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Third order optical non-linearities of nematic liquid crystals[†]

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Liquid crystals can exhibit large third order optical non-linearities. Using the Z-scan technique, we have measured the intensity dependence of the non-linear absorption and non-linear refractive indices on time-scales ranging from milliseconds to picoseconds for nematic liquid crystals. This method allows the determination of the non-linear absorption coefficients as well as the signs and magnitudes of the non-linear refractive indices for different polarizations. A two pulse technique further enables estimation of the response time of the dominant mechanism. Using CW argon and Q-switched and mode-locked pumped dye lasers, we have carried out Z-scan measurements on aligned liquid crystal samples as a function of temperature, as well as wavelength. In the geometries studied, director reorientation is not expected to take place. On the nanosecond time-scale, all materials studied were self-focusing for polarization perpendicular to the director, and self-defocusing for parallel polarization. On the picosecond timescale, the samples were self-focusing for all polarizations, but strong non-linear birefringence was typically observed. An attempt is made to relate the bulk response to the molecular structures.

1. Introduction

The non-linear optical response of liquid crystals has been the subject of considerable study in recent years [1–4]. A large variety of mechanisms ranging from collective reorientation to electronic hyperpolarizability can contribute to the optical non-linearities in these materials. In recent papers, [5–7], measurements of third order non-linearities have been reported on liquid crystals 5CB (4-cyano-4′-*n*-pentylbiphenyl), 8CB (4-cyano-4′-*n*-octylbiphenyl) and E7 (a commercial mixture of biphenyls and terphenyls) on time-scales ranging from picoseconds to milliseconds using the Z-scan method. It has been pointed out that, on the millisecond timescale, the major contributing mechanism to the large optical non-linearities in these materials is laser heating due to linear absorption, which changes the orientational order and hence alters the refractive indices. On the picosecond time-scale, the dominant mechanism most probably arises from the electronic contributions. The dominant mechanism in the nanosecond time regime has yet to be identified.

Although many techniques have been developed to study third order non-linear optical effects, the single-beam Z-scan technique [8] is attractive because of its

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simplicity and sensitivity in measuring both the non-linear refraction and non-linear absorption. The technique is based on the transformation of phase distortion induced by the non-linear medium to amplitude distortion during beam propagation. The sensitivity of the Z-scan method has allowed the determination of third order susceptibilities of liquid crystals in the nematic phase on the nanosecond time-scale for the first time [6], using very thin samples where scattering due to director fluctuations does not pose a problem. We have undertaken further nanosecond Z-scan measurements on a variety of liquid crystals, in order to understand better the origins of the optical non-linearities. In this paper we report the results of these measurements.

The samples were aligned in such a way that director reorientation is not expected to occur. Measurements were taken at different temperatures, using nanosecond pulses from a frequency doubled Nd:YAG laser. Both the non-linear refractive indices and non-linear absorption coefficients for light polarized parallel (denoted by $\|$) and perpendicular (denoted by $\perp$) to the nematic director were determined. The effects of adding a dye to one material (8CB) were studied. In the case of 5CB, the response was studied as a function of intensity, and measurements at the fundamental wavelength of 1·06 μm were also made. In addition, a two-pulse Z-scan experiment was developed and used to estimate the response time of the non-linearity. Millisecond pulses from a CW Ar$^+$ laser operating at 514 nm wavelength were also used to study the effects of laser heating.

2. Z-scan experiment

The details of the Z-scan method and the experimental arrangement have been described elsewhere [5–7]. The samples consisted of a 10 to 120 μm thick layer of liquid crystal between parallel glass plates. The plates were coated with polyimide and buffed, to give alignment of the nematic director in the plane of the plates. The samples were housed in a precision-controlled, thermostatted stage (Instec) on a computer controlled translation stage. A gaussian laser beam, propagating in the z-direction, was focused to a narrow waist using a lens. The sample was moved along the z-direction through the focal point, and the transmitted intensity was measured using a photodiode behind an aperture. The polarization was either parallel or perpendicular to the nematic director. The refractive index n is

$$n = n_0 + \frac{n_2}{2}|E|^2, \tag{1}$$

where n_0 and n_2 are the linear and the non-linear refractive indices, and E is the electric field, while the absorption coefficient is

$$\alpha = \alpha_0 + \beta I, \tag{2}$$

where α_0 and β are the linear and non-linear absorption coefficients. By analysing [5–7] the Z-scan data, the n_2 and β can be calculated.

Using the experimental scheme described above, we have carried out measurements on 8 different liquid crystals. Five of these materials are commercially available; however, OPL-7-1, OPL-10-1 and OPL-10-2, were synthesized by the group of L. C. Chien at the Liquid Crystal Institute at Kent State University. In addition to pure liquid crystals, a dyed (anthroquinone dye d_{27} from BDH) sample of 8CB was studied. The experimental results for these materials are summarized in tables 1, 2 and 3. The molecular structures are also shown. λ is the wavelength at which the measurements were carried out, δ is the laser pulse width, and T is the sample temperature. The

Table 1. Summary of the measurements at 532 nm wavelength and 7 ns pulse width.

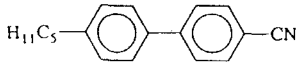
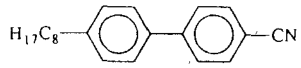
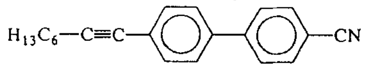
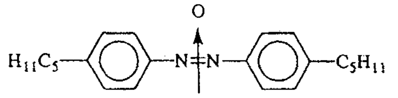
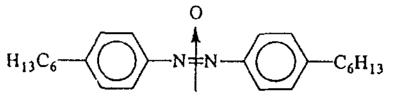
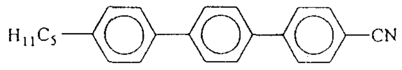
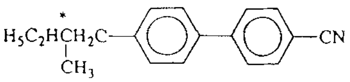
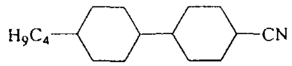
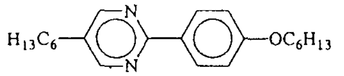
Material	n_2/esu	β/cm/GW	T/°C
5CB 4-cyano-4′-*n*-pentylbiphenyl 	$\parallel$: -54×10^{-11}	$\parallel$: 265	24
	$\perp$: $+8{\cdot}3\times10^{-11}$	$\perp$: 36	24
	iso: -24×10^{-11}	iso: 114	40
8CB 4-cyano-4′-*n*-octylbiphenyl 	$\parallel$: -26×10^{-11}	$\parallel$: 246	22
	$\perp$: $3{\cdot}7\times10^{-11}$	$\perp$: 20	24
d_{27} doped (<0·2 per cent) 8CB	$\parallel$: -152×10^{-11}	$\parallel$: 380	22
	$\perp$: $+10{\cdot}5\times10^{-11}$	$\perp$: 30	22
	iso: -48×10^{-11}	iso: 193	40
OPL-7-1 4-(1-octynyl)-4′-cyanobiphenyl 	$\parallel$: -27×10^{-11}	$\parallel$: 112	37
	$\perp$: $+7{\cdot}0\times10^{-11}$	$\perp$: 19	37
	iso: $-5{\cdot}5\times10^{-11}$	iso: 33	60
OPL-10-1 4-4′-dipentylazoxybenzene 	$\parallel$: $-9{\cdot}9\times10^{-11}$	$\parallel$: 55	40
	$\perp$: $+4{\cdot}5\times10^{-11}$	$\perp$: 3·7	40
	iso: $-2{\cdot}4\times10^{-11}$	iso: 11	80
OPL-10-2 4-4′-dihexylazoxybenzene 	$\parallel$: -15×10^{-11}	$\parallel$: 38	50
	$\perp$: $+2{\cdot}0\times10^{-11}$	$\perp$: 4·2	50
	iso: $+5{\cdot}0\times10^{-11}$	iso: 21	66
T15 4-cyano-4″-*n*-alkyl-*p*-terphenyl 	$\parallel$: -52×10^{-11}	$\parallel$: 270	180
	$\perp$: $+21\times10^{-11}$	$\perp$: 18	180
E7	$\parallel$: -38×10^{-11}	$\parallel$: 284	24
	$\perp$: $+3{\cdot}3\times10^{-11}$	$\perp$: 40	24
CB15 	iso: $+7{\cdot}4\times10^{-11}$	iso: 38	24
ZLI 1538 Cyclohexylcyclohexane 	$\parallel$: ~0	$\parallel$: ~0	70
	$\perp$: ~0	$\perp$: ~0	70
	iso: ~0	iso: ~0	90
ZLI 2303 Phenylpyrimidine 	$\parallel$: -20×10^{-11}	$\parallel$: 67	45
	$\perp$: $+3{\cdot}0\times10^{-11}$	$\perp$: 8·2	45
	iso: $-3{\cdot}8\times10^{-11}$	iso: 19	85

Table 2. Summary of the measurements at 532 nm wavelength and 33 ps pulse width.

Material	n_2/esu	β/cm/GW	T/°C
5CB	$\parallel$: $+1\cdot 04\times 10^{-11}$	$\parallel$: 2·26	24
	$\perp$: $+0\cdot 69\times 10^{-11}$	$\perp$: 0·78	24

Table 3. Summary of the measurements at 514 nm wavelength and 10 ms pulse width.

Material	n_2/esu	β/cm/GW	T/°C
5CB	$\parallel$: -10×10^{-4}	$\parallel$: 0	24
	$\perp$: $+2\cdot 0\times 10^{-4}$	$\perp$: 0	24
	iso: $-2\cdot 0\times 10^{-4}$	iso: 0	40
T15	$\parallel$: $-0\cdot 68\times 10^{-4}$	$\parallel$: 0	180
	$\perp$: $-0\cdot 092\times 10^{-4}$	$\perp$: 0	180
CB15	iso: $-0\cdot 25\times 10^{-4}$	iso: 0	22
ZLI 1538	$\parallel$: $-0\cdot 43\times 10^{-4}$	$\parallel$: 0	70
	$\perp$: $0\cdot 13\times 10^{-4}$	$\perp$: 0	70
	iso: $-0\cdot 35\times 10^{-4}$	iso: 0	97
ZLI 2303	$\parallel$: $-0\cdot 97\times 10^{-4}$	$\parallel$: 0	45
	$\perp$: $+0\cdot 082\times 10^{-4}$	$\perp$: 0	45
	iso: $-0\cdot 3\times 10^{-4}$	iso: 0	85

subscripts $\parallel$ and $\perp$ indicate polarization parallel and perpendicular to the director, and iso denotes the isotropic phase. The uncertainty in the figures is approximately 10 per cent. Also, in tables 1, 2 and 3, previous results on 5CB, 8CB and E7 are included for the purpose of comparison.

In order to identify the dominant mechanism responsible for the observed large non-linearities in the nanosecond regime, it is useful to have an estimate of the characteristic time of the contributing process. To estimate this time, we have devised a time resolved double pulse Z-scan scheme. The experimental setup is shown in figure 1. A portion of the beam from the laser is first delayed and then recombined with the original beam, resulting in two pulses of nearly identical amplitude separated in time. By performing Z-scan measurements using these two pulses, it is possible to determine if the first pulse affects the response to the second. If it does, then the response time of the process cannot be less than the temporal separation of the pulses. For this scheme to work, it is essential that, at the sample, the two beams be parallel, and that both pulses pass through the same region of the sample.

The time delay between the two pulses can be varied by changing the length of the delay line. The energy of each pulse can be adjusted independently by changing the angles between the $\lambda/2$ plate and the Glan prisms. In our experiment, the two pulses had

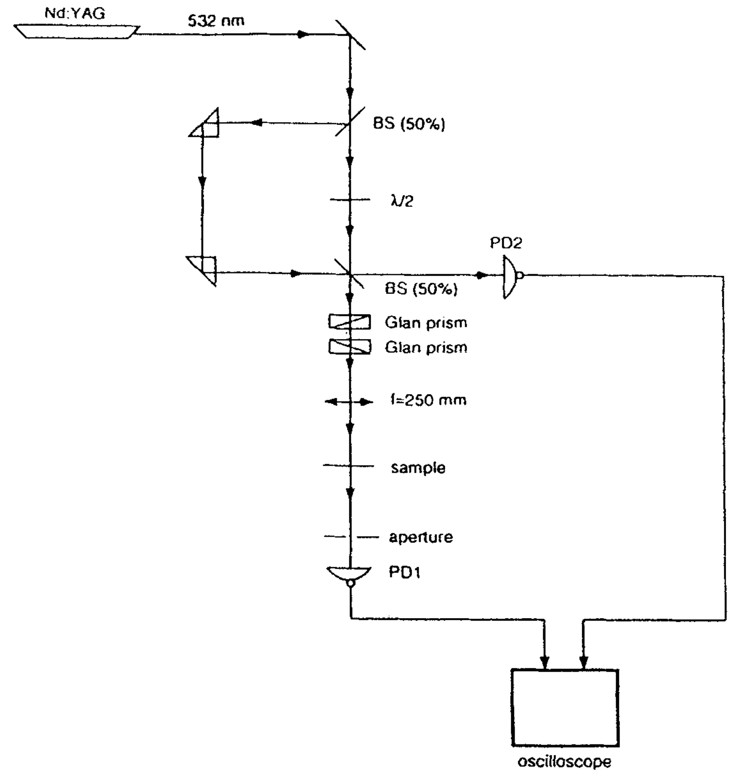
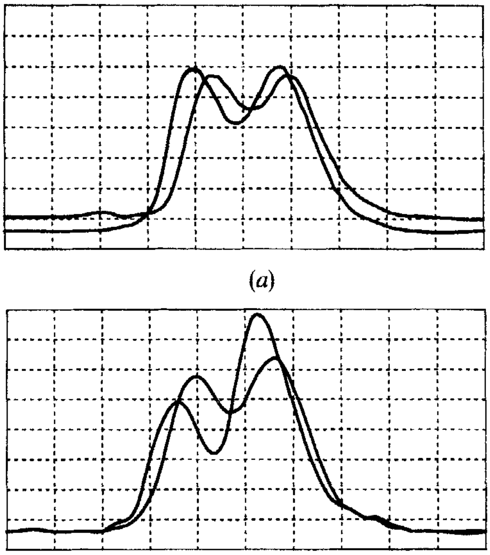


Figure 1. Two-pulse Z-scan experiment. BS is a beam splitter, and PD1 and PD2 are photodiodes.

nearly the same energy and a time delay of 11 ns. The incident and transmitted intensities were recorded on the oscilloscope. The sample was 5CB at 24°C. The incident polarization of both pulses was parallel to the director. Figure 2 shows the oscilloscope record when a small aperture was placed in front of the photodetector PD1. Figure 2 (*a*) shows the transmitted pulses when the sample was placed far away from the focal point. The two transmitted pulses have almost the same height, since the intensity is low and non-linear effects are negligible. However, when the sample is moved close to the focal point, at a particular sample position, the first pulse is suppressed due to non-linear absorption and non-linear refraction, while the second one is increased rather than decreased. Such an example is shown in figure 2 (*b*). The increase in the amplitude of the second transmitted pulse is clearly due to the effect of the first pulse, since when the first pulse is blocked, the second pulse decreases also. This behaviour implies that, regarding non-linear refraction, the second pulse 'sees' the effect of the first pulse. However, if the total transmittance is measured without an aperture in front of the detector, i.e. all transmitted light is detected, the two transmitted pulses have the same response regardless of sample position relative to the focal point. This implies that, regarding non-linear absorption, the second pulse does not see the effect of the first.

We have also carried out measurements of the temperature dependence of the non-linear response of 5CB on the nanosecond scale at 532 nm wavelength. We found, as in the millisecond case, that $n_{2\parallel}$ and $n_{2\perp}$ in the nematic phase have opposite signs, and that there is an abrupt change in these values across the nematic–isotropic transition.



(*a*)

(*b*)

Figure 2. Oscilloscope traces of the reference and transmitted beam intensities in the two-pulse Z-scan experiment. The time-scale on the horizontal axis is 5 ns Div.$^{-1}$ (*a*) Sample far from focal point; (*b*) sample near focal point.

However, unlike in the millisecond case, [5, 6], the values of $n_{2\parallel}$ and $n_{2\perp}$ do not change appreciably with temperature in the nematic phase, and remain nearly constant up to the nematic–isotropic transition temperature. Figure 3 illustrates the temperature dependence of the parallel component of n_2 and β. We note, as shown in figure 3 (*a*), that $n_{2\parallel}$ is constant to within 5 per cent from 0 to 10°C below the transition; the transition was approached to within less than 400 mK. Similar behaviour holds for $\beta_{\parallel}$, figure 3 (*b*). However, there is an abrupt jump at the transition temperature both for $n_{2\parallel}$ and $\beta_{\parallel}$.

We have also measured the intensity dependence of the non-linear absorption coefficient $\beta_{\parallel}$ and refractive index $n_{2\parallel}$ for 5CB at 532 nm using ns pulses. The sample has a thickness of 25 μm and the sample temperature is 24°C. In this set of measurements, for each incident energy, we performed a Z-scan measurement and calculated the non-linear refraction and absorption coefficients. In this way, n_2 and β were determined as a function of incident intensity. Figure 4 shows the result for the geometry where the incident polarization is parallel to the director. The horizontal axis represents on-axis laser intensity I_0, defined as $I_0 = 2P/(\pi\omega_0^2)$, where P is the power and ω_0 is the beam waist. As can be seen in figure 4, the non-linear refractive index $n_{2\parallel}$ remains essentially constant within our experimental error, as expected for a third order process. Interestingly, however, the effective non-linear absorption increases linearly with the intensity.

We have also attempted to measure the non-linear response at the fundamental $\lambda = 1{\cdot}06\,\mu$m output of the Q-switched Nd:YAG laser. Our preliminary experimental results for 5CB show very weak non-linearities at this wavelength; below the damage threshold, the non-linear contribution to the transmittance could not be effectively separated from noise.

Finally, photoacoustic measurements were made to study the process of dissipation of the absorbed energy. A sensitive accelerometer consisting of a piezoelectric element

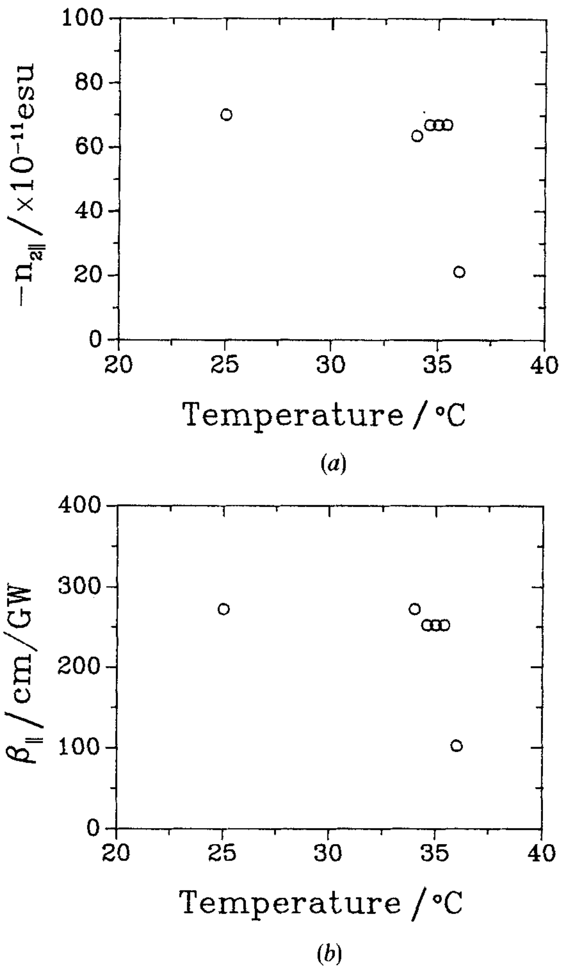


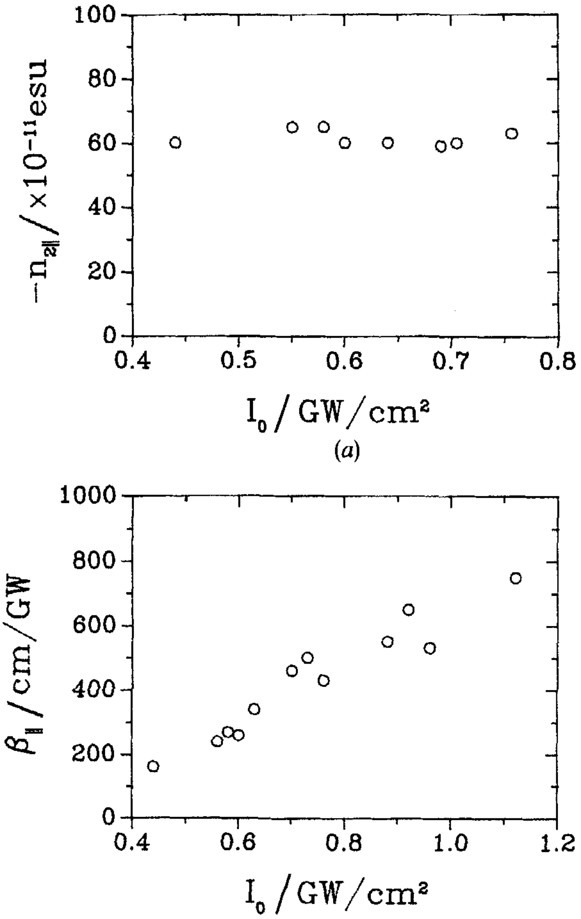
Figure 3. Temperature dependence of (*a*) non-linear refractive index $n_{2\parallel}$, and (*b*) non-linear absorption coefficient $\beta_{\parallel}$ of 5CB, 25 μm thickness and 532 nm wavelength ($E \parallel n$).

was attached to one glass plate of a 120 μm thick 5CB sample; the sample was then exposed to 532 nm pulses. The incident polarization was parallel to the director and the pulse energy was 64 μJ. With the sample positioned near the focal point of the lens, the transmittance was ~0·5. At this intensity, a signal was detected by the accelerometer, indicating that acoustic excitations play a role in the dissipation process. Details of these measurements will be published elsewhere.

3. Discussion

Of all the pure materials studied, on the nanosecond timescale, 5CB shows the largest non-linearities. To interpret the nanosecond measurements, it is useful briefly to summarize the results of the millisecond measurements given in table 3.

In our geometry, where reorientation is not expected to take place, the non-linearity on the millisecond time-scale originates from laser heating due to linear absorption. The resulting temperature increase causes a decrease in the degree of orientational order and in the density, with the result that, in most materials, the extraordinary index decreases while the ordinary index increases. This gives rise to $n_{2\parallel} < 0$ and $n_{2\perp} > 0$, as



(*a*)

(*b*)

Figure 4. Intensity dependence of (*a*) non-linear refractive index $n_{2\parallel}$, and (*b*) non-linear absorption coefficient $\beta_\parallel$ of 5CB at room-temperature (24°C), 25 μm thickness and 532 nm wavelength ($E \parallel n$).

observed in the case of 5CB. Furthermore, $-n_{2\parallel}$, $n_{2\perp}$ and the non-linear birefringence $n_{2\perp} - n_{2\parallel}$ all increase dramatically as the nematic–isotropic temperature is approached from below [5]. At the intensities used in these measurements, no non-linear absorption is observed. The signs of the two non-linear refractive indices measured for 5CB and ZLI 2303 are in accordance with the above model. However, for ZLI 1538 and T15, both non-linear refractive indices are negative. ZLI 1538 is the only material studied whose core consists of cyclohexane rather than benzene rings, and hence is without conjugation. It is likely that due to the lack of the conjugation, the linear polarizability and the refractive indices are small, and hence order parameter changes are overwhelmed by the effect of thermal expansion. However, T15 has three benzene rings instead of two, and the reason why both non-linear indices are negative is not clear. It is possible that photostimulated conformational changes [9] play a role, but more study is needed to understand this behaviour. The observed non-linearities seem to be relatively insensitive to structural changes other than the presence of benzene rings. For example, the addition of a chiral branched alkyl chain in CB15 does not change the non-linear index in the isotropic phase appreciably.

Next, we consider possible mechanisms responsible for the non-linearities on the nanosecond time-scale. Strong non-linear refraction, non-linear birefringence and non-linear absorption are observed for these materials. By noting that the temperature dependence of the non-linear indices on the nanosecond timescale is fundamentally different from that on the millisecond scale, we conclude that the dominant mechanism is not laser heating due to linear absorption. This is further substantiated by the observations that n_{iso} for CB15 and $n_{\perp}$ for T15 change sign as the pulse width is reduced from ms to ns.

Although many other mechanisms, such as direct optical field induced orientational effects, electrostrictive effects, and electrostrictive effects combined with shear alignment, may contribute to the observed non-linearities, order of magnitude calculations based on simple theoretical models indicate that they cannot be the primary cause. The intensity dependent measurements on 5CB indicate that n_2 is independent of intensity, and therefore it is a third order process. Analysis of the measured peak and valley positions on the Z-scan curves is consistent with this. Two-pulse measurements indicate that the mechanism is slow; that is, the response time cannot be less than ~5 ns. One possibility is that the non-linear refraction originates from an excited state associated with one-photon absorption. On the other hand, for 5CB, intensity dependence measurements show that the non-linear absorption coefficient β is nearly proportional to the intensity. This is a signature of a 5th order process; two pulse measurements furthermore show that the associated response time is less than ~5 ns. It appears likely therefore, that at least in the case of 5CB, two different processes are operating simultaneously—a slow third order process which contributes primarily to the non-linear refraction, and a faster 5th order process which contributes primarily to the non-linear absorption.

If the measured β was due to three photon absorption, then picosecond measurements should show very large values of β, since the intensities are more than one order of magnitude higher. However, β measured with 33 ps pulses is smaller; values are given in table 2. It is likely therefore that the response time of the absorption process is long compared to picoseconds (but short compared to 10 ns), and this accounts for the decrease of β seen in the picosecond measurements. Such a process could be excited state absorption from a two-photon excited state. Since the non-linear refraction which dominates on the nanosecond time-scale is slow, it will be attenuated by more than two orders of magnitude in the picosecond measurements. The picosecond n_2 values thus originate from another mechanism, such as non-resonant electronic hyperpolarizability. The result that both n_2 and β are very small at $\lambda = 1{\cdot}06\,\mu$m is not inconsistent with this model. The contribution of the excited state at this wavelength to the molecular polarizability could be much smaller than that at 532 nm, and the multiphoton absorption cross-section is certain to be very different.

The non-linear behaviour is linked to the presence of the benzene rings in the molecules. For example, for ZLI 1538 no observable non-linearities (either non-linear refraction or absorption) have been detected; this material does not have benzene rings. Conversely, the addition of the anthroquinone dye d_{27} to 8CB significantly enhances the observed non-linearity, without changing its character (i.e. signs of n_2 are unchanged from that of the pure material; both non-linear refraction and non-linear absorption increase). Janossy [10] had observed an anomalous reduction of the threshold intensity required for the optical Fréedericksz transition in similarly dyed nematics. However, other features of molecular structure do not seem to play an important role in determining the non-linearity. As can be seen in table 1, the addition of the acetylene group (OPL-7-1) does not significantly contribute to the non-linearity. Similarly, varying the linkage by adding small conjugated structures (azoxy group) also has little effect on the nanosecond response.

In conclusion, our key findings on nanosecond time-scale experiments are the following: the non-linear refraction in a number of liquid crystals is anomalously large, the non-linear refraction is accompanied by large non-linear absorption, and the magnitude of the non-linearity is closely linked to the number of benzene rings in the molecules and appears insensitive to the presence of other conjugated units. Our results indicate that in 5CB, a slow third order process is responsible for the non-linear refraction, while a faster fifth order process is responsible for the non-linear absorption. Further work is needed to understand thoroughly the origins of the observed non-linearities in these materials.

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References

[1] Tabiryan, N. V., Sukov, A. V., and Zel'dovich, B. Ya., 1986, *Molec. Crystals liq. Crystals*, **136**, 1.
[2] Khoo, I. C., 1988, *Progress in Optics, XXVI*, edited by E. Wolf (North-Holland).
[3] Janossy, I., 1990, *Perspective in Condensed Matter Physics*, edited by L. Miglio (Kluwer Academic Publisher).
[4] Palffy-Muhoray, P., 1990, *Liquid Crystals: Applications and Uses*, Vol. 1, edited by B. Bahadur (World Scientific), Chap. 18, p. 493.
[5] Yuan, H. J., Li, L. and Palffy-Muhoray, P., 1991, *Molec. Crystals liq. Crystals*, **199**, 223.
[6] Palffy-Muhoray, P., Yuan, H. J., Li, L., Lee, M. A., Desalvo, J. R., Wei, T. H., Sheik-Bahae, M., Hagan, D. J., and Van Stryland, E. W., 1991, *Molec. Crystals liq. Crystals*, **207**, 291.
[7] Jiang, J. P., and Rentzepis, P. M., 1991, *J. appl. Phys.*, **70**, 5125.
[8] Sheik-Bahae, M., Said, A. A., Wei, T. H., Hagan, D. J., and Van Stryland, E. W., 1990, *I.E.E.E. J. Quant. Electron.*, **26**, 760.
[9] Odulov, S. G., Reznikov, Yu. A., Soskin, M. S., and Khiznyak, A. I., 1993, *Soviet Phys. JETP*, **58**, 1154.
[10] Janossy, I., 1991, *Molec. Crystals liq. Crystals* (*Proceedings of the IV International Meeting on the Optics of Liquid Crystals*, Cocoa Beach, Florida).