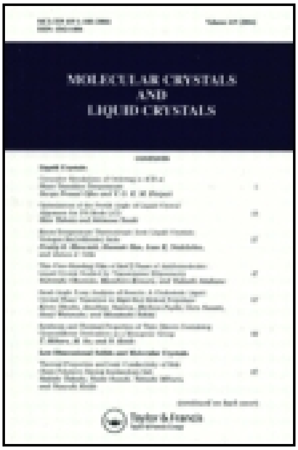

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Light Induced Reorientation in AZO-DYE Doped Liquid Crystals: The Relative Role of Surface and Bulk Effects

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LIGHT INDUCED REORIENTATION IN AZO-DYE DOPED LIQUID CRYSTALS: THE RELATIVE ROLE OF SURFACE AND BULK EFFECTS

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We report an experimental investigation on the origin of the large optical nonlinearity in azo-dye doped nematic liquid crystals. We show that a very large response is obtained for extremely low input light intensity, of the order of a few tens of μ*W/cm*^{2}*, and that it is mediated by the action of the photo-induced voltage on the specific surface coupling agent, which is an ionic surfactant. By performing circular polarization experiments we show that, during the reorientation, the nematic director follows a three-dimensional trajectory composed by in and out-of-plane motion with respect to the incidence plane of the light. We suggest that the bulk contribution is dominated by the photoisomerization of the azo-dye molecules and we report a new kind of self-sustained gratings.*

Keywords: large optical nonlinearities; nematic liquid crystals; azo-dye dopants; surface effect

INTRODUCTION

Light-induced reorientational phenomena in nematic liquid crystals (NLC) has been the subject of intense research interest during the last 20 years [1]. Giant optical nonlinearities have been observed for a suitable choice of the incident light polarization and nematic liquid crystal director $\vec{n}$ [2]. More recently, Janossy has shown that NLC doped with dye may give even

We gratefully acknowledge Tomoyuki Nagaya for helpful discussions and for his advices in many technical problems. We are grateful to Jean-Charles Bery for manufacturing the mechanical parts, to Jean-Claude Bernard and Arnaud Dusaucy for the electronics of our home-made rubbing, spin-coating and withdrawing machines. This work has been supported by the ACI of the French Ministry of Research (2218 CDR 2).

stronger nonlinear response [3]. In addition to their large optical reorientational nonlinearities, several research groups have found that they exhibit different properties, like surface mediated reorientation [4] connected with the ***trans-cis*** photoisomerization of azo-dye molecules [5] and photorefractive effects due to space charge modulation [6]. Further studies by Khoo showed extremely large sensitivity of a particular mixture: a small amount ($< 1\%$) of Methyl Red (MR) in 5CB [7]. This was interpreted as a large photorefractive effect, arising from an optically induced space charge field in combination with a bias dc field. Another possible interpretation is the one given by Simoni and cowokers [8], who have shown that the director reorientation originates from light-induced modifications of the anchoring conditions. This conjecture is supported also by other recent papers on the effect of ion-controlled anchoring transitions in NLC [9–12]. In particular, in [12] it is shown that the surface polarization observed in nematic samples can have an ionic origin. In another recent paper, it has also been demonstrated the effect of photo-alignment which is related to the presence of dye-doped anchoring layers [13].

In general, surface and bulk contributions may be simultaneously present and it is the interplay between these two effects which finally lead to a stable grating formation. Bulk reorientation has been reported as the consequence of the ***trans-cis*** photoisomerization of the azo-dye molecules under irradiation in the absorption band of the dopants [14]. Surface and bulk driven reorientations may also be combined for technological applications, such as the recording of high resolution permanent gratings [15]. Another important effect is the light-induced dye adsorption [16], leading to accumulation of dye molecules at the bounding plates of the cell, which can also play a role in the surface-induced reorientation [17].

In our set of experiments we show that the large optical nonlinearity of dye-doped NLC is indeed mediated by the specific surface alignment agent. We report here a systematic investigation on the influence of the surface conditions, performed by testing a large part of the known alignment agents that give homeotropic orientation. The result of our research is that an extremely high sensitivity can be obtained only by treating the surfaces with an ionic surfactant [18]. However, may questions still remain open, which are related to the relative weight of surface and bulk contributions to the whole reorientation process. Indeed, once the reorientation has started at the surface as a consequence of the light-induced weakening of the anchoring strength, the director motion propagates in the bulk of the cell, where it couples with other mechanisms which are usually resumed under a mean-field description in terms of guest-host interaction [19]. In the details, this interaction strongly depends on the particular type of liquid crystals, especially on their polar or non-polar nature, on the molecular conformation of the azo-dye dopants and on the incident light polarization, wavelength, propagation direction.

By testing our homeotropic cells both for linear and circular polarization of the pumps, we show here that the surface and bulk contributions combine in such a way that the resulting motion of the director is a three-dimensional trajectory leaving the plane of incidence of the incoming laser beams [20]. This motion starts with a fast in-plane reorientation, due to the surface effect. Then, a much slower contribution brings the director out-of-plane, leading to a continuous increase of the light absorption because of the dye dichroism. The subsequent photoisomerization of the dye molecules induces on its turn further rotation of the director. Finally, at the stationary state the director lies in a plane almost parallel to the bounding plates, that is, the reoriented cell is very similar to a planar one. Once written, the grating is self-sustained, that is, it is still present and stable even when we switch off one of the two pump beams.

In the first part of the article we present the methods for preparation of the homeotropic cells, we discuss the results obtained with different alignment agents in comparison with the ionic surfactants and we present the intrinsic instability of the extremely sensitive cells. Then, we describe the experimental setup and we present the results obtained in the diffraction experiments as well as in the one-beam experiments for linear polarization of the pump beams. We report also a mixed cell experiment, showing evidence of the surface effects. Then, we present the circular polarization experiments and we outline the memory effects related to the photoisomerization of the azo-dye dopants in the volume of the cell. Finally, we discuss the experimental results and we suggest the possible mechanisms which could be at the basis of the surface and bulk effects, respectively.

THE LIQUID CRYSTAL CELLS

Preparation and Coating of the Glass Plates

All our cells were made by ITO coated glass plates (Asahi Glass). The size of each glass plate is 20×30 mm^2. The plates were cleaned in ultra sound bath at 25°C for 15–20 minutes with a Micro 90 cleaning solution (Bioblock Scientific). After cleaning, the slides were rinsed 5 times, 5 minutes each time, in a highly purified water ($R \simeq 18\,M\Omega$). We dried the plates with filtered compressed air. Then, the clean glass plates were used for deposition of the alignment agent.

Homeotropic alignment of nematic liquid crystals can be obtained by different methods and by the use of different anchoring agents [21]. We have tested most of the standard techniques, such as spin-coating and deposition of a Langmuir film. All the technological procedures were performed in a clean bench. Spin-coating of the glass plates was used to treat the surfaces with Lecithin or with a specific poly-imide, provided by Nissan Chemicals. Lecithin was just spin-coated over the plates whereas Nissan Chemicals ploy-imide was prepared by two-step curing, at 80°C during 30 minutes after the spin-coating, then at 180°C during about 60 minutes.

We have also prepared cells by treating the surfaces with chlorosilanes, which are well known to provide good homeotropic alignment [21]. Deposition of N, N-dimethyl-N-octadecyl-3-amino-propyl-trimethoxysilyl chloride (DMOAP) was done according to the protocol described in [22]. Clean glass plates were dipped into a 0.1% wt DMOAP water solution and kept about 20–30 minutes. Then, the plates were rinsed, dried and cured at 110°C during 1 hour. We have also tested commercial cells from Linkam Scientific Instruments, treated to provide homeotropic alignment. For all the cells, the final quality of the liquid crystal alignment was tested by observing the sample under a polarizing microscope.

Another approach to obtain homeotropic alignment is to depose a surfactant mono-layer over the glass substrates [21]. We have followed this procedure with two different surfactants, hexadecyl-trimethyl-ammonium-bromide (HTAB) and hexadecyl-trimethyl-ammonium-chloride (HTAC). Both HTAC and HTAB belong to the group of ion pair reagents. The deposition of the HTAB and HTAC mono-layer film was obtained by withdrawing the glass plates very slowly out of a water solution. The withdrawing speed was about 5 mm/min and typical concentration of surfactant was in the range $10^{-6} \div 10^{-5} M$. We have prepared different solutions at different surfactant concentrations, both for HTAB and HTAC. Indeed, it is known that for weak concentrations of the surfactant there is a transition from the stable homeotropic alignment to a planar alignment with the easy axis oriented along the withdrawing direction [23]. Therefore, we expect that the HTAB (HTAC) concentration may play a role in the reorientation phenomena.

Filling the Cells and Alignment Instability

All the cells were filled with the same mixture of 0.3% MR (Aldrich Chemicals) in 5CB (Merck) and typical cell thickness was $d = 10\,\mu\text{m}$. Before filling the cells, the azo-dye doped liquid crystals were filtered, by centrifuging with Millipore filters of 0.22 μm, as well as degassed in a vacuum oven. All the differently prepared cells have shown perfect homeotropic orientation.

In the case of the cells treated with an ionic surfactant, we have also observed perfect homeotropic orientation at all concentration of the surfactant. However, for low HTAB (HTAC) concentrations the homeotropic alignment is not stable. In this case, after a few days a spontaneous reorientation takes place from the homeotropic to the planar state. The reorientation time depends on the temperature and on the illumination conditions. There is also an influence of the glue used to seal the glass plates. Indeed, in the cells sealed with Araldite epoxy glue the reorientation start much earlier than in the cells sealed with photosensitive polymer NOA. In any case, the reorientation starts from the sealed sides of the cell and eventually propagates to the entire cell in a few weeks.

The total surface of the reoriented area strongly depends on the HTAB (HTAC) concentration. This behavior shows that the surface coupling force can be controlled by changing the concentration of the ionic surfactant. Indeed, lowering the HTAB (HTAC) concentration leads to a weakening of the coupling force and to the alignment instability, which can be assimilated to a spontaneous reorientation. Normal illumination conditions give rise to a low photovoltage, which is enough to induce a change of the ion distribution close to the surface-liquid crystal interface. As a consequence, the liquid crystal reorientation starts at the points more favored by the boundary conditions, for example because of the presence of the glue. In a similar way, spontaneous reorientation [24] has been

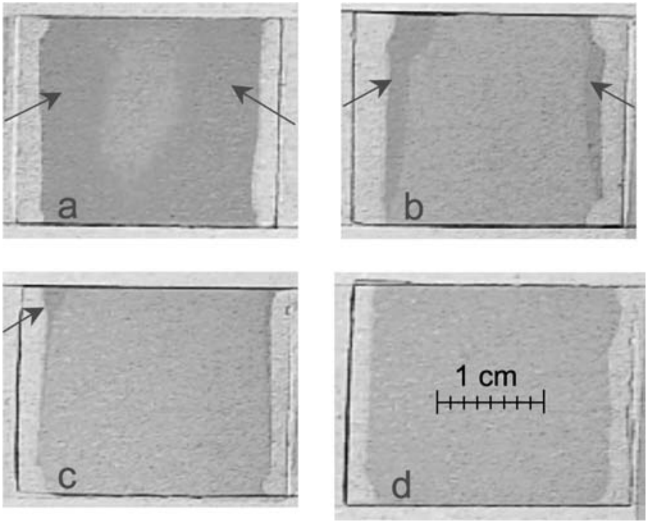

FIGURE 1 (see COLOR PLATE XXXX) Alignment instability in HTAC coated cells for different concentrations of HTAC in water solution: a) 1×10^{-5} M, b) 5×10^{-5} M and c) 1×10^{-4} M. For comparison, in d) we show a cell prepared with Lecithin. Arrows indicate the regions from where reorientation starts. All the images were taken one week after the cell preparation.

explained on the basis of the ion adsorption at the liquid crystal solid interface [9,12,25].

We show in Figure 1 some images of the liquid crystal cells prepared with low concentration of the surfactant and undergoing the alignment instability. It can be noticed that the spontaneous homeotropic-to-planar reorientation always takes place starting from the boundaries and then propagates towards the middle of the cell. Under normal illumination conditions the spontaneous reorientation is very slow and may take from one to 100 days depending on the surfactant concentration. In Figure 1d we show also a cell made with Lecithin. In this case no spontaneous reorientation is observed, as well as in the case of cells prepared with Nissan Chemicals or DMOAP alignment agents.

Another test on the influence of the surfactant concentration has been performed by preparing a cell with a HTAC concentration of about 10^{-4} M, by illuminating it with two interfering Ar^+ laser pump beams and by observing the grating formation under the polarizing microscope. When the pump beams are polarized parallel to the withdrawing direction, we observe grating formation at a total input power $I_{in} = 1\,\text{mW/cm}^2$. When the pumps are polarized orthogonal to the withdrawing direction, the grating formation requires a much higher intensity, up to $I_{in} = 30\,\text{mW/cm}^2$. This result can explain the existence of an easy axis in the cell, Which is related to the symmetry breaking due to the withdrawing procedure.

THE LIGHT INDUCED REORIENTATION

The Experimental Setup

The experimental setup is shown in Figure 2. The cell was placed at the intersection of two linearly polarized Ar^+ laser beams. The angle between them was $\alpha \simeq 1°$. For the typical cell thickness ($10\,\mu\text{m}$) and MR concentrations (0.3%), the cell absorption was approximately equal to $65\,\text{cm}^{-1}$, as we measured for both s and p polarization. Notice that for homeotropic alignment and normal incidence, and if there is no director tilt in the NLC cell, the absorption coefficient does not depend on the input light polarization. The two Ar^+ beams propagates in the $x - z$ plane. We choose normal incidence geometry, that is, the two Ar^+ beams are symmetrically place with respect to the normal of the cell. A linearly polarized 0.8 mW He-Ne laser was used to probe the grating.

We performed several experiments with different kind of NLC cells, but we found extremely high sensitivity for low input light intensity $\sim 100\,\mu\text{W/cm}^2$ only for cells prepared with HTAB or HTAC coated glass

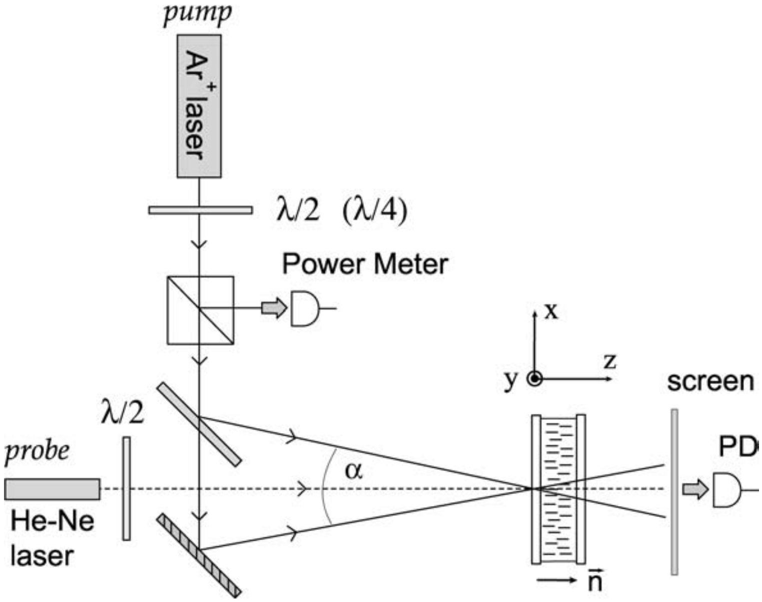

FIGURE 2 Experimental setup, PD: photodiode; $\vec{n}$: liquid crystal nematic director; $\lambda/2(\lambda/4)$: half-wave (quarter-wave) plate.

substrates. In this case, diffraction efficiency is very high ($\eta \simeq 0.20$) even at normal incidence and without any bias voltage applied. Neither Linkam S.I. cell nor the cells prepared with Lecithin, Nissan Chemicals or DMOAP alignment agents give such a large reorientational effect. The threshold intensity also depends on the ITO resistivity, as we checked by testing different ITO coated glass windows. The highest sensitivity was found for lowest ITO resistivity, at about 10 Ω/cm^2, and for low concentration of the ionic surfactant.

The Diffraction Efficiency in the Two – Beam Experiments

A typical diffraction pattern observed for a HTAB cell is shown in Figure 3. This pattern was obtained for a total input light intensity of 250 $\mu\mathrm{W/cm}^2$ and for a cell prepared with a low HTAB concentration, approximately 10^{-5} *M*. In Figure 3 we show also the measured first-order diffraction efficiency $\eta = I_{+1}/I_{probe}$ where I_{+1} is the intensity of the first diffracted order and I_{probe} is the total intensity of the probe beam. We observe diffraction rising when pump and probe beams are othogonally polarized and in two different geometries , pump $\|$ (probe $\perp$) and pump $\perp$ (probe $\|$) with

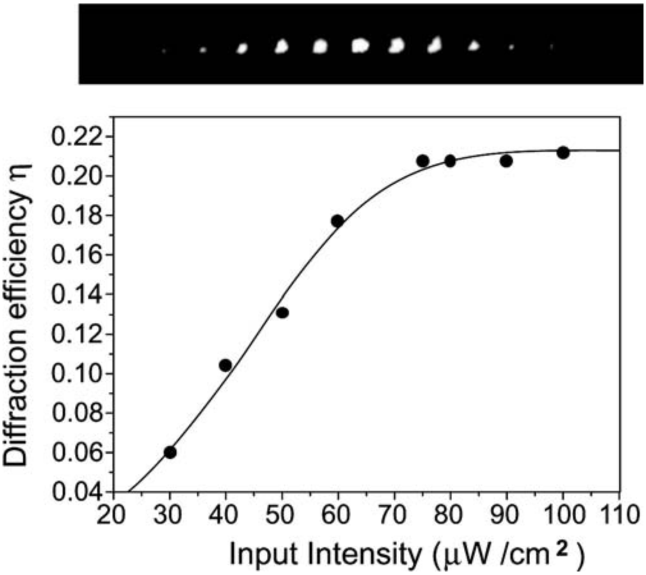

FIGURE 3 Diffraction pattern and diffraction efficiency.

respect to the $\vec{n}$ plane. However, maximum diffraction was obtained for horizontal pump polarization. This means that an easy axis selection is provided by the additional contribution of charge modulation in the x direction.

As usual [7], we can express the refractive index change as $\Delta n = n_2 I_{in}$ and estimate the coefficient n_2 from the first-order diffraction efficiency in the Raman-Nath regime, $\eta \simeq (\pi \Delta n d/\lambda)^2$. By substituting $\eta \sim 0.20$ at $I_{in} = 100\,\mu\text{W/cm}^2$ $\lambda = 0.632$ and $d = 10\,\mu\text{m}$, we get $\Delta n \simeq 1.0 \times 10^{-2}$ and thus $n_2 \simeq 100\,\text{cm}^2/\text{W}$ which is an extremely large value of the nonlinear coefficient [18].

Typical response time is about 20 seconds, as it can be seen on Figure 4a, where the diffraction efficiency is reported as a function of time and for a total pump intensity $I_{in} = 100\,\mu\text{W/cm}^2$. For comparison, in Figure 4b it is reported the photo-induced voltage measured for $I_{in} = 2\,\text{mW/cm}^2$. Typical values of the photovoltage are of the order of 10 mV. As it was already noticed [8], such a field is much lower than the one usually required for director orientation, especially at the very low total input power at which we observe the light induced reorientation. However, close to the ITO layer an interface is formed between the ionic surfactant and the cyano-heads of 5CB and the photo-induced voltage may change the mobility and hence the concentration of ions and counter-ions at this interface. As a result, at the

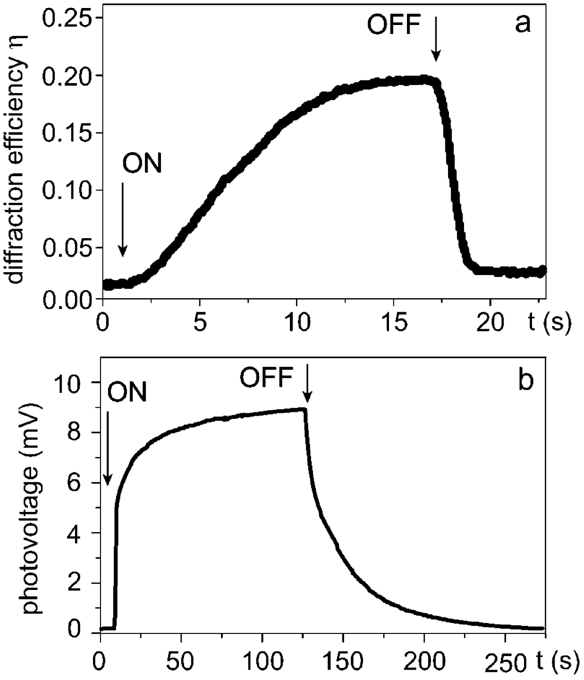

FIGURE 4 Temporal response of the HTAB coated cell for switching on and off of the writing beams: a) diffraction efficiency and b) photo-induced voltage as a function of time.

incidence surface the anchoring strength is weakened so that liquid crystals close to this surface start to reorient.

In order to better specify our statement, we can say that the action of the photo-induced voltage on the ionic layer adds to the NLC free energy a term of the form $\vec{P}_s \cdot \vec{E}_{ph}$, where $\vec{P}_s$ is the surface polarization and $\vec{E}_{ph}$ is the electric field associated to the photovoltage. Since the vector $\vec{P}_s$ points outwards the ITO coated surface, the presence of the product $\vec{P}_s \cdot \vec{E}_{ph}$ leads to a weakening of the anchoring strength at the illuminated side of the cell, thus triggering the onset of the liquid crystal reorientation. The same rise time observed both for the diffraction efficiency and the photovoltage gives a strong indication of the correlation between these two processes.

Self-diffraction is not observed in the whole range of very low light intensities in which we operate. Note however, self-diffraction appears at higher intensities as well as in the transient regime that characterizes the passage from one geometry to another, that is, by switching the pump polarization from one direction to the orthogonal one. This transient

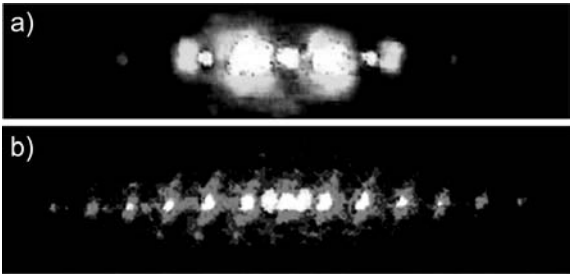

FIGURE 5 (see COLOR PLATE XXXXI) a) Self-diffraction and b) probe diffraction at $I_{in} = 1.5$ mW/cm^2.

behavior shows that the LC reorientation is first established in the plane orthogonal to the pump polarization.

In Figure 5a it is shown a typical self-diffraction pattern observed for horizontal pump polarization at $I_{in} = 1.5\,\mathrm{mW/cm^2}$. Notice that for these values of I_{in} the index grating becomes unstable since the out of axis reorientation leading to self-diffraction is also responsible of an increased light absorption, due to the dichroism of the azo-dye dopants. A probe diffraction pattern in this unstable regime is shown in Figure 5b, where a large light scattering appears in all directions. This is a signature that the NLC film is approaching the transition to the isotropic phase.

THE ONE-BEAM EXPERIMENTS

We have performed pump-probe experiments with only one pump beam at normal incidence. The probe was polarized either parallel or orthogonal to the pump and analyzed by a crossed polarizer after the cell. The pump input was blocked by a red filter after the passage through the cell. The pump polarization was horizontal, that is, in the x–z plane. When the pump is incoming on the cell, for both s and p polarization of the probe we observe a signal on the photodiode. Maximum signal is observed for a probe polarization at 45° with respect to the pump polarization, in agreement with the standard analysis techniques [24].

In Figure 6 we show the transmitted probe intensity I_{tr}, observed after a crossed polarizer for different orientation of the probe polarization and for different values of the total input intensity I_{in}. These observations show that the LC reorientation is out of plane and composed of two contributions, parallel and orthogonal to the pump polarization direction, respectively. Similar results were reported by Simoni [8], who showed that both ordinary and extraordinary components are involved during the reori-

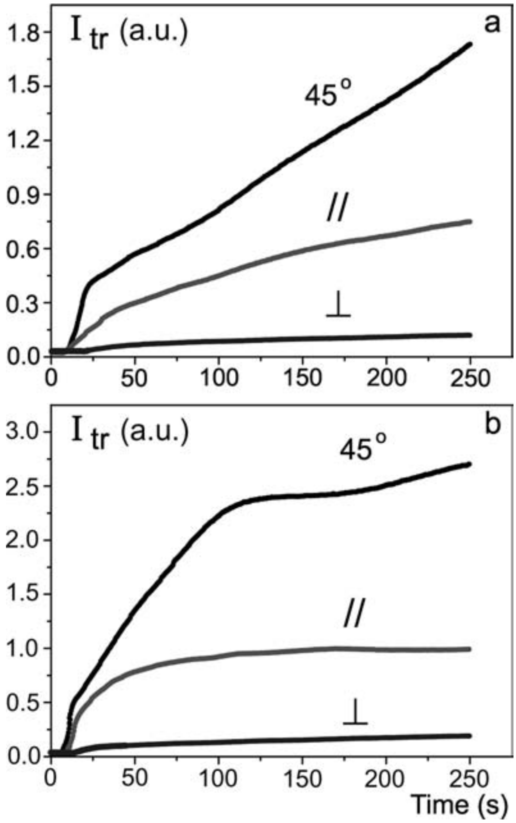

FIGURE 6 Temporal response of the HTAC cell in the one-beam experiment for a) $I_0 = 0.6$ mW/cm^2 and b) $I_0 = 0.8$ mW/cm^2. Probe polarization is indicated close to each corresponding curve.

entation and who gave the first evidence that the light induced reorientation in azo-dye doped NLC does not need the presence of a charge grating. Indeed, all the observations indicate that the index grating is mainly due to the local reorientation at the surface in combination with the photoisomerization of the dye molecules [4,5,8,18].

More precisely, the light induced reorientation starts at the surface and then propagates in the bulk. Because of the dye dichroism, dye-doped liquid crystals absorb more and more light during the reorientation. This bulk process is responsible for the long time scale and is accompanied by the *trans-cis* photoisomerization of the dye molecules. By comparing Figure 6a and b it can be seen that both signal presents a second slope starting approximately 20 seconds after switch on of the pump and that the corresponding slow growth saturates after a time that decreases by increasing the input light intensity. The first rise of the signals is instead a signature of the surface induced reorientation, characterized by the same short time scale that characterize the rise of the diffraction efficiency and of the photovoltage.

Finally, the one-beam experiments show also a dependence of the easy-axis on the withdrawing direction of the glass plates. In the absence of other mechanisms capable to break the symmetry in the longitudinal plane of the cell, it is the withdrawing direction which imposes a preferential direction. If we perform the same experiments as before but for a vertical pump polarization, that is, for a polarization orthogonal to the withdrawing direction, we find that the input light intensity needed to induce LC reorientation is more than 10 times larger than the one needed in the case of horizontal pump polarization.

THE MIXED CELL

In order to prove the influence of the ionic surfactant on the large sensitivity of the azo-dye doped NLC, we have built mixed cells, with one side coated with Lecithin and the other one treated with HTAC. We have made three cells with different thickness, 10, 20 and 50 μm. In the case of 10 μm thickness the threshold intensity for the appearance of the diffraction orders strongly increases up to a few mW/cm^2. For this reason, we have

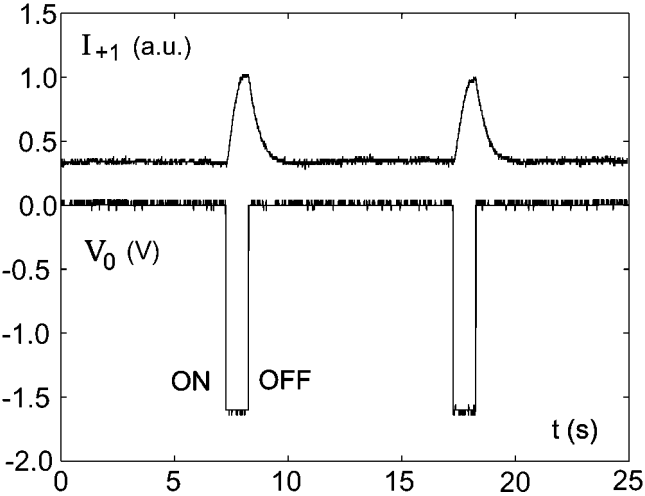

FIGURE 7 Temporal response of the mixed cell for switching on and off of the applied voltage V_0.

diminished MR concentration to 0.05% to avoid grating degradation due to photoisomerization of the dye and we have performed experiments with cell thickness 50 μm. The larger thickness also permits to enhance the decorrelation between the two surfaces of the cell. Without any voltage applied, the mixed cell does not display diffraction at low input power. However, when we apply a small voltage, 1.6 V, at $I_{in} = 800\,\mu W/cm^2$ and for a tilted geometry (incidence angle $\simeq$ 22.5°) we observe diffraction with efficiency $\eta = 0.1$, for horizontal polarization of the pump and of the probe. At 2 V applied to the cell, the diffraction efficiency increases dramatically to $\eta \geq 0.30$ and the grating becomes permanent. We can erase the grating by simply switching off the applied voltage.

The diffraction is observed only for probe polarized in x–z plane, because of the tilted geometry. Very important is the dependence of the observed phenomena on the electrical polarity. When we apply positive voltage to the HTAC coated side there is no diffraction. Only when we apply negative voltage to HTAC coated side we see clearly the appearance of diffraction orders. For a thick Cell (50 μm) the grating also depends on the incidence direction of the light. Indeed, for the thick cell we do not observe diffraction when the pump beams are incoming form the lecithin side. This is consistent with the presence, close to the sidewall, of charge carriers whose density decreases exponentially over the cell length. A similar ***optical-diode*** behavior was already reported for a mixed homeotropic cell [26].

A typical switching behavior of the cell is depicted in Figure 6 for an applied negative pulse with amplitude 1.6 V. It was found that the rising time is about 250 ms, which is the typical time for light induced director reorientation [1,2].

THE CIRCULAR POLARIZATION EXPERIMENTS

In order to get informations about the trajectory of the nematic director during the light induced reorientation, we have checked the response of the liquid crystal cells under the action of circularly polarized laser beams. In the experimental setup, as shown in Figure 2, we have inserted a $\lambda/4$ wave-plate at the exit of the Ar^+ laser, so that the two pump beams are circularly polarized, both in the same direction.

In Figure 8, it is shown a typical self-diffraction pattern observed after a HTAC coated cell for a total input light intensity $I_{in} = 2.0\,\mathrm{mW/cm^2}$ and for right handed circular polarization of the two pump beams (for symmetry reasons, left handed polarization leads to the same results). The response time is very slow, and in particular it takes quite a long time (several tens of seconds) to see the appearance of the first diffraction order. In Figure 9 the

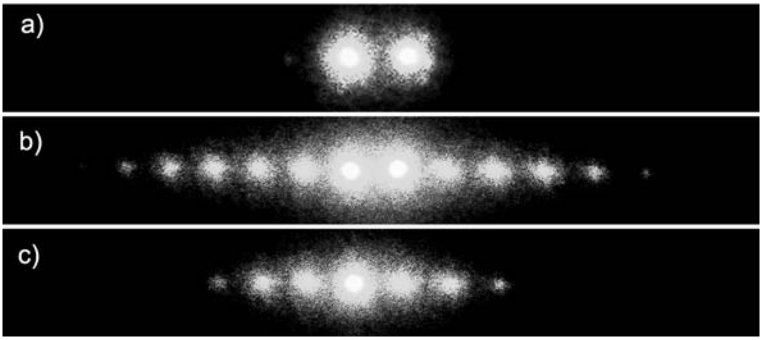

FIGURE 8 (see COLOR PLATE XXXXII) Self-diffraction of the two circularly polarized pump beams: a) start-up signal and b) stationary diffraction pattern. c) Stationary pattern observed once one of the two pump beams has been switched off.

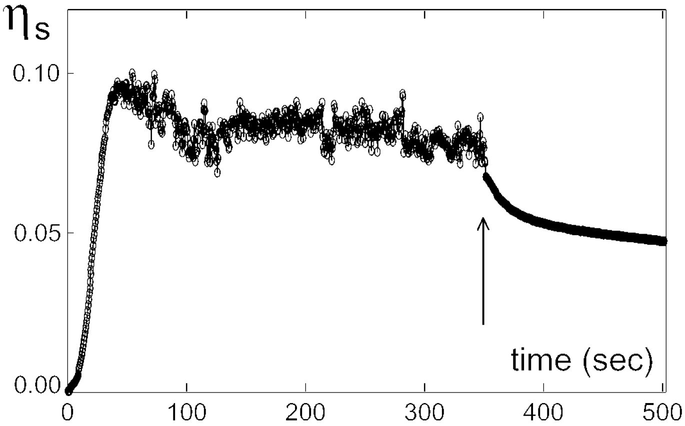

FIGURE 9 Self-diffraction efficiency η_s as a function of time. The arrow indicates the point where one of the pump beams was switched off.

self-diffraction efficiency $\eta_s \equiv 2I_{+1}/I_{in}$ is plotted as a function of time. I_{+1} is the intensity measured for the first self-diffracted order of one pump and $I_{in}/2$ is the intensity of one pump. It can be noticed that once the diffraction grating is established, the signal is characterized by large fluctuations. Indeed, since the pump beams are circularly polarized, the self-diffracted signal is the sum of the projections of the nematic director in the transverse plane (plane *x*-*y* in Fig. 2), thus very sensitive to fluctuations, both along the radial and the azimuthal directions. Once we switch off one of the pumps, as marked by the arrow in the plot, the amplitude of the fluctuations decreases drastically and the signal stabilizes in long time onto a lower value but does not go to zero. The corresponding diffraction pattern is shown in Figure 8c. Similar memory effects have also been observed in other liquid crystal cells coated with photoconductive polymer and filled with the same mixture of MR in 5CB [27]. In that case it was shown that the bulk photoisomerization of the dye can be controlled by pre-illumination of the sample.

Pump-probe experiments are performed for linearly polarized probe, both s and p components, analyzed by a crossed polarizer after the liquid crystal cell. For p-polarized probe, the intensity I_p transmitted after the analyzer is given by the usual formula [24]:

$$I_p = I_0 \sin^2(2\theta)\sin^2(\Delta\Phi/2), \tag{1}$$

where I_0 is the probe input intensity, $\Delta\Phi = (2\pi/\lambda)\langle\Delta n(z)\rangle d$ is the total phase shift integrated over the cell length and $\Delta n(z) = n_e(\theta,\beta,z) - n_0, n_e$ and n_0 being the extraordinary and ordinary refractive indices of the liquid crystals. $0 < \theta < \pi/2$ and $0 < \beta < \pi/2$ are the in-plane and out-of-plane reorientation angles, respectively, where the plane of reference is the incidence plane of the light, which is also the plane containing the nematic director $\vec{n}$ before the onset of the reorientation (plane x–z in Fig. 2). For s-polarized probe, the intensity I_s passing through the analyzer is given by the same formula, Eq. 1, with β replacing θ.

As shown in Figure 10, when we switch on the pumps, for both s and p polarization of the probe we observe a signal on the photodiode. The diffraction efficiencies $\eta_\theta \equiv I_{p+1}/I_0$ and $\eta_\beta \equiv I_{s+1}/I_0$ are evaluated by normalizing the intensities I_{p+1} and I_{s+1} of the first orders to the total probe intensity I_0. During the build-up of the grating there is first a signal for the p-polarized probe (Fig. 10a) whereas there is no signal for the s-polarized component (Fig. 10b). This indicates that a relatively fast reorientation takes place in the plane of incidence of the light. Then, the in-plane motion stops (correspondingly the signal in Figure 10a decreases) and a slow out-of-plane motion starts, as it is indicated by the rise of the signal in Figure 10b. At stationary state η_θ has considerably decreased, which means that the final configuration of the initially homeotropic cell is very similar to a planar one, with an almost vertical director. By switching off one of the two pumps (arrows in Fig. 10), we observe a decrease of η_β accompanied by an increase of η_θ, reflecting the reversed motion of the director along his original trajectory. Then, the two signals stabilize at intermediate values but they do not go to zero, that is, the grating is still present, according to the self-diffracted signal.

The fact that the first component of the director motion is the in-plane one is related to the presence of a small symmetry breaking at the surface of the cell. Indeed, this can be associated to the direction of withdrawing of the glass plates during the deposition of the surfactant layer. If we turn the

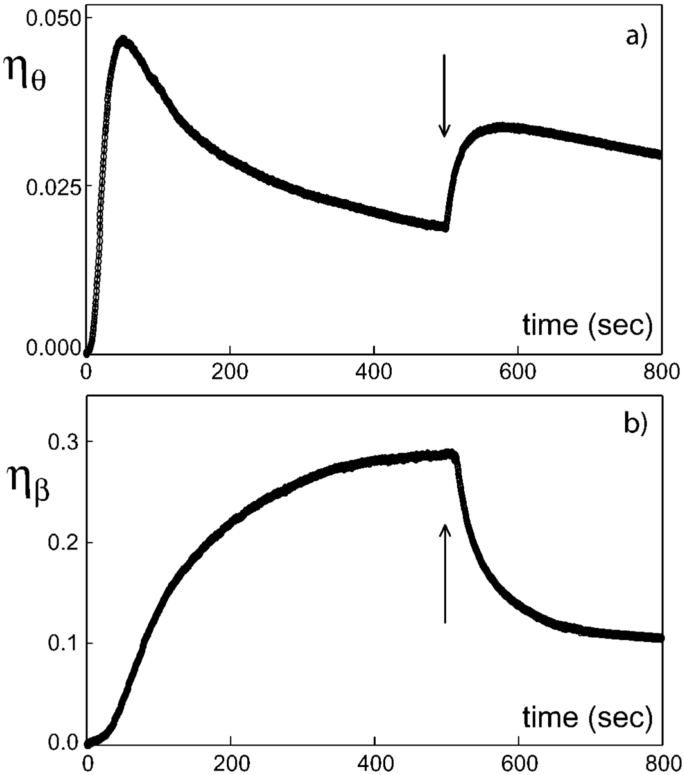

FIGURE 10 Diffraction efficiency a) $\eta_\theta = I_{p+1}/I_0$ for p-polarized probe and b) $\eta\beta = I_{s+1}/I_0$ for s-polarized probe. Arrows correspond to switching off one of the pumps.

cell by 90°, we observe the same behavior for the probe diffraction but the role of s and p polarizations is exchanged, that is, the first and fast component of the director motion is the one out-of-plane whereas the successive slow component is the in-plane one. These observations support the conjecture that the first and relatively fast component of the director motion is the one resulting from the surface-induced reorientation.

As a final test, we have prepared a planar cell by treating the surfaces with rubbed poly-vinyl alcohol(PVA) and we have illuminated the cell with circularly polarized pumps. The director $\vec{n}$ is initially along the x axis. The threshold for the director reorientation has increased up to $I_{in} = 20\,\mathrm{mW/cm^2}$ since the anchoring strength is much higher for PVA than for HTAC [21]. However, once the cell is illuminated with a light intensity high enough to overcome the anchoring strength, the director reorientation takes place in a very short time (~100 ms) and always in the x–z plane, as

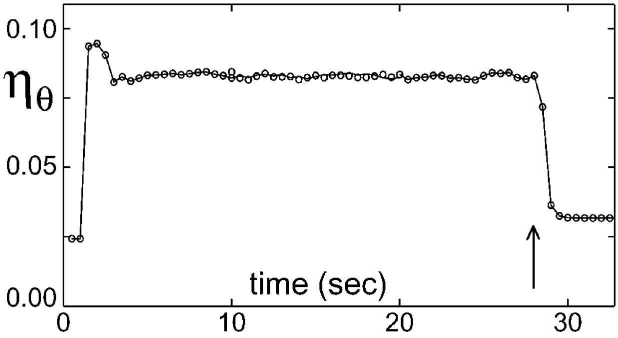

FIGURE 11 Diffraction efficiency η_θ for p-polarized probe in the case of a planar cell. The grating disappears once we switch off one pump (arrow in the plot).

revealed by the diffraction of a p-polarized probe (Fig. 11). For s-polarized probe, no diffracted signal is observed. This shows that the director motion is confined to the *x–z* plane and that at stationary state the cell becomes very similar to an homeotropic one. These observations can be explained by considering that in the planar case the light absorption is already maximized by the in-plane component, so that there is no reason for the director to reorient out-of-plane. This is again a confirmation of the role of the photoisomerization of the dopants and of their dichroism in determining the motion of the nematic director.

We have also tested homeotropic cells prepared by using Lecithine or Nissan Chemicals coated plates, for 10 µm thickness of the cell as well as for larger thickness such as 50 or 100 µm. In no one of these experiments, we have seen the same phenomenon, neither any diffraction until input light intensities of the order of 200 W/cm^2, which are completely out of the range of low input light intensity to which we are concerned in the case of large optical nonlinearities, as observed for the cells treated with ionic surfactants.

DISCUSSION OF THE RESULTS: THE RELATIVE CONTRIBUTION OF SURFACE AND BULK EFFECTS

All our observations demonstrate that the motion of the nematic director is composed of two contributions, parallel and orthogonal to the light incidence plane, respectively. The two contributions follows two different time scales, the first one being related to a relatively fast (tens of seconds) motion and to the surface contribution, the second one being characterized by the slow (hundreds of seconds) features of the ***trans-cis*** conformation of the azo-dye dopants in the bulk of the cell. Both linear and circular polarization experiments have shown the presence of two separated time scales, thus giving indication that the whole reorientation process results from two different contributions, related to surface and bulk effects, respectively.

The extremely high sensitivity of the cell treated with ionic surfactants is a strong indication of the surface effect. Indeed, the action of the photo-induced voltage on the ionic layers may be at the basis of the huge nonlinear response observed for this kind of cells. Note that this huge nonlinearity cannot be obtained with another kind of known alignment agent. Even the recently observed behavior of pure 5CB cells [28] could be explained on the basis of the photo-induced change of ion distribution at the surface-liquid crystal interface. Indeed, 5CB molecules have a polar cyano head [29] and applying a dc field creates a space charge close to the electrodes. All these considerations are consistent with the results reported by several authors [4,8,9–12], which all converge to indicate that liquid crystal reorientation does indeed originate from a charge modulation at the surface - liquid crystal interface.

The role of the surface driven reorientation is confirmed in the case of the mixed cell. In that case the polarity dependence of the diffraction grating cannot be explained without invoking a surface effect which adds to the NLC free energy a term of the form $\vec{P}_s \cdot \vec{E}_{ph}$, where $\vec{P}_s$ is the surface polarization and $\vec{E}_{ph}$ is the photo-induced voltage. More precisely, for the mixed cell there is an extra term due to the difference of the two surface anchoring coefficients, leading to a difference in the absolute value of the surface polarization $\vec{P}_s$. This does indeed reinforce the asymmetric effect, as it has also been observed also in other mixed cell experiments [26].

While the surface effect controls the relatively fast component of the director motion, the slow motion of the director seems to be more related to the photoisomerization of the dye dopants and to their dichroic properties. Indeed, the presence of *trans-cis* isomers not only enhance significantly the optical torque but also may lead to complex reorientational phenomena, resulting as a consequence of the dye dichroism and of the different strengths at which the*trans* and *cis* compounds contribute [30]. An intuitive explanation is that the out-of-plane reorientation leads to increased light absorption which on its turn leads to further reorientation, so that a slow accumulation of isomers takes place together with the reorientation. This process may be associated to the slow features of the director motion that are observed for the one-beam linear polarization experiments and for the circular polarization experiments. This interpretation is also confirmed by the planar cell behavior in the presence of circularly polarized illumination, where the dye dichroism stabilize the in-plane orientation. In the one-beam experiment, it is also shown that the slow response saturates after a time that decreases by increasing the input light intensity [18], which supports the conjecture that photoisomerization plays a crucial role in the bulk reorientation. Eventually, if I_{in} is too large (more than a few mW/cm^2) the photoisomerization of the dye may lead to permanent gratings. This may result from processes of dye adsorption onto the confining plates, in agreement with the results reported in recent papers [17,19].

CONCLUSIONS

We have presented a large number of measurements of the nonlinear optical response in azo-dye doped NLC cells. We have changed the surface anchoring conditions and investigated different types of alignment agents. We have tested the cells in different experimental geometries, either with two or one pump beams, either for linear or circular polarization of the pumps. All the results give indications that the high sensitivity of homeotropically aligned azo-dye doped NLC is related to the presence of ionic surfactant on the side-walls of the cell. We have also realized a new type of mixed cell that can be used as optical switch with a low dc voltage applied (1.6 V). The switching can be controlled either electrically or optically.

By illuminating NLC cells with two pump beams both circularly polarized in the same direction, we have shown that the motion of the nematic director is characterized by a relatively fast in-plane component followed by a much slower and out-of plane component. We suggest that the two contributions are associated to the surface and bulk effects, respectively. Finally, we have shown that the diffraction grating presents memory effects, which are related to the photoisomerizaton of the azo-dye dopants in the bulk of the cell. These preliminary observations, showing that gratings may be self-sustained in the case of circular polarization of the pumps, open the way to investigate the dynamics of the nematic director in the general framework of molecular motor systems [31].

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