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DEUTERIUM NMR SPECTROSCOPY AND FIELD-INDUCED DIRECTOR DYNAMICS IN LIQUID CRYSTALS

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DEUTERIUM NMR SPECTROSCOPY AND FIELD-INDUCED DIRECTOR DYNAMICS IN LIQUID CRYSTALS

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Deuterium NMR spectroscopy together with spectral simulations have been used to investigate the field-induced director dynamics in a nematic liquid crystal, 4-pentyl-4′-cyanobiphenyl (5CB), confined in a slab between two electrodes. The NMR spectra have been measured when turning the electric field on and turning it off. Measurements were also made at different temperatures to explore how the temperature effects the director relaxation. At higher temperatures, some complications arise as peculiar oscillations are observed in the spectra. With spectral simulation this phenomena is shown to result from the relaxation of the director on a timescale comparable to that of the experiment which is the effective spin-spin relaxation time. The simulated spectra are compared with the experimental spectra for the specifically deuteriated 5CB-d_2.

Keywords: liquid crystals; director dynamics; deuterium NMR; spectral oscillations

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INTRODUCTION

A key quantity in determining the switching speed for a liquid crystal display is the rotational viscosity coefficient, γ_1. This can be measured by changing the director orientation via the application of an external field and then monitoring the time dependence of the angle between the director and the field. Deuterium NMR spectroscopy has proved to be an especially powerful technique to determine the director orientation in liquid crystals [1]. This is because the deuterium spectrum is directly related to the angle between the magnetic field and the director, in addition its form is simple compared to the proton NMR spectrum. For a nematogen containing a group of equivalent deuterons, the deuterium NMR spectrum consists of a single quadrupolar doublet when the dipolar ineraction is negligible. The quadrupolar splitting, $\Delta\tilde{\nu}$, depends on the angle θ between the director and the magnetic field according to

$$\Delta\tilde{\nu} = \Delta\tilde{\nu}_0 P_2(\cos\theta), \tag{1}$$

where $\Delta\tilde{\nu}_0$ is the splitting when the director is parallel to the magnetic field. This kind of NMR experiment is characterised by two timescales; τ, the field-induced director relaxation time and T_2, the effective spin-spin relaxation time which determines the time taken to record the spectrum via the free induction decay (FID). The relative magnitude of these times then determines the appearance of the NMR spectrum. Provided $\tau \gg T_2$ the director does not move during the time taken to record the FID and the spectrum consists of a simple quadrupolar doublet whose splitting gives the director orientation according to Eq. (1). As the relaxation time τ decreases with respect to T_2 so the director orientation changes during the measurement of the FID. This is expected and is found to lead to new features in the NMR spectrum.

In this paper we describe an investigation of the field-induced director dynamics for the specifically deuteriated nematogen 4-pentyl-4′-cyanobiphenyl (5CB-d_2) contained as a thin slab in a flat cell. Our particular interest was to study how the temperature affects the relaxation time of the director (and thus the form of the spectra) and to explain the artefacts observed in the spectra at higher temperatures. Theoretical spectra have been calculated for a range of values for τ/T_2. With an optimised value for this ratio the resultant simulated spectrum has an appearance similar to that observed for 5CB-d_2 at temperatures near the nematic-isotropic transition. The angle, θ, between the director and the magnetic field has previously [2] been shown to vary with time according to

$$\tan(\theta - \theta_\infty) = \tan(\theta_0 - \theta_\infty)\exp(-t/\tau) \tag{2}$$

which has been obtained analytically from the torque-balance equation (3). In the equation θ_0 and θ_∞ refer to the initial angle (the angle before turning the electric field off/on) and the final angle (the angle the director approaches after an infinite time), respectively. Deuterium NMR measurements at lower temperatures have previously been used by Luckhurst *et al.* [2] to obtain the rotational viscosity coefficient and the diamagnetic anisotropy for 5CB-d_2. The relaxation rate for the director could be obtained by observing the quadrupolar splitting at different stages of the relaxation process and then fitting the results for the director orientation to Eq. (2). Because of the complications in the spectrum this approach cannot be used at higher temperatures without spectral simulations.

EXPERIMENTAL

The sample used in the experiments was the nematic liquid crystal 5CB-d_2, deuteriated in the α-position of the pentyl chain. It has a nematic-isotropic transition at 308 K and both the dielectric and diamagnetic anisotropies are positive, hence the director aligns along an electric or a magnetic field. The sample was contained in a 56 μm thick flat cell made of two glass plates coated with indium/tin oxide. Wires were soldered to the surface and a function generator was used to provide an AC electric field to the cell. The experimental geometry is illustrated in Figure 1.

A JEOL Lambda 300 NMR spectrometer was used to record the deuterium NMR spectra. Measurements were made at several temperatures ranging from 283.0 K to 302.5 K and the director dynamics were studied when the electric field was turned on (the director moves towards the

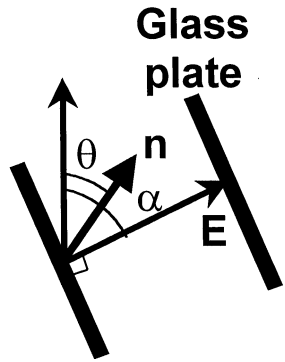

FIGURE 1 The experimental geometry. The angles θ and α define the orientations of the director, **n**, and the electric field, **E**, respectively, with respect to the magnetic field, **B**.

direction of the electric field) and when the field was turned off (the director is aligned along the magnetic field). An AC electric field of 50 to 60 V_{rms} was applied to the sample in order to align the director away from the magnetic field. The value for the angle α between electric and magnetic fields was chosen to be about 50° in all the experiments because starting from 90° causes some additional complications [4,5] as the director no longer rotates as a monodomain. A standard quadrupolar echo sequence ($(90°)_x$ – *delay* - $(90°)_y$ – *delay* - FID) was utilised to measure the spectra (see Figure 2).

The delay, t_d, after turning the field off/on was varied from 0 to 10 ms so as to follow the director relaxation at different stages of the relaxation process.

SPECTRAL SIMULATIONS

Simulations were performed to emulate the experimental spectra as closely as possible, thus all the values for the acquisition and processing

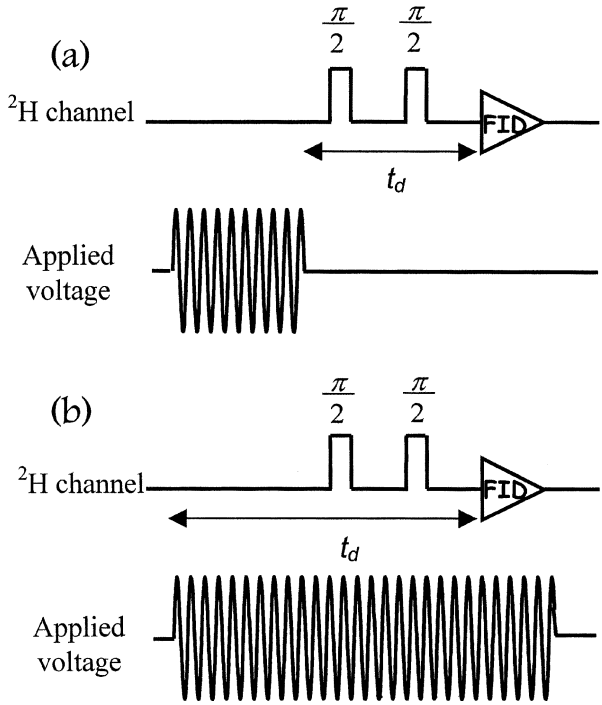

FIGURE 2 The pulse sequences for (a) the turn-off and (b) the turn-on processes.

parameters (number of data points, spectral width, acquisition time, window function) were taken from the experiments. The angle that the director made with the magnetic field when the electric field was on, linewidths and line-shapes as well as the noise level were adjusted to those of the static experimental spectra and the only parameter varied in the simulations of the dynamic spectra was the field-induced relaxation time for the director. In addition, a narrow gaussian distribution of the angle between the director and the magnetic field was introduced to allow for better fitting with the experimental data. This is easily justified; the observed spectral lines are wider with the field on and during the dynamic process, thus it can be reasoned that the director is distributed over a small range of angles. As the linewidth seems to be practically conserved during the dynamic process, we can safely assume that the director moves as a monodomain and just introduce a narrow gaussian distribution in the simulations. This distribution could be due to temperature gradients over the sample, surface interactions, inhomogeneous magnetic field, inhomogeneous electric field resulting from the thickness of the cell not being exactly the same through the whole sample, or a combination of these reasons. However, it is important to realise that introducing a gaussian distribution is merely cosmetic as it only affects the line-shapes and linewidths but not the essential features such as the peak positions in the spectrum. The use of the quadrupolar-echo sequence instead of a single pulse sequence does not create any additional difficulties for the simulations as the spin system at the beginning of the FID remains the same in the two experiments except for the relaxation effects which influence the overall intensity of the signal. The simulations were performed simply by generating an exponentially decaying ($exp(-t/T_2)$ FID and letting the angle θ in Eq. (1) change according to Eq. (2). The frequency spectrum was obtained by Fourier transforming this simulated FID. All of the simulations were performed using the program MATLAB [6].

RESULTS AND DISCUSSION

Experimental spectra obtained from a series of turn-off experiments at different temperatures, but at the same time (0.4 ms after turning off the electric field) are shown in Figure 3. They clearly demonstrate that as the temperature of the sample is increased, the relaxation rate of the director increases giving rise to significant oscillatory artefacts in the spectra. For the spectra recorded at 283.0 K and 288.0 K Eq. (2) can be used to obtain a value for the director relaxation time simply by measuring the quadrupolar splitting at different stages of the relaxation

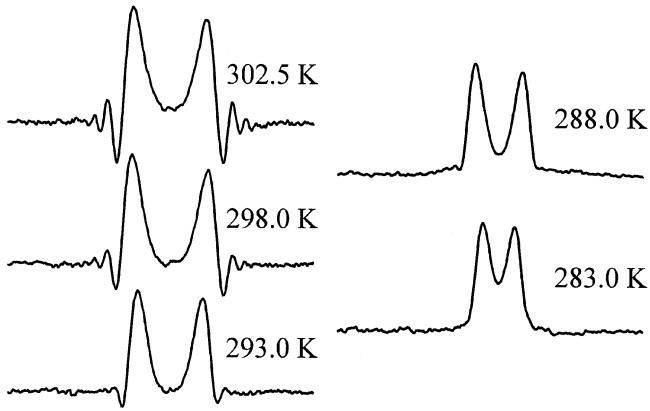

FIGURE 3 Deuterium NMR spectra from the series of turn-off experiments measured for 5CB-d_2 at different temperatures. All of the spectra were collected 0.4 ms after turning off the electric field.

process and fitting the observed splittings to Eqs. (1) and (2). This analysis yields the values $\tau = 3.5$ ms at 283.0 K and $\tau = 2.5$ ms at 288.0 K.

Experimental spectra for both the turn-on and the turn-off experiments at 302.5 K are shown in Figure 4. At the bottom are the static spectra with and without the electric field on. The rest of the spectra follow the dynamic process as the director aligns back along the magnetic field after turning off the electric field (see Figure 4 (a)) or towards the applied electric field after turning the electric field on (see Figure 4 (b)). From the figure it is clear that the director moves rapidly during the measurement of the FID and the corresponding spectrum is no longer a simple doublet. Due to the movement of the director the observed splitting no longer corresponds exactly to the actual angle θ and thus cannot be utilised to obtain an accurate value for the director relaxation time from Eq. (2) as was posible at the lower temperatures. With spectral simulations, the artefacts in the spectra can be shown to result from the rapid movement of the director. When the director relaxation time approaches that for the effective spin-spin relaxation, the director moves considerably during the measurement of the FID. This is illustrated in Figure 5 which shows some simulated spectra obtained using four different values for the ratio τ/T_2. Oscillations similar to those observed in the experimental spectra start to appear when the ratio of the two times $\tau/T_2 \approx 10$ (see Figure 5 (b)).

To test the simulation method, one of the experimental spectra recorded immediately after turning the electric field off (i.e. at $t_d = 0^+$ ms) from the turn-off series at 302.5 K was simulated (see Figure 6). The best fit was obtained with the value $\tau = 2.0$ ms, which is a

reasonable result when compared with the value obtained for the sample at 283.0 K ($\tau = 3.5$ ms) as the temperature is higher (302.5 K) and the director relaxation is expected to be faster. It is also in relatively good agreement with the value of 1.76 ms [2] for 5CB-d_2 at 293.0 K, especially as the possible error arising from ignoring the fast relaxation was not considered in that case. Thus the simulations appear to be a promising new way to obtain the relaxation time from a single spectrum provided the director relaxation is comparable to the effective spin-spin relaxation time.

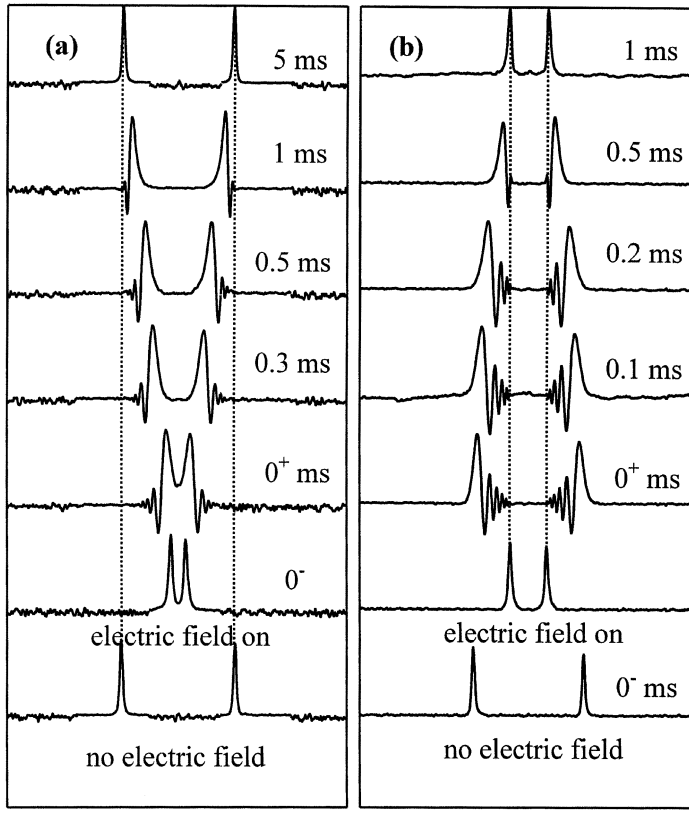

FIGURE 4 Deuterium NMR spectra from the series of (a) turn-off and (b) turn-on experiments measured for 5CB-d_2 at 302.5 K. At the bottom is the static spectrum with no electric field. The next is for a static sample spectrum with the field (50 V) on, corresponding to the director tilted at 49° (a) and 42° (b) to the magnetic field. The remainder of the spectra are for different stages after switching the electric field off/on.

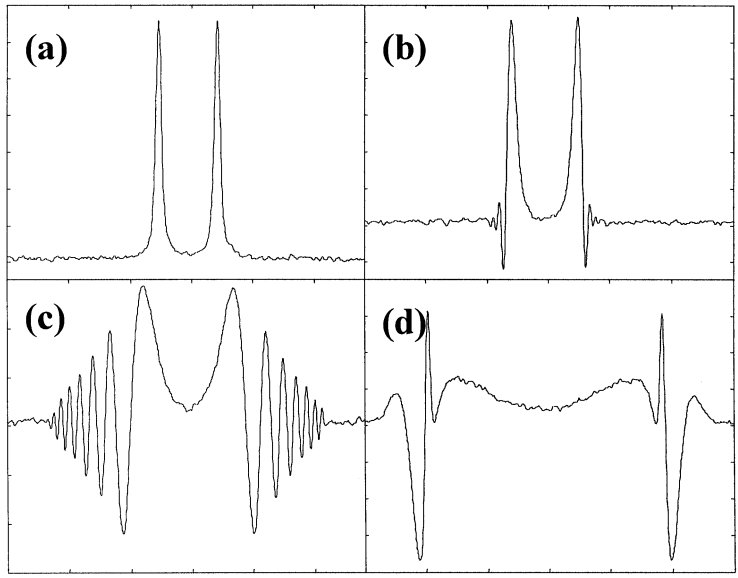

FIGURE 5 Simulated spectra illustrating the effect of changing the director relaxation time with respect to that for the effective spin-spin relaxation. (a) A spectrum when the relaxation of the director is very slow in comparison with the effective spin-spin relaxation ($\tau \gg T_2$). (b) A spectrum as the relaxation time of the director approaches the effective spin-spin relaxation time ($\tau \sim 10\ T_2$). (c) A spectrum when the two time constants are of the same magnitude ($\tau \sim T_2$). (d) An extreme case showing a spectrum when the director is fully relaxed well before the FID signal has decayed to zero.

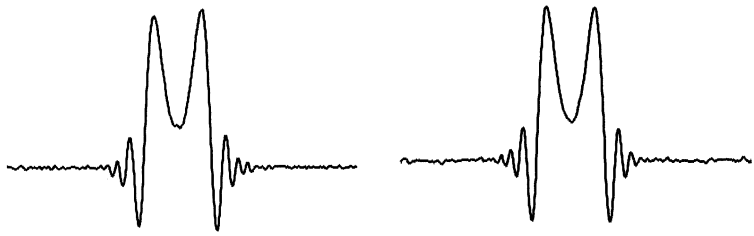

FIGURE 6 Experimental (left) and simulated (right) spectra for the turn-off process at 302.5 K obtained immediately after turning off the electric field.

CONCLUSIONS

Deuterium NMR has been used to investigate the dynamics characterising the field-induced director alignment of a nematic. With spectral simula-

tions, we have shown that the oscillations visible in the dynamic spectra at higher temperatures result from the rapid movement of the director during the time taken to record the FID. These spectral simulations can be used to determine the field-induced director relaxation time and thus the rotational viscosity coefficient for the nematic sample even at the higher temperatures where the conventional method is problematic. Although spectral simulation seems to be a promising method to obtain the director relaxation time from the deuterium NMR data, more simulations need to be undertaken to confirm the results. This more detailed exploration will be made in the near future.

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