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Louis A. Madsen[a]; Edward T. Samulski[a]
[a] Department of Chemistry, University of North Carolina, Chapel Hill, 27599 NC

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Addressing non-idealities in NMR experiments on rotating liquid crystals

LOUIS A. MADSEN and EDWARD T. SAMULSKI*

Department of Chemistry, University of North Carolina, Chapel Hill, 27599 NC, USA

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Unequivocal evidence for a biaxial nematic phase in low-molar-mass calamitic thermotropic liquid crystals has been challenging to generate. Recently we provided NMR evidence that nonlinear calamitic mesogens based on the oxadiazole heterocycle exhibit a biaxial nematic phase (*Phys. Rev. Lett.*, 2004, **92**, 145505). Herein we probe the robustness of that claim by exploring potential variations of the director distribution from the ideal one that would apply to nematics rotated about an axis perpendicular to the spectrometer magnetic field. Moreover, we demonstrate that our methodology, when applied to the high temperature uniaxial nematic TBBA, yields a biaxial order parameter η=0.0, thereby confirming the validity of our procedures. Our findings suggest that the original claim of biaxial order (η~0.1) as reflected by probe molecule studies of oxadiazole mesogens is still valid.

1. Introduction

Nuclear magnetic resonance (NMR) experiments allow quantitative measurements of various orientational order properties of liquid crystals (LCs). These assessments are made possible by the ability to readily define the spin Hamiltonian for a given NMR experiment, and then calculate a simulated spectrum to compare with data. The intricate models and assumptions sometimes involved are rigorously testable using calibration and control experiments, as well as statisitical tests on model/data agreement. The body of work in NMR of LCs [1–3], especially using selective deuterium labelling, demonstrates that these methods are sound and can provide exquisite information content. Confidence in these quantification methods is supplemented by the huge range of work done in solution and solid state NMR spectroscopy, as well as in magnetic resonance imaging (MRI) [4–6], allowing for revolutions in chemical and materials analysis and in medical procedure since the 1960s. Of course, the ability to quantify LC order parameters is limited by the ability to adequately derive a theoretical model with which to fit an experiment, or alternatively by the ability of the experimentalist to realize the 'ideal' conditions specified by an existing model. Liquid crystallographers who are not NMR experts naturally ask: What are the artifacts or non-idealities in NMR experiments that might give erroneous measurements of order parameters? Here we attempt to address some of these concerns related to the determination of biaxiality in LCs.

NMR experiments to determine LC biaxiality have shown their effectiveness by quantifying biaxiality in smectic phases [7–10], whereas they have until recently [11] only refuted biaxiality in nematics [9, 12]. The initial assumptions and theoretical framework for rotating-sample NMR [7] have been supplemented to analyse special cases of these experiments, such as high rotation rates [9], and a preceding study explored the use of an elliptical function to describe director distributions in the context of rotating-sample EPR (electron paramagnetic resonance) experiments [13]. Here we hope to guide future magnetic resonance experimentation and simulation by presenting a consolidation of these theories along with example NMR spectra simulations, and their relationships to biaxiality parameter extraction.

We also present new NMR data on terephthal-bis-(4-*n*-butylaniline) (TBBA), a uniaxial liquid crystal with similar transition temperatures [14, 15] and critical spinning rate to ODBP-Ph-C_7. Using the same theory used to fit the ODBP-Ph-C_7 data [11], which uses a uniform cylindrical director distribution, we can fit the TBBA nematic and SmA spectra and extract biaxiality parameters of η=0 to within error bars. This serves as a control experiment in support of our experimental observations of biaxiality in the ODBP nematics.

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*Corresponding author. Email: et@unc.edu

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2. Background

LC NMR of deuterium-labelled molecules differs from solid state NMR because the dominant quadrupolar interaction is pre-averaged by liquid-like molecular reorientation and diffusion. As a result, relative to solids reduced spectral widths are found in LCs wherein the magnitude of the quadrupolar splitting ν_Q depends on the orientation of the LC director **n** relative to the spectrometer magnetic field $\mathbf{B}_o$. In static experiments with uniaxial nematics, **n** is aligned parallel (perpendicular) to $\mathbf{B}_o$ for positive (negative) diamagnetic susceptibility LCs, see figure 1 (*a*). In viscous smectic phases that do not macroscopically orient in the magnetic field, a superposition of quadrupolar splittings is observed; figures 1 (*b*) and 1 (*c*) show 3D and 2D powder patterns, respectively. A 3D powder, in the case of a nematic, requires an isotropic porous substrate with pore size smaller than the nematic's magnetic correlation length in order to anchor the director distribution to the pore walls [16]. Herein we focus on 2D powder patterns which can be realized by rotating a nematic with positive diamagnetic susceptibility about an axis perpendicular to $\mathbf{B}_o$ at a sufficiently high rate.

3. Simulations and experiments

Several liquid crystallographers (including ourselves) have voiced the concern that director distributions in rotation NMR experiments may not be uniform. Figure 2 (*a*) shows a schematic of the NMR coil and rotating sample, with a uniform cylindrical (also termed an isotropic radial or '2D powder') director distribution depicted by the radial arrows. Equation (1) describes the NMR spectrum in this situation for Gaussian lineshapes, typically seen when observing a small probe molecule, and has been extensively used and verified in rotation NMR experiments on LCs [7–9, 12, 17]. We refer readers to other references for a complete description of this model and its assumptions [7, 11, 12, 17].

$$S_{\mathrm{cyl}}(\nu) = C\int_0^{2\pi}\left\{\exp\left[\frac{-\left(\nu-\nu'_{\mathrm{cyl}}(\theta)\right)^2}{2\sigma_{\mathrm{R}}^2}\right] + \exp\left[\frac{-\left(\nu+\nu'_{\mathrm{cyl}}(\theta)\right)^2}{2\sigma_{\mathrm{R}}^2}\right]\right\}\mathrm{d}\theta \qquad (1a)$$

where

$$\nu'_{\mathrm{cyl}}(\theta) = (1/4)\nu_Q\left[\left(3\cos^2\theta - 1\right) + (1/2)\eta\sin^2\theta\right] \qquad (1b)$$

is the dependence of the spectral line (nuclear quadrupole) splitting as a function of the polar angle θ of the partially averaged quadrupole tensor principal axis with respect to the magnetic field axis. The quadrupole splitting ν_Q, measured when the LC is static (not rotating) and aligned in the magnetic field, is a function of the primary nematic order parameter and thus the temperature of the LC. η is the biaxiality parameter of the LC phase and is also anticipated to exhibit temperature dependence. C is an overall intensity factor. The NMR linewidth due to spin relaxation is σ_{R}, which we assume is independent of angle θ. σ_{R} angular dependence has been observed in some LC systems [9], and may be included as a fitting factor in equation (1 *a*). In our experiments,

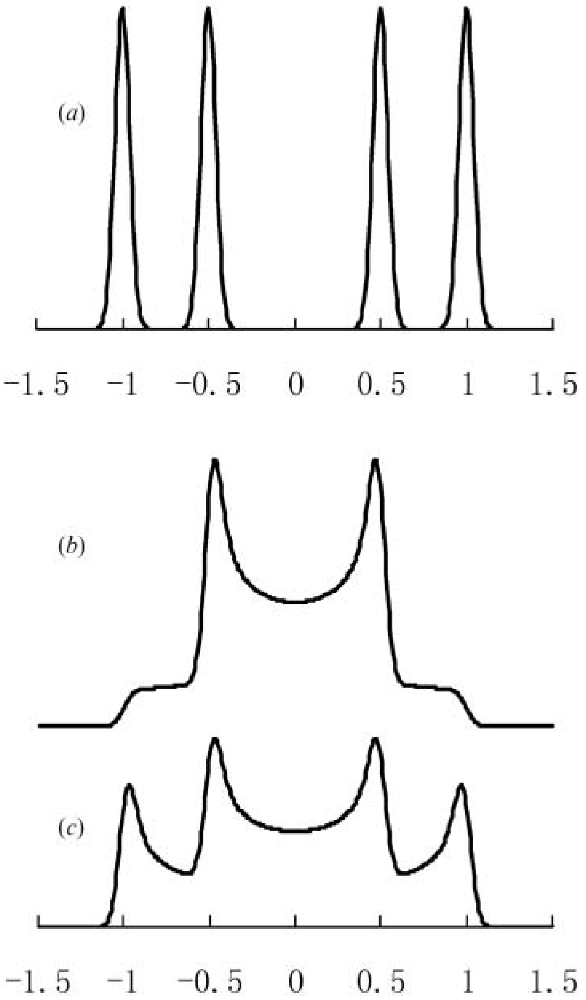

Figure 1. (*a*) Static non-rotating quadrupole NMR spectra for a deuterium-labelled LC with director along the magnetic field (outer lines) or perpendicular to the magnetic field (inner lines). (*b*) NMR lineshape for a spherical isotropic 'powder' distribution of LC directors. This distribution comes from summing up doublet NMR spectra, as in (*a*), for all director components. (*c*) NMR lineshape for a cylindrical isotropic '2D powder' distribution of directors. This shape is derived as in (*b*), but is the typical radial distribution found in rotation NMR experiments.

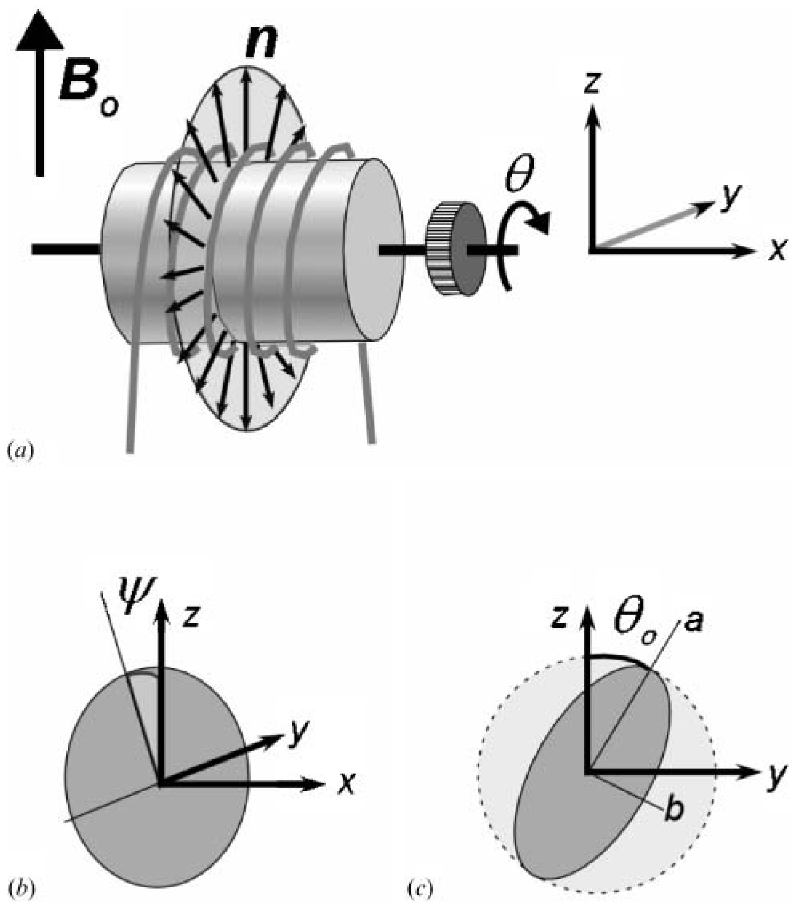

Figure 2. (*a*) Rotation-NMR apparatus schematic with cylindrical distribution of nematic major directors **n**. The cylindrical sample is mounted on a rotor inside a solenoid coil with an axis x perpendicular to the magnetic field $\mathbf{B}_0$. The magnetic field axis z provides the restoring torque on **n**, while the viscous torque of rotation spreads the director radially with angle θ about the spinning axis x. (*b*) A deviation of angle ψ away from the plane perpendicular to the rotation axis is equivalent to a deviation of the angle the rotation axis makes with $\mathbf{B}_0$, and thus we term this an axial distribution of angles. (*c*) If the rotation rate is not sufficiently above the critical rotation rate, an elliptical distribution results in the plane perpendicular to the rotation axis. The semiaxis ratio $\varepsilon=b/a$ and the inclination angle θ_0 of the major semiaxis describe this director distribution.

adding such a linewidth (T_2 relaxation) fitting factor did not improve fits, and thus is omitted from this discussion. If a substantial linewidth overestimate was obtained in a static spectrum due to a director distribution or temperature spread over the sample, then the linewidth extracted from the powder spectrum fit would actually appear smaller than that measured in the static spectrum. The absence of this effect from our data has also prompted us to neglect this factor from the current discussion. The term in square brackets in equation (1*a*) may be replaced with Lorentzian functions if that lineshape is observed in the static (non-rotating) NMR experiments, as is typical for directly deuterium-labelled liquid crystals.

When using high rotation rates on viscous LCs, especially smectics, Photinos and Doane observed that director distributions began to approach a spherical distribution [9]. We may investigate this crossover between cylindrical (2D) and spherical (3D) distributions via an out-of-plane (axial) distribution, shown in figure 2(*b*), which may be described by the following equation in the non-rotationally averaged case, assuming a Gaussian distribution of directors with angular halfwidth $\sigma_{\rm A}$.

$$S_{\rm ax}(\nu)=C\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\int_{0}^{2\pi}\left\{\exp\left[\frac{-\left(\nu-\nu'_{\rm ax}(\theta)\right)^2}{2\sigma_{\rm R}^2}\right]+\exp\left[\frac{-\left(\nu+\nu'_{\rm ax}(\theta)\right)^2}{2\sigma_{\rm R}^2}\right]\right\}\exp\left(\frac{-\psi^2}{2\sigma_{\rm A}^2}\right)\mathrm{d}\theta\,\mathrm{d}\psi \qquad (2a)$$

where

$$\nu'_{\rm ax}(\theta)=(1/4)\nu_{\rm Q}\left[\left(3\cos^2\theta*\cos^2\psi-1\right)+(1/2)\eta\sin^2\theta\right] \qquad (2b)$$

is the dependence of the spectral line splitting as a function of both the polar angle θ and the axial angle ψ of the quadrupole tensor principal axis with respect to the magnetic field. Figure 3 shows simulated spectra as a function of σ_A. We have explored the possibility that our experiments on ODBP nematics have given erroneous biaxiality parameters by fitting our data using equation (2). A best fit by allowing σ_A, ν_Q, σ_R and C to freely vary and fixing $\eta=0$ gives an exceedingly poor match of the axial distribution model to the data where the best fit produces $\sigma_A<0.5°$.

Another possibility for a director distribution under sample rotation, an elliptical distribution, was explored by Carr *et al.* in the context of rotation EPR experiments [13], and this is depicted in figure 2 (*c*) and described (for the NMR case) by the following equation.

$$S_{\text{ell}}(\nu)=C\int_0^{2\pi}\left\{\varepsilon^2/2\pi\left[\varepsilon^4\cos^2(\theta-\theta_0)+\sin^2(\theta-\theta_0)\right]\right\}\times\left\{\exp\left[\frac{-\left(\nu-\nu'_{\text{cyl}}(\theta)\right)^2}{2\sigma^2}\right]+\exp\left[\frac{-\left(\nu+\nu'_{\text{cyl}}(\theta)\right)^2}{2\sigma^2}\right]\right\}\mathrm{d}\theta \tag{3}$$

Here $\varepsilon=b/a$ is the ratio of the elliptical semiaxes and θ_0 is the steady state inclination angle the major semiaxis makes with the magnetic field under rotation. Figure 4 shows simulated spectra for various elliptical distributions. For the original EPR experiments employing spinning rates just below or nearly at the critical spinning rate, this distribution fit the spectral lineshapes without the need for biaxiality. Thus, it is prudent to attempt to fit any rotation spectra using equation (3) in order to determine whether the lineshape is characteristic of biaxiality or of simply an elliptical director distribution. We have constructed two examples to assess whether our data on ODBPs might give an apparent biaxiality due to an elliptical distribution. Figure 5 (*a*) shows an ODBP-C$_7$ rotation spectrum with the best fit using equation (3). The fit was conducted by allowing ε, θ_0, ν_Q, σ_R and C to freely vary and fixing $\eta=0$. This is more generous than our previous fit using biaxiality [11], since we only allowed η, σ_R and C as parameters and fixed ν_Q based on our static spectrum measurement, see figure 5 (*c*). If ν_Q is fixed at the experimentally observed value of 5980 Hz, the fit using equation (3) is dramatically worse, as shown in figure 5 (*b*).

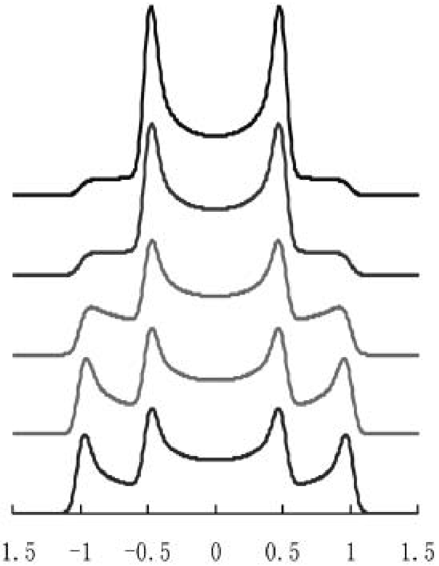

Figure 3. Simulations of a cylindrical isotropic (2D powder) distribution with the axial out-of-plane distribution of equation (2) for various axial angle halfwidths σ_A, and NMR line halfwidth $\sigma_R=0.043$ on the frequency axis shown ($\nu_Q=2$). This linewidth choice relates to specific experimental results described below (see figure 7). The curves are all normalized to unit area. From bottom to top, $\sigma_A=0$, 6, 17, 45 and 90 degrees. Note that the top spectrum is a 3D powder lineshape, as expected.

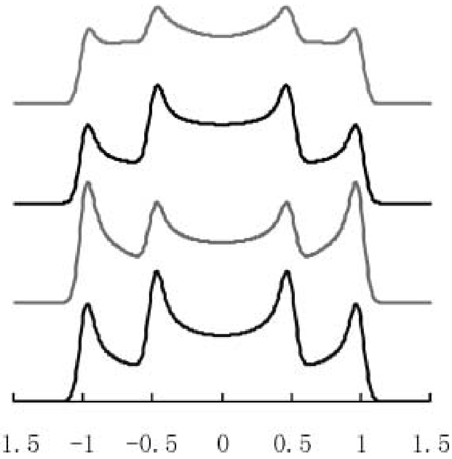

Figure 4. Simulations of elliptical director distributions of equation (3) for various semiaxis ratios ($\varepsilon=b/a$) and orientation angles θ_0, and NMR linewidth $\sigma_R=0.043$ on the frequency axis shown ($\nu_Q=2$). The curves are all normalized to unit area. From bottom to top $\varepsilon=1$ (cylindrical), 0.8, 0.8, and 0.6, and $\theta_0=0$, 20, 45 and 35 degrees, respectively. All of these elliptical simulations represent calculated example values [13], but are for rather extreme b/a ratios, compared with what has been observed in typical rotation-NMR lineshapes. Note that all of these lineshapes show only minimal perturbation of the inner and outer peaks from the 1:2 ratio typical of the cylindrical distribution.

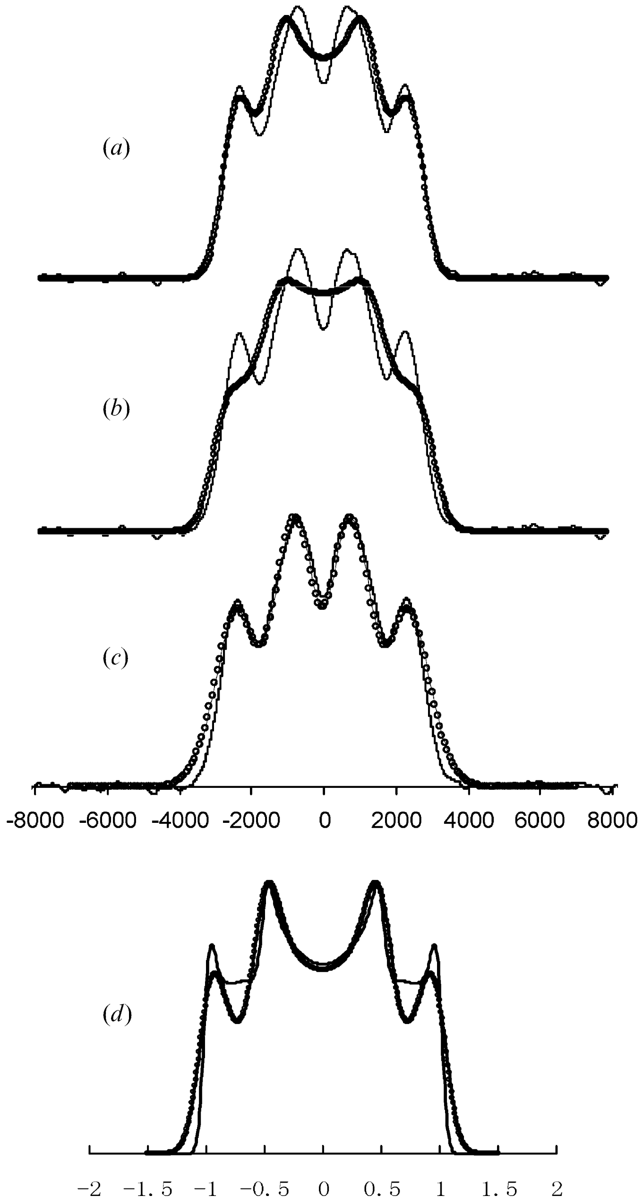

Figure 5. (*a*) Data (solid line) for the ODBP-Ph-C_7 nematic, and elliptical distribution fit (line with circles) using equation (3). This fit used five adjustable parameters: ε=0.82, θ_0=0.63, ν_Q=5340 Hz, σ_R=334 Hz and C=16900. (*b*) Data and elliptical distribution fit with fixed (measured in static spectrum) quadrupole splitting ν_Q=5980 Hz. This fit used four adjustable parameters: ε=0.62, θ_0=0.70, σ_R=378 Hz and C=12300. (*c*) Data and rotationally averaged biaxial fit using equation (4), ω_s=230 Hz and ν_Q=5980 Hz. This fit used three adjustable parameters: η=0.11, σ_R=376 Hz and C=620000. (*d*) Simulation of an elliptical distribution lineshape (thin solid line, same as top lineshape in figure 4 with σ_R=0.043), with fit using the non-rotationally averaged biaxial theory of equation (1). This fit used three adjustable parameters: η=0.11, σ_R=0.100 and C=0.212. We generated all nonlinear least-squares fits using Mathematica 4.1, and varied the initial parameter values to avoid achieving local least-squares minima.

Note that we have made comparisons between a fit using rotationally averaged theory (with biaxiality, see below) and the non-rotationally averaged elliptical distribution. While in principle we can derive rotationally averaged elliptical distribution theory [9], it adds substantial complexity to these simulations and thus is left for future studies. However, we can make a further comparison of these models by taking a specimen elliptical distribution simulation and fitting that using the non-rotationally averaged biaxial theory of equation (1) to extract a (false) biaxiality parameter. Figure 5 (*d*) shows such a fit using the elliptical distribution with the four parameters used in figure 5 (*b*), where we extract η=0.11. This represents a 'fair' comparison of the models of equations (1) and (3) since neither include rotational averaging. We note that although we can obtain an η for the fit, the lineshape agrees far less well than in fits of biaxiality to our ODBP data, see figure 5 (*c*). We also conducted the same exercise using various axial distribution simulations, equation (2), fit with equation (1), and in those cases we never obtained $\eta \geqslant |0.01|$, regardless of lineshape agreement. Thus, it is only possible that an elliptical distribution could add some error to our assessment of the biaxiality, but we believe that the error is substantially smaller than the measured values of $\eta \sim 0.1$.

Most thermotropic LCs investigated by rotating-sample NMR experiments have isotropic transitions below 100°C, and thus have exhibited low critical rotation rates (<50 Hz) to achieve isotropic planar director distributions. As the rotation rate ω_s (in Hz) begins to approach the spectral splittings or linewidths ($\omega_s \sim 1/5$ of the linewidth$=2\sigma_R$), rotational averaging becomes apparent in the spectrum. Equation (4), based on the Photinos and Doane formalism, describes the NMR spectrum under rotational averaging for Gaussian lineshapes [9].

$$\begin{aligned} S_{\text{rot}}(\nu) = {} & J_0^2[z] \times C\left\{ \exp\left[\frac{(\nu-E)^2}{2\sigma_R^2}\right] + \exp\left[\frac{(\nu+E)^2}{2\sigma_R^2}\right] \right\} \\ & + \sum_{i=1}^{\infty} J_i^2[z] \times C\left\{ \exp\left[-\frac{(\nu-E+2\omega_s)^2}{2\sigma_R^2}\right] \right. \\ & + \exp\left[-\frac{(\nu-E-2\omega_s)^2}{2\sigma_R^2}\right] \\ & + \exp\left[-\frac{(\nu+E+2\omega_s)^2}{2\sigma_R^2}\right] \\ & \left. + \exp\left[-\frac{(\nu+E-2\omega_s)^2}{2\sigma_R^2}\right] \right\} \end{aligned} \qquad (4)$$

where $J_i[z]$ is the Bessel function of the first kind

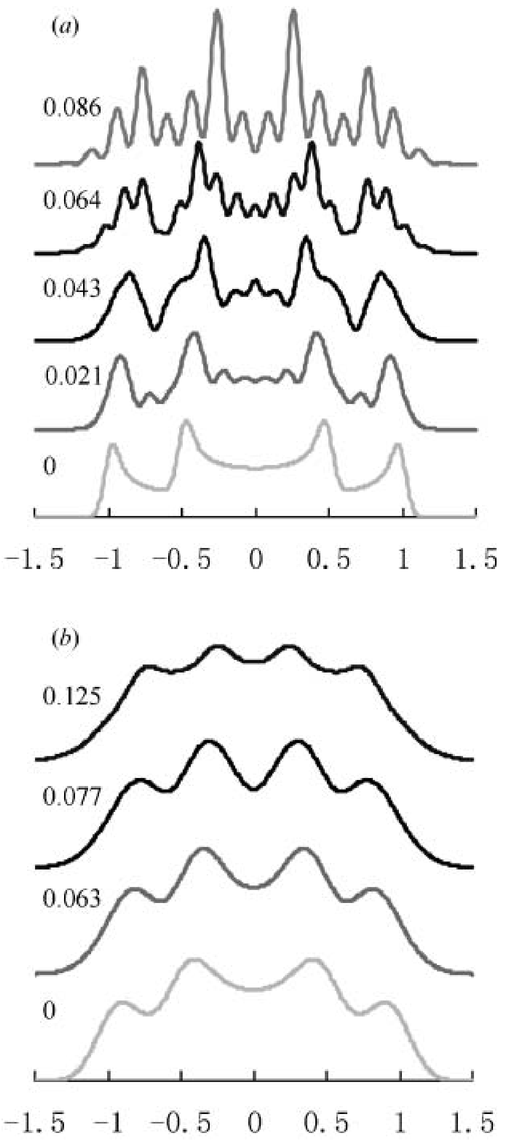

Figure 6. Rotationally averaged spectra as a function of rotation rate ω_s for the two linewidths observed in the TBBA experiments with $\eta=0$ (*a*) $\sigma_R=160$ Hz and ODBP-Ph-C_7, (*b*) $\sigma_R=376$ Hz. The rotation rates ω_s are shown to the left of each plot as a fraction of the full-width quadrupole splitting ν_Q, which is set equal to 2 in these plots. Note that $\omega_s=0.064$ for the TBBA experiment when shown on this scale, and $\omega_s=0.077$ for the ODBP experiment.

with integer order *i*, $E=\nu_Q(1+\eta)/8$, and $z=\nu_Q(3-\eta)/16\omega_s$.† Figure 6 shows simulated NMR spectra as a function of σ_R and ω_s. Notably, as the rotation rate becomes comparable to or larger than the linewidth, the spectrum has little resemblance to rotation spectra taken at negligible rotation rates.

Although the rotation NMR technique has been extensively used and proven on many liquid crystals, previous studies have not explored materials with such high transition temperatures and associated low viscosities. In order to further substantiate our biaxiality measurements on the ODBP molecules, we investigated TBBA [15], another nematic widely considered to be uniaxial, but with similar transition temperatures and critical rotation rates to the ODBPs. Using equation (4), fits to the data on TBBA for the SmA and N phases yield $\eta=-0.01$ and $0.01+/-0.03$, respectively. These simulations assume perfect cylindrically symmetric distributions of directors under rotation. Figure 7 shows the data and simulation for the N phase, where

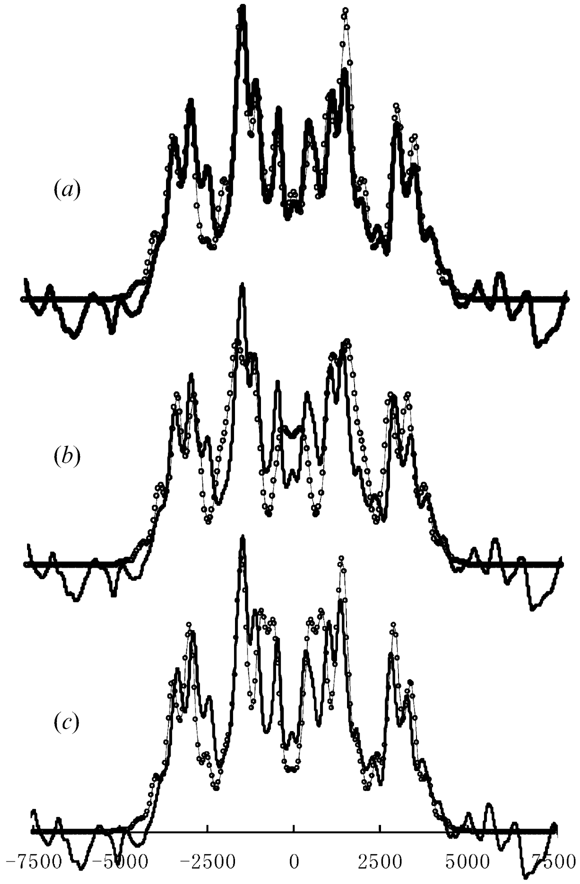

Figure 7. (*a*) Data (solid line) and best-fit simulation using equation (4) ($\eta=0.01+/-0.03$, $\sigma_R=160$ Hz, and $C=330000$; line with circles) for TBBA in the N phase at 192°C, $\omega_s=240$ Hz, and $\nu_Q=7450$ Hz. We acquired this ^{2}H spectrum at 55.28 MHz on a Bruker DMX 360 spectrometer using a 50 kHz sweep width, 0.6 s relaxation delay and 1.5 µs pulse in 16k 1024-point FIDs. (*b*) and (*c*) Data and simulations with $\eta=-0.1$ and $\eta=+0.1$, respectively. For the SmA phase of TBBA, we obtained a best-fit $\eta=-0.01+/-0.03$.

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†Note that we have slightly changed notation relative to our recent paper [11]. *J*[*i*, *z*] has become $J_i[z]$ to better follow standard notations. Also, we have corrected the fact that in this equation the Bessel functions are squared, which was omitted in equation (3) of that publication.

we note the striking agreement of the rotational sidebands between simulation and experiment. As in the previously published ODBP experiments [11], these spectra were obtained using the perdeuterated hexamethyl benzene (HMB-d_{18}) probe molecule at 1 wt%, and were best fit with Gaussian lineshapes in static and rotating cases, as is usual for small diffusing probe molecules. The larger biaxiality error bar reflects the lower sensitivity of these spectra relative to the ODBP-Ph-C_7, which had approximately twice the ^{2}H spin density due to higher probe molecule concentration. We also note that compared with the ODBP measurements, TBBA/HMB exhibits a much smaller linewidth ($2\sigma_R=320$ Hz fwhm) relative to the rotation rate ω_s (240 Hz) compared with ODBP-Ph-C_7 ($\omega_s=230$ Hz, $2\sigma_R=752$ Hz), thus dramatically enhancing the rotational sideband structure.

In sum, we have illustrated how axial and elliptical director distributions can express themselves in rotational NMR experiments, with the hope of giving theorists and experimentalists a better appreciation of the artifacts or features that might arise in such studies. Apparently, for sufficiently high rotation rates, these distributions appear to be inconsequential, as evidenced both by nonlinear least-squares fitting studies, and by the quantitative fit to spectra for the uniaxial LC TBBA using a uniform cylindrically symmetric director distribution and yielding $\eta=0$. These observations lead us to conclude that our original report [11] of a biaxial order parameter $\eta\sim0.1$ in the low temperature nematic phase of the ODBP mesogen is still valid.

Acknowledgement

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