Zero-Field NMR of Nematic Liquid Crystals with Positive and Negative Magnetic Susceptibility Anisotropies

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Nematic liquid crystal systems with positive and negative magnetic susceptibility anisotropies are studied by NMR in high and zero magnetic fields. The behavior of the system in zero field is dictated by the form of the zero-field Hamiltonian, the symmetry of the liquid crystal phase, and the initial state of the magnetization. Zero-field evolution is initiated both with and without the use of dc pulsed fields in the field cycle. Pulsed dc fields are also used to remove the effects of residual field inhomogeneities by zero-field spin echoes. The order parameters measured in an applied field and in the absence of a field are found to be the same within experimental error for both types of liquid crystal.

Introduction

Measurements of molecular ordering in liquid-crystalline systems are often conducted in large applied magnetic or electric fields.[1] These large fields cause the liquid crystal molecules to orient, on average, at a fixed angle with respect to the field direction. The anisotropic magnetic susceptibility of the molecules determines the direction and degree of alignment in a magnetic field.[2] NMR experiments are a sensitive means of distinguishing features of the alignment through the magnitudes and angular dependence of the relevant NMR Hamiltonian parameters.

In the absence of a field, the orientational, motional, and symmetry characteristics of the thermotropic liquid-crystalline mesophase determine the magnitude and form of the zero-field NMR Hamiltonian parameters. Until recently, the behavior of a liquid-crystalline system in the absence of an applied magnetic field could not be studied by NMR. Field cycling time domain zero-field NMR techniques[3] have since provided a means to measure both the bulk ordering and molecular order parameter without the influence of an applied field.[4] In order to observe the evolution of a spin system in zero field, the initial state of the spin system in zero field (e.g. magnetization) and the zero-field Hamiltonian must not commute. For liquid crystals which remain aligned with the field direction, this is not the case; it was demonstrated that in such cases pulsed dc fields can be used to alter the initial condition and observe the dipolar spectrum of a solute molecule dissolved in a nematic liquid crystal.[4] In this paper, we explore the alternative possibilities of changing the zero-field Hamiltonian through the use of liquid crystal systems with different magnetic susceptibilities.

Nematic Liquid Crystal Phases

As mentioned above, the ordering of the liquid crystal molecules is influenced by their magnetic susceptibility, χ, which relates the molecular diamagnetic moment, M, to the applied field B by[2]

$$M = \chi B \qquad (1)$$

For uniaxial nematics, the magnetic susceptibility can be represented by a symmetric tensor with elements equal to $\chi_{\parallel}$ and $\chi_{\perp}$ relative to the long axis of the molecule. An anisotropy of the magnetic susceptibility, $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, results when these two components are unequal, and its sign is determined by their relative magnitudes. Examples of the alignment for the two possibilities of $\Delta\chi > 0$ and $\Delta\chi < 0$ are shown in Figure 1. The elongated molecules in a domain of the sample align on average in a single direction with no resulting positional, only orientational order. This alignment is described by an axis called the director which may be uniform for an entire aligned sample. For molecules with a positive value of $\Delta\chi$, the directors align with the magnetic field as shown in Figure 1a. In contrast, the molecules with a negative

value of $\Delta\chi$ align on average perpendicular to the field direction, as illustrated for a single domain in Figure 1b. The molecules have the same rotational and translational freedom in both cases although in the latter the domain director axis can have any direction in the plane perpendicular to the external field. An interesting feature of these nematic liquid crystals is that in binary mixtures they display an unusual temperature-dependent phase behavior.[5] The apparent anisotropy in the magnetic susceptibility ranges from positive to negative with changing temperature and, at a certain transition temperature, appears to be zero.[6]

In a strong enough applied field, regardless of the ordering of the liquid crystals, the field direction determines the relevant spin interaction frame as illustrated by the axes in Figure 1, a and b. After the removal of the field, the relevant axis system is determined by the motional and symmetry properties of the liquid crystal molecules. This is illustrated for a single sample domain in Figure 1, c and d, and would describe the entire system as a monodomain in the former if it were aligned in a magnetic field. In contrast, although the director axes in Figure 1d are all perpendicular to the field direction (z), they are randomly distributed in the xy plane as shown in Figure 2 and therefore, a single director axis does not describe the entire system. Thus between high field and zero field, or $\Delta\chi > 0$ and $\Delta\chi < 0$, the interaction frames which aptly describe the spin systems may differ. The spin system can consist of the liquid crystal molecules themselves or a probe molecule dissolved in the liquid crystal which will be constrained to the symmetry of the phase.[7] This aids one in studying the liquid-crystalline phase via simpler spin systems (without requiring selective isotopic labeling). The ordering of a two spin rodlike solute molecule in the liquid-crystalline phase can be described by an order tensor, S, which describes the average alignment of the internuclear vector with respect to a director axis.[8]

Experiments and Results

The samples consisted of approximately 5 wt % CH_2Cl_2 in EBBA (*p*-ethoxybenzylidene-*p*-butylaniline, Frinton Laboratories)

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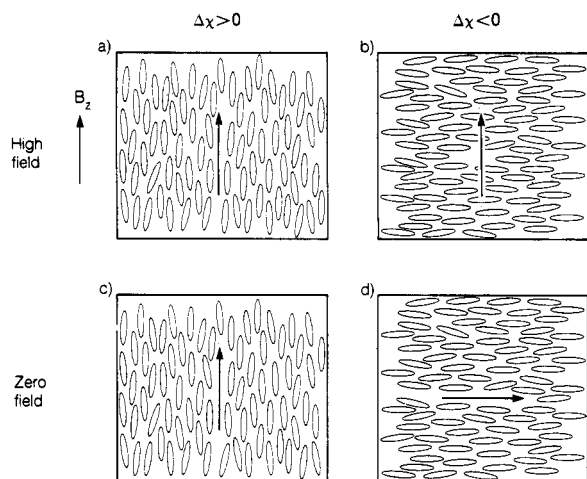
Figure 1. Alignment of nematic liquid crystal molecules with positive and negative magnetic susceptibility anisotropies in high and zero fields. The molecules align on average in a single direction described by a director axis. The molecules fluctuate rapidly about the director axis and rotate about their long axes. In the presence of a large field, the director axis of a domain of the system with $\Delta\chi > 0$ will be aligned with the field as in (a) while it will be perpendicular for a system with $\Delta\chi < 0$ as shown in (b). The arrows indicate the quantization axes of the spin interactions in high field. In the absence of a magnetic field, the director axes of a domain (as shown by the arrows in (c) and (d)) will determine the quantization axes of the spin interactions in zero field. Note that while the molecules remain aligned in both cases, the direction of the quantization axis does not change between high and zero field in the $\Delta\chi > 0$ case, while for $\Delta\chi < 0$ it does.
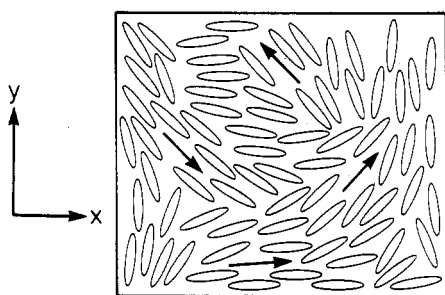

Figure 2. Cross section perpendicular to the field direction for a liquid crystal sample with $\Delta\chi < 0$. The separate domains are characterized by director axes which are all perpendicular to the field direction and there is a distribution of director directions in the xy plane.

with a $\Delta\chi > 0$, or ZLI 1167 (EM Chemicals, a mixture of propyl-, pentyl- and heptylbicyclohexylcarbonitriles) with a $\Delta\chi < 0$. The samples were prepared by dissolving the solute via thorough heating and mixing of the mixture above its clearing point.

Zero-field experiments were conducted on a homebuilt 180-MHz (^{1}H) NMR spectrometer modified for the field cycling experiments.[9] Two basic field cycles were used and are illustrated in Figure 3. After demagnetization, both field cycles employ a sudden transition in the intermediate field to zero field. This may or may not be followed by a pulsed dc field which acts as a rotation on the spin state and alters the initial condition in zero field.[10] Additionally, a dc refocussing π pulse was often applied in the middle of the field cycle to cancel the effects of residual field inhomogeneities in analogy to Hahn spin echoes[11] in high field. Employing the field cycle of Figure 3a on a sample uniformly aligned along the applied field ($\Delta\chi > 0$) results in the spectrum shown in Figure 4a. This spectrum is indicative of a liquid crystal sample remaining aligned in zero field due to the absence of
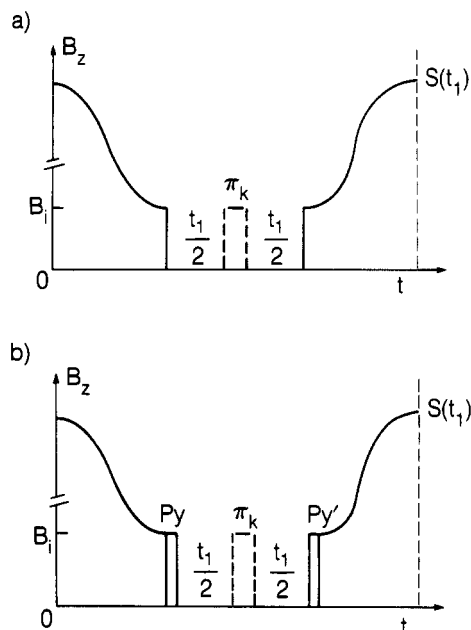
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Figure 3. Field cycles for the zero-field NMR experiment. Both field cycles incorporate demagnetization from a large field (42 kG) to an intermediate field, B_i, of approximately 50 G. The intermediate field is switched off suddenly as in (a) or can be followed by a $\pi/2$ dc field pulse (1–3 μs) as in (b) to initiate evolution in zero field. The evolution continues for a period t_1 which may be divided in half by a π_k dc pulse (along the x, y, or z direction of the laboratory) cancelling the effects of residual fields. The zero-field period is terminated by reapplication of the intermediate field, with or without a prior dc pulse, as illustrated in (a) and (b), respectively. The sample is then remagnetized and the magnetization is sampled in high field as a function of t_1. This produces the zero-field free induction decay or echo signal which, when Fourier transformed, yields the frequency domain spectrum.

evolving signal.[4] Improperly prepared samples, such as those with large bubbles, result in observable zero-field NMR signals due to the disruption of uniform alignment caused by surface effects and/or mechanical mixing. An example of such a spectrum showing broad peaks at the dipolar frequencies appears in Figure 4b and a schematic picture of the possible disordering induced by a bubble appears in Figure 5.

High-field and zero-field NMR spectra were obtained to compare the order parameters of the solute with and without the presence of a large magnetic field. The high-field dipolar spectrum of CH_2Cl_2 in EBBA appears in Figure 6a. The solute signal was observed independently by sampling only the longer T_2 component of the signal. Nematic liquid crystal samples have been found to remain aligned on the time scale of the zero-field experimental field cycle.[4] Thus in order to observe the zero-field spectrum, the field cycle with $\pi/2$ dc field pulses (Figure 3b) must be used to produce a different initial condition. Figure 6b is the resulting zero-field dipolar signal of CH_2Cl_2 in EBBA taken with a π_x echo pulse in the field cycle. Peaks appear at frequencies corresponding to $\nu_d = 3h\gamma^2S/8\pi^2r^3$ where the two-proton dipolar interaction is scaled by S. The order parameters measured in high field ($S = 0.064 \pm 0.001$) and zero field ($S = 0.063 \pm 0.001$) are identical within experimental errors.

On the other hand, the initiation of zero-field evolution can be produced by using samples with $\Delta\chi < 0$ in which the axis of quantization for the nuclear spins changes on going from high to zero field. Unlike the $\Delta\chi > 0$ case, no dc pulses are needed to initiate zero-field evolution and the sudden transition field cycle of Figure 3a was used with a π_z echo pulse. The high-field and zero-field spectra of CH_2Cl_2 in ZLI 1167 ($\Delta\chi < 0$) appear in Figure 7, a and b. In this case, the observed frequencies of the dipolar coupling are different in high and zero field. Due to the perpendicular alignment, one would expect the zero-field dipolar splittings to be twice as large as those in high field. The order parameters may be calculated to be $S = 0.100 \pm 0.001$ and $S = 0.101 \pm 0.001$ in high and zero field, respectively.
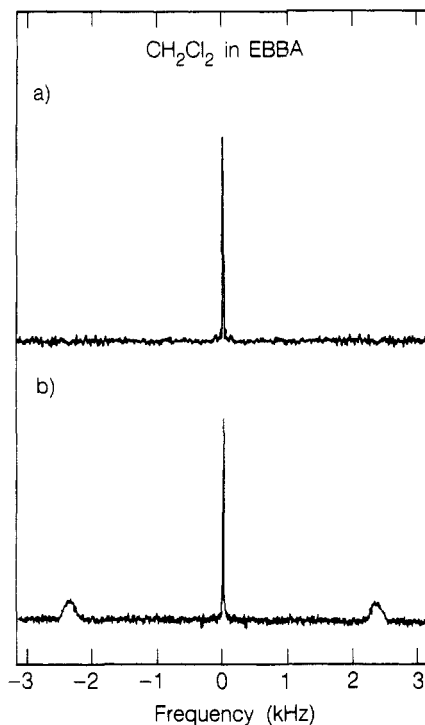
Figure 4. CH_2Cl_2 in the nematic phase of EBBA with $\Delta\chi > 0$. The spectrum shown in (a) results when the sudden transition field cycle of Figure 3a is used. This lack of dipolar signal indicates that the sample remains aligned; there is only a zero frequency signal from nonevolving magnetization. Samples in which large bubbles are present do display dipolar signals as shown in (b) and can be explained by disruption of the ordering of the liquid crystal molecules.
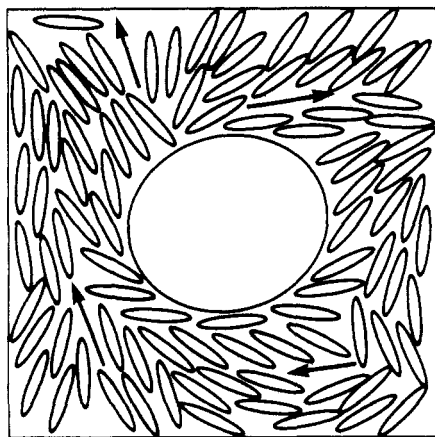

Figure 5. The uniform alignment of the sample is disrupted through the presence of a bubble in the sample. This effect may be due to either sample mixing in shuttling and/or surface effects. A possible scenario is shown above in which the director axes are anchored by a bubble and caused to point away from the z axis. This distribution of directors will alter the relative intensities of the possible zero-field lines.

Spin Hamiltonians in High Field and Zero Field

The dependence of the high- or zero-field NMR spectrum of a liquid crystal/solute system on field strength, the sign of $\Delta\chi$, and initial condition can easily be understood through the form of the NMR Hamiltonian. In the absence of an applied field, the liquid-crystalline phase alone determines the truncation of the Hamiltonian. Only two frames of reference are needed to describe the interactions present, the principal axis system (PAS) of the dipolar interaction and the director frame of the liquid crystal which conforms to the symmetry of the phase in zero field. The Hamiltonian in zero field can be written as a product of second rank spherical tensor operators[12]

$$H_D = \sum_{m,m'=-2}^{2} (-1)^m T_{2-m} \, A_{2m'} \langle D^2_{m'm}(\alpha\beta\gamma) \rangle \qquad (2)$$
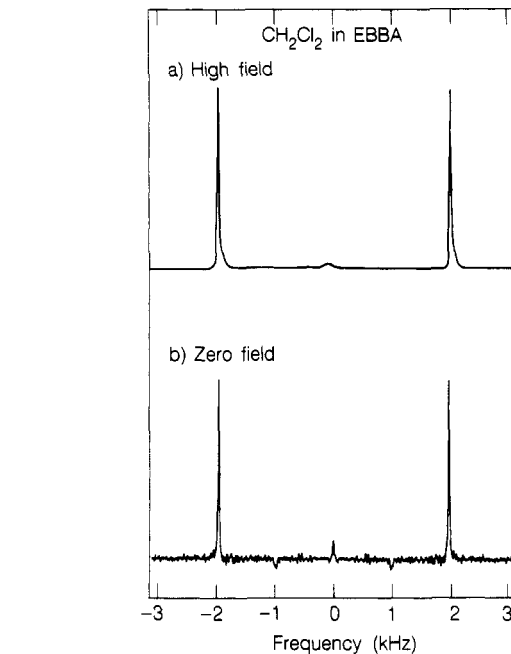

Figure 6. High-field and zero-field spectra of 5 wt % CH_2Cl_2 in EBBA ($\Delta\chi > 0$). The high-field spectrum in (a) was obtained with a $\pi/2_x$–τ–π_x–τ sequence with τ chosen to detect only the solute signal. The order parameter calculated from the observed splitting is 0.064 ± 0.001. In (b), the zero-field spectrum using the field cycle of Figure 3b with dc pulses equal to $\pi/2$ and a π_x refocussing pulse. The order parameter measured in zero field ($S = 0.063 \pm 0.001$) is identical with that in high field within experimental error. The intensities and dependence of the signal on dc pulses is indicative of a sample still aligned with the original field direction.
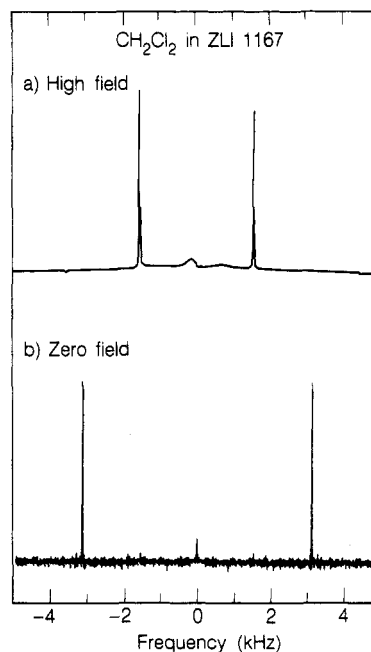

Figure 7. CH_2Cl_2 (5 wt %) in ZLI 1167 with $\Delta\chi < 0$. The high-field spectrum was obtained with a $\pi/2_x$–τ–π_x–τ sequence with τ chosen to echo only the solute signal. The high-field splitting observed in (a) is reduced by a factor of -0.5 relative to that in zero field due to the truncation of the Hamiltonian with respect to the field. The high-field order parameter is calculated to be 0.100 ± 0.001. The zero field spectrum in (b) was obtained by using the sudden transition field cycle of Figure 3a with a π_z refocussing pulse. The order parameter is identical with that calculated in high field within experimental error with $S = 0.101 \pm 0.001$.

where T_{2m} and $A_{2m'}$ represent the director frame spin and PAS spatial variables, respectively. The $D_{m'm}(\alpha\beta\gamma)$ term, averaged over

molecular fluctuations, transforms the PAS spatial terms into the director frame. The transformation depends on the Euler angles α, β, and γ describing the relative orientations of the two axis systems.[13] Due to the axial symmetry of the dipolar interaction and the uniaxial nature of the nematic phase, there can be no γ or α dependence. Therefore, with

$$D^2_{m'm}(\alpha\beta\gamma) = e^{-i\gamma m'}d^2_{m'm}(\beta)e^{-i\alpha m} \qquad (3)$$

the only term which survives is that with m and m' equal to zero and the director frame Hamiltonian then reduces to

$$H_D^0 = T_{20}A_{20}\langle D^2_{00}(\beta)\rangle = T_{20}A_{20}\,\tfrac{1}{2}\langle 3\cos^2\beta - 1\rangle = T_{20}A_{20}S \qquad (4)$$

The order parameter, $S = \frac{1}{2}\langle 3\cos^2\beta - 1\rangle$, describes the average over the relative orientations of the PAS z (internuclear vector) and director axes. This truncation holds regardless of the orientations of the liquid crystal molecules. That is to say, there is no dependence of the bulk alignment of the molecules as the interaction need only be considered in the local director frame. Thus for samples with $\Delta\chi > 0$ or $\Delta\chi < 0$ the form of the zero-field Hamiltonian is identical. This similarity in zero field is apparent for CH_2Cl_2 in EBBA and ZlI 1167; the spectral splittings differ due to different order parameters but the general appearance of the spectra is the same.

Although the zero-field Hamiltonians have the same form for the two phases, it may not yet be evident why dc pulses are required in the case with $\Delta\chi > 0$ to initiate evolution in zero field, but not when $\Delta\chi < 0$. Using either field cycle, the initial condition prepared in high field is proportional to I_z, and if this commutes with the zero-field Hamiltonian evolution will not occur with the sudden transition in field. For example if the sample in zero field remains aligned along the original field direction, then the zero-field Hamiltonian truncated with respect to the director axis has the same quantization axis as in high field and they commute. Applying a dc pulse and changing the initial state to I_x initiates evolution in a manner analogous to applying an rf pulse in high field. The normalized signal as a function of t_1 after a $\pi/2$ dc pulse is calculated as follows:

$$S(t_1) = \text{Tr}\,\{I_x\,\exp(-iH_Dt_1)I_x\,\exp(iH_Dt_1)\} = \cos(\omega_Dt_1) \qquad (5)$$

where $\omega_D = 3\gamma^2hS/4\pi r^3$. If the liquid crystal sample is aligned perpendicular to the field direction, then the zero-field and high-field frames are no longer coincident and the magnetization will precess in zero field. One may picture this as if the liquid crystal (or the averaged local field) is now shifted by 90° rather than the magnetization. In order to calculate the zero-field spectrum, a transformation between the lab frame and zero-field/local-director frame must be included. The normalized signal as a function of t_1 becomes identical with eq 5

$$S(t_1) = \text{Tr}\,\{RI_zR^{-1}\,\exp(-iH_Dt_1)RI_zR^{-1}\,\exp(iH_Dt_1)\} = \cos(\omega_Dt_1) \qquad (6)$$

where $R = \exp(-i\phi I_z)\exp(-i\theta I_y)$ relates the zero field to laboratory frame and $\theta = 90°$ for $\Delta\chi < 0$. In both cases represented in eq 5 and 6, all the magnetization evolves if the alignment is uniform

over the sample. In fact it is clear that there is no ϕ dependence in the signal function due to the overall axial symmetry of the phase around z. Thus the intensities in the zero field spectrum and the dependence on the field cycle used are indicative of the bulk alignment of the sample.

In a similar manner, the relative scaling factors of the high-field spectra may be understood by describing the Hamiltonian in high field. The Hamiltonian can again be represented by eq 2 although now an additional transformation from the director frame to the lab frame is required. This will then be written as

$$H_D = \sum_{m,m',n}^{2} (-1)^m T_{2-m}A_{2n}D^2_{nm}\langle\psi\theta\phi\rangle\langle D^2_{m'm}(\alpha\beta\gamma)\rangle \qquad (7)$$

where the $D^2_{nm}(\varphi\theta\phi)$ term relates the director and lab frames. This angular term is not averaged over molecular motions since the fluctuations of the director with respect to the field direction are slow[2] on the time scale of the experiment. Since the liquid crystal and laboratory (field direction) frames are uniaxial, only the angle θ is needed to make the transformation. For $\Delta\chi < 0$, $\theta = 90°$ and the $D^2_{00}(\theta)$ term in eq 3 equals $-\frac{1}{2}$, while for $\Delta\chi > 0$ the angle is zero and the term is equal to 1. The high-field spectra will then be scaled by this factor of $-\frac{1}{2}$, in addition to S, as is apparent in Figures 6 and 7.

Summary

The liquid crystal samples were found to remain aligned in zero field on the time scale of the experimental field cycle. For systems with $\Delta\chi > 0$, the ordering of the sample remains along the original field direction and dc pulses are necessary to produce a dipolar signal in zero field. Since the alignment of the liquid crystal molecules with $\Delta\chi < 0$ is perpendicular to the laboratory z axis, signal results with the sudden transition in intermediate field. High-resolution spectra may be obtained with refocussing dc pulses and allow for determination of the order parameters which were found to remain constant. In mixtures of liquid crystal solvents with $\Delta\chi < 0$ and $\Delta\chi > 0$ in concentrations and at temperatures close to their sensitive phase transition region, preliminary results indicate that although these samples are very sensitive to these experimental limits, even removal of the field does not cause a change in the aligned state.

Overall the bulk ordering of the sample may be determined through the intensities of the lines in the zero-field spectrum and the behavior of the system under specific zero-field NMR field cycles. The truncation and symmetry of the NMR Hamiltonian in the absence of a magnetic field is illustrated in the zero-field spectra of liquid-crystalline samples. Other systems which are of interest are those of smectic and lyotropic phases in which aligned samples may not be obtainable. In these systems the order parameters and possible effects due to biaxiality of the phases may be observed in the zero-field spectrum.[14]

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