies of the number N of the aberration rings on the incident radiation power.

Experimental dependencies of N on the power of femtosecond and CW beams for three samples—matrix E63, matrix E63 doped with the dye D4, and the "mixture A" matrix—are shown in Figs. 4–6, respectively.

For the pure E63 matrix we observed nearly the same number of aberration rings N over a wide range of the light-beam power

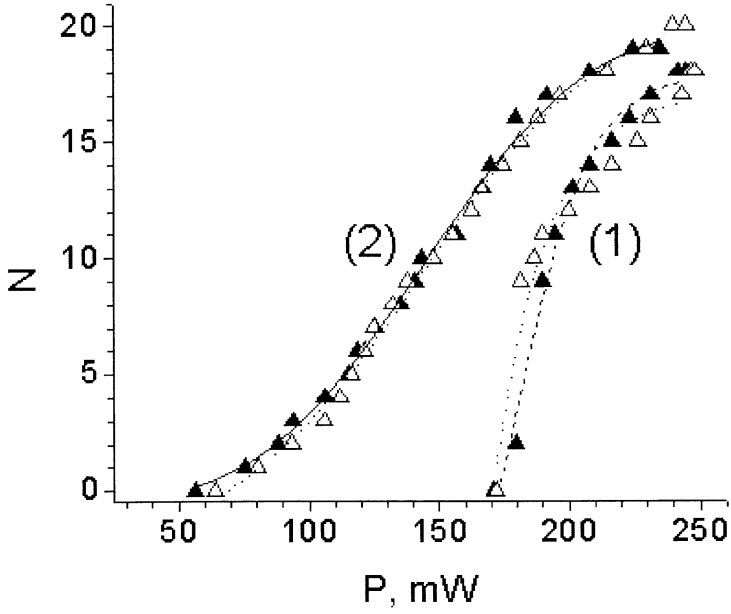

FIGURE 4 Experimental dependencies of the number of aberrational rings N on the laser-beam power ($\lambda = 773$ nm; ▲, cw radiation, Δ, femtosecond pulses) for E63 NLC sample: (1) normal incidence and (2) oblique incidence at an angle $\alpha = 15^{\circ}$.

(Fig. 4). Equal efficiencies of the action of femtosecond and CW radiation bears witness to no substantial influence of photoelastic stresses, flow, and heating produced by femtosecond radiation.

For E63 matrix doped with dye D4, the number of aberration rings (and the director-reorientation angle) was less in the field of femtosecond pulses as compared to the field of CW radiation (Fig. 5). Similar difference was also observed for the "mixture A" matrix (Fig. 6).

Let us consider the possible reasons of this difference.

DISCUSSION

We supposed that the observed difference might be caused by several possible mechanisms.

1. First of all, the observed difference could be caused by the presence of extinction of the femtosecond radiation because of one- or multiphoton absorption. However, if this were the case, the absorbed

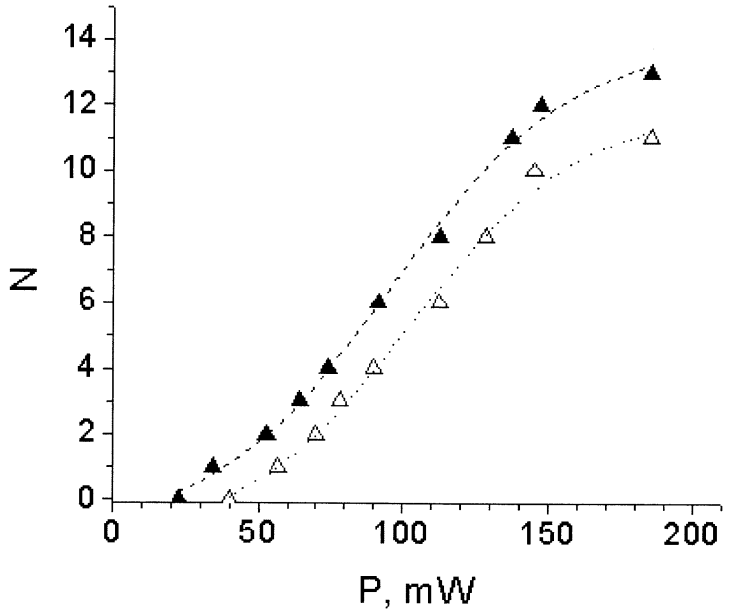

FIGURE 5 Experimental dependencies of the number of aberrational rings N on the laser-beam power ($\lambda = 773\,\text{nm}$; ▲, cw radiation, Δ, femtosecond pulses) for NLC E63 + 0.15% D4 sample for oblique incidence at an angle $\alpha = 25^\circ$.

power would result in substantial thermal effects such as the transition from the nematic to the isotropic phase or the change of the refractive index characterized by short ($<0.1\,\text{s}$) establishment and relaxation times. No such effects were, however, observed in our experiments. For our radiation wavelengths, which are out of the absorption band, we estimated the increase of the temperature in the beam waist area resulting from the residual absorption as a value of 2–5°C. The relaxation time of the thermal nonlinearity for "mixture A" sample could be estimated as $10^{-2}\,\text{s}$ [20].

2. Another possible reason for the observed difference in the influences of femtosecond and CW radiation could be intermolecular interaction and appearance of an additional torque caused by the change of intermolecular forces under two-photon absorption (TPA) of the femtosecond radiation. If this torque is opposed to the torque caused by induced dipoles in the NLC matrix, the director rotation angle decreases and the number of aberration rings also decreases. The negative (outward of the light field) director reorientation was observed in Ref. 19 for the D4-doped NLC in

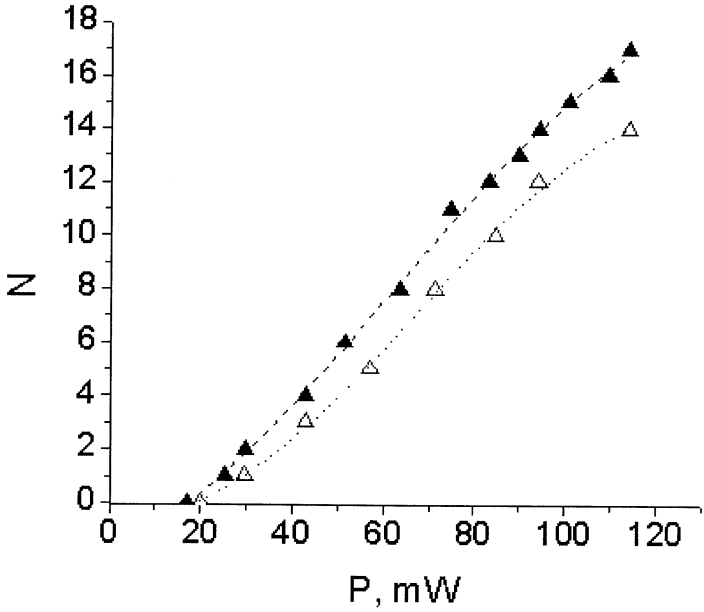

FIGURE 6 Experimental dependencies of the number of aberrational rings N on the laser-beam power ($\lambda = 773\,\text{nm}$; ▲, cw radiation, Δ, femtosecond pulses) for "mixture A" sample for oblique incidence at an angle $\alpha = 25^\circ$.

the case of one-photon absorption of green and red light. Such negative reorientation was also observed in our early experiments under CW radiation in the "mixture A" sample [20]. The studies of the changes of intermolecular forces at TPA of the femtosecond radiation have not been discussed in the literature up to now.

3. There is one more possible reason for the observed difference in reorientation efficiency for femtosecond pulses and CW radiation. This reason is mainly based on the distinction between the effects of femtosecond and CW radiation on the anchoring conditions at the NLC surfaces.

Let us consider the last two reasons in more detail.

Estimation of the Two-photon Absorption Cross Section

Let us estimate the value of TPA cross section of D4 dye that is necessary for the significant influence of the bulk torque caused by the TPA. In the case of one-photon absorption, the corresponding

torque $\mathbf{\Gamma}_{\text{abs}}$ can be represented as $\mathbf{\Gamma}_{\text{abs}} = (\Delta\varepsilon_{eff}|\text{A}|^2/8\pi)(\mathbf{ne})[\mathbf{n} \times \mathbf{e}]$ [5], where $\Delta\varepsilon_{eff}$ is the effective optical anisotropy—the parameter determined by absorption, the change of the intermolecular forces at the dye-molecule excitation, and the spatial-orientational correlation function; A is the light-field amplitude; and $\mathbf{n}$ is the director. According to Ref. 5, $\Delta\varepsilon_{\text{eff}} \sim \sigma^{(1)} c_{\text{d}} \zeta$, where $\sigma^{(1)}$ is the one-photon absorption cross section, c_{d} is dye concentration, and ζ is the parameter depedent on molecular properties in the ground and excited states and on the correlation function (by order of magnitude $\zeta \sim 0.5$). For rough estimation in the case of TPA we replace $\sigma^{(1)}$ with the quantity $\sigma^{(2)}F$ (where $\sigma^{(2)}$ is the TPA cross section and F is the photon flux density) and find $\Delta\varepsilon_{\text{eff}} \sim \sigma^{(2)} F c_{\text{d}} \zeta$. Furthermore, we notice that the required torque Γ_{abs} can be evaluated as $\Gamma_{\text{abs}} \sim \mu\Gamma_{\text{tr}}$, where $\Gamma_{\text{tr}} = (\Delta\varepsilon|\text{A}|^2/8\pi)(\mathbf{ne})$ $[\mathbf{n} \times \mathbf{e}]$ is the torque caused by the direct orientational influence of the light field on the induced dipoles, $\Delta\varepsilon$ is optical anisotropy of E63 matrix, and μ is the relative difference between the number of aberrational rings for femtosecond and CW radiation, observed at the same power (according to Fig. 5, $\mu \sim 0.2$). Then, we arrive at the relationship $\Delta\varepsilon_{\text{eff}} \sim \mu\Delta\varepsilon$ and, finally, to the estimation $\sigma^{(2)} \sim \mu\Delta\varepsilon/c_{\text{d}}F$. In our experiment ($P \sim 200\,\text{mW}$, off-duty ratio $Q = 10^5$, beam waist $w = 100\,\mu\text{m}$), the photon flux density of femtosecond pulses is $F \sim 4PQ/\pi w^2 \sim 10^{27}\,\text{cm}^2\,\text{s}^{-1}$ ($\lambda = 770\,\text{nm}$), $\Delta\varepsilon = 0.74$, and $\text{c}_{\text{d}} \sim 0.2 \cdot 10^{19}\,\text{cm}^{-3}$. Therefore, $\sigma^{(2)} \sim 10^{-46}\,\text{cm}^4 \cdot \text{s}$.

For experimental verification of the role of TPA in the observed difference between the influence of CW and femtosecond radiation, the TPA cross section was measured in an independent experiment. When TPA is registered from the secondary process, fluorescence, it is convenient to use not the TPA cross section but its product by the quantum yield of two-photon fluorescence (TPF) [25]. We used the algorithm based on the comparison of TPF cross section of the dye under study with the TPF cross section of a reference dye [26] under the same conditions. The main part of the experimental setup in this case is shown in Fig. 7. The parameters of the pulses produced by the Ti-sapphire laser were given previously. The femtosecond radiation was focused by a lens L1 ($f = 10\,\text{cm}$) into the cavity with the sample solution and excited fluorescence of the dye by a two-photon mechanism. As a result, the beam track into the cavity was observed. The intensity of the fluorescence depends on the TPF cross section and on the fluorescence quantum efficiency. The fluorescence signal was collected by a lens L2 ($f = 4\,\text{mm}$) through the collateral border of the cavity. For the registration of the TPF spectra and the spectra of laser radiation we used the spectrograph and digital CCD system.

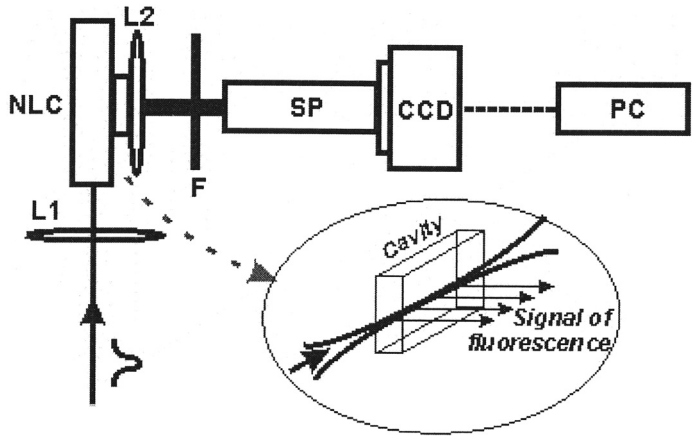

FIGURE 7 Experimental setup for TPF cross-section measurements: (L1 and L2): lenses, (NLC): sample, (F): glass filter, (SP): spectrograph, (CCD): digital CCD system, and (PC): personal computer.

We have chosen a quartz cavity with the solution of Rhodamin 6G in chloroform with the concentration of $4 \cdot 10^{-4}$ M as a reference sample. The TPA cross section of Rhodamin 6G in ethanol is known to be $\sigma^{(2)} \sim 40 \cdot 10^{-50}\,\mathrm{cm}^4\,\mathrm{s}$ [26]; the fluorescence quantum efficiency is closer to 100%. The sample under study was a D4 chloroform solution with the concentration of $4 \cdot 10^{-4}$ M.

Although the TPF spectra of Rhodamin 6G in chloroform was easily measurable with the aid of our experimental setup, the sensitivity of this setup proved to be insufficient to register the TPF signal from D4 dye. We thus concluded that the TPA cross section of D4 dye in chloroform solution is much less than the TPA cross section of Rhodamin 6G and could be estimated as $\sigma^{(2)}(\mathrm{D4}) \ll 40 \cdot 10^{-50}\,\mathrm{cm}^4 \cdot \mathrm{s}$. It is well known that the environment of the dye (the solvent) could greatly affect the TPA cross section. For example, the TPA cross section of a dye in Plexiglas matrix is, typically, several times less than the cross section of the same dye in solution [27]. The effect of the environment cannot, however, affect the order of magnitude of the estimated value of $\sigma^{(2)}$ for D4.

As a result we can conclude that the additional bulk torque produced by the changes of the intermolecular forces caused by TPA plays no important role in the director reorientation under femtosecond pulses. Thus, the bulk torque caused by the TPA cannot explain the observed difference between the influence of femtosecond and CW radiation, at least in the case of E63 doped with D4 dye.

Possible Role of Light-Induced Surface Phenomena

In this section we analyze the light-induced variation of the anchoring conditions as a reason for the observed difference in the influence of femtosecond and CW radiation.

The effect of light on the orienting properties of the NLC surfaces has been extensively studied for a considerable period of time (see, e.g., Refs. 28–32), with the primary attention paid to the memorized modification of the anchoring conditions. Studies [33–35] showed that this modification can be reversible—after switching off the illumination the initial anchoring conditions are rapidly restored. Modifications induced by the light beam on the NLC boundary surface affect the director orientation in the bulk of the sample through the elasticity of the medium, thus resulting in the change of the nonlinear phase shift and the number of aberrational rings. We believe that the reversible changes in the anchoring conditions produced by femtosecond pulses can account for our experimental results.

Let us discuss this in more detail. First of all, we consider the geometry of the interaction between the light wave and the NLC cell (Fig. 8). The decrease in the number N of the aberrational rings, appearing on the changeover from CW to femtosecond radiation, implies that the extraordinary refractive index is decreased. That is, the angle ψ_m, made in the sample bulk by the director $\mathbf{n}$ and light field $\mathbf{E}$, is decreased by a certain number δ_b. It is evident from Fig. 8 that such a decrease can only be produced if, in the case of femtosecond pulses, the director at the sample surfaces is rotated away from the light field with respect to the case of CW radiation (from the $\mathbf{n}_o$ to $\mathbf{n}_s$ orientation).

The physical reason for the light-induced changes of the anchoring conditions, as they have been discussed in the literature up to now, could be the light-induced adsorption and desorption of excited molecules (see, e.g., Refs. 31 and 35). Namely, it was concluded that the director rotation away from the light-field direction is due to the process of the light-induced desorption. As the rotational diffusion of the molecules in the surface layer is suppressed with respect to the molecules in the bulk, the light-absorption coefficient required for the anchoring-condition modification is lower than that required for bulk modification. Therefore, the TPA of the femtosecond radiation in our case can be sufficient for the surface-mediated director reorientation.

To estimate the TPA cross section required for the anchoring-condition modification we consider a very simplified, two-dimensional model, in which the absorbing molecules of dye D4 or the molecules of

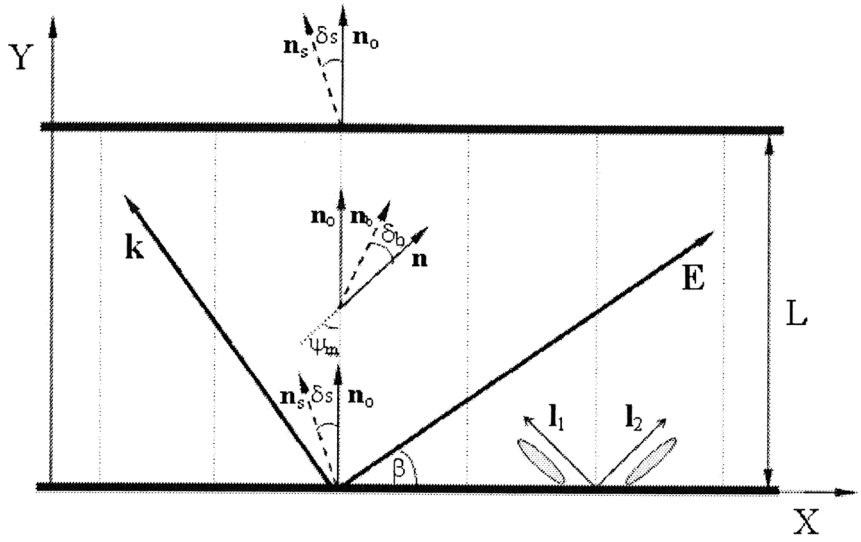

FIGURE 8 Influence of the light-induced variation in the anchoring conditions on the director field: **E**, **k**, and β are the electric field, wave vector, and the angle of refraction of the light wave, respectively; $\mathbf{n}_o$ and **n** are the director orientations at the surface and in the bulk of the NLC with unmodified anchoring properties of the surfaces, respectively (the case of CW illumination; $\mathbf{n}_o$ also specifies the initial homeotropic orientation); $\mathbf{n}_s$ and $\mathbf{n}_b$ are the director orientations at the surface and in the bulk of the NLC with modified anchoring properties of the surfaces, respectively (the case of femtosecond illumination); δ_s and δ_b are the changes in the director rotation angles at the NLC surfaces and in the NLC bulk in passing from *cw* to femtosecond radiation; $\mathbf{l}_1$ and $\mathbf{l}_2$ are mutually orthogonal unit vectors specifying two possible orientations of the light-absorbing molecules at the NLC surfaces within the model discussed ($\mathbf{l}_1$ and $\mathbf{l}_2$ make the angle $\pi/4$ with the NLC surfaces); and L is the NLC thickness.

the mixture A at the NLC surface can only take two mutually perpendicular orientations, specified by the unit vectors $\mathbf{l}_1$, and $\mathbf{l}_2$ in Fig. 8. Such simplification was employed in Ref. 36 in consideration of the light-induced realignment of the dye molecules at the polymer–liquid-crystal interface. Furthermore, we assume that the energy u of the interaction between the light-absorbing molecules and the nematic environment has the form similar to the mean-field (Maier–Saupe) potential $u(\mathbf{n}, \mathbf{l}_i) = -u_0(\mathbf{n}\mathbf{l}_i)^2$ (where the constant $u_0 \sim 4.5\,k_BT$, $i = 1, 2$). Then, the total energy of the interaction between the light-absorbing molecules at the NLC surface and the

nematic matrix is

$$U = -u_0[c_1(\mathbf{nl}_1)^2 + c_2(\mathbf{nl}_2)^2], \tag{2}$$

where c_1 and c_2 are the surface concentrations of the molecules with the orientations specified by $\mathbf{l}_1$ and $\mathbf{l}_2$ respectively. Using the orthogonality of the vectors $\mathbf{l}_1$ and $\mathbf{l}_2$, the orientation-dependent part of the energy U can be represented as

$$U = -u_0 \Delta c(\mathbf{nl}_1)^2, \tag{3}$$

where $\Delta c = c_1 - c_2$. Without light illumination $c_1 = c_2 = c_o/2$ (c_o is the total density of the light-absorbing molecules at the surface) and $U = 0$. The incident light changes the concentrations c_1 and c_2. We assume that each act of the light-quantum absorption by a molecule results in its detachment from the surface. Then, the number δc_i of the molecules with the orientation $\mathbf{l}_i$ escaped from the surface during a time interval τ can be estimated as $\delta c_i = c_i \tau \sigma_i^{(2)} F^2/Q^2$, where $\sigma_i^{(2)}$ is the TPA cross section of the molecules with the ith orientation, F is the photon flux density of the femtosecond pulses, and Q is the off-duty ratio. It is logical to assume that $\sigma_i^{(2)} \sim (\mathbf{el}_i)^4$. Then, with regard to the experimental value $\beta \approx 15^\circ$ (see Fig. 8), we find $\sigma_2^{(2)}/\sigma_1^{(2)} = 9$, and, hence, $\Delta c = \delta c_2 - \delta c_1 = 4\tau c_o \sigma_2^{(2)} F^2/9Q$. Finally, using Eq. (3) we arrive at

$$U = -W_0(\mathbf{nl}_1)^2, \tag{4}$$

where the parameter $W_0 = -4\tau c_o \sigma_2^{(2)} F^2 u_0/9Q$ has the sense of the anchoring energy.

Our previous consideration did not include the processes that are opposed to the orientationally selective desorption—for example, the dark- and light-induced adsorption and the thermal transitions between the two orientational states—which determine the equilibrium concentration of the molecules at the surface or restrict the τ values that can be used in our model. In principle the characteristic time periods of these processes may be rather long (e.g., tens of seconds in Ref. 33). This is also indirectly confirmed by the observation of the memorized modification of the anchoring conditions observed in the visible range for homeotropically aligned samples of E63 + D4 [32] and "mixture A" [37]. In our estimation we assume $\tau \sim 1\,\mathrm{s}$.

The typical energy of the photoinduced anchoring energy is $10^{-4}\,\mathrm{erg/cm^2}$ [29]. The estimate for the TPA cross section required to yield this value follows immediately from Eq. (4)

$$\sigma^{(2)} \approx 9W_0 Q/4\tau c_o F^2 u_o. \tag{5}$$

The parameter c_0 entering this relation can be estimated from the typical molecular dimension $a \sim 10^{-7}$ cm by the simple formula $c_o \sim a^{-2}$. Substituting $c_o = 10^{14}\,\mathrm{cm}^{-2}$ into Eq. (5), $\mathbf{W}_0 \sim 10^{-4}\,\mathrm{erg/cm}^2$, $\mathbf{Q} = 10^5$, $\mathbf{F} \sim 10^{27}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, and $u_0 = 1.6 \cdot 10^{-13}\,\mathrm{erg}$, we find $\sigma^{(2)} \sim 10^{-54}\,\mathrm{cm}^4 \cdot \mathrm{s}$. This value of the TPA cross section is much lower than that required for the bulk reorientation ($\sigma^{(2)} \sim 10^{-46}$ $\mathrm{cm}^4 \cdot \mathrm{s}$) and is beyond the sensitivity of the previously described experiment.

Therefore, the TPA, inherent to femtosecond radiation alone, might be responsible for the observed difference between the influence of femtosecond and CW radiation. This effect of adsorption could be a subject of additional study.

CONCLUSIONS

Direct experimental comparison of the interactions of the succession of femtosecond pulses and CW light radiation with NLC has been performed. For transparent nematic E63 matrix, the nonlinear orientational responses were found to be equal provided that the average power of the femtosecond pulses coincides with the power of CW radiation. For nematic matrix "mixture A" and E63 matrix doped with anthraquinone dye D4, the influence of femtosecond pulses proved to be less effective than that of CW radiation.

The results obtained indicate the absence of the significant effect of the photoelastic stresses, flow, and heating at irradiation with the femtosecond radiation.

To elucidate the role of the bulk torque arising from the modification of the intermolecular forces at TPA, we estimated the required value of the TPA cross section of dye D4 both theoretically and experimentally. The results showed that this value is too small to explain the experimental results by the bulk torque mentioned.

The observed difference could be attributed to the difference in the influence of the femtosecond and *cw* radiation on the anchoring properties of the NLC surfaces.

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