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Computer Simulation of the Deuterium NMR Spectra Reflecting the Director Distribution for Multi-Domains in a Thin Nematic Cell

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Deuterium NMR spectroscopy is widely employed to investigate the static and dynamic director alignment for low molar mass nematics contained in a thin sandwich cell. When the director is not uniformly aligned the appearance of the deuterium NMR spectra, recorded in the measurements, reflects the form of the director distribution. This occurs because the observed spectrum is a weighted sum of the spectra from all director orientations in the sample. In order to obtain the form of the director distribution function by simulating the spectra it is necessary to know how the spectral lineshape varys with the director orientation. As well as being of practical relevance, when the director distributes thermally with the average director orientation in multi domains, this contribution to the lineshape is of fundamental interest for nematic behaviour. Here we explore ways to vary the aveage director orientation using an electric field and employ this to measure the voltage dependence of the NMR lineshapes for the nematic phase of 5CB-d_2. This approach is investigated by using a computer simulation of the NMR lineshapes.

Keywords Deuterium NMR; director distribution; director orientation; liquid crystal

1. Introduction

Deuterium nuclear magnetic resonance (NMR) has proved to be especially important for the investigation of many aspects of liquid crystalline behaviour [1,2]. The strong dependence of the quadrupolar splitting for deuterons in the liquid crystal phase on the angle between the director and the magnetic field means that deuterium NMR spectroscopy can be employed to investigate the static and dynamic director alignment in thin nematic films following the application or removal of an electric field [3,4]. Of particular importance is the observation that when the director is not uniformly aligned with respect to the magnetic field of the NMR spectrometer

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the spectrum develops features that reflect the form of the director distribution. This situation obtains because when the director is not uniformly aligned the observed spectrum is a weighted sum of the spectra from all director orientations provided, of course, that the molecular diffusion between regions with different director orientations is slow with respect to the NMR timescale. For nematics of low molar mass this is usually the case. The spectral analysis requires a knowledge of the angular variation of the quadrupolar splitting which is relatively easy to obtain. In addition, it is necessary to know how the spectral lineshape as well as the linewidths varys with the director orientation. As we shall see the directors distribute thermally with the average director orientation. The director distribution function needs to be explored experimentally and theoretically, and this is more of a challenge.

In this paper, we describe our attempt to determine the director distribution function by varying the static director orientation in a thin nematic liquid crystal film subject to competing constraints, namely electric and magnetic fields. The nematogen used in our experimental approach is 4-α,α-d$_2$-pentyl-4′-cyanobiphenyl (5CB-d$_2$) specifically deuteriated in the α-position of the pentyl chain which in the aligned nematic phase has a particularly simple NMR spectrum containing a single quadrupolar doublet. The sample was confined between two glass plates and subject to magnetic and ac electric fields. The normal to the plates and hence the electric field makes an angle, α, with the magnetic field of the spectrometer (see Fig. 1). In the absence of the electric field the director for nematic 5CB-d$_2$ is aligned parallel to the magnetic field. When an electric field is applied the director is aligned towards the electric field because the anisotropic susceptibilities, $\Delta\tilde{\varepsilon}$ and $\Delta\tilde{\chi}$, are both positive for 5CB and so the director orientation with respect to the magnetic field can be varied over the range from 0° to just less than α depending on the strength of the electric field relative to the magnetic field.

The layout of our paper is as follows. In the next Section we give the theoretical background to the NMR method and to the equilibrium alignment of the nematic

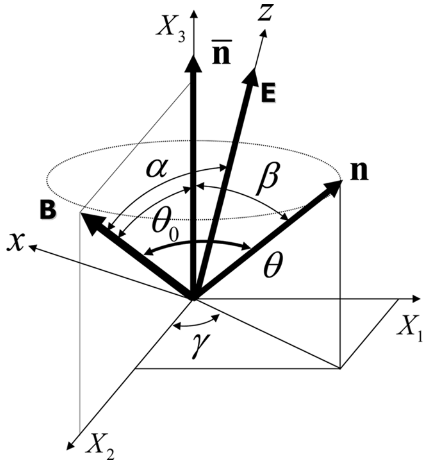

Figure 1. The experimental geometry used in this study. The average director, n̄, orientation and the electric field, E, make the angles θ_0 and α with respect to the magnetic field, B, respectively. The angle θ is made by the arbitrary director, n, with the average director orientation. In this frame the spherical polar coordinates for the arbitary director are β and γ.

director subject to static magnetic and electric fields. In Section 3 we describe the NMR experiments. The results for the measurements and computer simulation of the lineshapes are given in Section 4. Our investigation is summarized in Section 5, where we also draw our conclusions.

2. Theoretical Framework

Deuterium NMR provides a powerful technique with which to investigate the director orientation in a liquid crystal and we now describe briefly the background to this [1,2]. The nuclear spin of deuterium is one and so it possesses a quadrupole moment, which interacts with the electric field gradient at the nucleus, to give a tensorial quadrupolar interaction. This does not influence the number of lines in the deuterium NMR spectrum for an isotropic liquid because the random and rapid molecular motion averages the quadrupolar interaction in the static spin hamiltonian to zero. The NMR spectrum for a single deuteron, therefore, contains a single line composed of two degenerate spin transitions. In a liquid crystal phase the molecular rotation is no longer random and so the total quadrupolar tensor is not averaged to zero. In consequence the transitional degeneracy observed for the isotropic phase is removed. The deuterium NMR spectrum originating from a group of equivalent deuterons, with negligible dipolar interactions, for a nematic in which the director is parallel to the magnetic field consists of a doublet whose separation, the quadrupolar splitting, is denoted by $\Delta\tilde{\nu}_0$. This quadrupolar splitting is given, in a uniaxial phase, by [1,2]

$$\Delta\tilde{\nu}_0 = \frac{3}{2} q_{CD} \langle P_2 \rangle_{CD}, \tag{1}$$

where q_{CD} is the deuterium quadrupolar coupling constant and $\langle P_2 \rangle_{CD}$ is the orientational order parameter of the C-D bond. This result is valid provided the quadrupolar tensor is taken to be uniaxial about the C-D bond which is a reasonable approximation. When a sufficiently strong electric field is applied, the director tends to be aligned in the direction of the electric field provided the dielectric anisotropy is positive. Now, the dependence of the quadrupolar splitting, $\Delta\tilde{\nu}$, on the angle θ made by the director with the magnetic field of the NMR spectrometer is given by [2]

$$\Delta\tilde{\nu}(\theta) = \Delta\tilde{\nu}_0 P_2(\cos\theta), \tag{2}$$

where $\Delta\tilde{\nu}_0$ is the splitting when the director is parallel to the magnetic field and $P_2(\cos\theta)$ is the second Legendre polynomial. The form of this angular dependence results from the uniaxial symmetry of the motionally averaged quadrupolar tensor and does not depend on the symmetry of the total tensor or of the molecule. As the director moves from being parallel to the magnetic field the splitting is predicted, and observed, to decrease, pass through zero at the so-called magic angle ($\theta = 54.74°$) and then to increase to one half of $\Delta\tilde{\nu}_0$ when the director is orthogonal to the magnetic field. Strictly the quadrupolar splitting changes sign at the magic angle but the sign of the splitting is not directly available from the spectrum. This would create a difficulty when the splitting is less than or equal to one half of $\Delta\tilde{\nu}_0$; for example if $|\Delta\tilde{\nu}(\theta)|$ was exactly $1/2$ then the angle could be either 38.26° or 90°. Fortuntely this is not a problem in our experiments for as we shall see the quadruplar splitting varies continuously from $\Delta\tilde{\nu}_0$ and so its sign or rather its relative sign is not in doubt. Thus, the value of the angle θ can be determined directly from Eq. (2) by measuring the quadrupolar splittings, $\Delta\tilde{\nu}(\theta)$ and $\Delta\tilde{\nu}_0$.

As we have noted one of the prime advantages of NMR spectroscopy in studying the director orientation with respect to the magnetic field is that the form of the spectrum is also influenced by deviations of the distribution from a monodomain. Provided the functional form of the director distribution, $P(\theta)$, that is the probability density for finding the director at an angle, θ, to the magnetic field is known then the observed spectrum can be simulated from

$$I(\nu) = \int G(\nu, \tilde{\nu}_\pm(\theta), T_2^{-1}(\theta))P(\theta)\sin\theta d\theta. \tag{3}$$

Here $G(\nu, \tilde{\nu}_\pm(\theta), T_2^{-1})$ denotes the normalised shape of a spectral line centered at either $\tilde{\nu}_+(\theta)$ or $\tilde{\nu}_-(\theta)$ and with a linewidth related to T_2^{-1} (θ). We shall take the lineshape to be a Gaussian, that is

$$G(\nu, \tilde{\nu}_\pm(\theta), T_2^{-1}(\theta)) = \frac{T_2(\theta)}{\sqrt{2\pi}}\exp\left[-\frac{T_2^2(\nu - \tilde{\nu}_\pm(\theta))^2}{2}\right], \tag{4}$$

where the linewidth $T_2^{-1}(\theta)$ is half the distance between the points of maximum slope of the line. The angle dependent resonance frequency is

$$\tilde{\nu}_+(\theta) = \nu_\circ + (\Delta\tilde{\nu}_0/2)P_2(\cos\theta), \tag{5}$$

with an analogous expression for the resonance frequency, $\tilde{\nu}_-(\theta)$, for the other component of the quadrupolar doublet. In the spectral simulations it is convenient to set the central frequency, ν_0, coming from the Zeeman splitting to zero.

There are a number of mechanisms which contribute to a spectral line for deuterons. As we have already mentioned one of these is the deviation of the director distribution from a monodomain; in addition, the broadening is sensitive to the angle, θ_0, made by the average director orientation with respect to the magnetic field (see Fig. 1). To illustrate these two factors we need a director distribution function. A possible model for this function would be for multi domains having a monodomain director orientation in each domain. In this model the effect of Frank elasticity is ignored, in other words the orientations of the domains are not coupled with each other. A director distribution function [5] is given by

$$P(\beta) = \frac{\lambda^2}{2}[\lambda^2 - (\lambda^2 - 1)\cos^2\beta]^{-\frac{3}{2}}. \tag{6}$$

The parameter, λ, controls the width of the distribution which is maximal when λ is unity and tends to zero as λ approaches infinity; β is the angle made by the director with its average orientation. To simulate the spectrum we need the angle, θ, between an arbitary director and the magnetic field. To obtain this we establish a coordinate system with the z-axis parallel to the average director orientation and with the magnetic field in the xz-plane as shown in Figure 1. In this frame the spherical polar coordinates for the arbitary director are β and γ although the cylindrical symmetry with respect to the average director means that the orientational director distribution function is independent of the azimuthal angle, γ. The angle between an arbitary director and the field is found to be

$$\cos\theta = \cos\theta_0 \cos\beta + \sin\theta_0 \sin\beta \cos\gamma. \tag{7}$$

We see that θ is dependent on the angles β, γ and θ_0 and so the expression for the lineshape must be changed from the single integral in Eq. (3) to the double integral

$$I(\nu) = \iint G(\nu, \nu_{\pm}(\theta), T_2^{-1}) P(\beta) \sin\beta d\beta d\gamma, \tag{8}$$

where we now have to integrate over β and γ, using Eqs. (4)–(7), for a fixed orientation of the average director with respect to the magnetic field. The linewidth is taken to be independent of the angle between the director and the magnetic field which allows us to focus on the line broadening caused by the small distribution in the director orientations determined by λ.

The essential feature of our experimental study is to vary the average director orientation with respect to the magnetic field with the aid of an electric field applied across a thin nematic slab. By varying the strength of the electric field, the total balance of the magnetic field, the electric field, the surface torque and the elastic torque can be controlled. To see how the factors determine the director orientation in the presence of the two fields we consider a monodomain sample and ignore surface anchoring effects, which is a reasonable assumption for a thick cell (~200 μm) with untreated electrode surfaces. Since the director is uniformly aligned we can also ignore the elastic energy. The geometry for this system is shown in Figure 1 where the electric field makes an angle α with the magnetic field. The director orientation is obtained from the torque-balance equation which for a monodomain nematic [6] is

$$\frac{\Delta\tilde{\chi}}{2\mu_0} B^2[\sin 2\theta - \rho \sin 2(\alpha - \theta)] = 0, \tag{9}$$

where

$$\rho = \mu_0 \varepsilon_0 \left(\frac{E}{B}\right)^2 \left(\frac{\Delta\tilde{\varepsilon}}{\Delta\tilde{\chi}}\right), \tag{10}$$

μ_0 is the magnetic permeability and ε_0 the dielectric permittivity of a vacuum. The parameter, ρ, is the ratio of the anisotropic magnetic and electric energies. The equilibrium value of the director orientation, θ_∞, sometimes called the limiting angle, is given by

$$\cos 2\theta_\infty = \frac{1 + \rho \cos 2\alpha}{(1 + 2\rho \cos 2\alpha + \rho^2)^{\frac{1}{2}}}. \tag{11}$$

The director orientation depends, therefore, on the material property, $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$, and the known experimental parameters, E/B and α. In Eq. (11) $\rho = 1$ means that the two anisotropic field energies are equal. It is clear from Eq. (11) that the equilibrium angle is not exactly the same as the angle between the two fields because the values of ρ used in the calculation are insufficient to align the director parallel to the electric field. Indeed, for $\rho = 0.55$ the equilibrium angle first grows with α but then decreases and eventually returns to zero when α is 90° and the magnetic energy exceeds the electric. However, it is clear that provided ρ is larger than one the director orientation will be in the range $0^\circ < \theta_\infty < 88^\circ$, depending on the value of ρ. Given the relationship between the quadrupolar splitting and the director orientation (see Eq. (2)) then, $\Delta\tilde{\nu}$, will also show an analogous variation with ρ.

As we have just seen the angle, α, between the electric and magnetic fields is one of the important experimental parameters needed to investigate the static and dynamic director orientation. However, it is difficult to determine this angle precisely because the electric field strength used in our measurements is not quite high enough to align the director parallel to the electric field. As reported previously [7], Eqs. (2) and (11) show that the quadrupolar splitting ratio for a certain applied voltage, V, gives the limiting angle, θ_∞. This was achieved by rearranging Eq. (11) and combining it with Eq. (2) to give

$$g(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0) = \frac{1}{a\sin 2\alpha} \cdot \frac{1}{V^2} + \cot 2\alpha, \tag{12}$$

where

$$g(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0) = \frac{4(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0) - 1}{2\sqrt{[2 - 2(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)][1 + 2(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)]}}, \quad a = \frac{\mu_0\varepsilon_0}{B^2d^2}\left(\frac{\Delta\tilde{\varepsilon}}{\Delta\tilde{\chi}}\right), \tag{13}$$

and d is the cell thickness. The function $g(\Delta\tilde{\nu}/\Delta\tilde{\nu}_0)$ is seen to be linear in $1/V^2$, accordingly α and a, that is $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi}$, can be found from a linear least squares fit of the experimental NMR data for the voltage dependence of the quadrupolar splittings to Eqs. (12) and (13).

3. Experimental

The nematogen used for our study was 5CB-d_2 specifically deuteriated in the α-position of the pentyl chain. The extent of deuteriation was checked by ^{1}H-NMR and was found to be better than 98%. The nematic-isotropic transition temperature for this sample is 305 K. Thin nematic sandwich cell was prepared from glass plates coated with transparent In_2O_3 to act as electrodes; these were not treated in any way. The glass plates were held together by special glue which is stable in the presence of alkyl cyanobiphenyls and which can be cured using UV radiation for a few minutes. The cell thickness was controlled by Teflon spacers; it was determined optically and found to be $d = 194\,\mu m \pm 0.5\,\mu m$ (that is an inhomogeneity of about ±0.25% in the film thickness). The saturation voltage method [8] was employed to measure the surface anchoring strength at the interface of 5CB-d_2 with the substrate surface; the anchoring energy, A, was found to be $1 \times 10^{-7}\,Jm^{-2}$. This corresponds to a weak anchoring condition and so does not influence the director orientation in the presence of strong electric and magnetic fields. The NMR measurements in the nematic phase of 5CB-d_2 were made at 293 K. The spectra were recorded using a JEOL Lambda 300 spectrometer, which has a magnetic flux density, B, of 7.05T. The spectra measured for the static director orientation were obtained using a quadrupolar echo pulse sequence, with a 90° pulse of 5.5 μs and an interpulse delay of 25 μs, a delay of 35 μs after the second pulse and before FID and the post delay time was 30 ms. The number of free induction decays used to produce spectra with good signal-to-noise ratio varied from 4,000 to 8,000 depending on the sharpness of the spectral lines. The resolution in the frequency of a spectrum was set to be 25 Hz. The nematic cell was held in the NMR probe head so that the electric field, whose direction is normal to the substrate surface, makes an angle, α, with the magnetic field (see Fig. 1). An amplifier and a function generator were used to provide a sinusoidal ac electric potential of 1 kHz to the cell. This frequency is sufficient to overcome the effects of ionic conduction. On applying the electric field, the monodomain director orientation is expected to be confined to the plane defined by $\boldsymbol{B}$ and $\boldsymbol{E}$. A typical spectrum of 5CB-d_2 recorded at 293 K without an electric field showed the quadrupolar splitting of $\Delta\tilde{\nu}_0 = 54.6\,\mathrm{kHz}$. The final adjustment of the orientation of the cell, to ensure that the electric field makes the desired angle with the magnetic field, was carried out by switching on a high electric field (200 $\mathrm{V_{rms}}$) and rotating the cell by a few degrees using a ultrasonic stepping motor until the appropriate quadruploar splitting was obtained (see Eq. (2)). A voltage of 200 $\mathrm{V_{rms}}$ corresponds to $\rho = 2.15$ for the present experimental condition calculated using $\Delta\tilde{\varepsilon}/\Delta\tilde{\chi} = 9.09 \times 10^6$ [7].

4. Results and Discussion

The voltage dependence of the NMR spectra measured at a constant temperature of 293 K and with $\alpha = 89.1°$ is shown in Figure 2 where the angle between two fields was determined by a linear least squares fit using Eq. (12). The weak feature in the centre of the spectrum originates from the isotropic phase of 5CB-d_2, possibly dispersed in the glue holding the cell together. The spectra show that with increasing voltage the quadrupolar spacing between the lines is reduced, passes through zero and then increases again as θ_∞ tends to an angle less than 89.1°, as expected from Eqs. (2) and (11). It would seem that the director orientation changes more or less continuously from being parallel to the magnetic field to being almost parallel to the electric field, as the voltage grows. Also as the voltage and hence electric field are increased, the lines appear to broaden leading necessarily to a decrease in the signal-to-noise ratio. For higher voltages, however, the lines sharpen again resulting in an improved signal-to-noise ratio.

We now show that it is reasonable to attribute this voltage dependence to a distribution in the director orientations which grows with the angle θ_0 between the magnetic field and the average director orientation. That is, the sample does not adopt a monodomain director distribution which means that it is not possible to determine the voltage dependence of the line broadening with this method of changing the director orientation. This departure from a monodomain can be attributed to the variation in the cell thickness that was mentioned in Section 3. The inhomogeneity in the cell thickness means that the nematic is subject to an inhomogeneous electric field even though the applied voltage is constant. It follows from Eqs. (9) and (10) that the inhomogeneity in the electric field will result in a distribution in the equilibrium orientation of the director, θ_∞. The resultant increase in the width of the director distribution could then result in the observed inhomogeneous line broadening. In addition, the distribution width will increase with the angle between the electric and magnetic fields, as is apparent from Eq. (11), and so lead to greater line broadening.

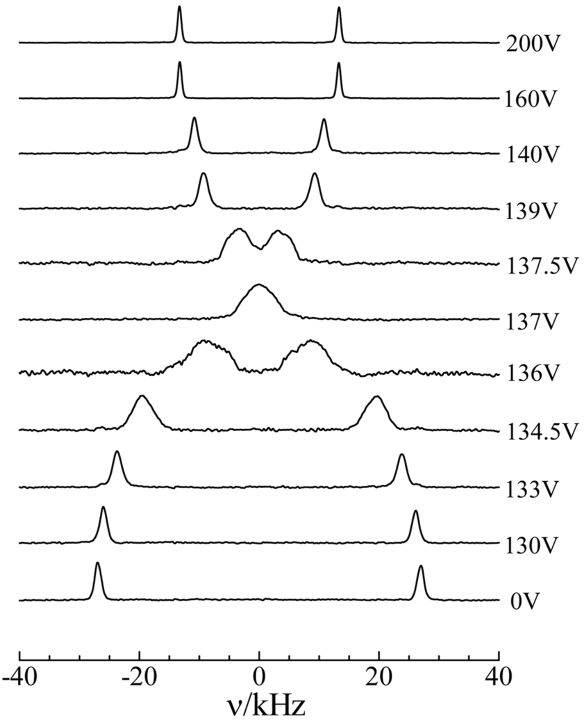

Figure 2. The voltage dependence of the NMR spectra measured at a constant temperature of 293 K and with $\alpha = 89.1°$.

To explore the maximum extent of the director distribution we have calculated θ_∞ from Eq. (11) for the minimum and maximum thicknesses of the cell. Thus for the cell with the average thickness of 194.0 μm the minimum thickness is 193.0 μm and the maximum is taken to be 195.0 μm. The curves for the dependence of θ_∞ on the voltage calculated for these extreme cell thicknesses then define the extreme values for the director orientation at constant V and α. These extremes are shown by the widths of the curves in Figure 3. It is clear from the curves that the range of director orientations is small for low values of the voltage; this occurs because the director alignment is dominated by the magnetic field. Around the threshold voltage ($V_{TH} = 136.0$ V) when the magnetic energy is equal to the electric energy ($\rho = 1$), the director orientation shows a significant distribution for larger angles of $\alpha = 89.1°$. For this value the largest spread in the director orientation is between 35.7°–53.9°. This spread then decreases with the increasing voltage until at 200 V it is just slightly larger than in zero electric field. It would seem, therefore, that the line broadening observed in Figure 2 originates in the inhomogeneity of the cell thickness.

As described in Section 2, there is another factor of the thermal director distribution (see Eq. (6)), which contributes to the deviation of the director distribution from a monodomain. In addition, the broadening is sensitive to the angle, θ_0, made by the average director orientation with respect to the magnetic field. It can be calculated for various voltages at a constant angle $\alpha = 89.1°$ using Eq. (11). To illustrate the lineshape we have simulated NMR spectra with the following parameters, the quadrupolar splitting, $\Delta\tilde{\nu}_0$, is 54.6 kHz, the intrinsic linewidth, T_2^{-1}, is 0.4 kHz

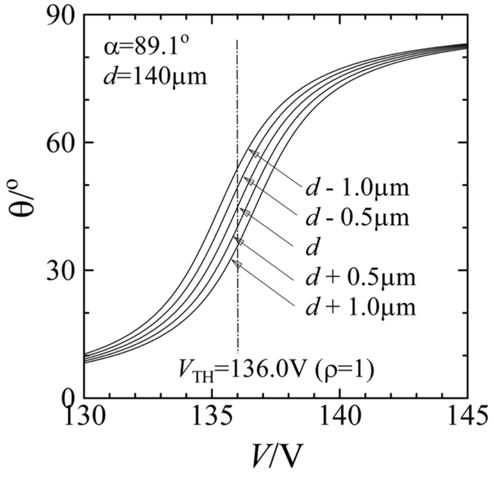

Figure 3. The voltage dependence of the director orientation, θ_∞, calculated for $\alpha = 89.1°$ using Eq. (11). Curves calculated correspond to different film thicknesses within the range 194.0 μm ± 1.0 μm. This inhomogeneity in d causes a distribution in the director orientation.

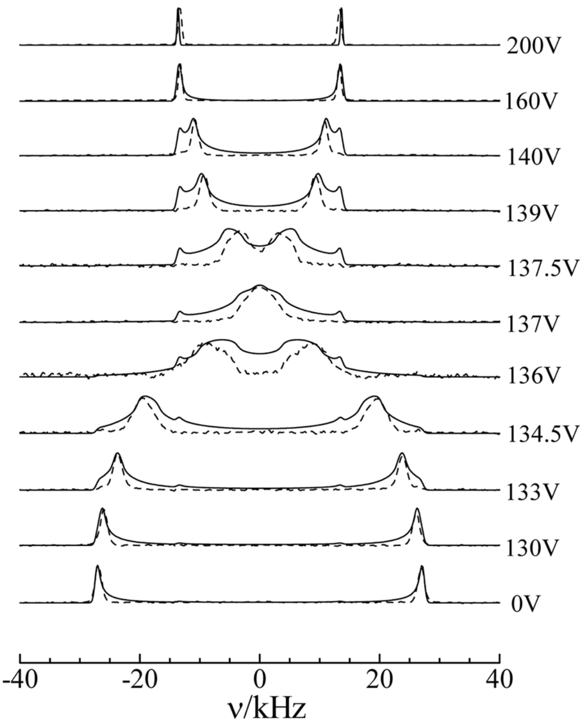

Figure 4. Simulated deuterium NMR spectra as a function of the electric field strength. The solid lines indicate the simulated spectra and the dashed lines show the experimental spectra which were taken from those shown in Figure 2 in order to compare the simulated results with experiment.

and λ is 4.5. This value corresponds to a director order parameter, $\langle P_2 \rangle_D$, of 0.59, which is taken to be a value reported as the molecular order parameter for 5CB at 293 K [9]. The spectra simulated with this set of parameters are shown in Figure 4. The spectral range used in the simulation was taken to be $-40\,\text{kHz} \le \nu \le 40\,\text{kHz}$ and is analogous to that of the experimental spectra. In Figure 4 the solid lines indicate the simulated spectra and the dashed lines show the experimental spectra which were taken from those shown in Figure 2 in order to compare the simulated results with experiment. The simulated spectra at different voltages are found to be in good agreement with the experimental spectra. This means that the broadening of the lineshape with the electric field is mainly described by the inhomogeneity of the film thickness and the distribution in the director orientation in the multi domains. The only significant exception to this is for the spectra around the magic angle where the line shapes in the experimental spectra are observed to be symmetrical as take to be a Gaussian in Eq. (4), but those predicted are to be unsymmetrical. To illustrate the possible origins of for such discrepancy we should consider a contribution to the broadening of the lineshape such as the angular dependence of the spectral line widths [10]. Nonetheless it is important to recognize that overall there is quite remarkable agreement between the experimental spectra and those simulated using the director distribution for multi domains model and an inhomogeneity in the film thickness. In other words the combination of deuterium NMR spectroscopy and continuum theory including a thermally director distribution for multi domains gives us a good understanding of the director distribution in a thin nematic film subject to competing constraints.

5. Conclusion

The angular dependence of the line broadening in the NMR spectrum of a nematic monodomain is important both from a fundemental point of view and for the practical investigation of the director distribution. To measure this angular variation it is necessary to change the director orientation in an NMR experiment by applying an electric field at a fixed orientation to the magnetic field. We have discovered that this method results in deviations from the monodomain character of the nematic sample. Analysis suggests that deviations from the monodomain character are caused by a small variation in the cell thickness and hence an inhomogeneous electric field. In addition we considered the thermal director distribution with respect to the average director orientations in multi domains in a sample. This director distribution function as well as the inhomogeniety of the film thickness were used to investigate the voltage dependence of the NMR spectral lineshapes for the nematic phase of 5CB-d_2. As a conclusion the combination of deuterium NMR spectroscopy and a computer simulation of the lineshapes based on a model including a thermally director distribution for multi domains gave us a good understanding of the director distribution in a thin nematic film subject to competing constraints.

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