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Neither Kerr Nor Thermal Nonlinear Response of Dye Doped Liquid Crystal Characterized by the Z-Scan Technique

A. A. Rodríguez-Rosales[1], R. Ortega-Martínez[1], M. L. Arroyo Carrasco[2], E. Reynoso Lara[2], C. G. Treviño Palacios[3], O. Baldovino-Pantaleón[3], R. Ramos García[3], and M. D. Iturbe-Castillo[3]
[1]Universidad Nacional Autónoma de México, Centro de Ciencias Aplicadas y Desarrollo Tecnológico, México
[2]Benemérita Universidad Autónoma de Puebla, Av. San Claudio y Rio Verde, Puebla, Mexico
[3]Instituto Nacional de Astrofísica, Óptica y Electrónica, Tonantzintla, Puebla, México

In the experimental characterization of the nonlinear optical properties of dye-doped liquid crystals by the Z-scan technique with CW lasers it is rather common to assign it a Kerr or thermal nonlinear response. In this work, we demonstrate that neither of them correctly describes all features of the Z-scan obtained in planar samples of methyl red doped 5CB liquid crystal using He-Ne CW illumination, where a strong nonlinear optical response is observed. The Z-scan curves depend strongly on the input polarization of the beam obtaining negative and positive nonlinear response for polarizations parallel and orthogonal to the director vector. We discuss and compare the effect of an additional incoherent linearly-polarized beam and plain heating source on Z-scan experiments. A theoretical model, valid for small and large phase modulation, is proposed based on the assumption that the sample can be considered as a thin lens with a photo-induced focal length dependent on the Gaussian beam radius ω^m (where m is an integer), obtaining good agreement with the experimental curves for $m = 3$, which is neither a Kerr nor thermal nonlinearity.

Keywords: liquid crystals; nonlinear optics; Z-scan

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Address correspondence to David lturbe-Castillo lnstituto Nacional de Astrofisica, Óptica y Electrónica, Luis Enrique Erro #1, Tonantzintla, Puebla 72840, México. E-mail: diturbe@inaoep.mx

1. INTRODUCTION

Liquid crystals are very attractive nonlinear material for low power applications owing to their extremely large birefringence. The nonlinear optical properties of liquid crystals have been studied for more than 30 years since the seminal paper of Zeldovich *et al*. [1] where a giant nonlinearity was reported. Later on, it was found that liquid crystal nonlinearity can be enhanced by two orders of magnitude by doping them with a small quantity of anthraquinone dyes [2]. Even higher nonlinear response is observed in azo dye doped liquid crystals [3–5]. Several techniques are routinely used to characterize the nonlinear optical response of liquid crystals. Z-scan is one of the most popular and powerful techniques due to its simplicity that allow to obtain both the sign and magnitude of the complex nonlinear refractive index of optical materials [6]. In this technique, variations of the transmittance of the samples are monitored as function of the sample position on the vicinity of the focal point of a fast lens. An aperture may be placed or not in front of a detector depending if close or open aperture Z-scan measurements are performed. Z-scan characterization in dyed doped liquid crystals has produced contradictory results showing either positive or negative nonlinearity depending on the host, dye, external electric field, wavelength, temperature or additional illumination. Although Z-scan is a simple technique, identification of the physical mechanism that gives rise to the nonlinearity it is not a simple task. Thus, for example either Kerr or thermal nonlinearity has been attributed to similar samples measured under different experimental conditions and liquid crystal sample preparation [7–13].

In this work we report Z-scan experiments in thin samples of methyl red doped 5CB liquid crystals illuminated with a low power CW He-Ne laser. The obtained transmittance curves show unambiguous experimental evidence of the simultaneous existence of positive and negative refractive indexes changes depending on the input polarization. In order to explain our results we use a simple model where the photoinduced lens is described as a beam's radius-dependent focal length [14,15]. We demonstrate that the dye-doped liquid crystal can be described by a photoinduced focal length lens of the form: $F = c[w(z)]^3$ where c is a constant and $w(z)$ is the incident Gaussian beam radius on the sample.

2. SAMPLE PREPARATION

5CB liquid crystal was doped with the azo dye methyl red at 1% wt and used to fill-up glass cells of 100 μm thickness; the samples were

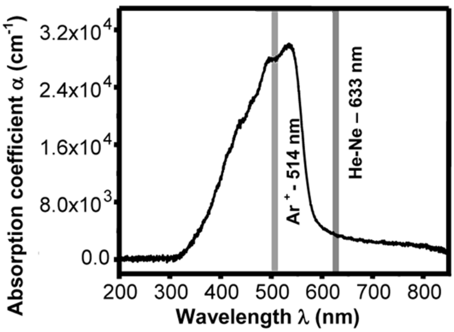

FIGURE 1 Absorption spectrum of 5CB doped sample, vertical lines correspond to the wavelengths of the He-Ne and Ar^+ ion laser.

fabricated without any prealignment process. Inspection of the samples with polarizing microscopy shows regions where the liquid crystal is well aligned. The selected wavelength ($\lambda = 633\,nm$) correspond to the low absorption region (see Fig. 1), and therefore contributions of the linear and nonlinear absorption to the transmission changes are negligible, as it was experimentally verified.

3. Z-SCAN SETUP

The Z-scan technique was implemented by using a nonpolarized laser beam from a 5 mW He-Ne laser. The direction of the incident polarization to the sample 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 4.5 cm of travel distance. A large area Si-photodetector was located at a distance $L \approx 1\,m$, much larger than the Rayleigh distance ($z_0 \approx 3\,mm$) from the focusing lens. A 1 mm diameter aperture was placed in front of the detector to measure the on-axis intensity changes. Additionally, a continuous-wave linearly polarized Ar^+ ion laser beam ($\lambda = 514\,nm$) was used to illuminate the sample at an angle of $\theta \approx 45^\circ$ (see Fig. 2). Since the green light lies on the absorption peak of the dye, it is expected that thermal heating (in addition of molecular reorientation) may be induced by the additional beam. In order to compare the heating effect of the Ar^+ ion laser and that produced by isotropic heating, a temperature-controlled oven was used to increase the temperature of the sample from 21.0°C up to 32.0°C. The photodetector signal was measured with a digital oscilloscope and recorded on a computer. Finally, all motion

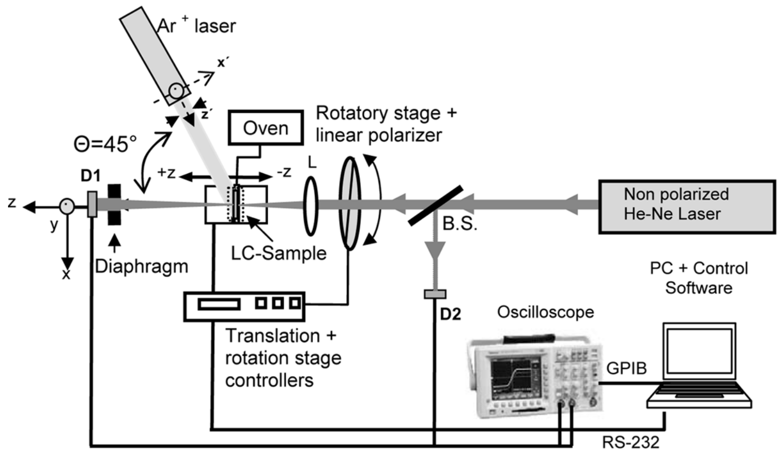

FIGURE 2 Z-Scan set-up with linear polarized light. A secondary light source (Ar^{3+} ion laser) and temperature controlled oven were also used. BS is a beam splitter, L is a lens, LC is a liquid crystal sample, D1 and D2 are detectors and PC is a personal computer.

systems and the administration of the set-up were automated via a LabView© control program.

4. EXPERIMENTAL RESULTS

4.1. Incident Polarization

By using a polarized microscope we identify a region where the director vector is well defined, and then we rotate the sample in such a way that the director vector was parallel to the vertical polarization. The Z-scan response of the dye-doped 5CB liquid crystal for different input polarizations is shown in Figure 3a. The 0° position corresponds when director vector and the input polarization of the He-Ne laser are parallel. In this case, the sign of nonlinearity was negative. The amplitude of the peak and asymmetry of normalized transmittance curves indicate a very large phase change, therefore a large nonlinear optical response to this wavelength [16,17]. By varying the input polarization in steps of 30°, we observed a drastic reduction of the peak-to-valley transmittance $\Delta T_{p\text{-}v}$ from 2.58 to 0.2, and a decrease of the peak-to-valley asymmetry. Eventually, a change on the sign of the nonlinearity for the orthogonal polarization was observed. It is important to emphasize that the peak-to-valley distance ($\Delta Z_{p\text{-}v}$) for the different polarizations was not constant and decreases as the amplitude of the curve did; from 5.5 mm for 0° polarization to 4 mm for 90° polarization.

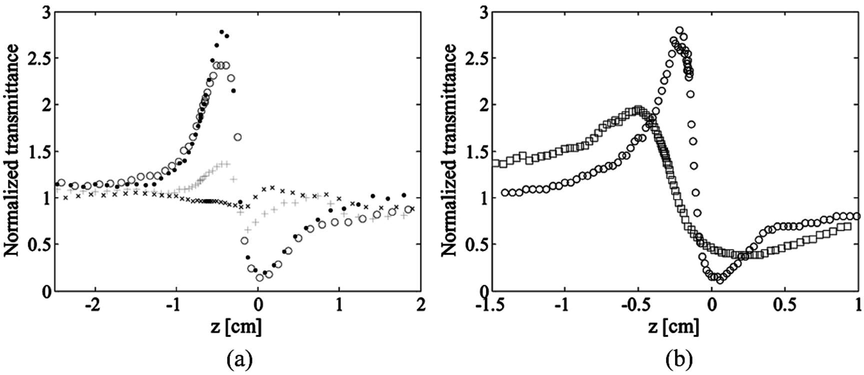

FIGURE 3 (a) Z-scan curves obtained at different input polarization for 5CB doped samples, exhibiting both negative and positive nonlinear refractive indexes for orthogonal polarizations. Incident power of 2.0 mW, focal length lens of 5 cm and input polarization of: 0° (filled circles), 30° (open circles), 60° (+) and 90° (×); (b) Z-scan curve obtained with different focal length lenses: 3.5 cm (circle) and 6 cm (square). The input polarization was 0°. Input power was of ≈1.7 mW.

4.2. Focal length of the focusing lens

In order to study the dependence of the Z-scan curve with the beam waist w_0 of the incident beam, we performed Z-scan experiments with two different focal length lenses (3.5 cm and 6 cm). The input polarization was adjusted to 0° and the incident power to 1.7 mW. The obtained results shows a decrease of $\Delta T_{p\text{-}v}$ from 2.6 to 1.5 when the 3.5 cm focal length lens is replaced by the 6 cm focal length lens, i.e., $\Delta T_{p\text{-}v}$ scales inversely with w_0. On the other hand, $\Delta Z_{p\text{-}v}$ changed from 2.6 mm to 7.6 mm for the same focal length lenses. It is important to note that regardless the experimental conditions, the nonlinearity exhibited by the dye-doped liquid crystal sample can not be considered as thermal one since in this type of nonlinearity the amplitude of the z-scan curve is independent on the beam waist (as it was experimentally demonstrated in [18]).On the other hand, in Kerr nonlinearity $\Delta T_{p\text{-}v}$ scales as w_0^{-2}, so once again neither thermal nor Kerr nonlinearity describe the experimental results correctly.

4.3. Effect of a Secondary Light Source ($\lambda = 514$ nm)

It is worth to mention that Z-scan experiments using two wavelengths ($\lambda = 514$ nm and $\lambda = 633$ nm) in dye-doped nematic liquid crystals have been reported earlier [13] showing a complex behavior: if the polarization of the two beams are parallel to the director vector, then the peak-to-valley distance $\Delta T_{p\text{-}v}$ initially increased with the intensity of the green light, reaching maximum and then decreasing for higher intensity. However, when the polarization of the red beam is orthogonal to the green (and director vector) no nonlinearity was excited. It was concluded that the thermal nonlinearity was the dominant one in that sample. To study the matter further, we characterize the effect of thermal heating induced by polarized light absorption and that produced by isotropic heating.

In our experiments, the Ar^+ ion laser beam was expanded to 1 cm diameter to ensure a uniform illumination around the area where the red beam is being focused (see Fig. 4). Figure 4a shows the transmittance curves when both beam polarizations are parallel and the green power beam was increased. The filled circles curve is the Z-scan obtained in absence of green light. Notice that increasing the input power of the green light affects both $\Delta T_{p\text{-}v}$ and $\Delta Z_{p\text{-}v}$ but in an asymmetric way. It is difficult to evaluate the temperature rise produced by the absorption of the green laser but is clear that some disorder of the director vector is induced, increasing dn/dT. An additional isothermal disorder may be induced due to the photoisomerization of the dye [19]. On the other hand, the green light was also increasing the ordering of the liquid crystal due to the electric field-induced torque; as a consequence both contributions tend to partially compensate each other since not much change on the Z-scan curves was observed.

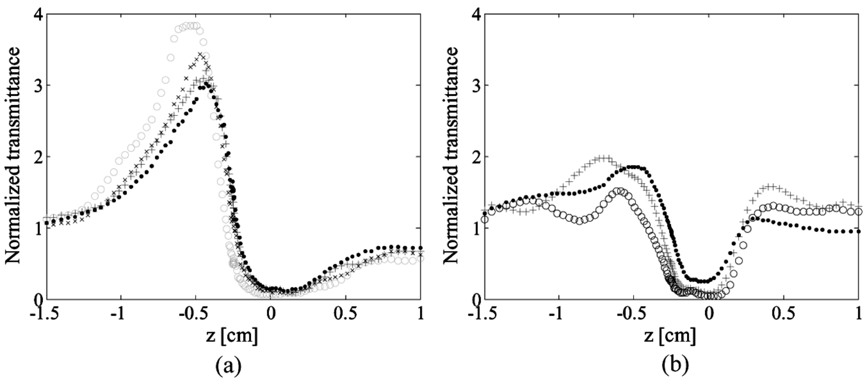

FIGURE 4 (a) Z-Scan curves with additional illumination from an Ar^{3+} laser beam with a polarization parallel respect to the He-Ne laser beam. Argon laser power of: 0 (filled circles), 20 (+), 30 (×) and 35 mW (open circles); (b) Z-Scan curves with an additional Ar^{3+} laser beam with polarization perpendicular to the He-Ne laser beam polarization. Argon laser power of: 12 (filled circles) 37 (+) and 50 mW (open circles).

Keeping the same polarization for the red light and illuminating with orthogonal polarized green light, the experimental curves show a dramatic change on the shape of the Z-scan curve (see Fig. 4b). The peak-valley feature typical of Z-scan curves almost disappeared. As we will shown later, this behavior can be explained by the competition between the positive (excited by the green light) and negative nonlinearity since the red laser "sees" both positive and negative nonlinearities.

4.4. Effect of Isotropic Heating

In order to study in more detail the effect of the temperature, we performed further experiments by using a home-made heating oven (sensitivity $\Delta T = 0.1°C$). Figure 5 shows the temperature dependence of the Z-scan curves for linear polarization of the He-Ne laser set at $0°$ (Fig. 5a) and $90°$ (Fig. 5b), respectively. In Figure 5a can be seen that the temperature rise produces a similar effect to the observed on the previous experiment. However, the temperature rise changes not only the amplitude $\Delta T_{p\text{-}v}$ and the position of the peak and valley but also broadens the peak.

Figure 5b shows the Z-scan curves for polarization perpendicular to the director vector ($90°$). It can be observed that only the positive nonlinearity was excited whose amplitude increase as the temperature approaches the phase transition temperature (35°C for 5CB). There is not significant change in the position of the peak-to-valley distance

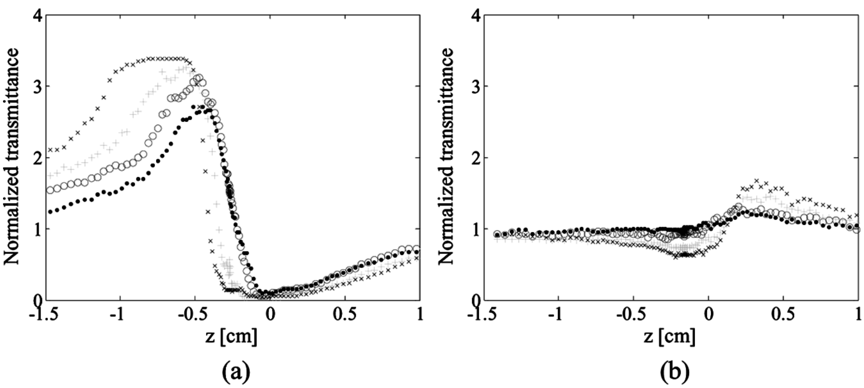

FIGURE 5 (a) Z-scan experimental curves at $0°$ input polarization of the He-Ne laser and sample temperature of: 21.1°C (filled circles), 22.2°C (open circles), 27.2°C (+) and 29°C (×); (b) Z-scan experimental curves at $90°$ input polarization of the He-Ne laser and sample temperature of: 21.1° (dot), 22.2° (circle), 26.2° (+) and 28.2° (×).

$\Delta Z_{p\text{-}v} = 5\,\text{mm}$. In this case, the rate of change of $\Delta T_{p\text{-}v}$ with temperature was larger than that obtained with the parallel polarization. Since no competition exists between the disorder and electric field reorientation, only the disorder dominates and therefore dn/dT becomes negative as expected.

It is important to mention that at higher temperature the Z-scan curves do not show the typical peak-to-valley feature probably because the thermal oscillations and pretransitional effects near the nematic-isotropic phase transition become important making difficult the interpretation of the curves.

5. THEORETICAL ANALYSIS AND DISCUSSION

In a previous paper we developed a simple model to explain many of the features of Z-scan valid under several circumstances [14]. In this model, the nonlinear response of the material is considered as a photo-induced thin lens with a focal length dependent on the incident Gaussian's beam radius. The model is valid for large phase modulation in samples thinner than the Rayleigh range and far field on axis detection. In particular, for dye-doped nematic liquid crystals good correspondence between experiments and theory is obtained when the photoinduced focal length F on the liquid crystal is considered to be of the form $F_{\pm} = c_{\pm}[w(z)]^3$; where $c_{\pm}$ is a constant (with units of length^{-2}) and $w(z)$ is the incident beam radius of the Gaussian beam on the sample. The constant $c_{\pm}$ carries information of the material (absorption, thermal conductivity, dn/dT, etc) and experimental (beam power for example) parameters. In order to take into account the polarization dependence, the dielectric anisotropy of the liquid crystals must be considered. In order to do this, it is well know that the effective refractive index depends on the angle of a linearly polarized light beam with the director vector. The transmittance of a linearly polarized beam making an angle θ with the director vector must be a combination of the positive (T_+) and negative (T_-) nonlinear transmittance of the liquid crystal of the form:

$$T = T_+ \sin^2\theta + T_- \cos^2\theta \tag{1}$$

where

$$T_{\pm} = \frac{F_{\pm}^2}{(F_{\pm} - z)^2 + z_0^2}, \tag{2}$$

is the normalized transmittance obtained in [14]. Here z_0 is the Rayleigh distance of the incident Gaussian beam and z is the sample position relative to the lens' focus. In order to reproduce the polarization dependence shown in Figure 3a, Eqs. (1) and (2) were fitted to the experiment obtaining a beam waist of $\omega_0 = 24\,\mu m$. The following fitted constants were obtained: $c_+ = 1.4 \times 10^8\,cm^{-2}$ and $c_- = -1.1 \times 10^7\,cm^{-2}$ i.e., the positive photoinduced focal lenght lens is larger than the negative, reflecting the experimental fact that T_+ is almost an order of magnitude smaller than T_-. With these parameters, the Z-scan curves obtained using Eqs. (1) and (2) at different angles for the incident polarization are shown in Figure 6. The general behaviour obtained in the experimental results, showed in Figure 3, was reproduced quite nicely by our model.

We tried to fit the same experimental results by using other type of nonlinearities for input polarization of 0° and 90°. For example, the value of $m = 4$, typical of Kerr nonlinearity, gives a reasonable fit but fails to reproduce the left wing of the peak and the amplitude of the valley. Figure 7b shows the theoretical fit for $m = 2$, typical of thermal nonlinearity, the fitting is not as good as that shown in Figure 6. It is important to mention that we tried several combinations of integer numbers without success. It is reasonable to assume that nonlinear response of liquid crystals may be a combination of Kerr and thermal response; however we did not find an adequate set of parameters to fit the experiment as good as with $m = 3$.

In Ref. 14 it was established that the photoinduced lens in the Z-scan experiments exhibits a particular behaviour with the spot

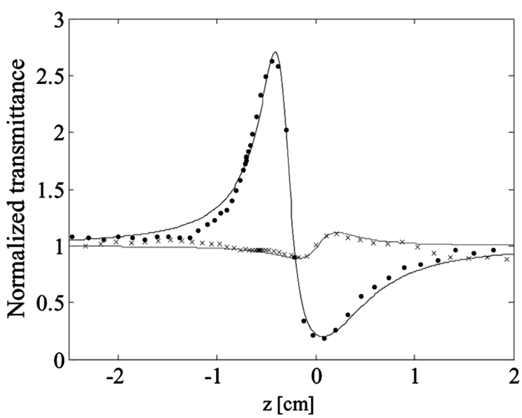

FIGURE 6 Calculated z-scan curves for different input polarizations. The fitted parameters were $c_+ = 1.4 \times 10^8$; $c_- = -1.1 \times 10^7$; $w_0 = 24\,\mu m$ and the following polarization angles: 0° (black) and 90° (gray). Symbols are experimental results for the same input polarizations from Figure 3.

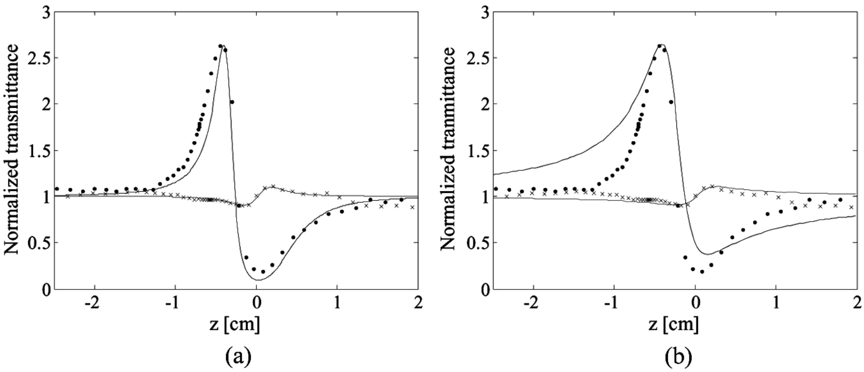

FIGURE 7 Theoretical curves obtained for values of m of: (a) 4 (the parameter were $c_+ = 5.5 \times 10^{10}$; $c_- = -2.5 \times 10^9$) m^{-3} and (b) 2 (the parameters were $c_+ = 5 \times 10^5\, m^{-2}$; $c_- = -4.5 \times 10^4\, m^{-1}$). Input polarization of: 0 (black) and 90 (gray). Symbols are experimental results for the same input polarizations from Figure 3.

size depending on the type of nonlinearity. In order to verify that the dependence proposed above ($m = 3$) give the best description of the nonlinear response of the liquid crystal, we made further simulations by using different spot sizes for the focused beam in a ratio corresponding to that used in the experiments. Simulations for spot sizes of 17 and

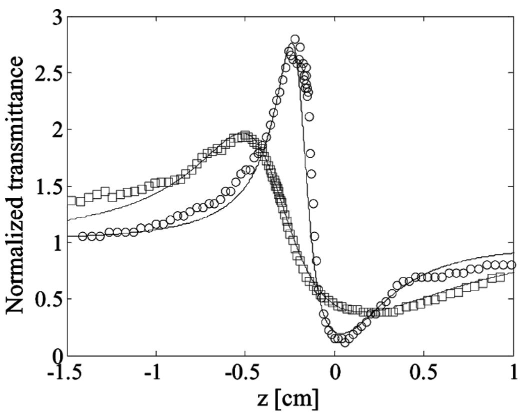

FIGURE 8 Calculated Z-scan curves for different focusing lenses with $m = 3$. The parameters were $c_+ = 1.6 \times 10$; $c_- = -1.4 \times 10^7$; input polarization of 0° and the following beam waists: 17 μm (black), and 30 μm (gray). Symbols are the experimental results for focal length lenses of: 3.5 cm (circles) and 6 cm (squares).

30 μm corresponding to focusing focal lenses of 3.5 and 6 cm, respectively, are shown in Figure 8. $\Delta T_{p\text{-}v}$ changed from 2.35 to 1.7 i.e., $\Delta T_{p\text{-}v}$ scales inversely with w_0 while $\Delta Z_{p\text{-}v}$ changed and from 2.4 to 6.9 mm for the two lenses. For the simulations the value of the constants was of $c_+ = 1.6 \times 10^8$; $c_- = -1.4 \times 10^7$. It is important to mention that other photoinduced focal length dependences give other dependences with the beam waist [14]. From these results it is not possible to consider that the nonlinearity exhibited by the liquid crystal can be considered as thermal because this type of mechanism does not produce any difference in the $\Delta T_{p\text{-}v}$ parameter with the beam waist.

In order to verify that other values of the parameter m produce a different amplitude dependence of the Z-scan curve in Figure 9 we plot the theoretical curves obtained with $m = 4$ and $m = 2$ to fit the experimental results. In the former case the peak and valley of the curves can be reproduced but not the general behaviour and the amplitude of the curve for the larger beam waist is smaller than that obtained experimentally. In the later case the amplitude of the z-scan curve did not change with the beam waist.

The effect of the secondary light source was simulated considering two cases: (i) when both laser beams have the same polarization (parallel to the vector director) and (ii) when the laser beams have perpendicular polarization (with the green light polarization perpendicular to the director vector). In the former case, increasing the incident green laser power is equivalent to decrease the value of the constant since $c_\pm$ scales inversely with the power. The results of

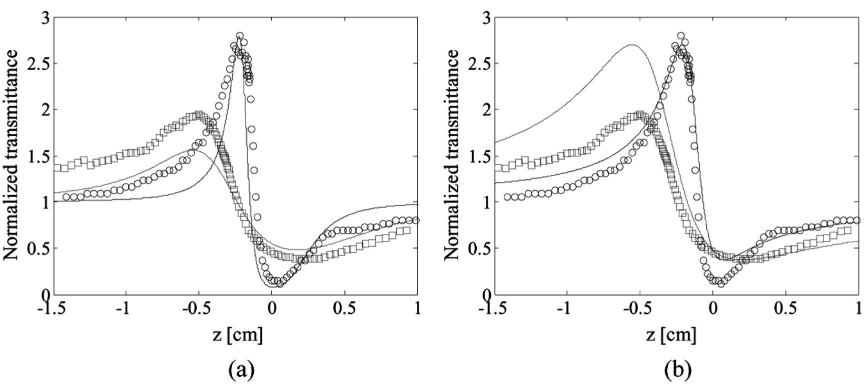

FIGURE 9 Theoretical curves obtained for different values of m: (a) 4 (The parameters were $c_- = -4.5 \times 10^9$ and $w_0 = 18\,\mu m$ (black) and $w_0 = 35\,\mu m$ (gray)) and (b) 2 (The parameters were $c_- = -4.8 \times 10^4$ and $w_0 = 16\,\mu m$ (black) and $w_0 = 26\,\mu m$ (blue)).

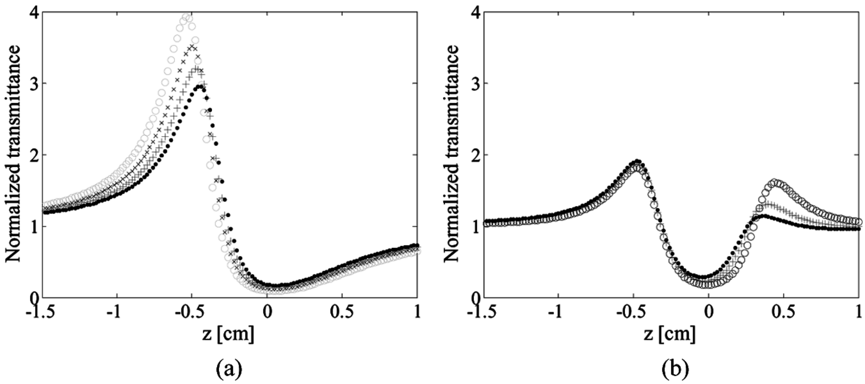

FIGURE 10 Calculated z-scan curves with additional polarized light at 514 nm and different powers. (a) Parallel polarizations (The parameters where the following, input polarization 0° and $c_-: -9.5 \times 10^6$ (point); -8.5×10^6 (+); -7.5×10^6 (×) and -6.5×10^6 (circle)). (b) Orthogonal polarizations (The parameters where the following, input polarization 42°, $c_-: -8.5 \times 10^6$ and $c_+ = 1.8 \times 10^7$(point); $c_+ = 1.4 \times 10^7$ (+) and $c_+ = 1 \times 10^7$ (circle)).

the simulation are shown in (Fig. 10), where we can observe an increase of the amplitude of the curve in the peak mainly. For the case of perpendicular polarization and due to the fact that the polarization of the additional illumination excites the positive response of the liquid crystal, in the simulation we considered that the magnitude of the positive constant decreased as the power increased.

6. CONCLUSIONS

In this work we present an experimental characterization of dye doped liquid crystal samples of methyl red in 5CB using the Z-scan technique with CW illumination at 633 nm. Strong nonlinear optical response, both positive and negative, was obtained for the samples. Focal length of the focusing lens, input polarization, additional illumination and sample temperature were varied in order to have the dependence of different parameters in the nonlinear response of this material. This novel dependence can not be considered as Kerr or thermal due that these nonlinearities are associated to fourth and square dependence on the Gaussian beam radius. The result obtained demonstrate that, based on the model presented in Ref. [14], the photoinduced focal length exhibited by the dyed doped liquid crystal samples under CW illumination depends on the third power of the incident Gaussian beam, whose physical source is still not fully understood.

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