

# Ultrafast all-optical response of a nematic liquid crystal

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**Abstract:** Liquid crystals are superior optical materials for large area displays, but it is considered that their collective and slow-millisecond response makes them useless for ultrafast optical applications. In contrast to that, we here demonstrate an ultrafast optical response of a nematic liquid crystal, which is induced by an intense femtosecond optical impulse. We show that the refractive index of the nematic liquid crystal pentylcyanobiphenyl can be modulated at a time scale as fast as 500 fs via a coherently excited optical Kerr effect. The change in the refractive index is in the order of  $10^{-4}$  at a fluence of 4 mJ/cm<sup>2</sup> and is strongly polarization dependent. This unprecedented result opens new ways towards ultrafast all-optical modulation in liquid crystal-based devices.

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OCIS codes: (160.3710) Liquid crystals; (160.1190) Anisotropic optical materials.

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## 1. Introduction

Nematic liquid crystals (NLCs) are superior optical materials for many applications, such as large flat screen displays, but the speed of their optical response is limited to the millisecond range, because of the collective reorientation of all molecules under an applied electric field. Improvement in the overall working speed might be achieved by a proper patterning of the LC cell [1], but still showing characteristic timescale of the order of 1 ms. To investigate shorter time scales laser systems are required. In this respect, nano- and picosecond laser-induced molecular reorientation in NLCs and dye-doped NLCs has been investigated since the 90's [2–5]. Recently, Borshch et al. [6] demonstrated tens-of-nanoseconds response of the refractive index of a NLC by applying an intense electric field of  $\sim 100$  V/ $\mu$ s to a thin layer of a NLC. This fast response is due to the enhanced degree of orientational order of the liquid crystalline molecules, which are forced to align along the strong electric field. On the other hand, in ordinary liquids, the electric field of a strong light pulse is known to modify the refractive index via the optical nonlinear Kerr effect on a 100 fs [7,8] to a picosecond time scale [9] by affecting the molecular electron density distribution. In the isotropic phase of NLCs, the optical Kerr effect can resonantly be enhanced on a 100 ps time scale because of the orientational interactions between the elongated LC molecules [10–14]. In the nematic phase, the persistent collective order gives rise to complex and much slower orientational dynamics [15–17]. Here we focus on the instantaneous optical response of collectively ordered liquid crystal molecules in the nematic phase to an applied  $\sim 100$  fs optical pulse. We observe a strong and fast transient response of the birefringence of the NLC in the order of  $\sim 500$  fs, which is polarization-dependent and is five to eight orders of magnitude faster than ever observed before [1–18]. In combination with self-assembly [19] and topology [20], which are inherent properties of nematic liquid crystals, our results not only promise implementation of NLCs in ultrafast photonic devices, but also demonstrate a new and absolutely unexplored aspect of LCs.

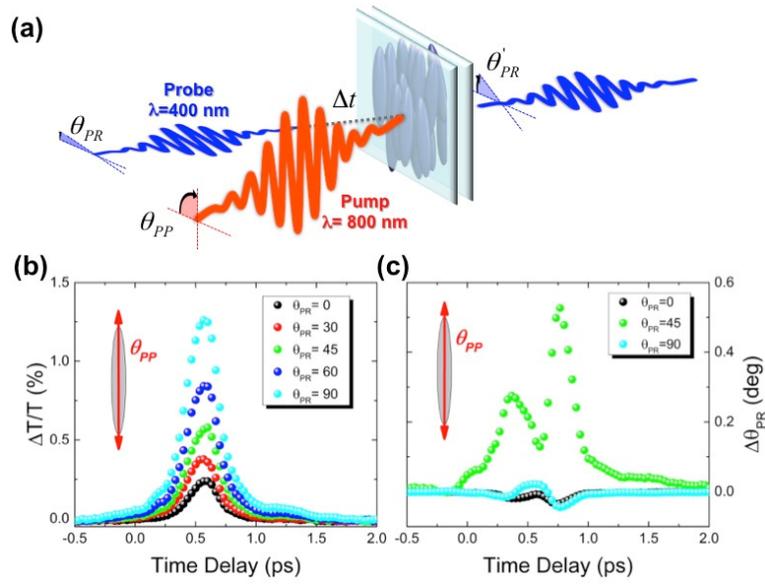


Fig. 1. Ultrafast response of nematic liquid crystals due to 100 fs excitation pulse in a pump-probe experiment. (a) Scheme of the pump-probe experiment, where  $x$  is the pump linear polarization axis and  $y$  is the probe linear polarization axis. (b) Time-dependence of the normalized relative transmission of the sample, with the pump (excitation) polarization along the director. The fluence of the pump beam is  $4 \text{ mJ/cm}^2$  and corresponds to an electric field strength of  $660 \text{ V}/\mu\text{m}$ . (c) Time dependence of the rotation of polarization of the probe beam for pump polarization along the director.

## 2. Experimental details

### 2.1. Sample preparation

The LC cell was prepared by sandwiching  $23 \mu\text{m}$  of commercial 4-cyano-4'-pentylbiphenyl, 5CB (K15, Merck) between two quartz glasses (1 mm thick, double polished, Mateck GmbH). The quartz glasses were previously ultrasonically cleaned with detergent (ALCONOX) for 30 min and rinsed with copious amounts of tap water, followed by acetone (99.8%, Merck) and 2-propanol (Fluka 99.9%). At last, they were blown dry with  $\text{N}_2$ . A thin layer of polyimide (PI) solution (2% w/w in pyrrolidone) was spin-coated on one surface of each quartz glass (2000 rpm, 107s) and baked at  $180^\circ\text{C}$  for 2h. The PI layers were subsequently rubbed with a velvet cloth. The LC cell was then assembled with the two rubbed surfaces facing each other at a distance of  $23 \mu\text{m}$  through a Mylar spacer (Dupont), keeping the rubbing direction parallel to each other, and glued with and epoxy resin (Epoxy Rapid, Bison). The cells were then filled with pentyl-cyanobiphenyl (5CB) by capillary force at  $40^\circ\text{C}$  ( $T_{\text{IN-5CB}} \sim 35^\circ\text{C}$ ). The filled cells were kept at  $40^\circ\text{C}$ , in the isotropic phase, for a few minutes before they were cooled to room temperature. The cooled cells were finally sealed with the same resin.

### 2.2. Pump-probe experiment

The laser-induced birefringence dynamics was studied by a time-resolved stroboscopic optical pump-probe technique at different temperatures, using an amplified Ti:sapphire system (repetition rate  $f = 1 \text{ kHz}$ , output power  $P_{\text{av}} = 1.2 \text{ W}$ , emission wavelength  $\lambda = 800 \text{ nm}$ , pulse duration  $\delta = 100 \text{ fs}$ ). The laser beam was split with a 85%–15% beam splitter to set up a noncollinear pump-probe scheme. The probe beam was doubled in frequency with a nonlinear Barium Boron Oxide crystal. The pump beam frequency was modulated by a chopper at 500 Hz. Both beams, after being delayed with respect to each other, were linearly polarized and

then superimposed on the sample. The size of the pump-beam in the focus was approximately 120  $\mu\text{m}$  while that of the probe was 55  $\mu\text{m}$ . The fluence of the pump was carefully measured and varied in the range 2-10  $\text{mJcm}^{-2}$  to study the fluence dependence on the induced effects. The sample temperature was carefully controlled and set at 4 different temperatures: 23°C, 36°C, 40°C and 75°C. After interacting with the sample, the transmitted probe beam was collected on a balanced detection scheme. This includes a passage through a Wollaston prism that separates the incoming probe beam with unknown polarization into two orthogonal linearly polarized beams. These two separated probe-beams were then collected onto separated photodiodes, namely A and B. Only the sum  $A + B$  and the difference  $A - B$  signals were synchronously sent to two lock-in amplifiers triggered with the frequency of the chopper (500 Hz). In this way we can refer the signal  $A + B$  to the pump-induced transmission of the probe through the sample, while the signal  $A - B$  gives information about the rotation of the polarization axis of the probe with respect to the pump-off condition. The laser-induced changes in birefringence are studied by recording both transmission ( $A + B$ ) and rotation ( $A - B$ ) experienced by the probe beam as a function of the relative time delay  $t$  between pump and probe and as a function of the pump linear polarization axis and the probe linear polarization axis (both from horizontal, 0°, to vertical, 90°), as shown in Fig. 1(a).

### 3. Results and discussion

Figure 1(b) and 1(c) show the response of a nematic LC to a 100 fs pump light pulse with the electric field oscillating along the nematic director. Well within the first picosecond of the light pulse, we clearly observe ultrafast transients both in the normalized relative transmission  $\Delta T/T$  of the sample [Fig. 1(b)] and the rotation of the polarization of the probe beam [Fig. 1(c)]. Here,  $\Delta T$  is the pump-induced change in the total transmission of the sample and  $T$  is the total transmission before the pump arrival. In the nematic phase, the ultrafast optical response is maximal when the pump polarization is along the director, which clearly reflects the influence of the long-range orientational ordering of the NLC. This means that if an intense interacting electric field (pump) couples to the extraordinary axis of the NLC molecules, it can induce a major modification of its extraordinary refractive index. This OKE-induced change of the refractive index on the sub-ps time scale changes the reflectivity of the liquid crystal-glass cell interface and affects the probe transmission. To understand the nature of the ultrafast optical response of the NLC, we performed pump-probe experiments for different polarizations of the pump and probe beams, and at different temperatures; the results are shown in Fig. 2 and 3. Figure 2(a) shows the time dependence of the relative transmission of the sample for three different pump polarizations and five different probe polarizations in the nematic state (23°C). When the pump electric field is perpendicular to the director [Fig. 2(a), first panel from the left], the time response of the sample's relative transmission is smallest and isotropic, i.e. independent of probe polarization. In this case, the pump beam travels through the sample as an ordinary wave and has little effect on the two refractive indices. However, as we rotate the polarization of the pump beam towards the director [middle and right panels in Fig. 2(a)], the response is increasing and becomes anisotropic, i.e. dependent on the polarization of the pump beam. We obtain a maximum transmission transient when both pump and probe polarizations are along the director, i.e. along the mean orientation direction of NLC molecules. In this geometry, both pulses travel through the sample as pure extraordinary optical waves, and the optical response is the largest.

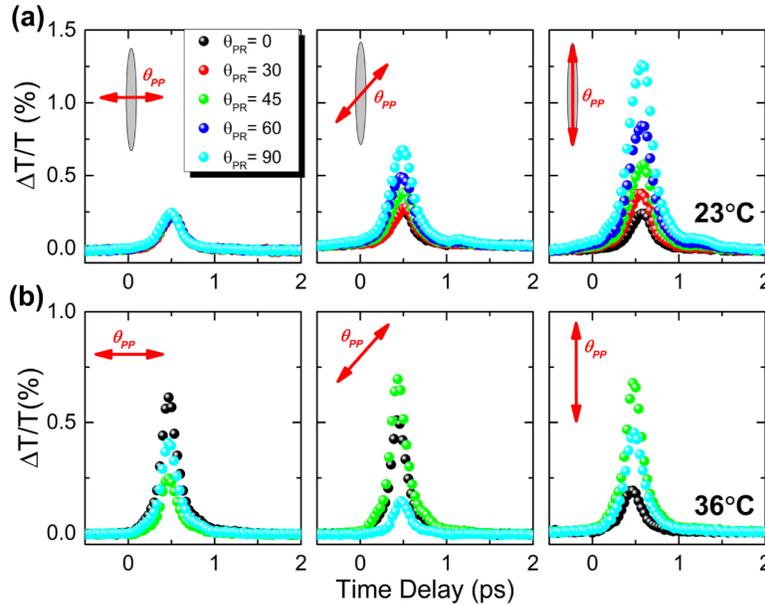


Fig. 2. Pump polarization dependence of the ultrafast response in the nematic 5CB liquid crystal. (a) In the nematic phase of 5CB, at 23°C, the normalized relative transmission is polarization-dependent, and the maximum is obtained when both pump and probe polarizations are along the long molecular axes of the NLC. (b) In the isotropic phase, at 36°C, the response does not depend on the direction of the pump polarization, and we get maximum response whenever the probe polarization is rotated into the pump polarization direction.

When the sample is heated into the isotropic phase of 5CB, we obtain at 36°C an isotropic optical response, which is typical for ordinary liquids. Figure 2(b) shows the time-dependence of the relative transmission of the 5CB in the isotropic phase for three different pump polarizations (with respect to the nematic director at lower temperatures) and for each of them we measured the response for three different probe polarizations. One can clearly see from the left panel of Fig. 2(b) that the maximum relative transmission is one half of the response in the nematic phase. This maximum is again obtained when the probe polarization is parallel to the pump polarization. When we rotate the pump polarization, we indeed obtain exactly the same maximal response when the probe polarization is set along the pump polarization. This can easily be understood in terms of the orientational disorder of the long molecular axes of rod-like nematic molecules. Because the light pulse is so short, it sees an instantaneous (i.e. frozen) picture of the molecular orientational distribution, which in this case is isotropic in 3D. For any chosen polarization there will be a certain number of nematic molecules pointing along that direction, therefore contributing to the optical response. This contribution will be largest for a probe polarization along the pump polarization, because of the optically induced Kerr polarization. The relative transmission measurements demonstrate that this nematic ultrafast response can be disentangled along two main directions, the ordinary axis contribution that shows a small isotropic excitation, and the extraordinary axis contribution, which shows a clear pump-polarization dependence with a maximum, when the excitation (i. e. the pump) electric field is along the LC director. This implies that cyano-biphenyl LC's (such as the n-CB family) are anisotropically Kerr-active in their ordered phase, i.e. the dominant Kerr-effect is obtained with the electric field of light set along the long-molecular axis. In order to estimate the induced birefringence we simultaneously measured the polarization state of the out-coming probe beam after the interaction with the NLC, i.e. the transient rotation of the polarization plane, [see Fig. 1(a)] and the ellipticity,  $\chi$ . The polarization rotation was measured simultaneously with the transmission signal, since it is the difference between the two orthogonal linearly polarized probe-beams. The latter were

separated by the Wollaston prism in the balance scheme detection, thus cancelling-out the static birefringence. The ellipticity measurements were performed by introducing a  $\lambda/4$  retardation plate before the detector and recording the difference in the balance detection (not shown). In contrast to the nearly feature-less transmission response, shown in Fig. 2, we observed that the time-dependence of the rotation of the polarization of the probe beam has a characteristic two-wing-like structure in the nematic phase, as shown in Fig. 1(c) and Fig. 3. This feature was analyzed for different polarizations of the pump and probe beams and at different temperatures and the results are shown in Fig. 3.

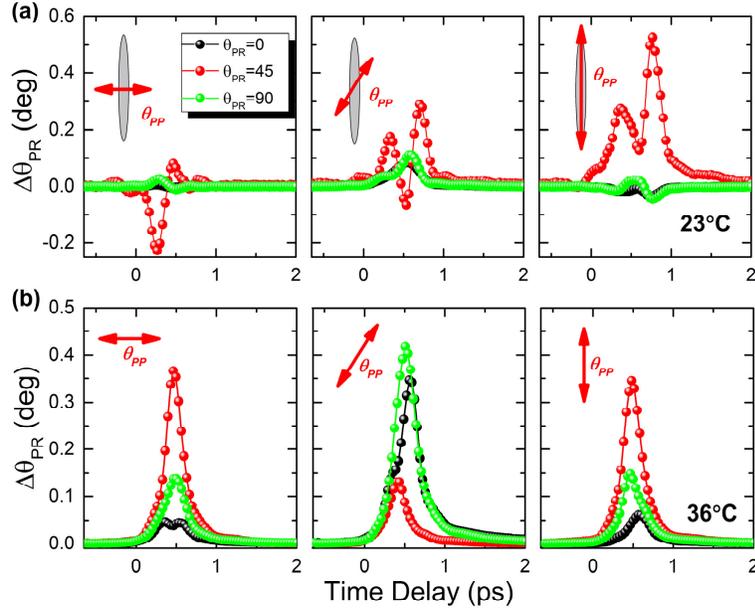


Fig. 3. Rotation of light polarization by light in the nematic 5CB liquid crystal. (a) In the nematic phase, maximum polarization rotation of the probe beam of  $\sim 0.5^\circ$  is observed when the pump polarization is along the director and the probe polarization is at  $45^\circ$ . (b) In the isotropic phase, maximum light-induced polarization rotation of the probe beam is independent of the pump polarization direction. For a given pump polarization, it is maximum when the probe polarization is at  $45^\circ$  with respect to the pump polarization.

This ultrafast transient is present for all pump polarizations, and corresponds to 2.7 THz ( $\sim 90 \text{ cm}^{-1}$ ), well within the frequency plateau observed by Tao et al. [21]. Even more interestingly, it is in the spectral range, where 5CB shows its most characteristic terahertz signatures [16,17]. The amplitude of this oscillation corresponds to a pump-induced rotation by half a degree on a time scale of 150 fs of the probe polarization. Since the signals of ellipticity and rotation are nearly equal in strength, and using the approximation  $2\chi \approx \delta$ , where  $\delta$  is the phase shift experienced by the two components of the probe optical field, the induced birefringence is given by [22]:

$$\delta n(t) \approx \frac{\lambda 2 \Delta \theta_{PR}(t)}{2\pi d} \quad (1)$$

Here,  $\lambda = 400 \text{ nm}$  is the probe beam wavelength,  $d = 23 \text{ }\mu\text{m}$  is the thickness of the NLC, yielding a maximum modulation of the refractive index of the order of  $\delta n \sim 10^{-4}$ , as shown in Fig. 4.

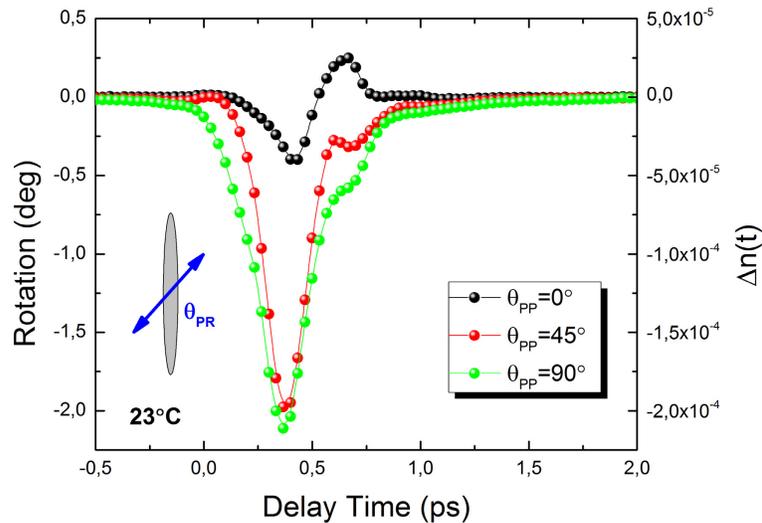


Fig. 4. Rotation signal (left axis) and calculated birefringence  $\Delta n(t)$  (right axis) as a function of the pump polarization axis and time, keeping the probe polarization fixed at  $45^\circ$ . The measurement has been performed at  $23^\circ\text{C}$  at a pump fluence of  $4\text{ mJ/cm}^2$ .

In addition to this quasi-oscillation, a Gaussian-like offset is present, which increases as we rotate the pump polarization towards the director [Fig. 3(a) center and right panels]. This is indeed expected for a Kerr-active sample. On the other hand, above the isotropic-nematic transition [Fig. 3(b)], the time-dependence of the polarization rotation does not show any oscillating behavior, but a simple Gaussian profile with a slightly longer life-time compared to that in the nematic phase. Based on the observed frequency, magnitude and time duration, we can understand the ultrafast Kerr response of 5CB in the nematic phase in terms of optically induced librational modes, i.e. intramolecular vibrations excited through a non-resonant channel, i.e. by stimulated Raman scattering. Since the frequency bandwidth of the pump pulse is of the order of 3 THz ( $\sim 100\text{ cm}^{-1}$ ), it contains both frequencies required to excite the low-frequency single vibrational modes of 5CB, collectively oscillating along the pump polarization axis. When the pump polarization axis coincides with the LC director, these single molecule vibrations will be coherently excited and result in an enhanced optical Kerr response, oscillating at 2.7 THz. Moreover it has been reported that in 5CB the average birefringence remains fairly constant over a wide range of frequencies, from 2 to 15 THz, with local variations in the vicinity of resonances [23]. This can explain the modest modulation we observe, since we are exciting those vibrations that do not correspond to the main resonances between 4 and 6 THz [24,25]. The fact that these modes thermalize just after the interaction with the pump pulse can be explained by the liquid nature of the NLC. Whereas in a crystal, the optical phonons excited by stimulated Raman scattering can survive much longer than the excitation itself ( $\sim 100\text{ ps}$ ), in a liquid the coherence of such intramolecular vibrational modes is lost immediately after the excitation and thermalizes within  $\sim 2\text{ ps}$  [10,15,18], as we observed.

#### 4. Conclusions

In summary, the demonstrated ultrafast optical modulation of the refractive index of the NLC 5CB via the optical Kerr effect, which reaches in 500 fs at a fluence of  $4\text{ mJ/cm}^2$ . This is 5 to 8 orders of magnitude faster than observed before and can therefore be exploited for ultrafast modulation of LC-based devices. The unique combination of crystalline and liquid behavior of NLC's makes the latter an excellent medium for ultrafast coherent modulation of its

birefringence. However, more importantly, there is a fundamental difference between liquid crystals and ordinary liquids: liquid crystals can self-assemble into fascinating photonic structures, such as tunable optical microcavities [26], microlasers [27] and microfibers [28], which ordinary liquids cannot. In combination with their ultrafast Kerr response, liquid crystals could enter into a new era as a foundation for ultrafast, all-optical soft matter. Our experiments not only show a new exploitable route to use LCs for ultra-fast applications, but pioneer a new field of research, where ordered soft matter and ultra-fast spectroscopy could be combined towards an all-optical ultrafast control in LC technology.

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