NONLINEAR REFRACTIVE INDEX MEASUREMENTS OF ISOTROPIC LIQUID CRYSTALS (U) ROYAL SIGNALS AND RADAR ESTABLISHMENT MALVERN (ENGLAND) A M SCOTT ET AL.
ROYAL SIGNALS & RADAR ESTABLISHMENT

NONLINEAR REFRACTIVE INDEX MEASUREMENTS OF ISOTROPIC LIQUID CRYSTALS

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SUMMARY

We have measured the nonlinear refractive index of a number of liquid crystalline materials in the isotropic phase. These materials show strong enhancement of the nonlinearity due to nematic like local ordering, and even materials which do not have a nematic-isotropic transition show this enhancement.

We also studied mixtures of liquid crystals and solvents and find that these mixtures also have an enhanced nonlinearity due to local ordering.

Absorption of the laser beam causes expansion which reduces the refractive index and can counteract the refractive index change due to reorientation.
1 INTRODUCTION

In areas such as phase conjugation, optical bistability and optical signal processing there is a need for identifying materials with large fast nonlinear refractive indices [1,2]. The most well known material with a large nonlinear refractive index is carbon disulphide [1] which has an $n_2$ of $1.2 \times 10^{-11}$ esu and a relaxation time of about 2 ps, resulting from molecular reorientation. Other materials can have substantially larger nonlinear refractive indices, and it was shown by Shen et al [3] that a sample of the nematic liquid crystal MBBA in the isotropic phase could have a nonlinear refractive index of up to a thousand times that of CS$_2$. In this memo we report on the measurements of the nonlinear refractive indices of a number of nonlinear liquids and provide data which may be of use in other investigations.

This data can be used both to screen various materials for their suitability in various applications and also to study the molecular dynamics of the liquids under investigation and the various phase transitions which occur in them. This latter aspect will only be touched on here and will be discussed more fully when published in the open literature in due course.

2 THE INTENSITY DEPENDENT REFRACTIVE INDEX OF LIQUID CRYSTALS

Before discussing the nonlinearity it may be useful to describe the characteristics of the liquid crystal phases. Liquid crystal molecules are long and rod-like (Figure 1) and their shape is responsible for their various phases.

At low temperatures the materials are crystalline, and when they melt they may form a number of different liquid crystal phases (although there are no simple rules indicating which phase they will form). In the nematic phase molecules tend to have their axes parallel to their neighbours, but their centres of gravity are randomly positioned. In the smectic phases they are not only aligned parallel to their neighbours but their centres of gravity align to
form layers. There are a number of different smectic phases with different ordering of the layers. Finally at higher temperatures the molecules are no longer aligned with their neighbours and they become isotropic.

The transition from nematic to isotropic is very weakly first order, i.e. there is only a small latent heat associated with the transition. As a result the isotropic mixture can show 'pretransitional' nematic-like behaviour. This means that nearest neighbours will tend to align up with each other, but this ordering does not extend over very long distances. This 'local ordering' is responsible for the very large nonlinear refractive indices [3].

When a laser field is applied to CS$_2$ or to isotropic liquid crystal molecules, the field tends to align the molecules with the field, so changing the refractive index. In CS$_2$ each molecule moves independently and the change in refractive index occurs in a period of about 2 ps.

However, in isotropic liquid crystals, the pretransitional behaviour means that as each molecule aligns itself, it tends to orient its neighbours. As a result the nonlinear refractive index is greatly enhanced, but the reorientation time may be greatly increased.

The theory of de Gennes [3] shows that

\[ n_2 = \frac{A}{T-T^*} \]  
\[ t_{\text{reor}} = \frac{c}{(T-T^*)} \exp \left( \frac{B}{T} \right) \]

where \( t_{\text{reor}} \) is the collective reorientation time, \( A, B \) and \( C \) are constants, \( T \) is the temperature, and \( T^* \) is some notional temperature which usually lies just below the nematic-isotropic transition temperature. (It can be seen that in the nematic phase the molecules are aligned without any field, and that they stay aligned; corresponding to \( n_2 \) and \( t_{\text{reor}} \) having become infinite). In MBBA it has been shown that within a few degrees of the transition \( n_2 \) may be 1000 times that of CS$_2$ and the reorientation time may be about 1 ns, while at higher temperatures \( n_2 \) is smaller and faster [3].
The change in the refractive index of a nonlinear material is given by

\[ n(t) = n_0 + \Delta n(t) \]  

(3)

\[ \Delta n(t) = \frac{n_2}{t_{\text{reor}}} \int_{-\infty}^{t} dt' |E(t')|^2 \left( \frac{t'-t}{t_{\text{reor}}} \right) e \]  

(4)

where \( n_2 \) is the intensity dependent refractive index, \( E(t') \) is the amplitude of the laser field at time \( t' \), and \( t_{\text{reor}} \) is the reorientation time constant.

If the reorientation time \( t_{\text{reor}} \) is much less than the laser pulse then this reduces to

\[ \Delta n(t) = n_2 |E(t)|^2 \]  

(5)

ie the refractive index change is proportional to the instantaneous power density.

If the laser pulse is much shorter than the reorientation time then

\[ \Delta n(t) = \frac{n_2}{t_{\text{reor}}} \int_{-\infty}^{t} |E(t')|^2 dt' \]  

(6)

ie the change in refractive index is proportional to the integrated energy density which has passed through the medium.

3 THERMAL EFFECTS IN THE NONLINEAR REFRACTIVE INDEX

If the medium is weakly absorbing then some laser energy is absorbed and the material heats up and expands, causing a reduction in the refractive index. In liquid crystals we find that competition between the molecular reorientational refractive index and the thermal refractive index can also be observed (see section 5).
4 EXPERIMENTAL DETAILS

The experimental arrangement for degenerate 4 wave mixing is shown in figure 2. The output from a laser amplifier system is split into 3 beams; 2 strong pump beams (beams 1 and 2) and a weaker probe beam. In this experiment the ratios of the intensities were 10:10:1 for beams 1:2:3.

The two pump beams (1 and 2) are adjusted to go in counter-propagating directions through the sample cell. The probe beam (beam 3) is reflected off a third beamsplitter and intersects the other two at a small angle in the cell. Interference between beam 3 and the other two beams produce two sets of interference fringes in the sample and the nonlinear refractive index causes two sets of refractive index gratings to be formed in the liquid. The grating formed by beams 1 and 3 scatters beam 2 and the one formed by beams 2 and 3 scatters beam 1 and this scattered signal passes back along the path of beam 3 to form a conjugate wave. The output from the laser and the conjugate wave are recorded on two photodiodes and the signals from these photodiodes are simultaneously digitised by two transient digitisers and transferred to a main-frame computer (figure 3). It is then possible to carry out a detailed computer fitting routine to estimate the molecular orientation effect responsible for the observed signal.

5 THERMAL GRATING

In general both molecular alignment and absorptive heating contribute to the change in refractive index. As a result one can observe situations in which the phase conjugate signal is initially generated by a molecular orientation grating; then as the pulse develops the thermal grating grows and first cancels the effect of the molecular grating and then reflects a signal which may be as large as the original molecular signal (figure 4) [5]. Using detailed computer fitting procedures it is possible to fit both the molecular and thermal contributions to this signal, and useful data can be extracted regarding the thermal properties of the liquid. This will be discussed in detail elsewhere and we simply note here that if the two pump beams 1 and 2 are polarised vertically and the probe beam is polarised horizontally then the thermal grating disappears (since the heat source for the gratings depends on $E_3 \cdot E_1$ and $E_3 \cdot E_2$) and purely molecular effects are observed.
We have observed thermal gratings in CHCl₃, C₆H₁₄, and most other organic materials, but we do not observe them in CS₂ or CCl₄. This suggests that absorption is due to an overtone of the C-H stretch mode.

6 DATA ANALYSIS

If the phase conjugate signal is much weaker than the signal beam (beam 3) then the amplitude of the conjugate field E₄ is given by

\[ E₄ = c₁Δn₁₃E₂L + c₁Δn₂₃E₃L \]

where \( Δn₁₃ \) and \( Δn₂₃ \) are the refractive index grating formed by beams 1 and 3 and beams 2 and 3 respectively; \( L \) is the interaction length and \( c₁ \) is a constant of proportionality.

Since beams 1, 2 and 3 all come from the laser source and they are all synchronised to arrive at the experimental cell at the same time, the incoming laser fields can be related to the laser pulse shape by

\[ E₁(t) = A₁ \sqrt{I(t)} \quad i = 1, 2, 3 \]

where \( I(t) \) is the normalised pulse shape of the laser, and \( A₁ \) are amplitude coefficients of the respective beams.

The expression for the refractive index grating becomes

\[ n₁₃ = \frac{n₂}{t_{\text{reor}}} \frac{A₁A₃}{A₁^₃} \int_{-∞}^{t} I(t') \exp \left[ -(t-t')/t_{\text{reor}} \right] dt' \]

following expression (4). A similar expression exists for \( n₂₃ \), where \( A₂ \) replaces \( A₁ \) in the above equation. The phase conjugate intensity is then given by

\[ I₄(t) = c₂ \frac{n₂}{t_{\text{reor}}} \frac{A₁A₂A₃}{A₁^2A₂^2A₃^2} \int_{-∞}^{t} I(t') \exp \left[ -(t-t')/t_{\text{reor}} \right] dt' \]

\[ \left( \int_{-∞}^{t} I(t') \exp \left[ -(t-t')/t_{\text{reor}} \right] dt' \right)^2 \]
The values of $I(t)$ and $I_4(t)$ are measured on the transient digitisers monitoring the laser output and the phase conjugate return respectively. The values of $n_2$ and $t_{\text{reor}}$ are computed using an iterative procedure which estimates $n_2$ and then uses a least squares fit to match a computed profile based on the right hand side of equation (9) with the observed conjugate return $I_4(t)$ (figure 5).

7 ERROR ANALYSIS

When the reorientation time becomes much less than the pulse length (eg $\text{CS}_2$ where $t_{\text{reor}} = 2$ ps) then expression (9) depends only on $n_2$ and becomes insensitive to $t_{\text{reor}}$. The error in estimating $t_{\text{reor}}$ is then large but this does not affect the estimate of $n_2$. When the reorientation time becomes very long (eg much longer than 100 ns) then expression (9) depends only on the ratio $n_2/t_{\text{reor}}$. In this regime errors in estimating $t_{\text{reor}}$ again became large but these now affect the estimated value of $n_2$.

The measurements of $n_2$ in the liquid crystal materials are calibrated by comparing results with those of $\text{CS}_2$. Although we are not measuring $n_2$ but rather $\chi^{(3)}$, we note that both $\text{CS}_2$ and the liquid crystals have a $\chi^{(3)}$ which is dominated by molecular reorientation so the ratio of the measured $\chi^{(3)}$ to $n_2$ is expected to be the same in both cases. For calibration purposes we take the value of $n_2$ in $\text{CS}_2$ to be $1.2 \times 10^{-11}$ esu.

8 EXPERIMENTAL RESULTS

In this memo we report on two types of experiment. In the first we have taken pure liquid crystals or mixtures of two liquid crystals and measured the nonlinear refractive index as a function of temperature. Samples were heated in an oven with a temperature stability of greater than 1°C and cross calibrated with $\text{CS}_2$.

In the second set of experiments we took a few samples of liquid crystals and diluted them with carbon tetrachloride or carbon disulphide and measured $n_2$ and $t_{\text{reor}}$ purely as a function of concentration. These measurements were all carried out at room temperature (approximately 24°C).
TEMPERATURE DEPENDENT MEASUREMENTS

We have carried out temperature dependent measurements for 5 different organic materials and two mixtures.

The chemical structure of the materials which were investigated are shown in figure 1. The materials K9, K15 and K30 are homologous types of cyanobiphenyls with two adjoining benzene rings and a hydrocarbon chain. The material Pyrimidene 7 is similar to the cyanobiphenyl but two nitrogen atoms replace two of the carbon atoms in one of the benzene rings, while ME75 is an ester containing two separated benzene rings. These materials all show various aspects of liquid crystal type behaviour. K15, ME75, pyrimidine and the mixtures of K15 and ME75 all undergo a nematic-isotropic transition between 30°C and 50°C while K30 undergoes a smectic-isotropic transition. The material K9 is crystalline up to 60°C and melts to form an isotropic fluid. However, it has liquid crystalline properties and for example can form a nematic phase when supercooled.

If we consider first those materials which undergo a nematic-isotropic transition we find that the susceptibility and relaxation times are very temperature dependent (figures 6-10). A plot of the reciprocal of the relaxation time shows that both are proportional to \( (T - T^*) \) where \( T^* \) lies just below the nematic-isotropic transition, in agreement with equations (1) and (2). The plot of the reciprocal of the reorientation time is quite curved in some cases and this is due to the exponential in equation (2) and the effect of this exponential can be seen by plotting \( n^2 / t_{\text{reor}} \) versus temperature (figure 11). This ratio has a much weaker temperature dependence and in the case of K15 the experimental error hides any systematic trend. However in the other materials the ratio \( n^2 / t_{\text{reor}} \) systematically increases with increasing temperature.

There are variations between the different materials with pyrimidene 7 and K15 having approximately comparable nonlinear susceptibilities while ME75 is somewhat weaker. When comparing the mixtures of ME75 and K15 with pure K15 and ME75 it is noted that the nonlinear susceptibility does not seem to change smoothly with concentration. More systematic experiments will examine whether this is real effect or an artifact associated with experimental errors.
In figure 12 we show the data for K30 which undergoes a smectic A-isotropic transition at $52^\circ C$. However, the nonlinear refractive index and reorientation time fit reasonably well with equations (1) and (2) with $T^*$ being about $40^\circ C$ and implies that the nonlinear susceptibility in the isotropic phase is determined by nematic like local ordering. One can independently estimate a notional nematic-isotropic transition temperature by extrapolating from measurements on other members of the homologous series and this yields a temperature of $42^\circ C$ which is consistent with our data; and this tends to strengthen our hypothesis of nematic local ordering.

Figure 13 shows data for K9 which melts from the crystal phase to form an isotropic liquid at $60^\circ C$, but can be supercooled to a nematic-isotropic transition of $25.5^\circ C$. The measurements of the nonlinear susceptibility and reorientation time show the same qualitative behaviour as the other results but the implied phase transition temperature implied by this temperature appears inconsistent with a simple interpretation based on nematic like local ordering. This may be due to a calibration effect and further investigations are continuing to determine the source of the anomaly.

10 MEASUREMENTS OF LIQUID CRYSTALS DILUTED BY A SOLVENT

One disadvantage of the liquid crystals described on the previous pages is that the measurements all need to be carried out at elevated temperatures above the nematic-isotropic transition. If solvents are added to nematic liquid crystals, a mixture is formed in which the nematic-isotropic transition temperature is reduced [6] so that isotropic samples can be prepared for room temperature experiments. Measurements of the nonlinear susceptibility have shown that this is still enhanced by nematic like local ordering with $n_2$ still proportional to $1/(T-T^*)$ where $T^*$ lies close to the new reduced nematic-isotropic transition [6].

The materials K15 and ME75 are miscible with organic solvents such as $CS_2$, $CCl_4$, and $CHCl_3$, and mixtures of about 92% K15 by weight are found to have an isotropic-nematic transition temperature at room temperature ($24^\circ C$). We therefore prepared a number of samples of lower concentrations and measured the nonlinear refractive index and reorientation time of these other mixtures at
room temperatures. The results are shown in figures 14 and 15 and reveal that at concentrations close to the critical value of about 92%, the nonlinear refractive index and reorientation time are both large, and as the concentration is reduced the nonlinearity decreases rapidly.

In order to interpret this it is necessary to turn to light scattering experiments. The nonlinear refractive index has been shown to be related to the strength of depolarised Rayleigh scattering [8], and it has been shown that in liquid crystal mixtures this is proportional to $1/(\rho^*-\rho)$ where $\rho$ is the density of liquid crystal molecules and $\rho^*$ some empirical parameter [9]. As the density is reduced by dilution the sample changes from nematic to isotropic, and it is found that $\rho^*$ is the density for which the sample is just nematic.

This implies that the ratio

$$\frac{n_2}{\rho} = A_1 + \frac{B_1}{(\rho^*-\rho)}$$

(10)

The critical density $\rho^*$ is approximately the density of liquid crystal such that the mixture has its N-I transition at room temperature and so $\rho^*$ can be determined independently.

In the case of K15 measurements were made at 50%-90% by weight in steps of approximately 10%. A plot of $n_2/\rho$ versus $1/(\rho^*-\rho)$ gives a good straight line fit as predicted by equation (10) (figure 14). We note that on this graph the point corresponding to 90% concentration is greatly displaced from the points corresponding to 80% and less (because $\rho^*$ corresponds to 92% and therefore $1/(\rho^*-\rho)$ is changing rapidly at 90%); so the straight line was fitted to the data excluding the 90% point and the fact that that point lies close to the line emphasises the good agreement with theory. Measurements between 80% and 90% concentration were made on a separate occasion when the lab temperature was about 3°C warmer. These points formed a straight line parallel to the line in figure 14 but were displaced because of the temperature dependence of the nonlinearity (equations (1) and (2)).

In the case of ME75 the points were more evenly distributed (in figure 15) and good agreement with equation (10) was observed.
The data on relaxation time suggest that in ME75 at least, the reorientation time is given by

$$t_{\text{reor}} = A_2 + \frac{B_2}{(\rho^*-\rho)} \quad (11)$$

Again this is in approximate agreement with the depolarised scattering data. In the case of K15 the agreement is not so satisfactory.

We also carried out some experiments on samples of K30 in CCl4 (figure 16). At room temperature K30 is crystalline and can only be dissolved in CCl4 to a concentration of up to 68% by weight and there is no nematic phase at this concentration. However it is possible to fit the value of $n_2/\rho$ to fit equation (10), using an iterative process to determine $\rho^*$.

Figure 16 shows that $n_2/\rho$ fits equation (10) reasonably well, and similarly the dependence of $t_{\text{reor}}$ versus $\rho$ also indicates reasonable agreement with an expansion of equation (11). This indicates that some enhancement of the nonlinear susceptibility in solution is due to nematic like local ordering.

11 CONCLUSIONS

We have studied a number of isotropic organic liquids which have liquid crystalline properties in other phases and have shown that they have large intensity dependent refractive indices due to molecular reorientation which is enhanced by pretransitional local ordering. This enhancement appears to occur even when the material does not go directly from the nematic to isotropic phase.

Our data can be used to determine the refractive index change for any arbitrary laser pulse.

The change in refractive index depends on the reorientation time, the laser pulse length and the laser intensity or energy and was discussed in section 2. If the reorientation is much shorter than the pulse length then from equation (5) the refractive index depends on the instantaneous power, and the power
FIGURE 6
DFWM data: thermal effects present

Laser Output

Phase Conjugate Signal

10 ns / division

Probe beam polarised parallel to pump beams

FIGURE 4
DFWM data: no thermal contribution.

Laser Output

Phase Conjugate Signal

10 ns / division

Probe beam polarised perpendicular to pump beams

FIGURE 3
FIGURE 2

WP : Waveplate
Pol : Polariser
Amp : Amplifier
a) Cyanobiphenyls (K9; K15; K30)

\[ R - \begin{array}{c} \text{C} \text{6}\text{H} \text{5} \text{CN} \end{array} \]

\begin{itemize}
  \item R = C_3H_7 for K9
  \item R = C_5H_11 for K15
  \item R = C_{10}H_{21} for K30
\end{itemize}

b) ME75

\[ \begin{array}{c}
  \text{C} \text{7H} \text{15} - \text{C} \text{O0} - \text{C} \text{5H} \text{11} \\
  \text{C} \text{7H} \text{15} - \text{N} \\
  \text{C} \text{7H} \text{15} - \text{CN} \\
\end{array} \]

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c) Pyrimidene 7

\[ \begin{array}{c}
  \text{C} \text{7H} \text{15} - \text{N} - \text{C} \text{6H} \text{5} \text{CN} \\
  \text{C} \text{7H} \text{15} - \text{N} \\
\end{array} \]
REFERENCES

Finally we note that this nonlinear refractive index is expected to be independent of wavelength and should extend over the whole visible region. If a refractive index change is produced by a beam of one wavelength, this change will affect all wavelengths, and this may be useful in controlling beams of one set of wavelengths with the beam of another wavelength. We have also observed that thermal absorption causes a decrease in the refractive index which can counteract the effects of molecular reorientation. In our experiments the absorption was caused by absorption associated with the C-H stretch, and this may be a problem which is restricted to the 1 \( \mu m \) region. The liquids are all colourless in the visible and absorption may not cause the same problems here, although absorption spectra will be required to compare absorption in the visible and 1 \( \mu m \) region.
density required to produce a given refractive index change (say $\Delta n = 10^{-3}$) is given by

$$I_0 = \frac{10^{-3}}{n_2} = \frac{10^{-3}}{A} (T - T^*)$$

by substitution using (5) and (1). This shows that the required intensity decreases as the temperature is brought closer to the phase transition temperature, but equation (2) emphasises that this reduction in the required power is achieved at the expense of a longer reorientation time.

If the reorientation time is longer than the pulse length then the refractive index change depends on the integrated energy density as implied by equation (6) and the energy density required to produce a given refractive index change (again say $\Delta n = 10^{-3}$) will be given by

$$E_0 = \frac{10^{-3} I}{n_2} = \frac{10^{-3} C}{A} \exp \left( \frac{B}{T} \right)$$

Close to the phase transition, the required energy density is much less sensitive to temperature than the power density referred to above, although the 'integration time' of the refractive index change is sensitive to temperature.

The comparison of different materials shows that the molecules considered all had broadly comparable nonlinearities, although the ME75 is somewhat weaker than the others.

It was also shown that measurements can be carried out at room temperature by adding a solvent to the liquid crystal, which reduces the nematic-isotropic transition. The strength and speed of the nonlinearity is sensitive to concentration, and is largest at high concentrations close to the nematic-isotropic transition. This did not depend much on the solvent used. The nonlinearity of the mixture is again expected to be temperature dependent in the same way that the nonlinearity of the pure material was. This provides a great deal of flexibility because the temperature, concentration and choice of solvent can all be varied to get a choice of $n$, $n_2$ and $t_{\text{reor}}$. 

**FIGURE 14**

- **K15 in CCl4**
  - Positive linear correlation
  - Equation: $y = 1.23x - 0.04$
  - Slope = 1.23
  - Intercept = -0.04
- **K15 in solvent**
  - Negative linear correlation
  - Equation: $y = -0.01x + 0.05$
  - Slope = -0.01
  - Intercept = 0.05
FIGURE 15
We have measured the nonlinear refractive index of a number of liquid crystalline materials in the isotropic phase. These materials show strong enhancement of the nonlinearity due to nematic-like local ordering, and even materials which do not have a nematico-isotropic transition show this enhancement. We also studied mixtures of liquid crystals and solvents and find that these mixtures also have an enhanced nonlinearity due to local ordering. Absorption of the laser beam causes expansion which reduces the refractive index and can counteract the refractive index change due to reorientation.