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Supra Optical Nonlinearities of Photosensitive Nematic Liquid Crystals

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A critical review of laser induced nonlinear index changing mechanisms in liquid crystals is presented. In some azo-compound doped nematic films, we have observed nonlinear index coefficient $\geqslant 1$ cm^2/W. The supra optical nonlinearities are attributed to photorefractivity, order parameter modification and dopant-nematic intermolecular torques. Using these nematic films, we show that it is possible to perform image processing with μW/cm^2 optical intensity, and optical limiting with μW power lasers.

Keywords: Nematic Liquid Crystals; Supra optical nonlinearity; image processing; optical limiting; micro Watt

INTRODUCTION

In nematic liquid crystals, the easy susceptibility of the birefringent director axis to reorientation by externally applied fields, and their broadband birefringence and transparency[1,2], have led to their ever increasing widespread use in various information display and processing devices [4-6]. Progress in the studies of their optical nonlinearities has also been in leaps and bounds. Over the last few years, the so-called optical nonlinearities of nematic liquid crystals have evolved from being among the largest to record breaking supra-nonlinear values. We have recently discovered the so-called supra-opitcal nonlinearity (SON) in nematic liquid crystals doped with two different kinds of azo compounds, namely, methyl-red dye and an azobenzene liquid crystal[6-8]. Our studies have shown that many processes appear to be at work in these SON liquid crystals, such as photo-induced photorefractive effects and flows[9-11], trans-cis isomerization process [8,12] and order parameter, and dopant-liquid crystal molecular torque induced director axis reorientation effect[13]. Both systems yield nonlinear index coefficients that are orders of magnitude larger than existing materials[14-20], c.f. Table 1. In the following sections, we review some of the pertinent observations, current (qualitative) understanding of the basic mechanisms, and preliminary feasibility demonstration of image processing and optical limiting applications.

NEMATIC NONLINEAR OPTICS

Figure 2 depicts schematically various processes that could occur in an aligned nematic film upon irradiation by an optical field. In nematics, the reorientation of the director axis

$\hat{n}$ is governed by the system's tendency to minimize the overall Free energy[3], which consists of several bulk and surface interaction terms, and the interaction energy with the applied field[1].

Table 1. Refractive Index Coefficients of Nonlinear Optical Materials

Materials	Order of Magnitude of n_2 (cm^2/W)
Nematic Liquid Crystal	
Purely optically induced[1]	10^{-4}
Thermal effect and order parameter change [1]	10^{-4}
Excited dopant assisted[13]	10^{-3}
Photorefractive -C60 doped [ref.9]	10^{-3}
Photorefractive -methyl-red doped[ref. 6]	**6**
BMAB doped NLC [ref. 8]	**2**
GaAs bulk [14]	10^{-5}
GaAs MQW [15]	10^{-3}
Photorefractive crystals and polymers [16,17]	10^{-4}
Bacteriorhodopsin [18]	10^{-3}
Organic Polymers[19]	10^{-13}
Cis-trans isomery [20]	10^{-3}

Note: n_2 is defined by: change of index $\Delta n = n_2 I$, where I is the optical intensity

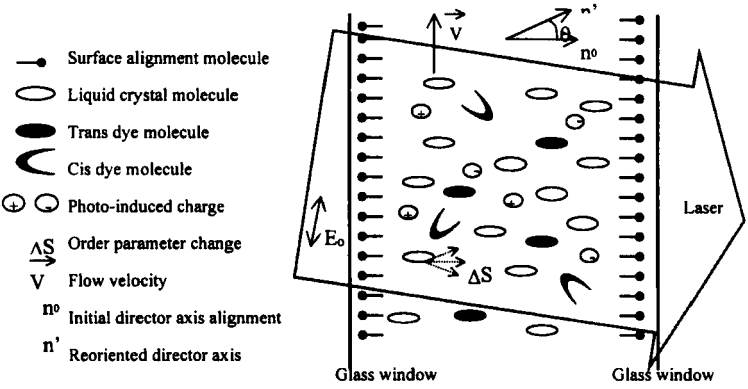

Fig. 1. Schematic depiction of various laser-induced photo-chemical and photo-physical processes in a nematic liquid crystal film.

In purely dielectric non-absorbing nematic liquid crystal, director axis reorientation is caused by the torque Γ_{opt} exerted by the optical electric field $\mathbf{E}$ and the director axis $\hat{n}$

$$\Gamma_{opt} = (\Delta\varepsilon/8\pi)(\hat{n}.\mathbf{E}^*)(\hat{n}\,x\mathbf{E}) \quad (1)$$

This torque competes with the elastic restoring torque Γ_{el}. Studies[13, 23] of nematic liquid crystals doped with anthraquinone or dichroic-dyes have shown that the excited dye molecules could exert an intermolecular torque Γ_{mole} that is much larger in magnitude than Γ_{op}, i.e.,

$$\Gamma_{mole} = \zeta\,\Gamma_{op} \quad (2)$$

where ζ can be > 100

Another mechanism, namely, orientational photorefractivity, could also result in very large optical nonlinearity. This effect occurs in nematic liquid crystals doped with photo-charge producing agents [9-11] such as Fullerene C_{60} or Rhodamine 6G dye, and requires the application of a small dc field to enhance the response. The effect originates from the incident optical field that excites and creates space charges the dopant molecules, which subsequently create dc space charge fields through ionic diffusion, migration and other electrodynamics processes. As shown in reference 9, the space charge fields consist of one photorefractive and two anisotropy components. The space charge fields, in combination with an applied dc field, creates a dc field induced torque of the form:

$$\Gamma_{dc} = (\Delta\varepsilon_{dc}/8\pi)(\hat{n}.\mathbf{E}_{int}{}^*)(\hat{n}\,x\mathbf{E}_{int}) \quad (3)$$

where the total internal dc field $\mathbf{E}_{int}$ contains the applied dc field $\mathbf{E}_{dc}$ and the generated dc space charge fields $\mathbf{E}_{sc}$. This causes director axis reorientation and refractive index change.

In addition to these space charge field induced effects, the flows of the charged ions and complexes under the applied dc field and the generated space charge fields, also contribute significantly to reorienting the director axis[9,21]. The combined action of the above space charge fields and the flow effects on director axis reorientation has been quantitatively formulated[9] and shown to describe experimental results very well. Furthermore, the flow-reorientation and adsorption of the excited dopant molecules on the surfaces are believed to be responsible for quasi-permanent and permanent director axis reorientation in Rhodamine 6G- and C_{60}^- doped nematic films, respectively.

In many azo-compound doped liquid crystals, photo-induced trans-cis isomerization of the dopant also provide another effective mechanism for refractive index modification, by causing an order parameter change and Γ_{mole} between the photo-excited dopant and the

NLC[13]. In general, the director axis reorientation associated with order parameter change ΔS tends to be randomly distributed, whereas Γ_{mole} gives rise to well-defined reorientation in dynamic grating experiment. As shown previously[6-8]and also described in the following section, polarization sensitive dynamic holography allows one to sort out the contribution from these mechanisms.

Our recent studies have shown that in nematic liquid crystals possessing supra optical nonlinearity, generally several mechanisms are at work simultaneously, depending on the interaction geometry and the excitation light intensity. It would require a treatise to delve into all the details. We shall contend ourselves here with a concise summary.

POLARIZATION DYNAMIC HOLOGRAPHY

Fig. 2 depicts schematically the grating diffraction experimental set up used to measure the intensity dependent refractive index changes in these nematic films. An Argon laser [λ = 488 nm] is split into two coherent writing beams which are overlapped on the sample. The films are made by sandwiching the doped nematic liquid crystal between surfactant treated glass windows for homeotropically alignment (director axis perpendicular to the surface), or rubbed polymer-coated windows for planar alignment (director axis parallel to the surface). The liquid crystal used is 5CB (Pentyl-cyano-biphenyl) or E7. Typical concentration [by weight] of the methyl-red dopant used is 0.05 %, and about 10 % for the other dopant, a azobenzene liquid crystal (4.4 butylmethoxy azobenzene BMAB)[12]. The molecular structures and absorption spectra of these dopants are shown in Fig. 3

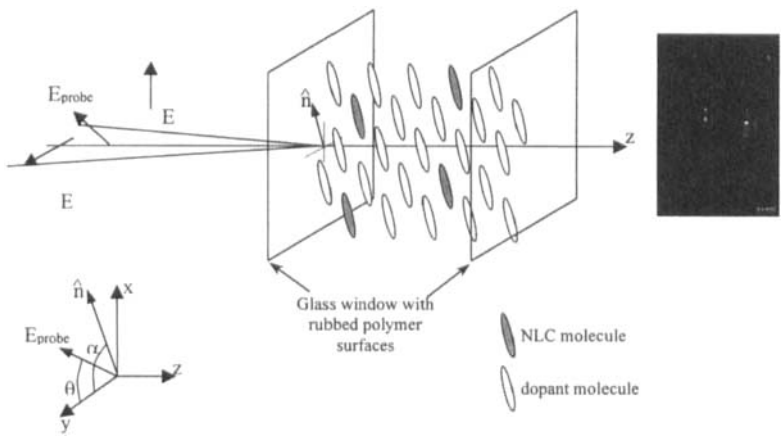

Fig. 2 The configuration of the various optical electric fields and the liquid crystal director axis $\hat{n}$ involved in the dynamic grating diffraction experiment, and photograph of the multi-order diffraction pattern.

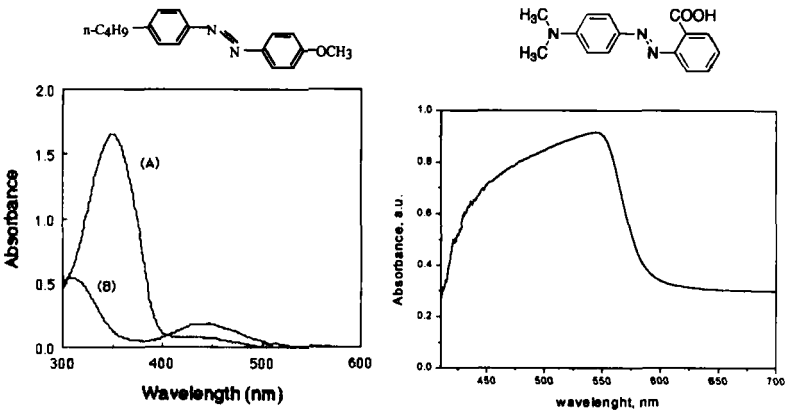

Fig. 3. (Left) Molecular structure and absorption spectra of Trans (curve A) and Cis (curve B) species of the azobenzene liquid crystals BMAB in the isotropic phase. (Right). Methyl-red dye.

MRNLC NONLINEARITY

In methyl-red doped nematic liquid crystal MRNLC, the optically induced space charge fields are so large that a sizable voltage drop is detected across the sample ITO-coated windows, and the external dc field is no longer necessary for generating observable diffraction. Unlike orientational photorefractivity discussed in preceding section, however, there is apparently no phase shift between the optical intensity function and the resultant spatial index change created in MRNLC. This and the fact that the reorientation tends to be along the grating wave vector have led us to conclude that flow effect plays an important role. The space charge fields cause flows of the charge-carrying dopant and liquid crystal molecules between the grating maximum and minimum, and from the entrance to the exit plane. The flows create shear torques that reorient the LC director axis[1,9,21], and also lead to ill-defined spatial phase shift between the optical intensity grating and the resultant index grating, and therefore vanishingly small two-beam coupling effect. Another evidence in support of the flow-reorientation model is the dependence of the grating diffraction efficiency on the sample thickness. It is observed that maximum diffraction usually occurs when the grating constant is on the order of twice the sample thickness – reminiscent of similar flow-orientation effect observed in photorefractive liquid crystals and other studies of flow alignment effects in nematic films[21].

Since methyl-reds are azo-dyes, one might expect order parameter modification caused by Trans-Cis Isomerization of these azo-dyes to play a role in the nonlinear response. However, such order parameter change gives rise to random director axis reorientation.

As pointed out in previous[6] studies, in general the reorientation tends to be well defined and directed along the input optical grating wave vector. We conclude that such trans-cis isomerization induced 'disorder' mechanism is not responsible for the supra-optical nonlinearity [SON] **observed in the low optical intensity regime[~1 mW/cm²]**. At higher writing beam intensity(10's of mW/cm^2), trans-cis isomerization induced order parameter and index change effects similar to those reported in reference[20] on MRNLC are detected. However, the n2 coefficient associated with such effects in MRNLC is **2 orders of magnitude smaller** than the SON effect.

Another possible cause of reorientation at low impinging light intensity is the intermolecular torque Γ_{mole} exerted by the photo-excited dye molecules on the NLC. This is particularly evident in experiments using input ***polarization grating*** on ***planar aligned sample***[7, 22].

BMAB-NLC OPTICAL NONLINEARITY

In BMAB doped nematic liquid crystal BMAB-NLC, director axis reorientation and refractive index changes are caused by two mechanisms, namely, order parameter modification ΔS caused by the trans-cis isomerization process and dopant-molecular torque Γ_{mole}. The latter is due to the tendency of the Trans- specis of the dopant to align with its transition moment perpendicular to the impinging optical polarization in order to minimize the interaction (absorption) energies.

We observed that, in general, if the writing beams are co-polarized, thus imparting an intensity grating, the resulting probe diffraction cannot be maintained at the maximal value, c.f. Fig.4a. This is attributed to diffusion of the Cis species from the intensity maxima to the minima, thus spreading the induced disorder ΔS throughout the sample, and degrading the index grating very much as thermal grating diffusion process.

Such degradation caused by Cis-species diffusion can be avoided if a writing optical polarization grating, formed by orthogonal polarized writing beams is used. Since the optical intensity is uniform, the order parameter change is also uniform(with small variation associated with the dichroic nature of the BMAM molecules). Therefore, the diffracted signal from the film comes primarily from director axis reorientation, which is due to the molecular torque exerted by the illuminated trans BMAB molecules on the NLC molecules. Since the orientation grating does not diffuse, the diffraction signal could build up to a large steady state value, as shown in Fig. 4b.

We have measured the dependence of the probe diffraction efficiency for various relative orientation of the probe polarization, and nematic director axis, c.f. Fig. 5. Detailed analysis of these results will be published in a longer article elsewhere. It suffices to say that these measurements further confirm that under a writing polarization grating, the predominant index changing mechanism arise from the director axis reorientation, with some small contribution from order parameter modification due to the dichroic absorption property of the BMAB molecules. From these experiments, the nonlinear

index coefficients of AZONLC are found to be on the order of 2 – 6 cm^2/W for writing optical intensity in the mW/cm^2 regime. At much higher intensity [~ 30 mW/cm^2], the concentration of Cis-species will build up to the point that the sample becomes isotropic.

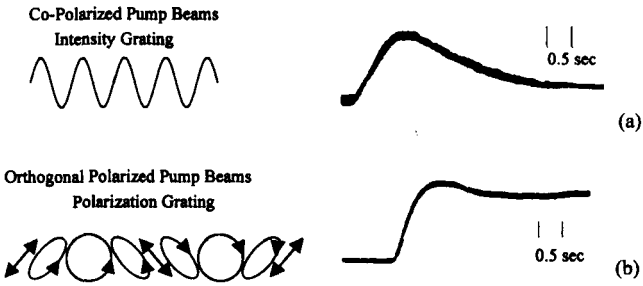

Fig. 4. Oscilloscope traces on the right depict the dynamics of the first order probe diffraction from BMAB doped planar nematic film for (a) input writing intensity grating (b) an optical polarization grating.

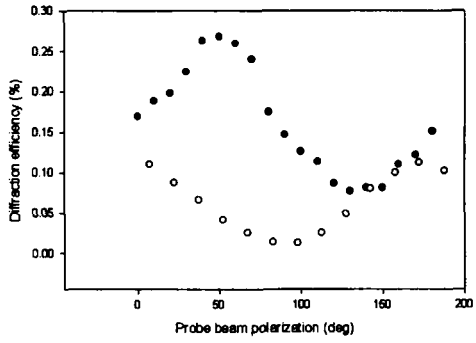

Fig. 5. Dependence of the probe diffraction on its polarization state [as the angle θ is varied] for two orientation of the director axis $\hat{n}$ of the planar aligned NLC's [Dots: α=45 degrees; circles: α=0 degree]. See Fig. 1 for definition of α and θ.

CONCLUSION

We have shown that it is possible to generate extremely large nonlinear refractive index change in nematic liquid crystals doped with efficient photo-charge producing agents or azo-compounds. These supra optical nonlinearities occur in the low optical intensity regime. A detailed quantitative theory for the basic mechanisms and analysis of the experimental data remain to be developed. Nevertheless, these preliminary observations

have already enabled the realization of several image processing and optical switching/limiting applications with extremely low optical power. In particular, we are able to demonstrate image contrast inversion using focal/image plane *phase modulation technique* [23], and *image conversion* with microwatt power laser [24]. *Optical limiting* with low threshold [nano - microWatt] and large dynamic range has also been demonstrated[24-26], c.f. Fig. 6; the limiting threshold is a few μWatt, and the operational dynamic range of the device exceeds 3000.

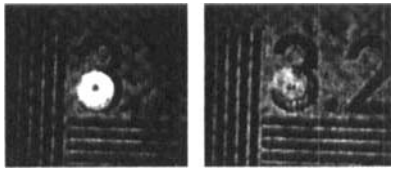

Fig. 5. Photograph of the transmitted laser beam (bright spot) and background image (i) without the MRNLC limiting effect, and (ii) with the MRNLC anti-jamming action on. [after ref. 24].

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