Impact of dyes on the nonlinear optical response of liquid crystals implementing the Z-scan technique

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Abstract. The study of the nonlinear refractive index response $\gamma$ of several organic dyes and their impact on the nonlinear optical (NLO) properties of nematic liquid crystals (LC) was performed via Z-scan measurements. For his purpose, a low power CW He-Ne laser system ($\lambda \approx 633$ nm) was implemented. Studies were carried out at the low absorption spectroscopic region of the implemented samples (dyes, liquid crystals and mixtures at different ratios of these materials). Samples were prepared at 1% weight of the used solvent (THF) and were sandwiched in glass cells with a gap thickness of ~100 µm. The implemented dyes have shown the largest optical nonlinearities and represent the main contributors to the cubic NLO-properties of the LC:Dye mixtures. In our particular studies, 5CB liquid crystal doped with DR1 azo-dye, resulted in the simultaneous positive and negative exhibition of nonlinear refractive indexes $\gamma$, depending on the polarization state of the excitation laser beam. Experimental conditions and results are described in detail.

Keywords: Nonlinear optics, Kerr effect, Z-scan, Liquid Crystals, Organic dyes.

1. Introduction

In previous papers [1,2,3], we have shown that nematic Liquid Crystals such as 5CB and MBBA doped with the organic dye Methyl Red (MR) exhibit significant third order (Kerr effect) nonlinearities. In the case of 5CB-LC, it shows simultaneous positive and negative exhibition of nonlinear refractive index $\gamma$. Both contributions are clearly identifiable from each other and mainly depend on the polarization states of the implemented laser source, where these two opposite $\gamma$-values appear normally for orthogonal polarization states. This peculiar result represents itself an interesting NLO-phenomenon which may be useful for several technological applications, since the studied materials also exhibit “giant” nonlinear refractive $\gamma$-values [3,4]. This work arises from the need to study and further understand these interesting phenomena, as well as to design novel nonlinear optical materials capable to exhibit controllable nonlinear refraction properties useful, for instance, in the generation of optical spatial solitons.

2. Organic molecular structures

In order to perform the Z-scan NLO-studies, different LCs, organic dyes and mixtures of these materials were used and prepared. The traditional Z-Scan technique [5,6,7,8] was slightly modified so that the polarization state of the incident laser source was able to rotate. In this way, an adequate spectroscopic analysis performed for each Z-Scan curve obtained at different input polarization states,
allowed to single out the positive and negative contributions of the NLO $\gamma$-values. In figure 1, the
different molecular structures of the studied nematic LCs materials are schematically represented
(5CB, MBBA and E7). Similarly, in figure 2, the different molecular structures of the studied organic
dyes (Methyl Red, Disperse Red 1 and Disperse Red 13) are represented. All these materials have
shown no negligible Kerr effects.

![Figure 1](image1.png)

**Figure 1.** Molecular structure of the implemented liquid crystalline structures: 

- **a)** MBBA or N-(4-Methoxybenzylidene)-4-butylaniline, 
- **b)** 5CB or (4-cyano-4'-n-pentylbiphenyl) and 
- **c)** E7 and derived liquid crystal mixtures.

![Figure 2](image2.png)

**Figure 2.** Molecular structure of the implemented organic dyes: 

- **a)** DR13/Disperse Red 13 or 4-[4-(Phenylazo)-1-naphthylazo]phenol, 
- **b)** DR1/Disperse Red 1 or N-Ethyl-N-(2-hydroxyethyl)-4-(4-nitrophenylazo)anilina and 
- **c)** MR/Methyl Red or 2-(4-Dimethylaminophenylazo)benzoic acid, 4-Dimethylaminoazobenzene-2'-carboxylic acid, Acid Red 2.

### 3. Experimental section

#### 3.1. Sample preparation

All dyes were dissolved in tetrahydrofuran (THF) at 1% wt. and the liquid crystals were doped with these solutions at 1% wt. The resulting mixtures were used to fill-up glass cells of ~100 µm thickness; the samples were fabricated without any prealignment process. Inspections of the samples with polarizing microscopy show regions where the liquid crystal is well aligned. The selected wavelength ($\lambda = 633$ nm) correspond to the low absorption region of these materials (see figure 3), and therefore
contributions of the linear and nonlinear absorption to the Z-Scan transmission curves are negligible, as it was experimentally verified. Experimental and theoretical analyses were performed as reported in the articles here referenced.

![Absorption spectra of organic dye](image)

**Figure 3.** Absorption spectra of the implemented organic dyes.

### 3.2 Basic equations

**Kerr effect:**

\[
n = n_0 + \gamma f(I) = n_0 + \left( n_2 / 2 \right) |E|^2
\]

(1)

**Nonlinear refractive index:**

\[
\gamma = \frac{\lambda}{2\pi} \frac{\Delta \Phi_0}{I_0 L_{\text{eff}}}, \left( m^2 / W \right)
\]

(2)

**Phase shift:**

\[
|\Delta \Phi_0| \approx \frac{\Delta T_{p-p}}{0.406(1 - S)^{0.25}}, \quad S: \text{diaphragm aperture}
\]

(3)

**Rayleigh range:**

\[
z_0 = \frac{\pi}{\lambda} w_0^2, \left( mm \right)
\]

(4)

**Waist radius:**

\[
w_0 = \frac{2f\lambda}{D\pi}, \left( mm \right)
\]

(5)

**Theoretical transmittance:**

\[
T_N \equiv 1 + \Delta \Phi_0 \frac{4. \frac{z}{z_0}}{1 + \left( \frac{z}{z_0} \right)^2 \left[ 9 + \left( \frac{z}{z_0} \right)^2 \right]}
\]

(6)

### 3.3 Z-Scan setup

The Z-Scan technique was implemented by using a nonpolarized laser beam from a 5 mW He-Ne laser system. The direction of the incident polarization was controlled by means of a linear polarizer mounted on a rotatory stage. The polarized laser beam was then focused on the sample by using a positive lens (\( f = 5 \) cm). The sample was attached to a translation stage of 2.5 cm of travel distance. A large area Si-photodetector was located at a distance \( L \approx 1 \) m, much larger than the Rayleigh range.
(\(z_0 \approx 3\) mm) from the focusing lens. A 1 mm diameter aperture was placed in front of the detector to measure the on-axis intensity transmission changes. The photodetector signal was measured with a digital oscilloscope and recorded on a computer. Finally, all motion systems and the administration of the set-up were automated via a LabView\textsuperscript{\textregistered} control program (see figure 4).

**Figure 4.** Z-Scan set-up with linearly polarized light, BS is a beam splitter, L is a lens, sample (LC, dye and LC+dye), D1 and D2 are the photo-detectors.

4. Experimental results

4.1. Organic dyes

The Z-Scan response of the studied dyes and their corresponding nonlinear refractive index values are shown in figure 5. In all cases, the sign of the nonlinearity was found to be negative.

**Figure 5.** Z-Scan transmittance curves obtained for the studied dyes and evaluated nonlinear refractive indexes.
4.2. Liquid crystals
The Z-Scan response of the studied liquid crystals and their corresponding nonlinear refractive indexes are shown in figure 6. These materials exhibited both positive and negative nonlinearities.

![Z-Scan response of liquid crystals](image)

**Figure 6.** Z-Scan transmittance curves obtained for the studied LCs and evaluated nonlinear refractive indexes.

4.3. Liquid crystals doped with organic dyes (LC:Dye mixtures)
The Z-Scan response of the LC:Dye mixtures and their corresponding nonlinear refractive indexes are shown in figures 7, 8 and 9.

![Z-Scan response of LC:Dye mixtures](image)

**Figure 7.** Z-Scan transmittance curves and evaluated nonlinear refractive indexes of 5CB LC doped with several dyes.
Figure 8. Z-Scan transmittance curves and evaluated nonlinear refractive indexes of MBBA LC doped with several dyes.

| LC+Dye     | $\gamma$ (m$^2$/W) | $n_2$ (esu) |
|------------|---------------------|-------------|
| MBBA+DR1   | -1.21E-10           | -4.53E-04   |
| MBBA+DR13  | -1.58E-10           | -5.91E-04   |
| MBBA+RM    | -7.51E-11           | -2.82E-04   |

Figure 9. Z-Scan transmittance curves and evaluated nonlinear refractive indexes of E7 LC doped with several dyes.

| LC+Dye     | $\gamma$ (m$^2$/W) | $n_2$ (esu) |
|------------|---------------------|-------------|
| E7+DR1     | -2.16E-10           | -8.11E-04   |
| E7+DR13    | -8.03E-10           | -3.01E-03   |
| E7+RM      | 1.49E-10            | 5.57E-04    |

4.4. Comparative representation of the Z-Scan curves obtained for the dyes, LCs and dye doped LCs

In Figures 10, 11 and 12 we present comparative Z-Scan curves of the NLO response evaluated in the implemented dyes, LCs and LC:Dyes mixtures, as well as their corresponding theoretical analyses. Experiments were performed at a fixed polarization state (without rotation of the polarizer). It is generally observed that when the implemented LC and dopant dye exhibit opposite nonlinearities, the...
corresponding Z-Scan curve resulting from their respective mixtures, shows a clear tendency to follow the nonlinearity of the dye or LC with stronger NLO-signal. That is to say, the resulting $\gamma$-value of the LC:Dye system has the same sign of that material exhibiting stronger NLO refractive index. These results are, up to now, according to our expectations.

**Figure 10.** Theoretical and experimental Z-Scan comparative studies of 5CB LC, the implemented dyes and the 5CB:Dyes mixtures.
**Figure 11.** Theoretical and experimental Z-Scan comparative studies of MBBA LC, the implemented dyes and the MBBA:Dyes mixtures.
Figure 12. Theoretical and experimental Z-Scan comparative studies of E7 LC, the implemented dyes and the E7:Dyes mixtures.
4.5. Rotation of the input polarization plane

As an example of the simultaneous observation of both positive and negative nonlinear refractive indexes with dependence on the laser input polarization states, figure 13 shows typical Z-Scan curves obtained for sample 5CB doped with dye DR1. Characteristic closed-aperture Z-Scan transmission curves with well defined and opposite nonlinearities were obtained under same experimental conditions as the polarization plane was rotated from 0° to 150° with respect to the horizontal laboratory reference plane (plane of the optical table). It is observed that well defined Z-Scan curves showing opposite nonlinear refractive indexes with $\gamma > 0$ and $\gamma < 0$ values are obtained for quasi-orthogonal input polarization states (at 70° and 150°). This kind of behaviour is similar to that previously discussed for 5CB LC doped with MR [1,2,3].

**Figure 13.** Z-Scan curves obtained for 5CB LC doped with DR1 dye at quasi-orthogonal input polarization states (curves were obtained at 70° and 150° input polarizing states). These experiments demonstrate the strong NLO and $\gamma$-sign dependence with the input polarization state of the Laser beam that some samples may experience under Z-Scan testing.

5. Discussion.

The experimental results have shown that the implemented dyes have a strong impact on the photophysical properties of liquid crystalline materials and play a key role on the observation of improved optical nonlinearities. Indeed, the nonlinear refractive indexes $\gamma$ of the LC:Dye mixtures are, in general, notably increased. At present, the study of 5CB LC doped with Methyl Red and DR1 dyes are able to exhibit both positive and negative $\gamma$-values depending on the polarization state of the laser beam. These results point out to potential photonic applications implementing selected LC:Dyes mixtures. Our results may provide some insights into the molecular mechanisms associated with this interesting phenomenon that will necessarily require several molecular simulation studies in order to further understand the molecular interactions between the LC-systems and the dopant dyes. In this way, a better representation of the possible molecular arrangements, guest-host intermolecular interactions and its dependence on the molecular electronic states, may be provided. Such studies are currently under way in order to complement the present report in a future scientific report.
6. Conclusions.
In this work, the impact of some organic dyes on the cubic nonlinear optical response of several well known liquid crystalline systems has been experimentally evidenced. Indeed, as the LC-materials are slightly doped with the organic dyes, the corresponding mixtures are able to exhibit larger cubic nonlinearities. Interestingly, it has been unambiguously demonstrated that some LC:Dye doped samples can exhibit both positive and negative nonlinear refractive indices depending on the polarization plane of the incident laser beam. Results suggest that both the magnitude and sign of the nonlinear refractive index of the LC:Dye mixtures have a strong dependence on the structure and nature of the liquid crystal and organic dye from which the LC-sample is doped. Moreover, the simultaneous exhibition of positive and negative nonlinear refractive indexes occurring at quasi orthogonal polarization states, is probably due to an existing NLO-birefringence associated to the LC:Dye molecular organization. On the other hand, most of our experiments show very asymmetric Z-Scan curves, making the traditional theoretical fitting a difficult task. According to these observations, it seems that an extended model will be required in order to satisfactorily describe our experimental results, given that the measured NLO refractive index - polarization dependence cannot be considered as a purely Kerr or thermal effect since these nonlinearities are mainly associated to the quadratic and fourth power dependence on the Gaussian beam radius. The obtained data demonstrate that, based on the model presented in Ref. [1], our Z-Scan results may exhibit a dependence on the third power of the incident Gaussian beam radius, whose physical source is until now not fully understood. The mathematical model describing this peculiar behavior is currently under development; however it can be reasonably inferred that it physical nature is mainly associated to the molecular orientation, material birefringence and molecular structures of the organic LC:dye systems. Current experiments and theoretical developments are underway in order to find more materials exhibiting the NLO-refractive index-polarization dependence and to further understand the physical mechanism causing the NLO-birefringence [9]. The understanding of this interesting phenomenon may present potential applications in the generation of dark and bright optical spatial solitons.

Acknowledgements.
CONACYT: U-49846F, 34921-E; DGAPA-PAPIIT-UNAM IN108900 Y BID-UNAM 1998.

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