



Nanosecond Electro-Optic Switching of a Liquid Crystal

Volodymyr Borshch, Sergij V. Shiyonovskii, and Oleg D. Lavrentovich*

Chemical Physics Interdisciplinary Program, Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

(Received 26 April 2013; published 6 September 2013)

Electrically induced reorientation of nematic liquid crystal (NLC) molecules caused by dielectric anisotropy of the material is a fundamental phenomenon widely used in modern technologies. Its Achilles heel is a slow (millisecond) relaxation from the field-on to the field-off state. We present an electro-optic effect in an NLC with a response time of about 30 ns to both the field-on and field-off switching. This effect is caused by the electric field induced modification of the order parameters and does not require reorientation of the optic axis (director).

DOI: [10.1103/PhysRevLett.111.107802](https://doi.org/10.1103/PhysRevLett.111.107802)

PACS numbers: 61.30.Gd, 42.70.Df, 42.79.Kr, 77.84.Nh

Nematic liquid crystals (NLCs) have revolutionized the way optical information is presented and processed [1]. The main feature that makes NLCs unique as an electro-optic medium is their long-range orientational order. NLC molecules are of an anisometric shape, in most cases resembling an elongated rod. Their average orientation is called the director $\hat{\mathbf{n}}$. The director is also the optic axis of an NLC with the birefringence $\Delta n = n_e - n_o$, where n_e and n_o are the extraordinary and ordinary refractive indices, respectively. Electro-optical applications exploit the so-called Frederiks effect, i.e., the reorientation of $\hat{\mathbf{n}}$ in a low-frequency electric field caused by anisotropy of dielectric susceptibility $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} > 0$; ε_{\parallel} and ε_{\perp} are the permittivities measured parallel to $\hat{\mathbf{n}}$ and perpendicular to it, respectively. When field \mathbf{E} is applied, the director $\hat{\mathbf{n}}$ realigns along \mathbf{E} if $\Delta\varepsilon > 0$ and perpendicular to \mathbf{E} if $\Delta\varepsilon < 0$. The reorientation time is approximately $\tau_{\text{on}}^F \approx \gamma/\varepsilon_0|\Delta\varepsilon|E^2$, where γ is the rotational viscosity and ε_0 is the electric constant. A strong field can realign an NLC rather quickly, within 100 ns [2]. However, a slow relaxation to the field-off state creates a bottleneck. When the field is switched off, the elastic nature of NLC forces $\hat{\mathbf{n}}$ to return to its original orientation set up by the surface treatment of the cell's plates (surface anchoring). The relaxation time of this passive process is determined by the elastic constant K of the NLC and by the thickness d of the cell, $\tau_{\text{off}}^F \approx \gamma d^2/K\pi^2$. For typical $K = 10$ pN, $d = 5$ μm , $\gamma = 0.1$ Pa s, the relaxation is slow, $\tau_{\text{off}}^F \approx 25$ ms.

In this Letter, we demonstrate an electro-optic effect in which both the field-on and field-off switching is fast, on the order of nanoseconds and tens of nanoseconds. The effect is based on electrically induced modification of the order parameters (EMOP) of NLCs rather than on the Frederiks reorientation of $\hat{\mathbf{n}}$.

The difference between the two types of electro-optic response is schematically illustrated in Fig. 1, using the concept of the dielectric tensor at optical frequencies (optic tensor). The two principal components of the optic tensor are $\tilde{\varepsilon}_{\parallel} = n_e^2$ and $\tilde{\varepsilon}_{\perp} = n_o^2$, such that $\Delta\tilde{\varepsilon} = \tilde{\varepsilon}_{\parallel} - \tilde{\varepsilon}_{\perp} > 0$, Fig. 1(a). Consider the case when the low-frequency

dielectric anisotropy is negative, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$. In the Frederiks effect, \mathbf{E} is applied parallel to $\hat{\mathbf{n}}$, so that the director reorients to become perpendicular to \mathbf{E} , Fig. 1(b) [1,3]. In the EMOP effect, \mathbf{E} is applied perpendicularly to $\hat{\mathbf{n}}$, to avoid director reorientation. The electric field changes the components of the optic tensor, Fig. 1(c):

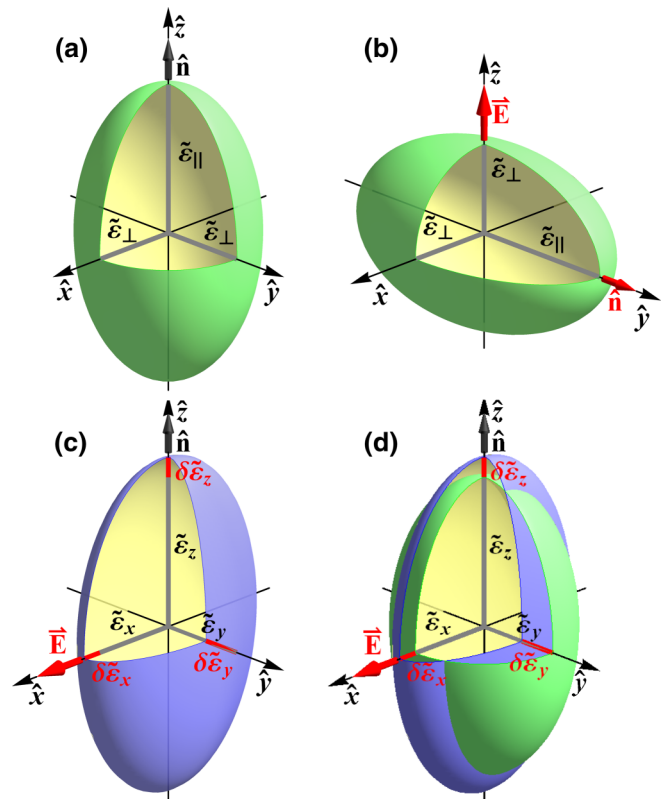


FIG. 1 (color online). Ellipsoid of optic tensor. (a) Uniaxial NLC with $\Delta n > 0$, $\Delta\varepsilon < 0$, and $\hat{\mathbf{n}}$ along the z axis. (b) Frederiks transition: $\hat{\mathbf{n}}$ reoriented by electric field \mathbf{E} applied along the z direction. (c) Electrically modified order parameter (EMOP) effect: Electric field \mathbf{E} along the x axis increases $\tilde{\varepsilon}_x$ and $\tilde{\varepsilon}_z$, while decreasing $\tilde{\varepsilon}_y$. (d) Field-off and field-on optical ellipsoids are shown together for comparison.

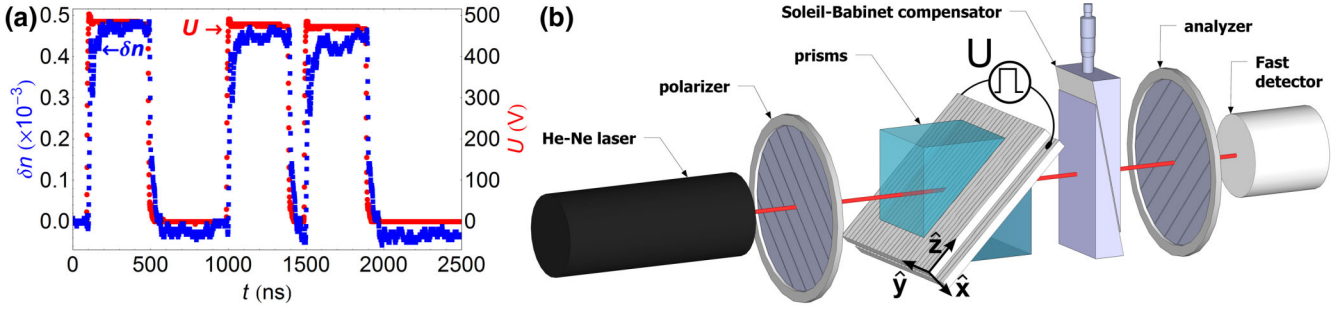


FIG. 2 (color online). (a) EMOP effect: field-induced changes in birefringence δn (blue) follow both the “on” and “off” edges of rectangular voltage pulses U (red) with a characteristic response time of about 30 ns; NLC CCN-47; $T = 45^\circ\text{C}$. (b) Experimental setup: NLC cell sandwiched between two 45° prisms.

$\tilde{\epsilon}_x = \tilde{\epsilon}_\perp + \delta\tilde{\epsilon}_x$; $\tilde{\epsilon}_y = \tilde{\epsilon}_\perp + \delta\tilde{\epsilon}_y$; $\tilde{\epsilon}_z = \tilde{\epsilon}_\parallel + \delta\tilde{\epsilon}_z$. These changes should manifest in phase retardation of light traveling through the NLC and thus provide the means for electro-optical switching. For example, when the NLC is viewed between two crossed polarizers, the change in phase retardation is converted into a change in light intensity, similar to the Frederiks effect. The principal difference is that the EMOP is a microscopic effect; its response time is determined by the coupling of the optic tensor of an NLC to \mathbf{E} . Such a response should be significantly faster than the off time $\tau_{\text{off}}^F \propto d^2$ of the Frederiks effect determined by macroscopic effects. Figure 2(a) demonstrates the main result of this work, an electro-optic switching of the NLC with the response time well below 100 ns to both the *field-on* and *field-off* driving.

The very possibility of the field-induced modification of the nematic order parameter (OP) is recognized and well known [4–7]. For example, if \mathbf{E} is parallel to $\hat{\mathbf{n}}$, it causes a uniaxial modification of $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$ and $\Delta\tilde{\epsilon} = \tilde{\epsilon}_\parallel - \tilde{\epsilon}_\perp$, see, e.g., Ref. [5], where the field-induced changes are described by the modification of the orientational ordering of the long molecular axes. The field applied normally to $\hat{\mathbf{n}}$ can lift the degeneracy of the transversal permittivity, producing a biaxial modification [5,6,8–11]. The field can also modify the fluctuations of $\hat{\mathbf{n}}$ [4,11–15]. The effect of fluctuations is detrimental; as when the field is switched off, they relax to their field-free spectrum slowly, with a characteristic time up to τ_{off}^F . We avoid the contribution of director fluctuations to the optical response by a special design of light propagation, as explained below.

We used 4′-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47) (Nematel GmbH, Germany) with the NLC phase in the temperature range $T = 31\text{--}58^\circ\text{C}$. CCN-47 is dielectrically negative, $\Delta\epsilon < 0$. At $T = 40^\circ\text{C}$, $\Delta n = n_e - n_o = 0.029$, and $\Delta\epsilon = -5.1$ at field frequencies (1–50) kHz. The NLC cell is $4.2\ \mu\text{m}$ thick. The anchoring direction is along the z axis in the plane of the cell, Fig. 2(b). The field is applied across the cell, along the x axis, by two indium tin oxide (ITO) electrodes of a small area, $A = 9\ \text{mm}^2$. Voltage pulses of amplitude U_0 up to 1 kV with nanosecond rise and fall fronts were generated by a pulse generator HV 1000

(Direct Energy). Their profile was experimentally determined with an oscilloscope Tektronix TDS 2014 (sampling rate 1×10^9 samples/s). The field changes the optic tensor

$$\begin{aligned}\delta\tilde{\epsilon}_x &= -\frac{1}{3}\delta\tilde{\epsilon}_u + \frac{1}{2}\delta\tilde{\epsilon}_b + (\langle n_x^2 \rangle_E - \langle n_x^2 \rangle_0)(n_e^2 - n_o^2), \\ \delta\tilde{\epsilon}_y &= -\frac{1}{3}\delta\tilde{\epsilon}_u - \frac{1}{2}\delta\tilde{\epsilon}_b, \\ \delta\tilde{\epsilon}_z &= \frac{2}{3}\delta\tilde{\epsilon}_u - (\langle n_x^2 \rangle_E - \langle n_x^2 \rangle_0)(n_e^2 - n_o^2).\end{aligned}\quad (1)$$

Here, $\delta\tilde{\epsilon}_u$ is the field-induced enhancement of optical anisotropy caused by the uniaxial OP change; $\delta\tilde{\epsilon}_b$ is the field-induced biaxiality of the optic tensor; $\langle n_x^2 \rangle$ is the average of the fluctuating director components along the x axis that depends on the electric field; the subscripts E and 0 indicate whether the value corresponds to the field-on or field-off case, respectively. We use a probing light beam that impinges on the NLC cell at 45° ; the light is polarized at 45° to the plane of incidence, Fig. 2(b). The field-induced quantities $\delta\tilde{\epsilon}_x$, $\delta\tilde{\epsilon}_y$, and $\delta\tilde{\epsilon}_z$ are small; thus the field-induced effective birefringence can be expanded in the power series, with the linear term corresponding to our setup,

$$\delta n = \frac{n_o^2(2n_o^2 - n_p^2)\delta\tilde{\epsilon}_z + n_p^2 n_e^2 \delta\tilde{\epsilon}_x - 2n_e n_o^3 \delta\tilde{\epsilon}_y}{4n_e n_o^3 \sqrt{n_o^2 - n_p^2/2}}.\quad (2)$$

Because the refractive indices of CCN-47, $n_o = 1.47$, $n_e = 1.50$, and the prisms, $n_p = 1.52$, are close, the contribution of slowly relaxing director fluctuations is practically eliminated, and the field-induced change δn of birefringence is determined by $\delta\tilde{\epsilon}_u$ and $\delta\tilde{\epsilon}_b$:

$$\delta n = \frac{1}{2\sqrt{n_o^2 + n_e^2}} \left(\delta\tilde{\epsilon}_u + \frac{3}{2} \delta\tilde{\epsilon}_b \right).\quad (3)$$

Dynamics of $\delta n(t)$ in response to the voltage pulses was determined by measuring the intensity of a He-Ne laser beam (wavelength $\lambda = 633\ \text{nm}$) probing the cell as shown in Fig. 2(b),

$$I(t) = I_0 \sin^2 \left\{ \frac{\pi [\delta n(t) + \Delta n_{\text{eff}}] d}{\lambda} + \frac{\phi_{\text{SB}}}{2} \right\},$$

where Δn_{eff} is the effective birefringence without the field; ϕ_{SB} is the adjustable phase of the Soleil-Babinet compensator. The phase ϕ_{SB} was adjusted in order to (a) maximize the sensitivity of measurements to $\delta n(t)$ by setting ϕ_{SB} to one of the $\phi_m = \pi(m + \frac{1}{2}) - (2\pi\Delta n_{\text{eff}}d/\lambda)$, where m is an integer, and (b) verify that the intensity change ΔI is caused by the EMOP effect ($\Delta I \rightarrow -\Delta I$ when $\phi_m \rightarrow \phi_{m+1}$) and not by the light scattering ($\Delta I \rightarrow \Delta I$ when $\phi_m \rightarrow \phi_{m+1}$) [16].

The most striking feature of the EMOP effect in Fig. 2(a) is that both the field-on and field-off switching show an extremely fast (tens of nanoseconds) response, a phenomenon very different from the Frederiks transition. In what follows, we analyze the EMOP dynamics and demonstrate that (a) the field-on and field-off response times are practically the same, and (b) the field-induced birefringence is a sum of the uniaxial $\delta\tilde{\epsilon}_u$ and biaxial $\delta\tilde{\epsilon}_b$ contributions to the optic tensor changes.

Figure 3(a) shows the birefringence change caused by a single voltage pulse of a duration 394 ns. To analyze the dependence $\delta n(t)$, we model the dynamics of the field-induced uniaxial $\delta\tilde{\epsilon}_u$ and biaxial $\delta\tilde{\epsilon}_b$ contributions to the optic tensor by the Landau-Khalatnikov approach [17]:

$$\tau_i \frac{d\delta\tilde{\epsilon}_i(t)}{dt} = \alpha_i E^2(t) - \delta\tilde{\epsilon}_i(t), \quad (4)$$

where the subscript i should read u if the equation describes the uniaxial contribution and b for the biaxial effect; τ_u and τ_b are the corresponding relaxation times; α_u and α_b are the susceptibilities to the applied field. Equation (4) has a general solution

$$\delta\tilde{\epsilon}_i(t) = \int_0^t \frac{\alpha_i E^2(t')}{\tau_i} \exp\left(-\frac{t-t'}{\tau_i}\right) dt' \quad (5)$$

$$E(t_{\text{on}} \leq t \leq t_{\text{off}}) = \frac{U_0}{d} \left[\frac{e^{-(t-t_{\text{on}})/\tau_a}}{1 - \tau_{\text{RC}}/\tau_a} - \frac{e^{-(t-t_{\text{on}})/\tau_{\text{on}}}}{1 - \tau_{\text{RC}}/\tau_{\text{on}}} - \frac{(\tau_a - \tau_{\text{on}})e^{-(t-t_{\text{on}})/\tau_{\text{RC}}}}{(\tau_a - \tau_{\text{RC}})(1 - \tau_{\text{on}}/\tau_{\text{RC}})} \right], \quad (6)$$

$$E(t > t_{\text{off}}) = E(t_{\text{off}})e^{-(t-t_{\text{off}})/\tau_{\text{RC}}} + \frac{U_0}{d(1 - \tau_{\text{RC}}/\tau_{\text{off}})} [e^{-(t-t_{\text{off}})/\tau_{\text{off}}} - e^{-(t-t_{\text{off}})/\tau_{\text{RC}}}],$$

where $\tau_{\text{RC}} = RC \approx 7$ ns is the RC time of the cell, $R \approx 43 \Omega$ is the resistance of cell electrodes, $C \approx 160$ pF is the cell capacitance measured at $T = 45^\circ\text{C}$. The characteristic times of the voltage pulse, namely, the rise time of the front edge τ_{on} , the fall down time of the rear edge τ_{off} , and the time of slow decay of the pulse amplitude τ_a , were obtained by fitting the pulse profile, Fig. 3,

$$U(t < t_{\text{on}}) = 0, \\ U(t_{\text{on}} \leq t \leq t_{\text{off}}) = U_0 [e^{-(t-t_{\text{on}})/\tau_a} - e^{-(t-t_{\text{on}})/\tau_{\text{on}}}], \text{ and} \\ U(t > t_{\text{off}}) = U(t_{\text{off}})e^{-(t-t_{\text{off}})/\tau_{\text{off}}}, \quad (7)$$

where t_{on} and t_{off} are the moments when the field is switched on and off, respectively. With the known $E(t)$,

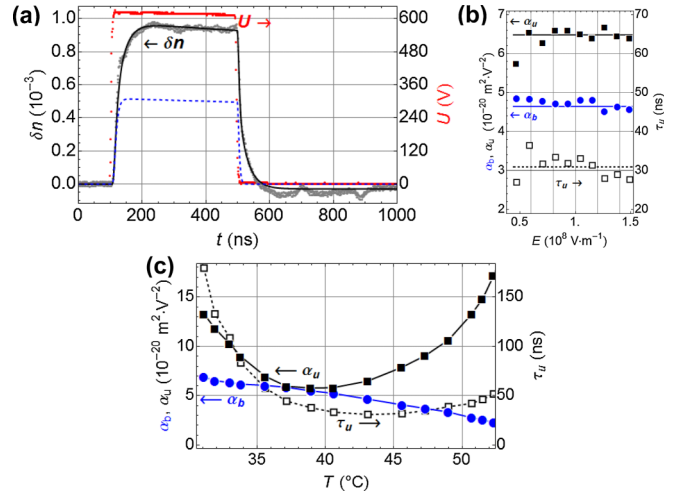


FIG. 3 (color online). (a) Birefringence change δn (gray dots) in response to a voltage pulse U (red) at $T = 43^\circ\text{C}$ is fitted with Eqs. (3) and (5), $\tau_u = 31$ ns, $\tau_b = 1.76$ ns, $\alpha_u = 6.5 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$, $\alpha_b = 4.7 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$ (solid black line). The blue dashed line shows the biaxial contribution with $\tau_b = 1.76$ ns and $\alpha_b = 4.7 \times 10^{-20} \text{ m}^2 \text{ V}^{-2}$. Fitting of the voltage profile by Eq. (7) with $U_0 = 626$ V, $t_{\text{on}} = 3.2$ ns, $t_{\text{off}} = 3.2$ ns, $\tau_a = 18 \mu\text{s}$, $t_{\text{on}} = 93$ ns, and $t_{\text{off}} = 487$ ns provides no visible deviations from experimental points. (b) The fitting parameters for uniaxial and biaxial contributions are field independent, as in the theoretical model. (c) Temperature dependences of α_u , α_b , and τ_u .

that is used to fit the experimental $\delta n(t)$. In the integrand, the time dependence $E(t)$ of the field acting on the NLC cell is described by a sum of exponential functions

we fit the experimental $\delta n(t)$ in Fig. 3(a) using the solutions (5) for the uniaxial and biaxial modifications of the optic tensor. The fitting parameters are τ_u , τ_b , α_u , and α_b .

The fitting shows that the response $\delta n(t)$ to the voltage change (including the on and off parts) is well described by the sum of two exponential processes of approximately equal amplitudes but with distinct relaxation times. One process is “slow,” with the relaxation time ~ 30 ns; the second process [dashed line in Fig. 3(a)] is very fast, with a relaxation time ~ 2 ns or even less (at the limit of our experiment accuracy).

The temperature dependences of α_u and α_b as one approaches the nematic-to-isotropic phase transition are very different from each other, Fig. 3(c). The value of α_u increases dramatically, while α_b shows a small decline.

This distinct behavior suggests that the slower process characterized by α_u should be attributed to the dynamics of uniaxial contribution $\delta\tilde{\epsilon}_u$ and that the faster process with α_b should be attributed to the biaxial contribution $\delta\tilde{\epsilon}_b$. The reason is that the free energy density near the nematic-to-isotropic transition has a vanishing dependence on the uniaxial OP and a sharp parabolic dependence on the biaxial OP [4]. The increase of susceptibility α_b at lower temperatures can be attributed to proximity of a hidden uniaxial-to-biaxial nematic phase transition. This transition is not observed experimentally, as the material transforms into a smectic A phase upon cooling. The latter might also explain why α_u increases at lower temperatures: formation of fluctuative smectic clusters near the nematic-to-smectic transition can be enhanced in presence of the electric field.

To summarize, we describe a new electro-optic effect in liquid crystals. We call it an EMOP effect, to stress that the phenomenon is caused by electrically induced modification of the order parameter (optic tensor) rather than by realignment of the director. The main distinctive feature of this effect is an extremely fast, nanoseconds and tens of nanoseconds, response to the electric field. The fast response characterizes both the field-on and field-off stages of switching. The nanosecond dynamics of the EMOP effect are drastically different from the slow (milliseconds) field-off director relaxation in the Frederiks effect. The field-induced changes of birefringence $\delta n \sim 10^{-3}$ might appear modest. Three comments are in order here. First, the quantity of interest in electro-optical applications is focused on the phase retardation $\Gamma(t) \propto L$, where L is the pathway of light that can be made large. Second, the measured values $\delta n \sim 10^{-3}$ are obtained for a material in which the natural field-free Δn is rather small (0.03); Δn and thus δn can be increased through chemical synthesis. Third, the EMOP effect can be enhanced in materials that are predisposed to a local biaxial order, such as bent-core mesogens. Further improvement in the switching speed can be achieved by using ultrashort voltage pulses to trigger only the fast (biaxial) EMOP response.

EMOP is a new member of the broad family of the Kerr-type effects, in which the field induced changes of birefringence grow with the square of an applied electric field. The classic Kerr effect is observed in isotropic fluids. Past research has revealed that the Kerr effect is strongly enhanced in the vicinity of the isotropic-to-nematic phase transition [5–7,18–21]. By staging the field-induced changes in the standard nematic and by eliminating the detrimental influence of director fluctuations, we demonstrate record-breaking response times and identify the mechanisms behind the effect, associated with uniaxial and biaxial modifications of the optic tensor. A complete description of the biaxial nematic phase requires four OPs which define the uniaxial and biaxial orders of the long and short molecular axes [22]. Our experiments are well fitted

with only two relaxation processes. The reasons might be as follows. First, the relaxation times of some of the four OPs might be similar to each other. Second, the EMOP effect is likely to be affected most strongly by the following two OPs: (i) uniaxial ordering of long molecular axes and (ii) biaxial ordering of short molecular axes. These two OPs are predicted to be dominant in the spontaneous biaxial nematic phase [23,24]. The same OPs are expected to be dominant in our experiment, since changes in the uniaxial ordering (i) cause strong changes in optical anisotropy and the biaxial ordering (ii) is affected by interactions of transverse molecular dipoles with the applied electric field. Further studies are needed to clarify the possible contributions of other OPs; this work is in progress.

The essence of EMOP embraces a much broader range of materials and driving forces than is presented in this Letter. Instead of the voltage pulses, one can employ the electric field of a light wave to modify the optic tensor, similar to what was extensively studied in the isotropic phase (see, e.g., [25] and references therein); instead of the low-molecular weight uniaxial nematic, one can use smectics and chiral nematics, polymers, etc. The nanosecond switching of optical properties of liquid crystals opens a new chapter in the fundamental science and applications of these materials.

The work was supported by DOE Grant No. DE-FG02-06ER 46331. We thank P. Bos, A. Jákli, P. Palffy-Muhoray, J. V. Selinger, and D.-K. Yang for reading the manuscript and useful discussions, R. Eidenschink (Nematel GmbH), now deceased, for providing us with CCN-47, and M. Groom for help with the experimental setup.

*olavrent@kent.edu

- [1] D.-K. Yang and S.-T. Wu, *Fundamentals of Liquid Crystal Devices* (John Wiley, Chichester, Hoboken, NJ, 2006).
- [2] H. Takanashi, J. E. MacLennan, and N. A. Clark, *Jpn. J. Appl. Phys.* **37**, 2587 (1998).
- [3] L. M. Blinov and V. G. Chigrinov, *Electrooptic Effects in Liquid Crystal Materials* (Springer-Verlag, New York, 1994).
- [4] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford Univ. Press, Oxford New York, 1993), 2nd ed.
- [5] C. P. Fan and M. J. Stephen, *Phys. Rev. Lett.* **25**, 500 (1970).
- [6] P. Palffy-Muhoray and D. A. Dunmur, *Mol. Cryst. Liq. Cryst.* **97**, 337 (1983).
- [7] I. Lelidis and G. Durand, *Phys. Rev. E* **48**, 3822 (1993).
- [8] J. A. Olivares, S. Stojadinovic, T. Dingemans, S. Sprunt, and A. Jákli, *Phys. Rev. E* **68**, 041704 (2003).
- [9] M. Nagaraj, Y. P. Panarin, U. Manna, J. K. Vij, C. Keith, and C. Tschierske, *Appl. Phys. Lett.* **96**, 011106 (2010).
- [10] R. Stannarius, A. Eremin, M. G. Tamba, G. Pelzl, and W. Weissflog, *Phys. Rev. E* **76**, 061704 (2007).

- [11] V. Borshch, S. V. Shiyankovskii, and O. D. Lavrentovich, *Mol. Cryst. Liq. Cryst.* **559**, 97 (2012).
- [12] P. G. de Gennes, *C.R. Acad. Sci. Paris B* **266**, 15 (1968) [<http://gallica.bnf.fr/ark:/12148/bpt6k480287r/f18.image.r=cr%20acad%20sc%20paris.langEN>]
- [13] J. L. Martin and G. Durand, *Solid State Commun.* **10**, 815 (1972).
- [14] Y. Poggi and J. C. Filippini, *Phys. Rev. Lett.* **39**, 150 (1977).
- [15] D. A. Dunmur and P. Palffy-Muhoray, *J. Phys. Chem.* **92**, 1406 (1988).
- [16] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.111.107802> for details of adjustment of phase retardation by the Soleil-Babinet compensator.
- [17] L. D. Landau and I. M. Khalatnikov, *Dokl. Akad. Nauk SSSR* **96**, 469 (1954) [*Collected Papers of L. D. Landau*, edited by D. Ter Haar (Pergamon Press, Oxford, 1965)].
- [18] J. C. Filippini and Y. Poggi, *J. Phys. D* **8**, L152 (1975).
- [19] H. J. Coles and B. R. Jennings, *Mol. Phys.* **36**, 1661 (1978).
- [20] S. Dhara and N. V. Madhusudana, *Eur. Phys. J. E* **22**, 139 (2007).
- [21] M. Gu, S. V. Shiyankovskii, and O. D. Lavrentovich, *Phys. Rev. E* **78**, 040702(R) (2008).
- [22] J. P. Straley, *Phys. Rev. A* **10**, 1881 (1974).
- [23] R. Berardi, L. Muccioli, S. Orlandi, M. Ricci, and C. Zannoni, *J. Phys. Condens. Matter* **20**, 463101 (2008).
- [24] S. V. Shiyankovskii, *Phys. Rev. E* **87**, 060502(R) (2013).
- [25] Hu Cang, J. Li, V. N. Novikov, and M. D. Fayer, *J. Chem. Phys.* **118**, 9303 (2003).