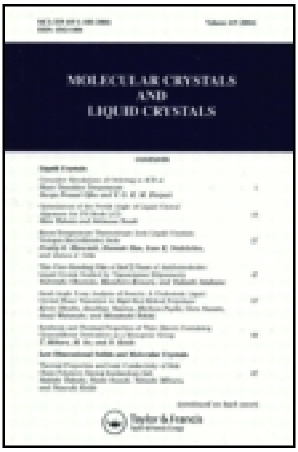

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STUDY OF THE FREEDERICKSZ TRANSITION IN 5CB USING TIME-RESOLVED RAMAN MICROSCOPY

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Abstract The study of the kinetics of electric field-induced reorientation of liquid crystals is a well-established field. However, the microscopic mechanism of reorientation at a molecular level is not well understood. A means of studying the time course of reorientation is time-resolved Raman spectroscopy[1]. Each Raman peak relates to a different region of the molecule, thus by investigating the transient change in intensity of a given peak, information about the reorientation process of distinct molecular fragments can be gained. The method therefore has an advantage over methods such as polarised optical microscopy, which study the time response of the director only.

Raman spectroscopy has been used previously by this group to study the switching dynamics of 5CB[1,2] immediately after the application of the electric field. This work extends the investigation to include the field-free relaxation of the molecules to their equilibrium configuration. A comparison is made between Raman bands associated with the core of the molecule, and those associated with the flexible alkyl chains. We also present the relative change of Raman intensity as a function of applied voltage.

INTRODUCTION

The development of Raman microscopy in the 1970s[3] enabled the spectroscopic study of micron-sized samples for the first time. The small laser spot size involved makes the technique ideal for the study of aligned liquid crystalline samples, which are typically films of the order of 10μm thick. Each peak in a Raman spectrum corresponds to a particular vibrational normal mode of the molecule, and thus it is possible to select a peak which corresponds to a vibration localised in a particular region of the molecule. In this way information about different sub-molecular fragments can be obtained. This fact can be exploited to study dynamic effects in liquid crystals, in particular the Freedericksz transition in nematics.

The intensity of a particular Raman peak depends upon the orientation of its polarisibility tensor relative to the polarisation of the exciting radiation. In a bulk sample such as a liquid crystal the orientation of the polarisability tensor is a function of the average orientation of the molecule. Thus the polarisibility tensor will re-orient with the director under the influence of an applied electric field, causing a change in the intensity of the Raman peaks. By monitoring this change in intensity using a time-resolved Raman spectrometer, information about the re-orientation of different sub-molecular regions can be obtained.

Previously this group has reported the use of time-resolved Raman spectroscopy to study the electric-field induced re-orientation of the 4-n-alkyl-4-cyanobiphenyl homologues 5, 6, 7 and 8CB[1,2]. It was found that the Raman bands corresponding to the rigid core and alkyl chain vibrations had distinct responses to the applied field. The core followed closely the response of the director, whereas the alkyl chain responded faster. This result has subsequently been observed using time-resolved infra-red spectroscopy[4,5,6].

References 1 and 2 studied the response of the Raman signal after the application of the electric field. In this paper we confirm these previous results, and extend the investigation to examine the re-orientation of the different sub-molecular regions during their relaxation to an equilibrium state when the field is removed. This provides a means of assessing whether the difference in response between the core and the pentyl chain is a result of some form of coupling to the applied field. We also present for the first time the relative change in Raman intensity for each band as a function of the applied voltage.

THEORY

The intensity of the Raman band associated with a particular bond vibration is a function of the orientation of the polarisibility tensor of that bond relative to the direction of polarisation of the exciting radiation. In the case of a liquid crystal molecule undergoing a Freedericksz transition, this orientation will change as the molecule reorients in the applied field. To analyse the time-dependence of such an intensity change we need to consider both the time-dependence of the orientation of the molecule, and the dependence of the Raman intensity on this orientation.

Consider the experimental geometry shown in figure 1. Initially, with no field applied, the director lies parallel to the direction of polarisation of the incident light. When a low frequency electric field **E** is applied, the director reorients along the field direction. The extent to which the director reorients depends upon the balance between the electric and elastic forces acting upon the molecules. It can be shown[7] that in the limit of small distortions, the intensity of Raman scattered light is given by

$$I = (A_0 + A_1 + A_2) - (A_1 + 2A_2)\psi^2 \tag{1}$$

where A_0, A_1 and A_2 are constants related to the molecular tensor components, and ψ is the angle between the director and the direction of polarisation of the incident light, as shown in figure 1.

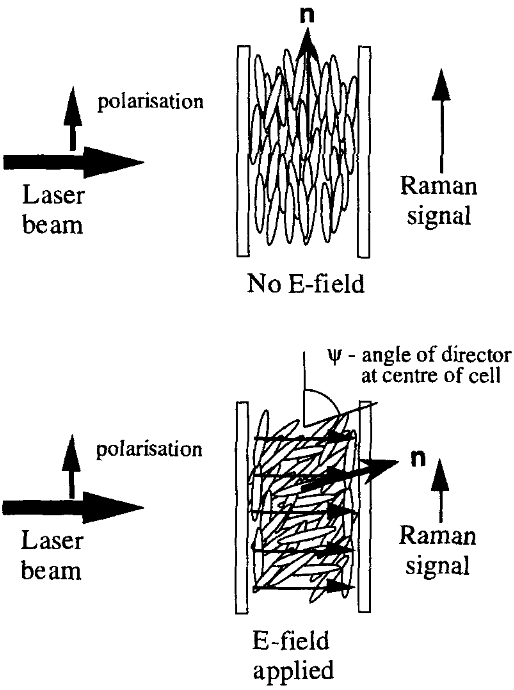

FIGURE 1 Experimental geometry.

The theory of Pieranski *et al.*[8] describes the time-evolution of the angle ψ for various geometries upon the application of a magnetic field. The analysis can easily be adapted to a situation where electric fields are used. There are two different situations described: one for the time-evolution after the application of the field, and the other following its removal. The simplest situation is when the deformation is purely twist, since no hydrodynamic flow occurs. For simplicity we will consider this case, and then describe how the results are adapted for our experimental geometry, where the deformation is a combination of splay and bend types. For the application of the field, ψ varies as follows

$$\psi_m^2(t)=\frac{\psi_m^2(\infty)}{1+\left[\frac{\psi_m^2(\infty)}{\xi^2}-1\right]\exp\left\{-\frac{2\varepsilon_0\Delta\varepsilon}{\gamma_1 d^2}\left(V^2-V_c^2\right)t\right\}} \tag{2}$$

where $\psi_m(\infty)$ is the maximum angle reached at the centre of the cell after an infinite time, ξ^2 is the time average of the fluctuations of the orientation of the undisturbed state at t=0, $\Delta\varepsilon$ is the dielectric anisotropy, γ_1 is a viscosity coefficient, d is the cell thickness, V is the root mean squared applied voltage and V_c is the critical voltage for the Freedericksz transition, given by:

$$V_c = \pi\left(\frac{k_{22}}{\varepsilon_0 \Delta\varepsilon}\right)^{\frac{1}{2}} \tag{3}$$

where k_{22} is the twist elastic constant. When the field is removed, the only forces acting on the molecules are viscous and elastic torques so the time-evolution of ψ is simply an exponential decay, determined by

$$k_{22}\frac{\partial^2 \psi}{\partial z^2} = \gamma_l \frac{\partial \theta}{\partial t} \tag{4}$$

Equation (2) and the solution of equation (4) can be combined with equation (1) to give the time-evolution of the Raman intensity after both the application and the subsequent removal of a voltage V. Specifically,

$$I\left(0 \le t \le t_{off}\right) = A - \frac{B}{1 + C\exp\left(-t/\tau_{on}\right)} \tag{5}$$

$$I\left(t_{off} \le t \le \infty\right) = A - B\exp\left(-\left(t - t_{off}\right)/\tau_{off}\right) \tag{6}$$

where A, B and C are constants for a given voltage and temperature, t_{on} and t_{off} are the times of application and removal of the field respectively, and the time constants τ_{on} and τ_{off} are given by

$$\tau_{on} = \frac{\eta_{splay} d^2}{2\varepsilon_0 \Delta\varepsilon} \frac{1}{\left(V^2 - V_c^2\right)} \tag{7}$$

$$\tau_{off} = \frac{\eta_{splay} d^2}{2\varepsilon_0 \Delta\varepsilon} \tag{8}$$

respectively. Here the viscosity factor γ_1 has been replaced by an effective viscosity η_{splay} to account for our experimental geometry. However, for small distortions of the director the difference between the two should be small.

By fitting the measured variation of Raman intensity to equations (5) and (6), the time constants can be found. Thus in the limit of small distortion, both η_{splay} and the elastic constant can be determined, assuming $\Delta\varepsilon$ is known. This is described in reference 1.

EXPERIMENTAL

The experiment was performed on a Raman microprobe apparatus developed by this group and described in detail elsewhere[2]. The apparatus used herein is shown in figure 2. A Coherent Innova 90 argon ion laser operating at 488nm is focused by a x50 infinity-corrected long-working distance microscope objective to a 5μm spot on the sample. The beam is intensity modulated at 1kHz by an electro-optic modulator to allow the use of a lock-in amplifier as part of the detection system. The Raman scattered light is collected by an identical microscope objective, which has a numerical aperture of 0.6. The beam is then passed to a Spex 1402 double monochromator via a notch filter and a spatial filter. The notch filter is of the holographic variety, and extinguishes unwanted light at the laser frequency by six orders of magnitude, whilst having a bandwidth of only 300cm^{-1}. The spatial filter ensures that only light scattered from the sample reaches the monochromator. A polariser selects the required component of the Raman-scattered light, and a Lyot depolariser is then used to randomise the polarisation as the light enters the monochromator. This is because the monochromator transmits horizontally polarised light six times more favourably than vertically polarised.

Light is detected by a Peltier-cooled photo multiplier tube, and the resulting signal is passed to a lock-in amplifier, which uses the beam-modulation frequency as its reference. This improves the signal-to-noise ratio, and can be used to reject fluorescence if the modulation frequency is increased[2,9]. The lock-in amplifier produces a dc signal proportional to that component of the ac input signal that is in-phase with the reference. This is recorded as a function of time by a Hewlett-Packard 54200 digitising oscilloscope, which passes the data to a 386-series PC via an IEEE-488 bus.

The liquid crystal studied was 4-n-alkyl-4'-cyanobiphenyl (5CB), supplied by Merck UK Ltd. and used without further purification. The sample cells consisted of glass plates coated with indium-tin-oxide and spaced with Kapton sheet, giving approximate thicknesses of either 15μm or 30μm. Planar alignment with low pretilt was achieved by the friction deposition of a thin film of poly(tetrafluoroethylene). Cells were held in a temperature-controlled jacket, stable to within 0.1°C. The geometry was as shown in figure 1.

A computer program has been written to control data acquisition. The user selects the end points of the range of voltages to be applied to the sample, and the increment between each successive voltage. Each voltage is applied and then removed a number of times so that the oscilloscope can build up an average waveform, improving the signal to noise ratio. The time intervals for which the field is applied or removed are set by the user.

The dominant Raman bands of 5CB[10] are shown in table 1.The first four bands are associated with the rigid core of the molecule, and the last one is the strongest band from the alkyl chain. Those associated with the rigid core have all been shown to reorient as one[1,2], and thus can be used to follow the motion of the core. The band at 826cm^{-1} is used to monitor the motion of the alkyl chains.

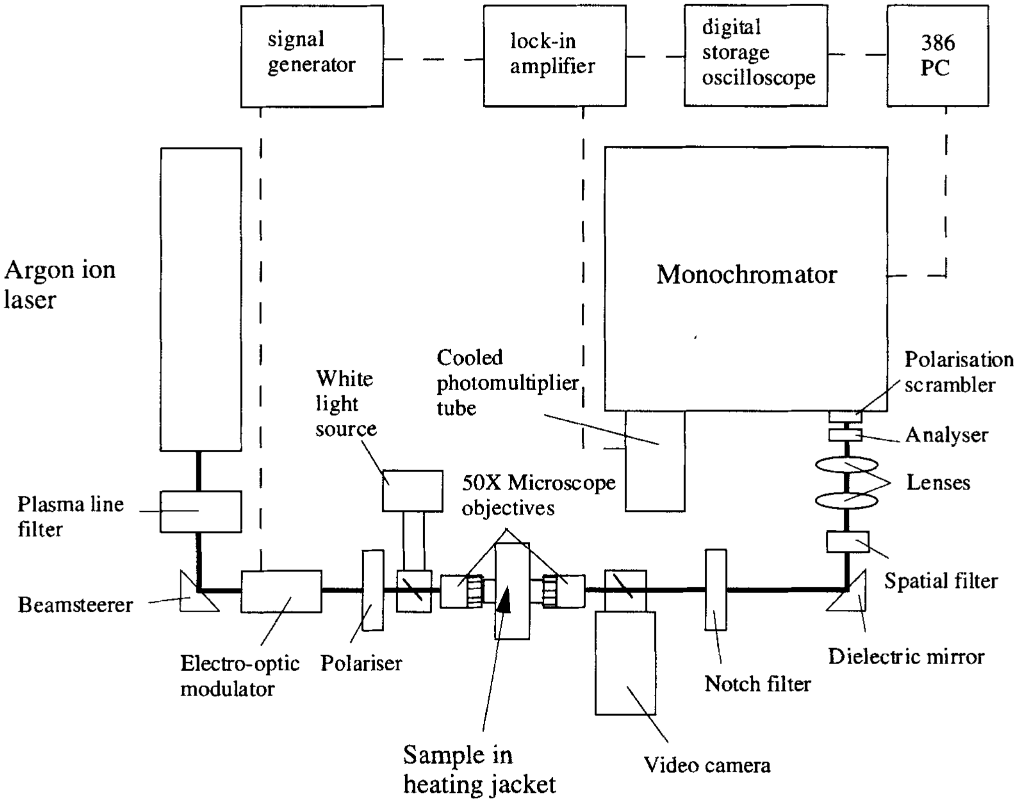

FIGURE 2 Schematic diagram of apparatus

TABLE I Raman band assignments for 5CB

Wavenumber (cm^{-1})	Band assignment
2224	CN stretch
1606	CC ring breathing
1285	CC biphenyl stretch
1185	CH ring in-plane
826	alkyl chain

RESULTS

Response to the application of the field

Following the approach outlined in section 2 we recorded the change in intensity of each Raman band as a function of time at a number of different voltages. The two bands studied were at $1606cm^{-1}$ and at $826cm^{-1}$, being representative of the core and chain respectively. Figures 3 and 4 show the response at a number of different voltages for the two Raman bands, with the best fit to the theoretical form of the curve superimposed for comparison. In this case the sample is contained in a 16.5μm cell with planar alignment. Clearly there is good agreement with the theory, particularly for the core bands.

Notice that the plots of the alkyl chain responses are considerably more noisy than the core responses. This is because the intensity of this band is nearly two orders of magnitude less than that of the core band. Consequently it is necessary to use signal averaging to improve the signal-to-noise ratio. Up to 10,000 averages may be required, depending upon the cell thickness.

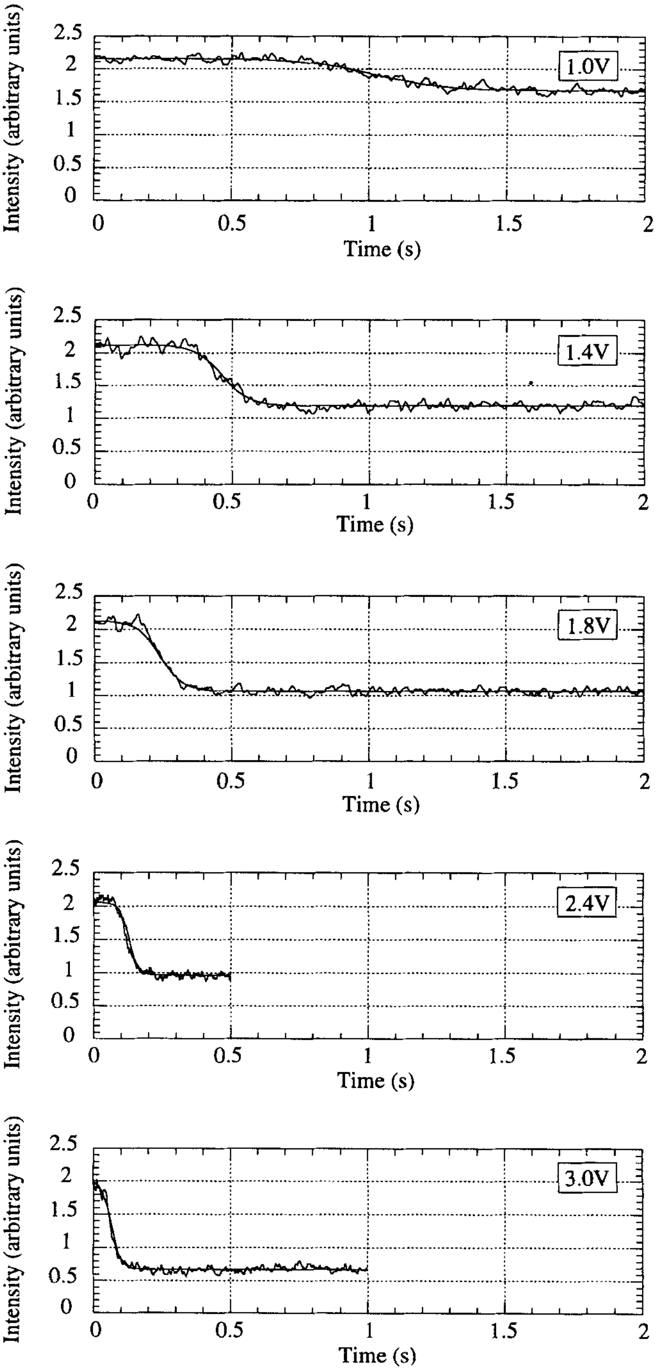

FIGURE 3 Response to the application of the field for core Raman band (1606cm-1) at various voltages. t = 0 corresponds to t_{on}.

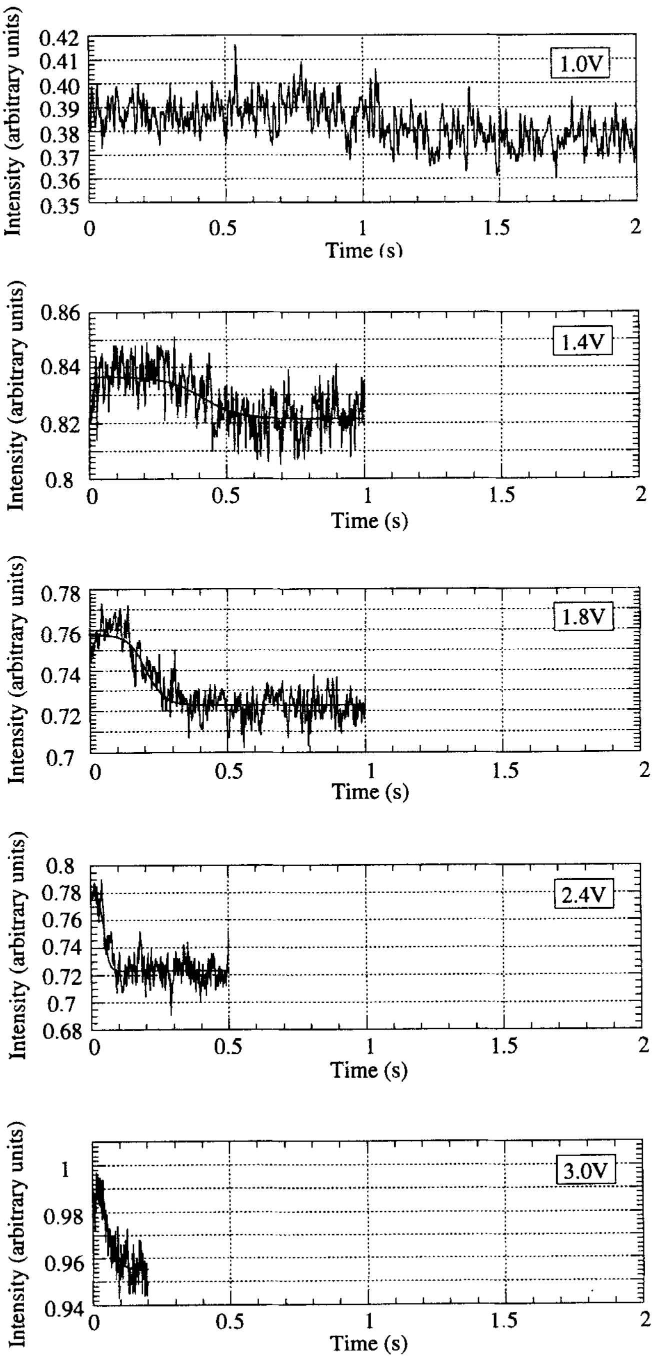

FIGURE 4 Response to the application of the field for alkyl chain Raman band (826cm-1) at various voltages. t = 0 corresponds to t_{off}.

From equation 7 it can be seen that a plot of the reciprocal of the time constant τ_{on} against the square of the applied rms voltage should give a straight line in the limit of small distortion of the director. Figure 5 compares the time constants for the core and chain in such a way, as in reference 1. It can be seen that the gradient for the response of the chain is steeper, suggesting that the chain responds faster than the core, particularly at higher voltages, but within the limit ($V < 2V_C$) of small deformations for this material.

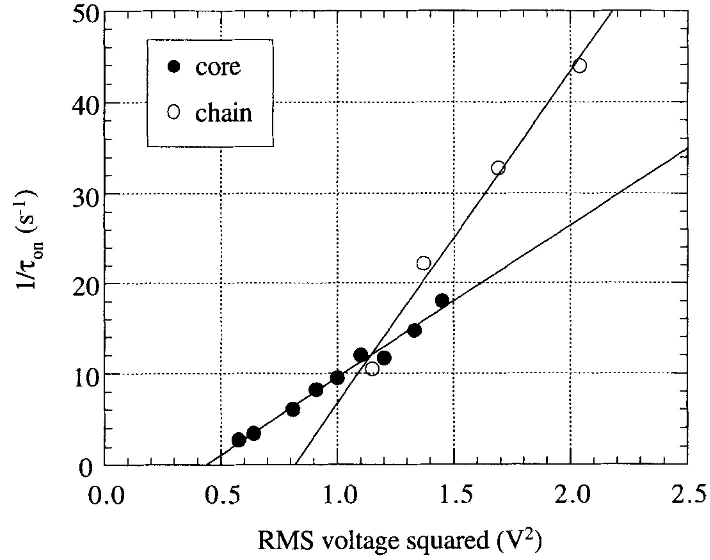

FIGURE 5 Inverse 'field-on' time constant versus the square of the applied rms voltage compared for rigid core and alkyl chain.

Response to the removal of the field

In this section we consider the relative response of core and chain during relaxation to an undistorted state after the field is removed. In this case the cell used was 32μm thick, again with planar alignment. Figures 6 and 7 show the field-free response of each band at a number of different 'pre-aligning' voltages and the corresponding fit to the theory. The fits are clearly good, and by inspection the time constants appear to be independent of pre-alignment voltage above approximately twice the threshold voltage. Figure 8 shows a comparison of these time constants as a function of voltage. Within experimental error there is little to distinguish between the core and chain relaxation near to the threshold, but further away (i.e. at $V > 2V_C$) the core bands relax approximately 20% faster in the field-free regime..

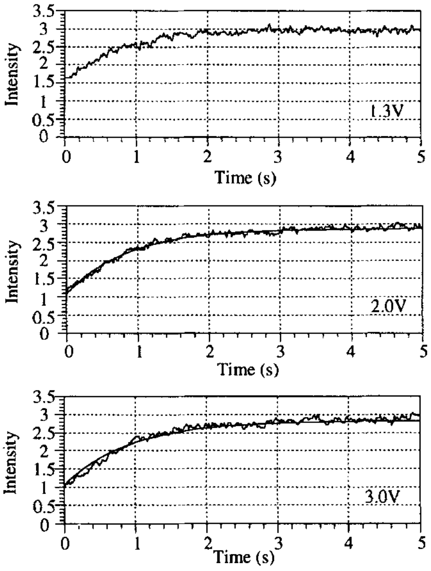

FIGURE 6 Response to the removal of the field for core Raman band (1606cm^{-1}) for different pre-alignment voltages.

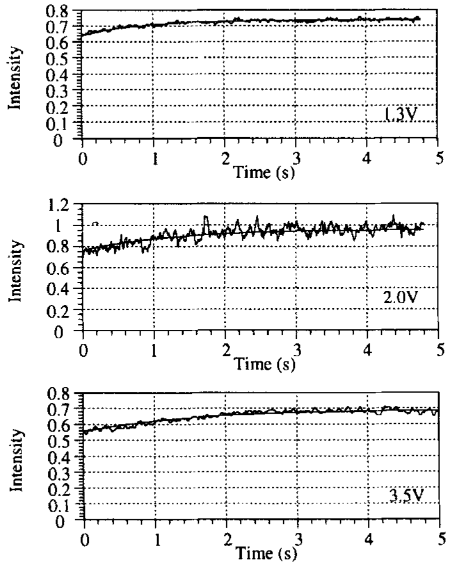

FIGURE 7 Response to the removal of the field for alkyl chain Raman band (826cm^{-1}) for different pre-alignment voltages.

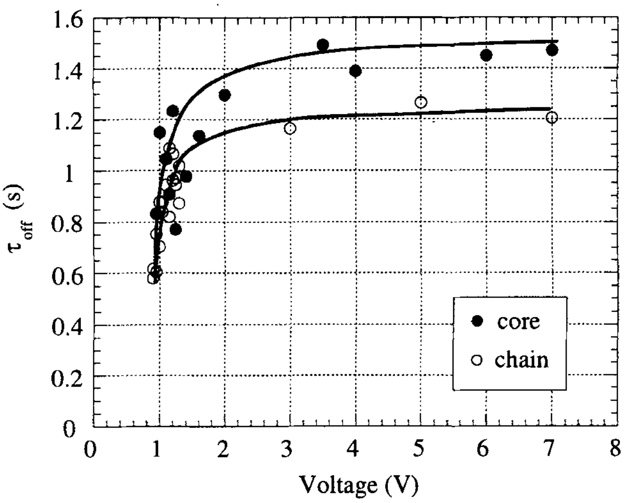

FIGURE 8 'Field-off' time constant versus applied rms voltage compared for rigid core and alkyl chain.

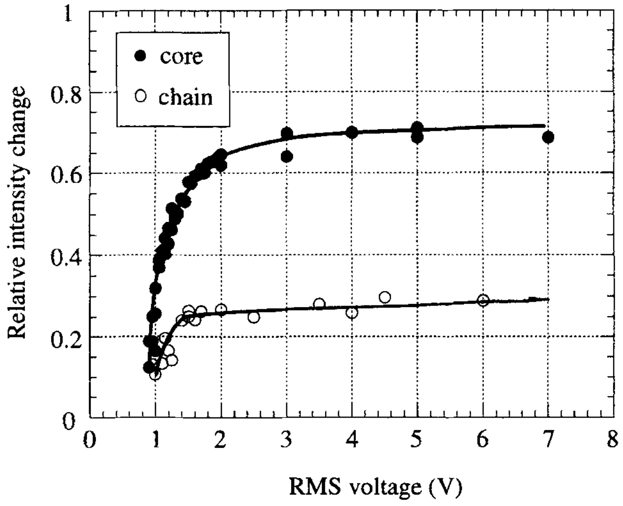

FIGURE 9 Relative change in Raman intensity for core and chain bands as a function of applied rms voltage.

Relative change in Raman intensity

From figures 6 and 7 it can be seen that the relative change in intensity at a given voltage is much greater for the Raman band associated with the core than it is for that associated with the alkyl chain. This is because the rigid core has a larger orientational order parameter than the more flexible alkyl chain[11] and so there is a greater degree of anisotropy in the Raman tensor associated with core vibrations. Figure 9 shows a comparison of the relative change in Raman intensity of the core and chain bands as a function of applied voltage.

Above between two and three times the threshold voltage the relative changes tend to saturate with increasing voltage, implying maximum induced re-orientation in the system. Below this 'saturation' voltage the induced re-orientation becomes markedly smaller supporting the notion of range of applicability of small deformation (i.e $V < 2V_C$) used in the above theory.

CONCLUSION

One of the primary motivations behind this work was to compare the response of the two bands after the application of the field with that during field-free relaxation to the undistorted state. Our results clearly show that after the field is applied, the response of the core and the chains differs considerably, with the chain moving with a faster characteristic time than the core. When the field is removed , there is only a minimal difference between core and chain within the resolution of the experiment and close to the threshold pre-aligning field. At higher voltages ($V > 2V_C$) there is a systematic difference in the relaxation times of the core and the alkyl chain bands. Again the chains appear to relax faster than the core. This suggests that the increased molecular flexibility leading to a lower order parameter is significant for the dynamic distortions of these nematic materials.

Clearly yet more work is necessary to understand the precise behaviour of the various sub-molecular fragments during re-orientation. However, our results once again show that time-resolved Raman spectroscopy (and the complementary technique of time-resolved infra-red spectroscopy) can provide a novel insight into the sub-molecular dynamics of liquid crystalline systems. It also highlights the need for molecular flexibility to be considered when deriving models to explain such dynamics.

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