Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Greeff, C. W. , Lu, J. and Lee, Michael A.(1993) 'Theoretical study of mechanisms of non-linear optical response in liquid crystals', Liquid Crystals, 15: 1, 75 — 85

To link to this Article: DOI: 10.1080/02678299308027840

URL: http://dx.doi.org/10.1080/02678299308027840

Liquid Crystals, 1993, Vol. 15, No. 1, 75–85

Theoretical study of mechanisms of non-linear optical response in liquid crystals

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(*Received 28 September 1992; accepted 16 February 1993*)

Here, we carry out a theoretical analysis of the *z* scan experiments used to measure the non-linear optical properties of liquid crystals, with the aim of clarifying the mechanism responsible for the observed non-linearity in the nanosecond regime. We consider various orders of non-linear absorption and non-linear refraction in order to illustrate their effects on the resulting *z* scan curve. The shape of the *z* scan curve, in principle, contains information about the order of the non-linearity. Qualitative features of the experimental *z* scan curves are consistent with a fifth order absorption and a third order refraction. However, given the level of disagreement between the calculated and experimental curves, it is not possible to make quantitative statements about the coeffients of the various orders. The magnitude of the refractive part of the non-linearity is consistent with laser heating due to linear absorption. The temporal profile of a two pulse experiment is also consistent with this mechanism. We suggest that the temperature dependence of the non-linear refraction might be explained in terms of a thermal mechanism by accounting for the temperature dependence of the rate of relaxation of the orientational order.

1. Introduction

Liquid crystals are known to exhibit large optical non-linearities, and these non-linearities have been the subject of considerable study in recent years [1–5]. In particular, the experimental group of Palffy-Muhoray have undertaken to measure the third order susceptibilities of a number of liquid crystal materials [3–5]. Using the *z* scan technique [6, 7] they have measured the non-linear index of refraction, $n_2 \propto \mathrm{Re}\,\chi_3$, and the non-linear absorption, $\beta \propto \mathrm{Im}\,\chi_3$, for pulse durations in the millisecond, nanosecond and picosecond regimes. They have also studied the dependence of these non-linear susceptibilities on temperature and on the intensity of the probing beam. They have carried out these experiments in geometries in which reorientation of the macroscopic director field is not expected to occur. In this paper we carry out a theoretical analysis of the experiments, focusing attention on measurements of 5CB (4-cyano-4′-*n*-pentybiphenyl) in the nanosecond regime where the mechanism underlying the observed non-linear refraction is not known.

The *z* scan technique is designed to measure the non-linear refractive index, n_2, which is proportional to the third order polarizability, χ_3, However, in many cases, due to the temporally and spatially non-local character of the response function, χ_3, the measured value of n_2 depends strongly on the geometrical and temporal

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properties of the measuring laser beam as well as intrinsic material properties. For example, if the measured response is due to laser heating of the sample, we expect

$$n_2 \propto \Delta n/I \approx \frac{dn}{dT}\frac{\alpha\tau}{C}, \tag{1}$$

where α is the linear absorption coefficient, C is the specific heat per unit volume, I is the beam intensity and τ is the pulse duration. In equation (1), we have assumed that the main source of heat is linear absorption of energy from the laser beam, and that the change in index of refraction, n, follows the equilibrium rate of change with temperature, dn/dT. Equation (1) also assumes that the pulse duration, τ, is short compared with the time scale for diffusion of heat across the beam profile, which is given by

$$\tau_D = \omega_0^2/D, \tag{2}$$

where ω_0 is the beam waist and D is the thermal diffusion constant. For values of D typical of liquid crystals, and for a beam waist of the order of $10\,\mu$m, we obtain, $\tau_D \approx 1$ ms, which is very long on the scale of the measurements we consider here, for which $\tau = 7$ ns.

The present analysis is concerned with addressing the mechanism behind the observed non-linear index of refraction for pulses on the nanosecond time scale. In particular, we focus on laser heating as a possible mechanism. Our consideration of laser heating is motivated by certain experimental facts. First, the signs of the observed n_2s are consistent with what is expected from laser heating. In particular, it has been observed [4] that in a large number of samples, n_2 is negative for polarization of the beam parallel to the nematic director, while n_2 is positive for polarization perpendicular to the director. This is what we would expect from a picture in which the main effect is due to a reduction of nematic ordering, and thus optical anisotropy, by heating of the sample. We also note that other potential mechanisms, namely field induced orientational order and electrostriction, predict a positive n_2 regardless of polarization. Non-resonant electronic hyperpolarizability effects tend to produce a positive n_2 for polarization parallel to the director and variable sign for the perpendicular polarization [8]. Second, the size of the observed non-linear refraction is consistent with what would be predicted given reasonable values of material parameters. This is shown more clearly in the following section where we show comparisons of calculated and experimental z scan curves. The reported non-linear refractive index [4] of -54×10^{-11} esu for 5CB measured with a 7 ns pulse is very large, and is more than an order of magnitude larger than the value obtained with a 33 ps pulse. Third, we note that equation (1) implies that if laser heating is the important mechanism, then the observed n_2 should scale in proportion to the pulse duration. Palffy-Muhoray *et al.* [3, 4] have measured n_2 for several nematic liquid crystals with pulses of both 10 ms and 7 ns of duration. It was concluded in [4] that the observed n_2 in the 10 ms case was due to laser heating. If equation (1) holds, then the observed n_2 in the 7 ns case should be $\sim 10^{-6}$ times smaller than that in the 10 ms case. In fact, the observed n_2 in the 7 ns case for 5CB and for ZLI 2303 are of the order 10 times larger than this prediction. We note, however, that 10 ms pulses are too long for equation (1) to hold. The response over 10 ms is expected to be reduced from the prediction of equation (1) by a factor $\sim \tau_D/\tau \sim 1/10$, and it is possible that the discrepancy could be explained by accounting for diffusion of heat in the 10 ms case.

Given these indications in favour of a thermal interpretation, we must note that in the case of the nanosecond pulses there is a shortcoming of this mechanism, which is that it apparently does not give the experimentally observed temperature dependence of n_2. Specifically, the strong temperature dependence of dn/dT near the nematic–isotropic transition is expected to lead to a corresponding temperature dependence of n_2. This is observed for 10 ms pulses, but in the case of the 7 ns pulses, n_2 is found to be essentially independent of temperature right up to the phase transition temperature. However, we point out that the equilibrium value of dn/dT gives an upper bound on the variation of n with T measured in a dynamical experiment. The temperature dependence of the index of refraction, n, is mainly due to the temperature dependence of the order parameter, S, with $dn/dT \propto dS/dT$. If the relaxation time for variations of the order parameter, τ_r, exceeds the duration of the pulse, then it is expected [1] that the observed n_2 will be reduced by roughly τ/τ_r. According to a theory of de Gennes [9], the orientational order relaxes according to

$$\gamma dS/dt = -\frac{\partial^2 F}{\partial S^2}(S - S_0), \tag{3}$$

where γ is a viscosity coefficient. This gives $\tau_r = \gamma/(\partial^2 F/\partial S^2)$. As we approach the nematic/isotropic transition from below, $\partial^2 F/\partial S^2$ approaches zero as $(T^\dagger - T)^{1/2}$, where $T^\dagger$ is the maximum superheating temperature, typically a fraction of a degree above the nematic–isotropic transition temperature. This leads to very large values of the relaxation time near the transition. At the same time $dS/dT \sim (T^\dagger - T)^{-1/2}$, so that for pulses that are short compared to τ_r, the effects of orientational relaxation may cancel the effects of rapid variation of S near the transition. Slowing down of the orientational relaxation has been observed directly [10, 11] in the isotropic phase using the optical Kerr effect, in which case $\tau_r \sim (T - T^*)^{-1}$. Relaxation times of the order of hundreds of nanoseconds have been seen in these experiments. In the calculations that follow, we will consider the measurements on 5CB at 25°C, which is 10°C below the nematic–isotropic transition, so that these slowing down effects may not be important. However, any attempt to describe the temperature dependence of the thermal non-linearity near the transition must include these effects if it is to be valid in the nanosecond regime.

2. Pulse propagation

In this section we present the theory behind our detailed simulations of z scan experiments. The z scan method is a single beam technique for measuring the non-linear absorption and non-linear refractive index of a sample [6, 7]. In this technique, the sample is moved along the axis of a focused beam, and the pulse energy transmitted through the sample is measured as a function of sample position. With an aperture in front of the detector, the measurement is sensitive to both non-linear refraction and non-linear absorption. Without an aperture, or with a large aperture, the total transmitted energy is measured, sensing only the non-linear absorption. Usually, both types of measurements are performed, the large aperture scan giving an independent measurement of the non-linear absorption. In our calculations, we assume that the incident pulse is represented by the fundamental gaussian beam [12],

$$E_{\mathrm{in}}(r, z_s, t) = E_0 \frac{\omega_0}{\omega(z_s)} \exp(-t^2/2\tau^2) \exp(i(kz_s - \Phi) - r^2(1/\omega(z_s)^2 - ik/2R(z_s))), \tag{4}$$

where ω_0 is the beam waist, and

$$\phi(z_s) = \arctan(z_s/z_0) \tag{5}$$

$$\omega^2(z_s) = \omega_0^2\left[1 + \left(\frac{z_s}{z_0}\right)^2\right], \tag{6}$$

$$R(z_s) = z_s\left[1 + \left(\frac{z_0}{z_s}\right)^2\right], \tag{7}$$

where z_0, the diffraction length, is given by

$$z_0 = k\omega_0^2/2 \tag{8}$$

and k is the vacuum wavenumber for the beam. We use the symbol z_s to denote the position of the sample along the beam axis, relative to the focus.

Given the field at the incoming surface of the sample, the effect of propagation through the non-linear medium is to attenuate the beam, and to distort the wave fronts through non-linear refraction. In the limit of a thin sample, $L \ll z_0$, these effects are represented by the equations

$$dI/dz = -(\alpha + \beta I + \mu I^2)I, \tag{9}$$

$$d\Delta\phi/dz = k\Delta n, \tag{10}$$

where α, β and μ are the linear, third order (two photon) and fifth order (three photon) absorption coefficients. Δn is the change in index of refraction due to non-linear effects, and in the present calculation, Δn is modelled by,

$$\Delta n(r,z,t) = \gamma I(r,z,t) + dn/dT\frac{1}{C}\int_{-\infty}^{t} dt'[f_\alpha \alpha I(r,z,t') + f_\beta \beta I^2(r,z,t') + f_\mu \mu I^3(r,z,t')]. \tag{11}$$

The first term in equation (11) represents a third order refractive effect which is instantaneous on the time scale of the pulse. The second term represents the effect of a change in temperature of the sample, due to the deposition of energy by the beam through the various absorption processes. The factors f_α, f_β and f_μ are included as adjustable constants, $0 \leqslant f \leqslant 1$, to account for the fact that only a fraction of the absorbed energy may be converted to heat in the duration of the pulse.

Having solved equations (9)–(11), the field at the exit surface of the sample is given by

$$E(r,z_s+L,t) = E_{\text{in}}(r,z_s,t)\sqrt{[I(r,z_s+L,t)/I_{\text{in}}(r,z_s,t)]}\exp(i\Delta\phi(r,z_s,t)), \tag{12}$$

where L is the sample thickness. To propagate the field from the sample to the detector, we make use of Kirchoff's integral in the Fresnel diffraction limit [13]. In our simulated z scans we vary the sample position, z_s, and calculate the pulse energy through the detector by integrating the intensity at the detector over the detector aperture and over time. We note that the theory presented here is not essentially different from that used in [6, 7], except that we do not make use of the gaussian decomposition [14] to propagate the field from the sample to the detector. We chose the present method over the gaussian decomposition, since the gaussian decomposition makes use of an expansion of $\exp(i\Delta\phi)$ in powers of $\Delta\phi$, which in our case is of order unity. Our method is convenient in practice, since the propagation from sample to detector is independent of any assumption about the propagation through the sample, enabling a great deal of flexibility with regard to the modelling of non-linear effects.

3. Results

All of the subsequent results were calculated with the following parameters for the laser beam, chosen to correspond to the experiments of [3–5]:

Pulse energy: 24 μJ,
Pulse duration (FWHM): 6·5 ns,
Beam waist: 7·5 μm,
Vacuum wavelength: 532 nm.

We assume a sample thickness of 25 μm throughout, and all of the following results are calculated for polarization of the beam parallel to the director.

Figures 1 and 2 show the results of a simulated z scan. The small aperture scan was calculated with $A=0{\cdot}01$, meaning that in the absence of non-linear absorption, 1 per cent of the incident light passes through the aperture into the detector. In the large aperture case, we integrate all of the intensity at the exit surface of the sample, so that the large aperture scan is sensitive only to non-linear absorption. The calculations are compared to the experimental results of [5] for the material 5CB, which shows some of the largest non-linearities of the materials studied [4]. The curves in figures 1 and 2 were calculated with the following material parameters, thought to be typical [1] for the materials under study:

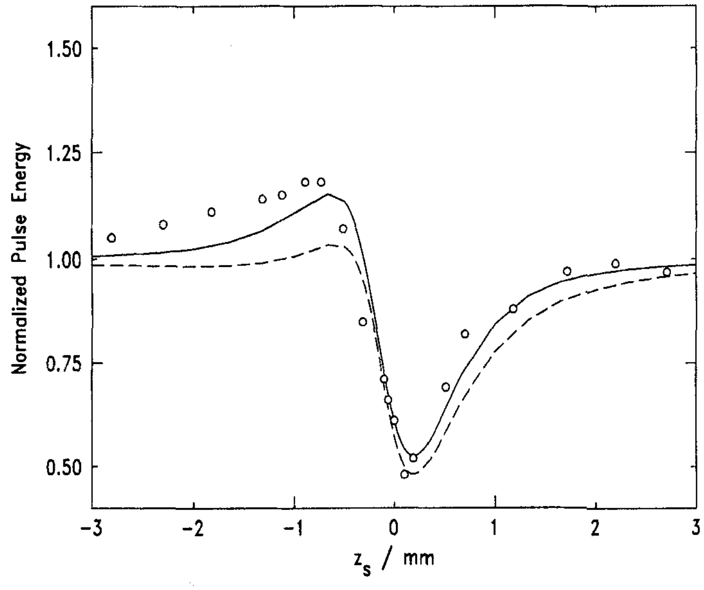

Figure 1. Simulated small aperture z scan. The dashed curve is calculated with purely third order absorption (see equation (9)), while the solid curve is calculated with purely fifth order absorption. Experimentation points (○) for 5CB are from [5]. The aperture transmission, A, is 0·01. ---, $\mu=0{\cdot}0$, $\beta=2{\cdot}8\times10^{-9}\,\mathrm{m\,W^{-1}}$; ——, $\mu=3{\cdot}5\times10^{-22}\,\mathrm{m^3\,W^{-2}}$, $\beta=0{\cdot}0$.

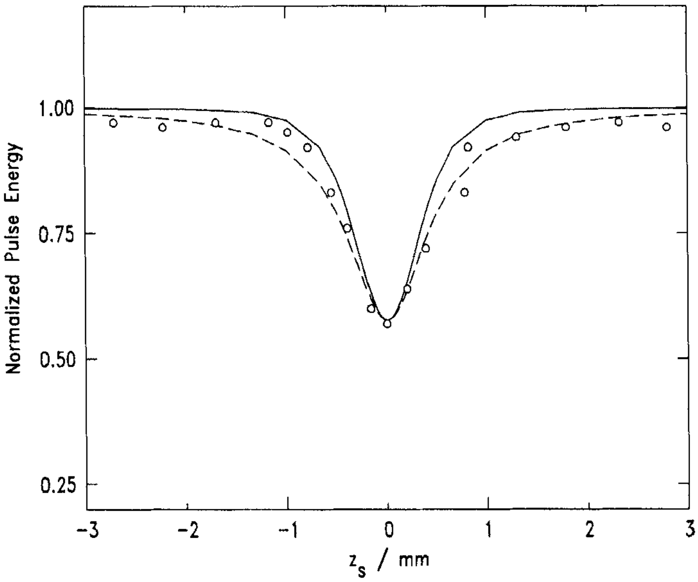

Figure 2. Simulated large aperture z scan. The curves are labelled as in figure 1. ---, $\mu=0{\cdot}0$, $\beta=2{\cdot}8\times10^{-9}\,\mathrm{m\,W^{-1}}$; —, $\mu=3{\cdot}5\times10^{-22}\,\mathrm{m^3\,W^{-2}}$, $\beta=0{\cdot}0$, ○, experimental data.

$$\left.\begin{aligned} dn/dT&=-3\times10^{-3}\,\mathrm{K^{-1}},\\ C&=2\times10^{6}\,\mathrm{J\,m^{-3}\,K^{-1}},\\ \alpha&=35{\cdot}0\,\mathrm{m^{-1}},\\ f_\alpha&=1{\cdot}0,\\ f_\beta&=0{\cdot}0,\\ f_\mu&=0{\cdot}0,\\ \gamma&=0{\cdot}0.\end{aligned}\right\}\qquad(13)$$

Using $f_\alpha=1{\cdot}0$, $f_\beta=f_\mu=0$, means that all of the energy absorbed through linear absorption is converted into heat, but none of the higher order absorption processes result in heating of the sample within the duration of the pulse. This results in a third order refractive process, that is, $\Delta n\propto I$. The linear absorption, α, was adjusted to match the peak to peak variation of the experimental z scan. Taking $\gamma=0{\cdot}0$ means that, in the calculations, all of the non-linear refraction comes from heating. This is done for illustrative purposes here, in order to show that the resultant magnitude of the non-linear refraction is in reasonable agreement with the measurements. However, if we take for γ the value measured with 33 ps pulses, where instantaneous effects presumably dominate, the resulting contribution to the phase shift, equation (1), is negligible.

The solid curves in figures 1 and 2 are for a purely fifth order absorptive process, where we put in equation (9) $\beta=0$, $\mu=3{\cdot}5\times10^{-22}\,\mathrm{m^3\,W^{-2}}$. Our consideration of fifth order absorption here is motivated by the experimental observation of [4] that the β obtained by fitting the data, assuming a third order absorption, in fact has a substantial linear dependence on the incident intensity. The dashed curves in figures 1 and 2 correspond to a purely third order absorption with $\mu=0$, $\beta=2{\cdot}8\times10^{-9}$ m W^{-1}. These values of β and μ were chosen to match the minimum of the large aperture scan. Some understanding of the relation between the shape of the calculated curve and the order of the underlying effect can be gained by recalling that one of the results of [6, 7] is that we can approximately think of non-linear absorption and non-linear refraction as operating independently. Then the small aperture scan curve can be thought of as the product of a refractive part, which has the peak-valley behaviour, with the non-linear absorption, which has a minimum at $z_s=0$. In general, a higher order effect tends to bring these features of the curve closer to $z_s=0$. For example, it was found in [7] that for a third order refraction, the maximum and minimum of the small aperture scan are separated by $1{\cdot}7z_0$, while for a fifth order refraction, the separation is $1{\cdot}2z_0$. The main effect of the fifth order absorption is seen in figure 2, which shows that the minimum of the large aperture scan is more concentrated near the origin, in contrast with the third order absorption. In the small aperture scan, figure 1, the refractive mechanisms for the two curves are the same. However, for the dashed curve, with the third order absorption, the peak at negative z_s which is normally associated with a defocusing medium [6, 7] ($n_2<0$) has been nearly swallowed by the broad absorption minimum. For the solid curve, which is calculated with a fifth order absorption, the narrower absorption minimum allows for a peak in the small aperture curve at negative z_s. We note that the experimental data do seem to show such a peak. We find that this feature is impossible to obtain with a purely third order absorption. The experimental large aperture scan also shows some sign of the narrower minimum characteristic of fifth order absorption, although this is difficult to distinguish from the scatter in the data. It is likely that more than one order of non-linear absorption is in effect. However, mixtures of third and fifth order absorption constrained to give the same minimum of the large aperture scan simply interpolate between the curves shown. Since this does not seem to result in any better fit to the data, particularly for the small aperture case, it does not seem to be possible to obtain definitive values for the coefficients by fitting a single z scan curve.

Non-linear absorption may contribute to heating of the sample. The experiments show that 40 per cent of the incident energy is removed from the beam by these processes in the situation we consider. If all of this energy were converted to heat, the sample temperature would rise by

$$\begin{aligned}\Delta T &\approx \mu I_p^3\tau/C\\ &\approx 4000\,\mathrm{K},\end{aligned}\tag{14}$$

where I_p is the peak, on-axis intensity. Clearly this does not occur. It may be that the energy absorbed by these higher order processes remains in long-lived electronic excitations for the duration of the pulse, or is carried away by fluorescence. This is not known. If some fraction of the energy absorbed by higher order processes is turned into heat during the pulse, then f_β and f_μ should not be strictly zero. In figure 3 we illustrate this possibility by calculating a small aperture scan where the refractive mechanism is entirely heating due to fifth order absorption. This results in a seventh order refractive effect. We have taken $f_\mu=1{\cdot}6\times10^{-3}$. The result of this

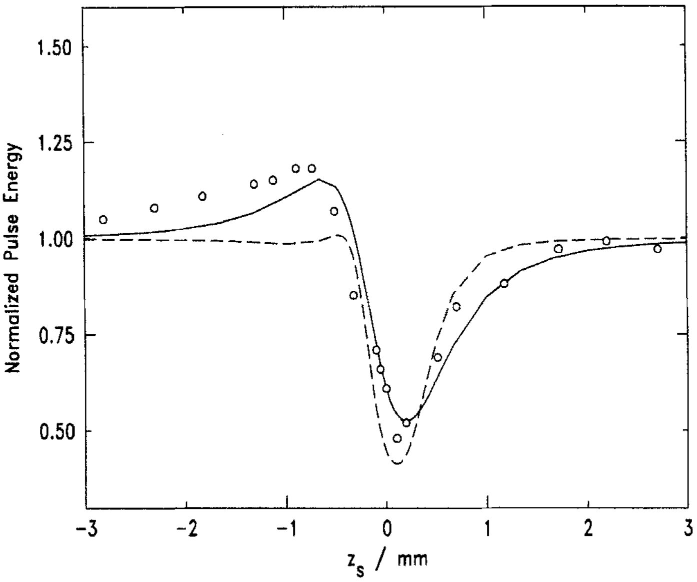

Figure 3. Effect of heating due to fifth order absorption. The solid curve is the same as in figure 1. The dashed curve shows the effect of heating due to fifth order absorption (see equation (11)). This is a small aperture scan, $A=0{\cdot}01$. ---, $f_\alpha=0{\cdot}0$, $f_\mu=1{\cdot}6\times10^{-3}$; ——, $f_\alpha=1{\cdot}0$, $f_\mu=0{\cdot}0$; ○, experimental data.

calculation is shown as the dashed line in figure 3 along with the solid curve of figure 1 and the experimental points [5]. The higher order refraction results in the peak of the curve being pulled in closer to $z_s=0$, where it is almost completely eliminated by absorption. This leads to worse agreement with experiment, particularly in the region of negative z_s. Since it was reported experimentally [4] that the measured n_2 is independent of the input intensity, it appears that the dominant refractive effect is truly second order.

With regard to the thermal mechanism, we note that although we have adjusted the value of α used in the calculations of figures 1 and 2 to fit the experimental data, the resultant value of $\alpha=35{\cdot}0\,\mathrm{m}^{-1}$ is well within what is considered reasonable, the precise value of α being difficult to measure [1]. From the comparisons of our calculations with the experimental data, we conclude that the magnitude of the observed non-linear refraction, as measured by the peak–peak variation of the z scan curve, is consistent with this mechanism. However, the main feature of the thermal mechanism is the way the non-linear refraction accumulates in time, as in equation (11). Since the z scan technique measures the integrated pulse energy, no information is obtained about the temporal character of the mechanism. Our z scan curves could have been calculated by putting $f_\alpha=f_\beta=f_\mu=0$ in equation (11) and using $\gamma=-2{\cdot}7\times10^{-16}\,\mathrm{m}^2\,\mathrm{W}^{-1}$ with nearly identical results. In order to gain information about the temporal behaviour of the non-linearities, Li *et al.* [4] have performed experiments in which they observed the temporal profile of the outcoming pulse with two closely spaced input pulses. Figure 4 shows a simulation of just such a situation. The material parameters are the same as those used for the solid curve of figure 1, with the non-linear refraction again being assumed to be entirely thermal. The solid

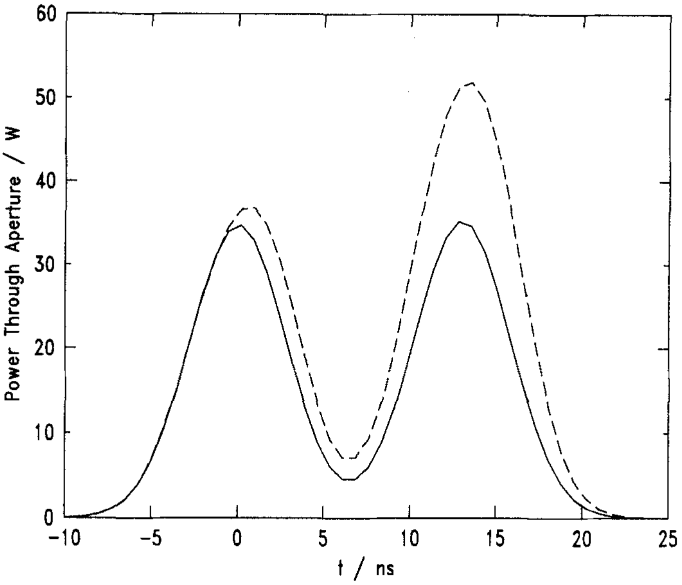

Figure 4. Temporal profile of a double pulse. The solid curve is for a sample position far from the focus. The dashed curve corresponds to a sample position near the maximum of the small aperture z scan (see figure 1). $A = 0{\cdot}01$, delay $= 13{\cdot}0$ ns. ——, $z_s = -3{\cdot}32$ mm; ---, $z_s = -0{\cdot}50$ mm.

curve of figure 4 shows the outcoming power through the small aperture for a case in which the sample is located far from the beam focus, so that non-linear effects are not important. In this case the output power is simply proportional to the input power. The dashed curve shows the case in which the sample is positioned near the maximum of the small aperture scan, figure 1. In this case there is important non-linear refraction, which tends to increase the energy flux through the aperture. This non-linear refractive effect builds up in time according to equation (11) with the accumulation of heat in the sample. Since there is effectively no diffusion of heat over the time scales we are considering, the heat accumulated during the first pulse is still in place during the second pulse, leading to a strong influence of the first pulse on the second. This type of behaviour has been observed experimentally [4].

4. Conclusions

We have performed numerical simulations of z scan experiments for comparison with the experimental results of Palffy-Muhoray's group [3–5]. In particular, we have considered the z scan experiments with 7 ns pulse duration and the material 5CB, which was the most extensively studied. We have shown calculations to illustrate the z scan signature associated with various orders on non-linear absorption and non-linear refraction. Qualitative features of the experimental z scan curves seem to be consistent with third order refraction and fifth order absorption. We find that the magnitude of the observed non-linear refraction is consistent with laser heating of the sample due to linear absorption. We have also shown a calculation of the temporal profile of the detected power through a small aperture in the case where the incident beam consists of two closely spaced gaussian pulses. Due to the cumulative nature of the thermal mechanism, the presence of the first pulse has a strong influence on the second. Our calculated result is qualitatively similar to the observation of [4], which clearly shows such a cumulative effect.

In our calculations, we have only considered one order of non-linear refraction or non-linear absorption at a time. In reality, various orders of non-linearity will be operative simultaneously. In principle, the shape of the z scan curve contains information about the coefficients of various orders. In practice we find the level of disagreement between calculated and experimental curves precludes any such detailed analysis. In addition to random scatter of the experimental points, which presumably results from fluctuations in laser pulse energy, there seem to be systematic deviations between calculation and measurement. One possible source of such deviations is imprecise location of the origin, $z_s=0$, in the experiments. We have not attempted to correct for this in the plots shown here. Instead of trying to obtain a very refined curve shape for a single pulse energy, it would seem to be fruitful to try to obtain the coefficients of the various processes by fitting z scan curves measured over a range of pulse energies. Energy dependent measurements are reported in [4], where the data were analysed to obtain pulse energy dependent 'effective' values for n_2, and β. The effective n_2 was found to be independent of intensity, while β was found to depend linearly on intensity, indicating the presence of fifth order absorption. A rough estimate of the fifth order absorption coefficient can be obtained from their plot using $\mu \sim \Delta\beta/\Delta I \approx 10^{-21}\,\mathrm{m^3\,W^{-2}}$. This compares favourably with the value $3{\cdot}5\times10^{-22}\,\mathrm{m^3\,W^{-2}}$ used in the plot of figure 1. More detailed fitting of energy dependent z scans to obtain definitive values of the coefficients would seem to be very profitable.

Both the magnitude and the temporal behaviour of the observed non-linear refraction are consistent with a thermal mechanism. We have noted that the thermal mechanism has one shortcoming with respect to explaining the observed n_2, and that is that the n_2 observed with 7 ns pulses is found to be nearly independent of temperature [4], while on the basis of equation (1) we expect that n_2 will have the temperature dependence of dn/dT, which has rapid variation near the nematic–isotropic transition. However, we point out that 7 ns is actually much shorter than the characteristic relaxation time, τ_r, associated with variations in the orientational order parameter, S, for temperatures near the transition. Given that τ_r has the same dependence on the temperature as dS/dT near the phase transition, it is quite likely that the observed lack of temperature dependence of n_2 is a result of the finite response time of S. We are currently investigating molecular orientational dynamics theoretically, and should soon be able to make more definite statements regarding the dynamics of the response of the orientational order to variations of temperature and external fields, and the resulting temperature dependence of n_2.

Further experimental data would also be very valuable in identifying the underlying mechanism of the non-linear optical response. For example, we have noted that the cumulative temporal behaviour of the non-linear refraction is characteristic of the thermal mechanism. However, we can imagine other mechanisms which would exhibit similar behaviour. Excited state refraction in which the molecular polarizability is changed through a one photon excitation would have a very similar signature. In fact, if the relaxation time of the excited state were long compared with the pulse duration, the theoretical description would be essentially identical with equation (11) except that the parameters would be interpreted differently. In the case of the thermal mechanism, we know that the decay time, which is essentially the diffusion time, equation (2), is indeed long. Therefore, if the thermal mechanism is the operative effect, we should not observe any diminution of the effect of the first pulse on the second in a double pulse experiment as the delay between pulses is increased to quite large values (~1 ms). This is a quite definite prediction of the thermal mechanism and any departure from this behaviour would be strong evidence against a thermal interpretation. Observations of fluorescence would help to determine the fate of the large amounts of energy removed from the beam by non-linear absorption. Also, the observation of fluorescence at wavelengths shorter than $\lambda/2$ would confirm the presence of fifth order (three photon) absorption.

This work was supported by DARPA through the U.S. Army Communications and Electronics Command, grant number DAAB07-88-C-F421, and by NSF under ALCOM grant number DMR85-20147. We thank P. Palffy-Muhoray for access to experimental data.

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