

Surface reorientation induced by short light pulses in doped liquid crystals

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Received February 27, 2003

Fast surface reorientation induced by a single 4-ns low-energy laser pulse in dye-doped liquid crystals is reported. The reorientation is due to light-induced modification of the surface anisotropy, which affects the liquid crystal's director through the appearance of a preferred direction on the irradiated surface. The detected signals can be interpreted as being the result of light-induced desorption and adsorption of dye molecules.

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OCIS code: 160.3710.

It is well established that the irradiation of Methyl Red- (MR-) doped liquid-crystal (LC) cells with polarized light induces stable director alignment over an initially isotropic boundary surface.^{1,2} Several experiments with combined cells [i.e., cells in which one substrate is treated to produce strong planar anchoring and the other is covered by an isotropic layer of poly(vinyl cinnamate) fluoride (PVCN-F)] have shown that MR adsorption on cell boundaries can be responsible for the observed permanent reorientation. Experimental evidence of surface reorientation in these kinds of cell has been given in Ref. 2, in which it was reported that free surface sliding of the nematic director was observed before a stable anchoring on the isotropic surface was reached. This effect was attributed to *trans-cis* photoisomerization of the dye. The subsequent permanent reorientation of the director parallel to the incident polarization was interpreted as being due to light-induced (LI) MR adsorption. Later it was shown that the processes of dye adsorption and desorption can account for director reorientation both toward and away from the incident optical field polarization.³ In the context of this scheme one can explain the appearance of an easy axis perpendicular or parallel to the pump-beam polarization by assuming that, after the cell is filled, a layer of adsorbed MR molecules (the dark adsorbed layer) grows over the PVCN-F-covered surface. Sub-

sequent irradiation with polarized laser light results in the development of an anisotropy axis on the boundary surface as result of competition between the LI desorption of dark-adsorbed molecules and the LI adsorption of dye molecules located close to the irradiated surface. Recent experiments have demonstrated that the phenomenon is quite general; it is responsible for director reorientation even in the transient regime.⁴ As discussed in Ref. 4, LI adsorption and desorption of MR molecules are surface effects that can be responsible for the modifications of surface conditions that led to the surface-induced nonlinear effect that was recently observed.^{5,6}

By studying the dynamics of the LI effects in combined cells for energy density below the threshold for permanent reorientation it is possible to verify the occurrence of transient surface reorientation. Such an observation would be in agreement with the model described above for which the irradiated boundary surface is considered the origin of the unusual nonlinear response observed in both homeotropic⁷ and planar⁸ cells, as suggested in previous papers.⁴⁻⁶

We carried out pump-probe experiments with combined cells, using pulsed laser excitation. Experimental data show that a single low-energy 4-ns pulse can induce fast dynamic LC reorientation consisting of two parts, outward and inward polarization. The two reorientations involve different rise and decay times,

which indicates that they are due to two distinct physical effects. Results are consistent with previously reported data on cw excitation that showed that light irradiation of combined cells can initiate two effects on different time scales.² The rise and decay times measured under pulsed excitation are much shorter than those that are typical of direct bulk reorientation, thus confirming that the observed effects are actually surface reorientations driven by the LI modification of the surface anisotropy.

Experiments were carried out with sandwich cells filled with a mixture of the nematic LC 5CB and the azo dye MR in a small concentration (0.1% by weight).

Different coatings were deposited onto two indium tin oxide-covered glass substrates. An isotropic unrubbed layer of PVCN-F covered one substrate; the second surface was treated with the commercial surfactant ACM72 for strong initial planar anchoring of the LC cell. The cell thickness was fixed at 23 μm with Mylar spacers.

The pump source was a frequency-doubled Nd:YAG laser that provided 4-ns pulses at $\lambda = 532$ nm. The pump beam impinged upon the cell at normal incidence from the side of the PVCN-F-coated surface with an optical energy density lower than 8 mJ/cm^2 . In general, with a laser pump beam traveling across a LC cell the induced thermal gradient can create a fluid flow that in turn will reorient the molecules through a flow-alignment mechanism.⁹ To prevent this effect from occurring we used a large pump beam diameter (4 mm). It is worth noting that thermal effects can be excluded because in our geometry they cannot contribute to the observed signal.

The irradiated region was probed by a linearly polarized low-power He-Ne laser impinging from the side of the rubbed surface. The probe polarization was parallel to the initial planar alignment of the cell. In these conditions the appearance of probe light behind the analyzer indicated a change of the LC orientation. Pump-probe measurements were performed for three values of angle β from the direction of pump polarization to the rubbing direction: $\beta = 0^\circ$, $\beta = 45^\circ$, and $\beta = 90^\circ$.

Curve a of Fig. 1 shows the typical shape of the signal obtained with $\beta = 45^\circ$, which corresponds to the geometry previously used in cw excitation.² A first fast peak with a rise time of the order of some tens of microseconds is followed by a second, slower signal that decays in ~ 10 ms. Both the rise and the decay times were evaluated by averaging over several curves obtained by use of time scales different from that in Fig. 1. No permanent director reorientation arises at the energy levels used. The detected signal exhibits some similarities to that reported for cw pumping.² There an initial sharp rise of the order of 0.5 s was followed by a decay to zero and then by a second, slower rise extending for a few minutes until stable reorientation parallel to the incident polarization was reached. The initial rise was due to a rotation of the director toward a direction orthogonal to the incident optical field in the plane of the isotropic surface.

By changing the pump's polarization it was possible to separate the contributions of the two signals shown

in Fig. 1, curve a. Curve b shows the signal detected in the same sample at $\beta = 0^\circ$. Only the first peak is present. The rise time is ~ 10 μs , and the decay time, evaluated with the assumption of exponential decay, is half a millisecond. Curve c shows the cell response at $\beta = 90^\circ$, which shows only the second, slower-rise-time contribution. The rise time is ~ 0.5 ms, whereas the decay time is of the order of 10 ms, as evaluated with reference to measurements over a longer time scale.

Examples of the decay times of the fast and slow signals are shown in Figs. 2 and 3, respectively.

The above observations indicate that the two distinct contributions of the detected signals are due to different mechanisms' occurring on different time scales, as in cw excitation. At $\beta = 0^\circ$, the pump polarization is parallel to the initial planar orientation of the cell. Under these conditions we expect to observe only director rotation away from the pump optical field E_{pump} , and we get only the fast signal that corresponds to the first peak of curve a. With $\beta = 90^\circ$, however, only the director reorientation toward E_{pump} should be observable, and accordingly we get a slower signal that corresponds to the long tail of Fig. 1, curve a. In this way the experimental data show the occurrence of two

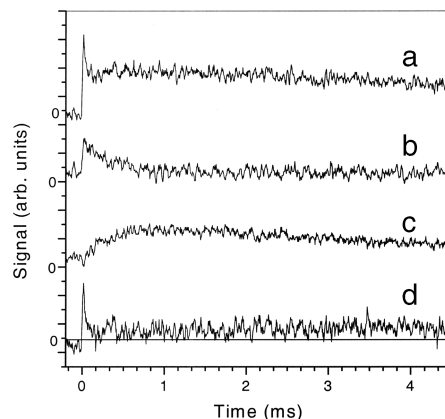


Fig. 1. a, Signal detected at $\beta = 45^\circ$; b, signal detected at $\beta = 0^\circ$; c, signal detected at $\beta = 90^\circ$. In all cases the incident energy density was 5 mJ/cm^2 . d, Difference between curve a and the sum of curves b + c. The y scale is linear for all the curves shown.

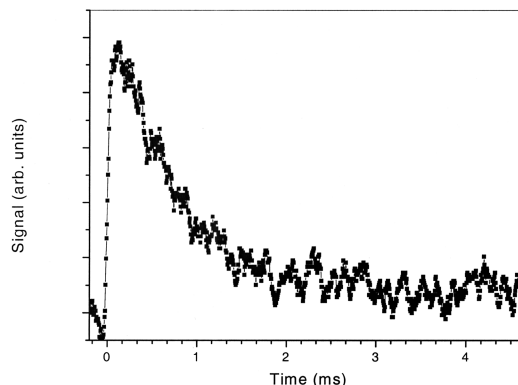


Fig. 2. Signal detected at $\beta = 0^\circ$, showing the decay time in detail. The incident energy is 3 mJ/cm^2 , and the decay time evaluated by fitting of the curve with an exponential decay function is 0.7 ms.

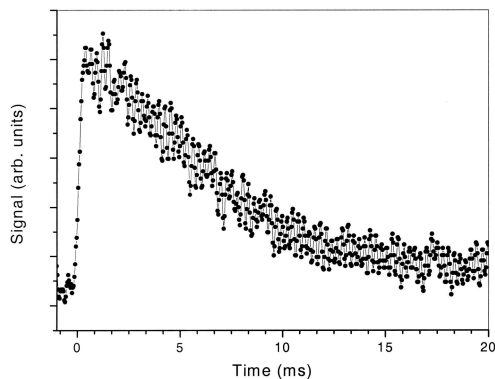


Fig. 3. Signal detected at $\beta = 90^\circ$, showing the decay time. The incident energy density is 3.5 mJ/cm^2 , and the decay time is 9.8 ms, evaluated by fitting of the curve with an exponential decay function.

distinct phenomena that lead to molecular reorientation toward two orthogonal directions.

Transient LC reorientation induced by a single nanosecond laser pulse has been reported and discussed by Hsiung *et al.*¹⁰ in the framework of the Ericksen–Leslie continuum theory. In that case a light-induced phase shift of ~ 0.1 rad was measured in a homeotropic nematic cell with a rise time in the range 10–100 μs . However, the decay time varied from 9 s for a 130- μm -thick cell to 23 s for a 190- μm -thick cell, which are characteristic values of the bulk reorientation. These values are 2–3 orders of magnitude higher than in our case. Moreover, for our sample thickness the expected bulk decay time would be ~ 0.4 s.¹¹ This experimental evidence strongly supports the hypothesis that we are dealing with surface phenomena, namely, with LI modification of the surface anisotropy, which in turn affects the LC's director through the appearance of a preferred direction on the PVCN-coated surface. The result is a molecular reorientation outward or toward the incident optical field, depending on the value of β . To our knowledge, this is the first direct evidence of fast surface reorientation in LCs.

Now, the objective is to understand what mechanism drives the modification of the surface anisotropy. The two signals that constitute the cell response are consistent with the theory of light-induced desorption and adsorption of MR molecules. According to the results of Ref. 4, LI desorption and adsorption can be effective even in the transient regime and can give rise to director reorientation away from and toward the incident polarization. Based on the experimental results and the considerations described above, the following interpretation can reasonably be proposed: The fast signal observed when $\beta = 0^\circ$, corresponding to outward reorientation, is due to LI desorption of dye molecules from the irradiated surface, which has already been pointed out as the origin of director reorientation perpendicular to the pump polarization.³ The slow signal, observed when $\beta = 90^\circ$ and corresponding to reorientation toward the incident polarization, is due to LI adsorption of dye molecules on the irradiated surface. Finally, when $\beta = 45^\circ$ a combination of the two

processes is observed. In this case we interpret the signal as due to LI desorption followed by LI adsorption. In curve d of Fig. 1 the difference between curve d and the sum of curves b + c is illustrated. The signal at $\beta = 45^\circ$ (curve a) consists of the superposition of the signals at $\beta = 0^\circ$ (curve b) and $\beta = 90^\circ$ (curve c).

In conclusion, pulsed pump–probe measurements of Methyl Red–doped liquid crystals have shown that cell irradiation with a single 4-ns pulse induces two distinct dynamic effects: a fast LC reorientation away from the pump polarization and a slow LC reorientation toward the incident polarization. Both phenomena are caused by light-induced modification of the surface anisotropy, leading to a preferred direction on the irradiated surface. The detected signals can be interpreted as the results of LI desorption and adsorption of MR molecules. We believe that the results reported in this Letter represent an important step toward a deeper comprehension of the complex phenomenology that underlies the photoinduced surface-mediated reorientation and the extraordinarily large nonlinear optical response in LCs.

We acknowledge financial support from the Istituto Nazionale per la Fisica della Materia (Project Progetto Avanzato InterSezione Light-Induced Molecular Adsorption and Orientation at Solid–Liquid Crystal Interfaces), Copernicus Concerted Action Photocom (European Community contract ERB IC15 CT980806), and the project Composite Liquid Crystal and Polymer Materials for Information Technologies of the National Academy of Science of Ukraine. We are grateful to V. Reshetnyak and A. Iljin for discussions. L. Lucchetti's e-mail address is lucchetti@popcsi.unian.it.

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