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The Never Ending Story of the Amazing Nonlinearities of Liquid Crystals: Recent Advances in Studying Electric Field Control

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The Never Ending Story of the Amazing Nonlinearities of Liquid Crystals: Recent Advances in Studying Electric Field Control

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We present a brief review of the story of the optical nonlinear response of liquid crystals from the Giant Optical Nonlinearity to the recently observed Colossal Optical Nonlinearity. We also report our latest results concerning the possibility of controlling this amazing nonlinearity by means of an external electric field.

Keywords: liquid crystals; optical nonlinearity; self phase modulation

INTRODUCTION: A BRIEF HISTORICAL REVIEW ABOUT THE LIQUID CRYSTALS AMAZING NONLINEAR BEHAVIOUR

The optical nonlinearities of liquid crystals (LCs) due to the collective reorientation of the molecular director represent a peculiar feature of these materials that have been studied for more than 20 years. After some theoretical previsions the first announcement of the Giant Optical Nonlinearity (GON) of LCs was given by Zel'dovich and coworkers in 1980 [1] after observing a strong self-focusing effect in nematic films using c.w. laser of moderate power. The GON denomination was motivated by a measured nonlinear permittivity 10^9 order of magnitude higher than in a common nonlinear liquid as carbon disulfide. In the following years several papers appeared confirming this observation and explaining in more details the connected phenomena both concerning the molecular orientation and the nonlinear optical propagation.

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The basic mechanism of the process is the Optical Torque on the molecular director n of the LC induced by the electromagnetic wave through its electric field. Due to the collective properties of these materials this effect allows a Kerr-like behavior were the nonlinear change of the refractive index is expressed by

$$\delta n = n_2 I$$

and n_2 is proportional to the square of the dielectric anisotropy and to the square of the film thickness and gets values of the order of $10^{-5}\,cm^2/W$. For this reason typical experimental conditions allowed observing these effects with light intensities in the range 10^2–$10^4\,W/cm^2$, namely using c.w. focused laser beams of 10–100 mW.

The fundamental nonlinear optical phenomena reported in the first year and widely studied and exploited in the following years were self-focusing, self-phase modulation, Optical Freedericks Transition and related threshold or non threshold effects dependent on the LC initial alignment and optical field polarization [2–5].

In spite of the easy experimental conditions necessary to observe these effects, an analytical theoretical description is possible only under restricted approximations since it involves the problem of coupling the Euler-Lagrange equations that minimize the free energy in the medium (considered as a continuum) with the Maxwell equations that describe the evolution of the field that affects the free energy of the medium. A useful solution of the problem has been given under the Geometrical Optical Approximation (GOA) [6] that holds when the reorientation of the director occurs on lengths much higher than the light wavelength.

A step forward in the way of studying GON have been done by the observation of the enhancement of this nonlinear response in nematic LC doped by antraquinone dyes: Janossy and coworkers [7] found a lowering of the OFT threshold by two order of magnitude with a correspondent enhancement of the nonlinearity of the medium. The further investigation performed on this effect has pointed out that it is possible to introduce a phenomenological additional torque due to the presence of dopant:

$$\Gamma_{dye} = \eta \Gamma_{opt}$$

where η represents the enhancement factor characteristic of the dye. The microscopic origin of the effect has been explained by Marrucci and Paparo [8] as dependent on the different interaction between dye and LC molecules occurring in the ground state and in the excited state of the dye and on the correspondent different diffusion constants.

Other experiments [9] have shown that a similar enhancement can be obtained by doping LCs with azo dyes provided that the two related

isomers *cis* and *trans* are treated as two different dopants associated with different enhancement factors.

Under these conditions the nonlinear refractive index n_2 can reach values up to $10^{-3}\,cm^2/W$ allowing light intensities in the range $10–10^2\,W/cm^2$, easily obtainable with focused laser beams of few mW in power.

Another development concerning optical nonlinearities of LCs started after the demonstration of the photorefractive effect in these materials [10]. In this case the long-range directional order allows a strong collective reorientation for a given space-charge field, and in contrast to photorefractive polymers, a weak electric field is able to induce directional charge transport and to enhance the quadratic electro-optic effect. In LCs other phenomena can play a not negligible role in the photorefractive response besides the "conventional" space charge generation and migration due to diffusion anisotropy: anisotropy of the dielectric permittivity and of the conductivity (Carr-Helfrich effect), thermal diffusivity of ions, and light-induced interfacial phenomena. These features make the photorefractive effect in LCs quite efficient so that in the usual geometry of wave mixing a nonlinear refractive index $n_2 \approx 10^{-2}\,cm^2/W$ can be reached using unfocused light beam of few mW with intensity on the sample in the range $0.1–1\,W/cm^2$. However we must keep in mind that such a strong nonlinearity is obtained with a spatially modulated light pattern as required to induce the photorefractive effect (two beams interfering in the nonlinear sample) while the Janossy effect is observable with a single beam impinging on the LC film.

Under the same geometry a "supranonlinear" response has been observed in nematic liquid crystals doped by Methyl-Red (MR) by Khoo and coworkers [11] without the application of an external bias voltage. In this case a nonlinear coefficient $n_2 \approx 6\,cm^2/W$ was measured and weak ($100\,\mu W$) unfocused light beams with intensity in the range $0.1–5\,mW/cm^2$ could be used to induce the nonlinear response. The evidence of a photovoltaic effect in these compounds supported the idea of a photorefractive-like effect, even if the low photo-induced voltage (of the order of mV) could not explain a strong director reorientation.

Several other experiments [12,13] have confirmed the supranonlinear behavior of MR-doped 5CB cells. In particular it has been proposed and supported by experimental observations that the origin of this amazing behavior is a surface-induced nonlinear effect (SINE) [14]. The basic idea being the light changing the anchoring conditions at (at least) one cell boundary, change that induces a bulk director reorientation which in turn affects the light propagation with the consequent

onset of a nonlinear optical response. Since the anchoring conditions can be modified by light absorption on a thin layer near the surface, very low pump intensity may be necessary to induce the effect.

It has been widely investigated that light-induced adsorption and desorption of MR molecules at the irradiated surface lead to transient or permanent modification of the surface conditions [15], therefore the SINE behavior is easily explained as due to the transient modifications occurring at very low pump intensity and at low dye concentration. It has been demonstrated that before any illumination a "dark" adsorbed layer of dye molecules is present on the boundary surface [16] and under weak illumination a partial desorption of these molecules occurs. This phenomenon is the basic one changing the surface conditions and being the origin of SINE. The most evident demonstration of this model is the dependence of the effect on the sample thickness d. While a real bulk optical reorientation leads to a square dependence on d, in this case a nonlinear coefficient independent on the thickness is expected [14]. As a matter of fact in this case any increase of the thickness increases losses so that the thinner is the sample and the higher is the nonlinear response. Following this idea it has been demonstrated that a "Colossal" nonlinear response is possible in these materials leading to $n_2 > 10^3\,cm^2/W$ in thin ($\sim 1\,\mu m$) randomly oriented samples, or $n_2 > 10^2\,cm^2/W$ in oriented samples with a weak anchoring surface. In this case, using the wave-mixing configuration, conventional for recording nonlinear gratings, unfocused beams with power ranging from 10 to 100 μW are used with intensities up to $1\,mW/cm^2$ [17].

The surface dependence of the Colossal behaviour makes very critical its reproducibility since it requires a good control of the initial surface conditions. For this reason we have made an extended investigation to get a reproducible Colossal behaviour by MR doped nematics without the need of a ideal control of the surface, studying the effect of temperature changes and of application of electric fields.

Even if the pretransitional behavior that has been reported [18] doesn't require a critical control of the surface, it does not appear practically useful to design optical devices based on this huge nonlinear response, since, on the other hand, it requires a critical control of the sample temperature.

On the contrary a low frequency electric field applied to the sample can easily give rise to a colossal behavior under reproducible experimental conditions [19]. In the following section we will review some recent achievements on this matter. Some new results obtained in one beam configuration will be also reported.

It is useful to summarize the main effects connected to nonlinear optical reorientation of liquid crystals in the following table.

Effect	n_2	Experimental conditions	Light intensity
GON	$10^{-5}\,cm^2/W$	undoped nematics single beam	10^3–$10^5\,W/cm^2$
JANOSSY	$10^{-3}\,cm^2/W$	doped nematics single beam	10^1–$10^3\,W/cm^2$
PHOTOREFRACTIVE	$10^{-2}\,cm^2/W$	doped nematics wave mixing	0.1–$1\,W/cm^2$
SUPRANONLINEAR	1–$10\,cm^2/W$	doped nematics wave mixing	0.1–$5\,mW/cm^2$
COLOSSAL	10^2–$10^3\,cm^2/W$	doped nematics wave mixing	0.01–$1\,mW/cm^2$

COLOSSAL NONLINEARITY CONTROLLED BY ELECTRIC FIELD

As already mentioned a "dark adsorbed" layer of dye molecules is present in the MR doped sample before any irradiation. Moreover several observations confirm that a photovoltaic effect is present in these materials. Additionally a strong increase of the Fredericksz threshold has been measured in dye doped samples [20]. All these arguments point out that before any irradiation a space charge distribution is present on the boundary surfaces and its effect is a strong screening of the electric field that can possibly be applied. On the other hand when light is impinging on the sample at low pump power dye desorption from surface takes place being dominant over the opposite dye adsorption of the excited molecules [15]. Under these circumstances a decrease of the space charge density on the surface is likely to occur, leading, as a consequence, to a lowering of the screening effect and to an increase of the electric field effective in the bulk of the material. In fact the effective voltage drop across the cell bulk can be written as:

$$V_{Bulk} \propto \left(V - 2\frac{\sigma q d}{\varepsilon_S}\right)$$

where V is the externally applied voltage, ε_S is the surface dielectric constant, d the cell thickness, and σq the surface charge density of ions collected in front of each electrode [21]. If σq is modulated by the optical field, the bulk voltage is modulated as well.

This effect has been recently reported by us [19], demonstrating that the Colossal nonlinear response can be easily controlled by a low frequency electric field applied to the sample.

In fact the following phenomenon can be observed in any LC cell doped by low concentration of MR to avoid memory effects. The planarly aligned sample is polarized by a bias voltage $V < V_{th}$, being V_{th} the threshold voltage to induce the electrical Fredericksz transition. Two light beams interfere on the sample producing a spatially modulated pattern (alternation of maxima and minima). In this way light induced desorption gives rise to a spatial modulation of the space charge distribution on the surface and, as a consequence, of the effective voltage applied to the bulk of the sample: in correspondence of light maxima desorption is strong and the resulting voltage is higher. When this value overcomes the Fredericksz threshold reorientation of the LC director occurs. In this way the spatially modulated optical pattern gives rise to a spatial modulation of the electric field induced reorientation, i.e. a phase grating. Of course an increase of the applied voltage over the Fredericksz threshold of the doped sample reduces the effect and can completely quench it when the whole sample is reoriented. On the contrary, keeping the applied field below threshold the effect of the interference pattern will be the spatial modulation of the applied voltage in the sample. Since this effect is induced by very low light intensity on the surface, it results in a strong nonlinear optical response.

Even if the strongest response (of the order of $10^3\,cm^2/W$) is obtained in randomly oriented samples, it is more suitable to use planarly aligned samples where one boundary surface is characterized by weak anchoring. In this way the conventional wave mixing configuration used for recording nonlinear gratings easily gives rise to a nonlinear refractive index $n_2 > 10\,cm^2/W$. An example of this behaviour is shown in Figure 1 where the diffraction efficiency under the action of the modulated field is reported for the first order of diffraction. The maximum reached efficiency is $\eta \cong 5\%$ for an optical intensity of $1.5\,mW/cm^2$, which corresponds to a nonlinear optical coefficient $n_2 = 25\,cm^2/W$. It should be stressed the very low pump intensity used in these experiments ($\cong 1\,mW/cm^2$).

All the experimental data show that the application of a static or quasi-static electric field below the threshold value correspondent to no light irradiation always allows reaching a huge nonlinearity, without requiring a critical control of the surfaces during cell preparation. Therefore the application of an external field of proper value provides a fully reproducible and easy way to get and control extremely high optical nonlinearity in thin MR-doped 5CB cells.

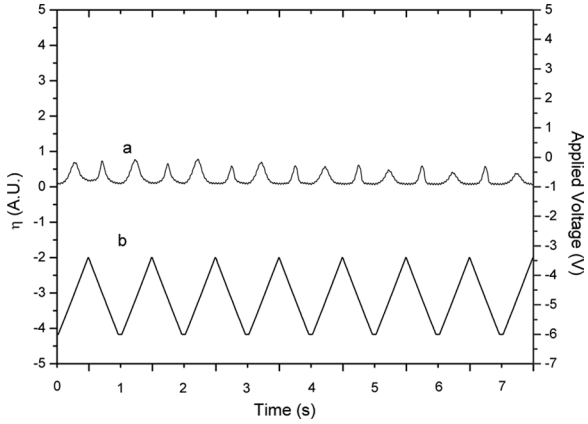

FIGURE 1 First order diffraction efficiency vs time under the action of an external low frequency bias. The cell has planar alignment.

The described mechanism has some similarity with effects observed by other authors under different experimental conditions [22–24], in particular for what concerns surface-mediated photorefractive effect or photo-induced carriers phenomena. However the effect reported here is not related to a particular combination of LC and alignment layer: it can be observed in cells with different substrate treatment (conventional coatings by PVA or DMOAP) or without any treatment (bare cleaned boundary). Therefore the involved charges necessarily come from the LC/MR mixture.

The ability to control the Colossal nonlinear response of a nematic liquid crystal should be considered an important achievement since it allows to have a reproducible control of the conditions allowing to get a nonlinear refractive index n_2 in the range $10–10^3\,cm^2/W$. Again we have to remind that this result is obtained under the wave mixing configuration leading to a spatially modulated light pattern on the sample.

A relevant question that arises is if it is possible to get the same Colossal nonlinear response using a single beam, i.e. under the usual self-focusing or self-phase modulation conditions for a single beam. The interest in answering this question is twofold. First of all it needs to be cleared yet how is the role of the spatially modulated pattern in the nonlinear response: the simplified model presented above introducing only a intensity depend light modulation could be corrected by introducing a contribution of surface photorefractivity which could play a not negligible role in presence of an applied field. On the other

hand the possible applications of a Colossal Nonlinear film in optical processing are evident.

The same samples described above (planar 5CB doped by MR) have been investigated under the following experimental conditions. A pump beam from a cw Nd:YVO_4 frequency doubled laser ($\lambda = 532\,\text{nm}$) is focused by a 22 cm plano-convex lens on the sample untreated surface at normal incidence. The beam is polarized in order to impinge the sample as a pure extraordinary wave. The incident power was varied between 30 and 1300 μW, corresponding to intensities in the range $(0.8 \div 40)\ \text{W/cm}^2$. It is worth noting that the intensity typically needed to observe SPM in pure liquid crystals is of the order of $10^3 \div 10^4 \text{W/cm}^2$ [25]. A static bias is applied perpendicular to the cell substrates. Cell thickness has been varied between 10 and 100 μm, which allows testing the dependence of the observed effect on the sample thickness. It is worth noting that cell thickness much lower than 10 μm is not desirable in this case, since SPM requires an induced phase shift higher than 2π to be observed.

Experimental results show that the typical SPM pattern is easily observed in all the analyzed cells even at the lowest intensity, but only if the external bias V is switched on. Once the ring pattern has been obtained, the number of rings N can be controlled by acting on V. In particular, an increase of V leads to an increase of N as shown in Figure 2. Above a certain value of about 2.5 V the SPM pattern collapses. A Similar behaviour was observed for anthraquinone dye doped materials by Tabiryan and Umeton, but at much higher power levels [26].

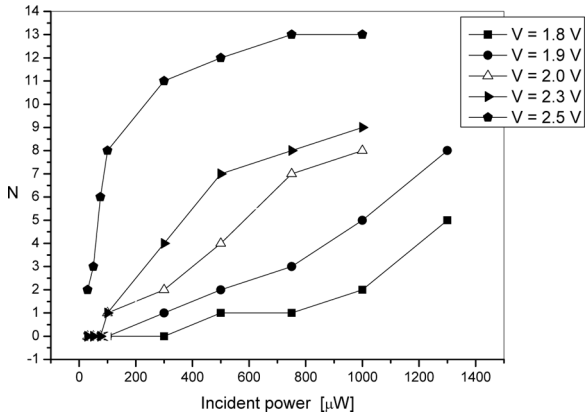

FIGURE 2 SPM rings as a function of the laser power, for different values of the external bias. The cell has planar alignment and is 13 μm thick.

The number of SPM rings is linked to the maximum induced birefringence Dn. This makes it possible to build up curves where Dn is plotted as a function of the incident laser intensity I. Figure 3 reports an example of this kind of curves.

By comparing the different curves it is easy to notice that the thinner is the cell the higher is the sensitivity. Moreover, the

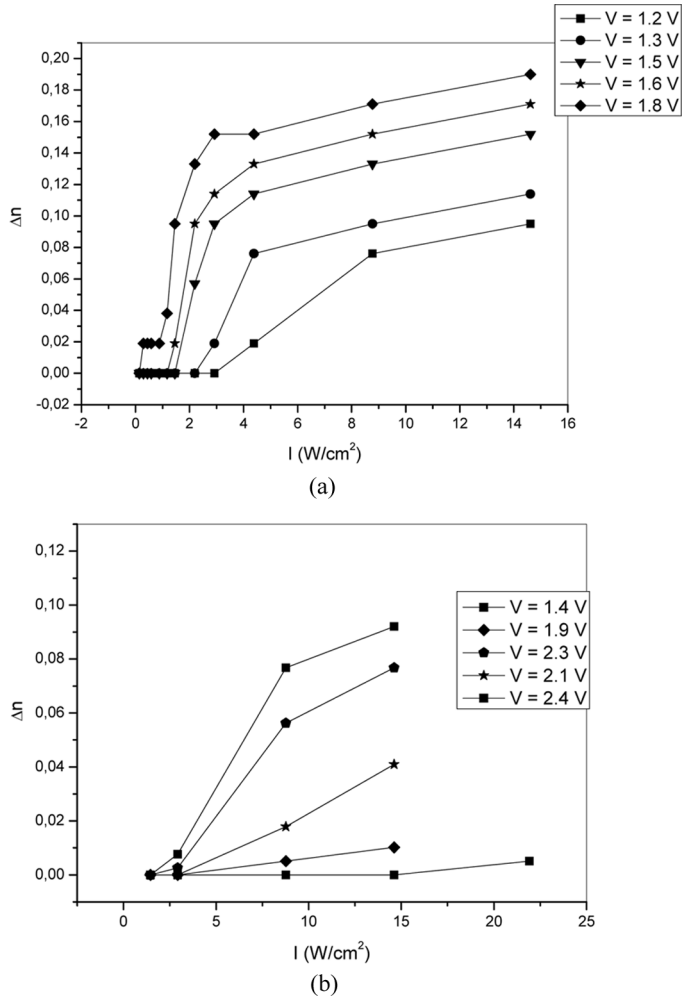

FIGURE 3 Light-induced birefringence Δn as a function of the laser intensity, for different values of the external bias. Cells are planar and are 10 μm (a) and 100 μm (b) thick.

maximum values of the induced birefringence are much higher in the thinner cell, reaching in some cases the total intrinsic birefringence of 5CB. From curves reporting Δn vs I it is possible to evaluate the nonlinear coefficient n_2 by a linear fit through the equation $\Delta n = n_2 I$ valid for Kerr media. The nonlinear optical coefficient can reach $0.1\,cm^2/W$. Worthy of note, this value is lower by about 2 orders of magnitude with respect to that obtained in similar cells in four-wave-mixing experiments assisted by an external dc field.

As already mentioned, the light-induced adsorption and desorption of MR molecules affect the surface charge density of ions. In our experimental configuration, light-induced desorption of dye molecules from the irradiated surface is expected to be dominant on adsorption and produces a lowering of the screening effect due to ion impurities and dopant, thus increasing the effective internal voltage. In this way the reduction of charge screening gives rise to a reduction of the actual Fredericksz threshold. When a Gaussian beam impinges on the cell, desorption is more effective in correspondence of the peak of the intensity distribution and this leads to an increase of the effective voltage in the same region. In other words, due to the Gaussian profile of the beam the threshold field results lower in correspondence of the Gaussian peak where the intensity is higher, and higher in correspondence of the tails. As a consequence the applied dc field produces a director distortion toward the homeotropic configuration only in the centre of the pump beam. This gives rise to the self phase modulation phenomenon. In this way we have a Fredericksz threshold voltage $V_{th}(I)$ dependent on the impinging light intensity, being maximum at $I = 0$ ($V_{th}(0)$ has been measured to be around 4 V for all the analysed cells). Therefore by increasing the bias voltage the director distortion increases thus increasing Δn and the number of rings until V approaches $V_{th}(0)$. At this stage the whole sample can be reoriented and the index modulation through the beam cross section decreases and becomes negligible at higher voltages (this explains why the SPM pattern collapses for external voltages higher than about 2.5 V).

CONCLUSIONS

We have reported a brief review about the LC optical nonlinear response, concerning in particular our recent results about the possibility of controlling the extremely high optical nonlinearity shown by MR-doped 5CB thin cells by external electric fields. Some new results about the effect of the external bias in single beam configuration have also been reported.

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