

appear which matched those observed by Sanchez and Spiro. Figure 9 shows the time development of the observed Raman spectrum at  $-0.8$  V which at long times became the spectrum of high-spin Fe(II). The time development of the spectroscopic changes at  $-0.8$  V contrasts the instantaneous changes observed in the reduction of adsorbed hemin and instead tracks the slow reduction of the entire solution volume.

Therefore, it is clear that the reduction product of dissolved hemin and adsorbed hemin have different structures. Our surface Raman data support an intermediate-spin 4-coordinate adsorbed Fe(II)PP and the resonance Raman spectrum of the reduced solution indicates a high-spin more highly coordinated Fe(II)PP structure. The electrochemical data suggest that at high Fe(II) concentrations Fe(II)PP dimers form in solution (see discussion of wave II<sub>a</sub>, Figure 3). In the absence of other ligands, the dimerization of dissolved Fe(II)PP may also explain the observation of low-spin Fe(II) in the resonance Raman spectrum of

the reduced solution. Apparently, the surface-bound reduction products are restrained from aggregating.

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## Zero-Field Nuclear Magnetic Resonance of a Nematic Liquid Crystal

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The molecular order parameter of CH<sub>2</sub>Cl<sub>2</sub> in a nematic liquid crystal was measured by using a version of zero-field NMR employing pulsed dc magnetic fields. Spectral frequencies and intensities are shown to reflect the ordering on a molecular and macroscopic scale, respectively. Samples oriented in high magnetic field did not significantly change their state of alignment during the time scale of the field cycle. Zero-field measurements of the order parameter yielded values within experimental error of those measured in high field. A zero-field echo experiment was performed to decrease the effect of residual fields on line width. Dipolar order was created in zero field by using a pulsed dc field analogue of the Jeener-Brokaert experiment.

### Introduction

Nematic liquid crystals consist of long rodlike molecules whose average orientation is described by a director  $\bar{n}$ . In the absence of a magnetic field the average orientation of the director is determined by convection and interactions with walls and surfaces of the container of the sample.<sup>1</sup> In a macroscopic sample,  $\bar{n}$  is a function of position throughout the sample owing to these effects. Since these materials have an anisotropic magnetic susceptibility defined by  $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ , they can be aligned by an applied magnetic field. Given a sample with positive  $\Delta\chi$  in an applied field of sufficient magnitude, the system will be describable by a single director whose average alignment is along the field. Molecules of the liquid crystal will on the average be aligned with their long axes parallel to the director.

The magnetic field strength dependence of the alignment on a macroscopic scale has been studied by light scattering,<sup>2</sup> optical<sup>3</sup> and magnetic<sup>4</sup> birefringence, and magnetic susceptibility<sup>5</sup> measurements. The unique feature of NMR is that it measures the alignment on a molecular scale. It has been suggested that the degree of ordering may differ on a macroscopic and molecular level in spite of the small energies of the order director fluctuations.<sup>6</sup> The order parameter and fluctuations are important in relaxation of liquid crystal systems,<sup>7</sup> and it is thus instructive to directly measure the order parameter of a probe molecule in a nematic liquid crystal in high and low fields. The recent pulsed field cycling technique<sup>8-10</sup> of zero-field NMR is ideally suited to this purpose. This paper presents the first applications of zero-field NMR to liquid crystals. A common approach to spectral simplification is to study the behavior of a solute dissolved in the liquid crystal<sup>11,12</sup> since the nematic phase causes the solute to acquire

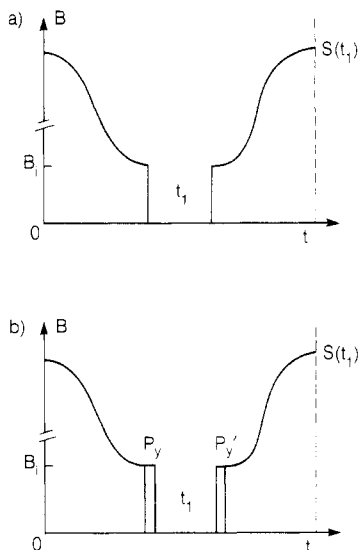
a preferred alignment with respect to the director.<sup>11-13</sup> The allowed motions of the solute reflect the anisotropic molecular tumbling in the uniaxial medium by characteristically averaging the dipolar interaction.<sup>14</sup>

### Experimental Section

The system chosen for study was composed of CH<sub>2</sub>Cl<sub>2</sub> dissolved in *p*-pentylphenyl 2-chloro-4-(*p*-pentylbenzoyloxy)benzoate (Eastman 11650). Samples were made homogeneous by thoroughly mixing after heating the liquid crystal/solute mixture to above its clearing point. The samples exhibited clearing points

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<sup>†</sup> On leave from Department of Physics and J. Stefan Institute, E. Kardelj University of Ljubljana, Yugoslavia.



**Figure 1.** Schematics of zero-field experimental field cycles. (a) After demagnetization to an intermediate field, the zero-field evolution period is initiated by the sudden switch-off of  $B_i$ . After a time  $t_1$ , the  $z$  component of magnetization is sampled by reapplication of the intermediate field and remagnetization to high field. The zero-field interferogram,  $S(t_1)$ , is produced by repeated field cycles for incremented values of  $t_1$ . (b) Sudden  $z$ /pulsed  $y$  field cycle. This field cycle is identical with (a) except for the application of pulsed dc magnetic fields corresponding to rotation angles given by  $\theta = \gamma B_{dc} t_p$ . For  $90^\circ_y$  pulses the density operator at the start of the  $t_1$  period is now proportional to  $I_x$  in the lab frame. Detection of the transverse component is completed by the final  $P'_y$  pulse and application of a field in the  $z$  direction to trap the magnetization before remagnetization to high field. The magnitude of  $B_i$  and the dc pulsed fields are typically on the order of 0.01 T.

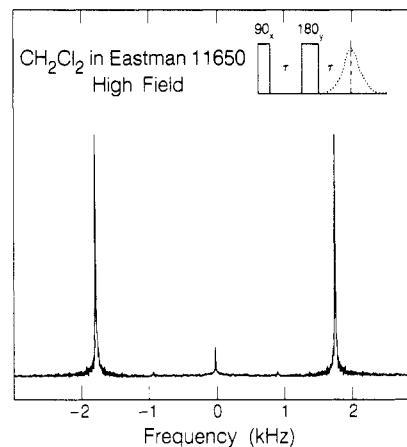
of  $\sim 65 \pm 2^\circ\text{C}$ , and the  $\text{CH}_2\text{Cl}_2$  concentration was estimated to be approximately 10–15 wt % in the nematic. Samples were sealed and remained unchanged for several weeks. Precautions were taken to minimize the presence of bubbles in the samples.

Descriptions of the zero-field NMR field cycling experiments have been presented elsewhere<sup>8,9,15</sup> and require little change when applied to liquid crystal samples aside from the application of orthogonal dc pulses in zero field. Field cycling schemes used in these experiments are shown in Figure 1. In the sudden transition experimental sequence of Figure 1a the zero-field magnetization at  $t_1 = 0$  is aligned along the laboratory  $z$  axis. In Figure 1b, dc pulses applied orthogonal to  $z$  rotate the initial magnetization to the  $x$ - $y$  plane. The pneumatic shuttling system employed for translation of the sample from  $B_0$  to  $B_i$  as well as the electronics for production of the zero field has also been described.<sup>15</sup> Minimum air pressures were used to reduce the physical shock of shuttling the sample.

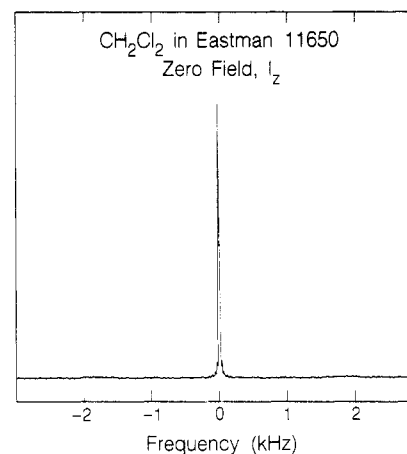
## Results

The high-field NMR spectrum of the  $\text{CH}_2\text{Cl}_2/11650$  system was obtained by using a  $90_x - \tau - 180_y - \tau$  echo sequence to reduce the effects of field inhomogeneities.<sup>16</sup> The signal intensity was measured as a function of  $\tau$ . The minimum time for the incremented variable  $\tau$  was chosen to echo only the solute signal and not that of the liquid crystal itself. The resulting dipolar spectrum is shown in Figure 2. The alignment of the proton-proton internuclear vector with respect to the director,  $\bar{n}$ , may be described by a single-order parameter  $S = 0.055 \pm 0.001$  as calculated from the observed splitting.<sup>14</sup>

Previous work<sup>9,17</sup> has shown that polycrystalline samples of isolated proton pairs yield a three-line frequency spectrum when subjected to the sudden transition experimental sequence of Figure



**Figure 2.** High-field NMR spectrum of  $\text{CH}_2\text{Cl}_2$  in Eastman 11650 taken as a function of  $\tau$  with the pulse sequence shown at upper right. The molecular order parameter of the solute is calculated to be  $S = 0.055 \pm 0.001$  from the observed splitting.



**Figure 3.** Spectrum of  $\text{CH}_2\text{Cl}_2$  in Eastman 11650 with the field cycle of Figure 1a. The single line at zero frequency indicates that no zero-field evolution occurred during the time  $t_1$ . The spectrum appears as expected for an ordered nematic in which the axis of quantization is the same in high as in low field.

1a. The three lines are of equal intensity and occur at zero frequency and  $\pm\nu_D = 3\gamma^2\hbar/8\pi^2r^3$ . If this sudden experiment is applied to the  $\text{CH}_2\text{Cl}_2/11650$  system using an echo as above to detect only the solute signal, one obtains the one-line spectrum shown in Figure 3. This line at zero frequency corresponds to the central line of the triplet found in the polycrystalline case and yields no dipolar information on the solute.

The experiment was thus performed with the sequence of Figure 1b. Figure 4 presents the results of a series of these sudden  $z$ /pulsed  $y$  experiments. The angles of the dc pulses corresponding to  $P$  and  $P'$  in Figure 1b were determined by a calibration procedure described previously.<sup>8</sup> The spectra consist of two lines corresponding to either the zero frequency or  $\pm\nu_D$  lines of the polycrystalline case. Calculation of the order parameter of the solute from the zero-field spectrum yields  $S = 0.054 \pm 0.001$ .

## Spin Hamiltonian in High Field

The  $T_{2-m}$  of the liquid crystal system in high- and zero-field experiments may be understood if one considers the Hamiltonian and the initial condition. The dipolar Hamiltonian in the average director frame may be written in spherical tensor notation as<sup>18</sup>

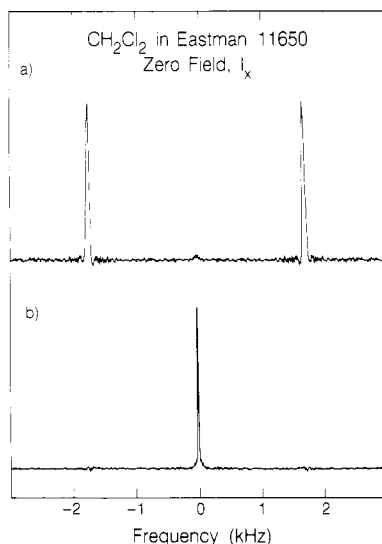
$$H_D = \sum_{m,m'=-2}^2 (-1)^m T_{2,-m} A_{2,m'} \langle D_{m',m}^2(\Omega) \rangle \quad (1)$$

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**Figure 4.** Spectra of the  $\text{CH}_2\text{Cl}_2/11650$  system obtained via the sudden  $z$ /pulsed  $y$  field cycle of Figure 1b. Direct current pulses used were (a)  $90^\circ_y, 270^\circ_y$ , and (b)  $180^\circ_y, 180^\circ_y$ . The observed spectra show the same dependence on pulse angle as given by eq 5, which was obtained assuming an ordered nematic liquid crystal in zero field. The molecular order parameter may be measured from the observed frequencies and was found to be  $S = 0.054 \pm 0.001$ , which is unchanged from high field within an experimental error of 2%. Line widths of  $\sim 45$  Hz may be attributed to residual fields.

Here  $T_{2,-m}$  and  $A_{2,m'}$  represent director frame spin operators and principal axis system (PAS) spatial variables, respectively, and the  $D_{m',m}^2(\Omega)$  effects the transformation between the two frames. The internuclear vector which is the  $z$  axis of the PAS frame is taken to be coincident with the  $z$  axis of the molecular frame. The brackets indicate a time average over the  $D_{m',m}^2$  terms which accounts for fluctuations of the alignment of the molecular frame with respect to the director frame. Truncation of the spin part of the Hamiltonian by a large magnetic field leaves only the  $T_{20}$  term nonzero. Furthermore, only the  $m' = 0$  term of the traceless second rank tensor  $A_{2,m'}$  is nonzero since the dipolar interaction is axially symmetric in the molecular/PAS frame. Therefore, the effective high-field dipolar Hamiltonian for a proton pair is given by<sup>14,18</sup>

$$H_D^\circ = T_{20}A_{20}S = \frac{\gamma^2\hbar^2}{4\pi^2r^3}S(3I_{1z}I_{2z} - \vec{I}_1 \cdot \vec{I}_2) \quad (2)$$

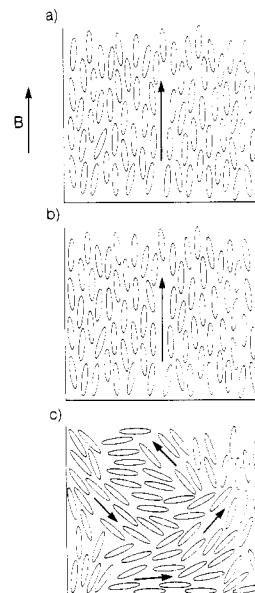
where the order parameter  $S$  is given by

$$S = \langle D_{00}^2(\Omega) \rangle = \frac{1}{2}(3 \cos^2 \beta - 1) \quad (3)$$

and  $\beta$  is the instantaneous angle between the director and the proton-proton internuclear vector. The Hamiltonian of a dissolved solute will have the same form as that above. The NMR experiment then measures the degree of ordering of the solute molecular frame with respect to the average director orientation. In the presence of a large applied magnetic field, the director is aligned along the field and the director and lab frames coincide as illustrated in Figure 5a. The high-field spectrum for a proton pair is then a two-line spectrum due to the scaled dipolar coupling, and the order parameter of the solute,  $S$ , may be calculated from the observed splitting  $\delta$  by  $S = 4\pi^2r^3\delta/3\gamma^2\hbar$ .<sup>14</sup>

### Spin Hamiltonian in Zero Field

**Aligned Systems.** The zero-field director frame dipolar Hamiltonian for a molecule of the nematic is unchanged from that in high field and is equal to  $H_D^\circ$  of eq 2. This is due to motional averaging about the average director which in an aligned system is oriented along the lab  $z$  axis, as in Figure 5b. Rotation about the long molecular axes and the uniaxial nature of the liquid crystal require that the terms in eq 1 with  $m'$  and  $m$  not equal to zero vanish.<sup>19</sup> In contrast to the high-field case, the truncation



**Figure 5.** Ordering in nematic liquid crystals. (a) The elongated molecules of the liquid crystal (ellipses) undergo rapid rotation about their long axes and fluctuations of these axes, thus having an average alignment with the director. In the presence of a magnetic field,  $B$ , the average orientation of the director (shown by the arrow) will be aligned along the magnetic field direction. (b) Order in the nematic remaining immediately after removal of the field. The sample maintains its average alignment along the laboratory  $z$  axis. Due to the rotational motions and symmetry of the liquid crystals, the dipolar Hamiltonian will also be truncated with respect to the  $z$  axis in the absence of a magnetic field. (c) Deigned system showing local domain structure. The alignment of the local directors is no longer in the laboratory  $z$  direction. The average orientation of the molecules is described by the local directors. The dipolar Hamiltonian of a local domain is now truncated with respect to the local director.

is accomplished through the spatial terms of the Hamiltonian. Again the solute Hamiltonian will have the same form as that above since the nematic environment imposes a preferred orientation and motion.

The sudden transition experiment results reported above can now be interpreted. Even in the absence of an applied field, a monoaligned sample with  $\vec{n}$  aligned along the lab  $z$  direction (Figure 5b) will have a zero-field Hamiltonian equal to the truncated lab frame dipolar Hamiltonian. The sudden switch-off of the intermediate field in the zero-field experiment of Figure 1a initiates zero-field evolution only if  $[\rho_0, H_{zf}] \neq 0$ . Since  $\rho_0$  is proportional to  $I_z$  before the transition, this condition is not met. No evolution occurs in zero field, and the resulting spectrum for an ordered sample in zero field is simply a line at zero frequency.

The zero-field spectrum of an aligned sample can still be obtained by use of a pulsed dc magnetic field to effectively change the initial condition from  $\rho_0$  proportional to  $I_z$  to some other operator that does not commute with  $H_D^\circ$ . In this case a pulse can be used to rotate the initial magnetization to the  $x$ - $y$  plane of the laboratory frame. Given a magnetization along some axis in zero field, a dc magnetic field pulse of duration  $t_p$  applied perpendicular to that axis will rotate the magnetization by an angle  $\theta$  given by<sup>8</sup>

$$\theta = \gamma B_{dc}t_p \quad (4)$$

If we define the direction of the dc field as the lab frame  $y$  and transform the initial density operator given above with a  $\theta = \pi/2$  pulse, then the density operator will be proportional to  $I_x$ . Since  $[H_D^\circ, I_x] \neq 0$  evolution is initiated. Exact calculation of the zero-field interferogram for a two-proton rodlike sample oriented in a liquid crystal subjected to the sudden  $z$ /pulsed  $y$  field cycle yields the normalized signal

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$$S(t_1) = \cos^2 \theta + \sin^2 \theta \cos \omega_D t_1 \quad (5)$$

where  $\theta$  is the angle of the dc pulse, and for a liquid crystal system we define  $\omega_D = 2\pi\nu_D$  by

$$\omega_D = S \frac{3h\gamma^2}{4\pi r^3} \quad (6)$$

in analogy with the polycrystalline case.<sup>9,17</sup> Resulting spectra obtained with the sudden  $z$ /pulsed  $y$  sequence may be seen in Figure 4 for different dc pulses. The molecular order parameter can be measured in zero field and is considered the same as that in high field within an experimental error based on the line widths and small-scale temperature fluctuations which may occur in the course of the experiment. The intensities in the experimental spectra have the same dependence on pulse angle as predicted by eq 5 for an ordered sample.

**Dealigned Systems.** The physical removal of the sample to low or zero fields might be expected to alter the alignment of the liquid crystal molecules. We consider the case where local ordering within a domain remains the same, while the alignment of the local directors of these domains changes orientation (Figure 5c). If it is assumed that the locally allowed motions and fluctuations within a domain are the same in zero-field as in the high-field monodomain, then the director frame order parameter of the solute will be the same in high and zero fields since the director frame Hamiltonian is unchanged. The distributions of director orientations will manifest themselves as changes in the intensities and/or frequencies of the zero-field lines. Thus, ordered and disordered nematics may be distinguished by the characteristic appearance of their zero-field spectra since the relative intensities of the zero-field lines will be indicative of the degree of disordering. As shown earlier, molecules initially aligned along the  $z$  axis of the lab frame with  $\rho_0$  proportional to  $I_z$  produce only a central line in the zero-field dipolar spectrum. When the magnetization is rotated to the  $x$ - $y$  plane, as with a dc pulse, only the outer lines of the zero-field spectrum result. General orientations will produce contributions of different intensities to the three lines. In the limit of an isotropic distribution of the local directors, the normalized zero-field signal for the sudden experiment or the sudden  $z$ /pulsed  $y$  version with both dc pulses equal to  $90^\circ$  is given by

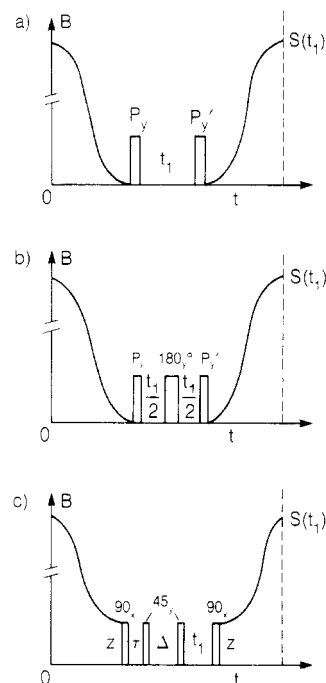
$$S(t_1) = \frac{1}{3}[1 + 2 \cos \omega_D t_1] \quad (7)$$

which is the same form as that predicted for the proton pairs in a polycrystalline hydrate.<sup>9,17</sup>

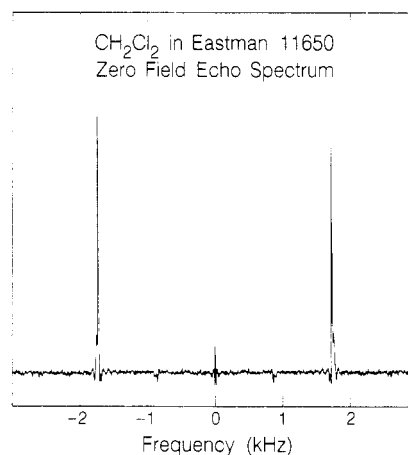
### Other Pulsed Zero-Field Experiments

**Demagnetization Experiments.** Further studies were also performed to observe the effect of complete demagnetization on the liquid crystal system. The field cycle, shown in Figure 6a, consists of demagnetization to zero field combined with a pulsed version of the experiment.<sup>8,9</sup> A spin temperature argument suggests that the density operator describing the initial demagnetized state in an aligned sample should be proportional to  $I_z$  since the motionally averaged dipolar and Zeeman Hamiltonians commute.<sup>20</sup> This predicts the zero-field signal will be described by eq 5. This is confirmed experimentally since spectra produced with the same dc pulses appear identical with those in Figure 4. Thus, the resulting state is not one characteristic of a demagnetized sample. If the demagnetization were to produce an initial condition other than  $I_z$ , then one expects an entirely different functional dependence for  $S(t_1)$ .

**Echo Experiments.** The effects of residual  $z$  fields on the line widths can be decreased in any of the zero-field experiments described by employing a transverse dc  $\pi$  pulse to form a zero-field echo. Figure 7 shows the results of a  $180^\circ$  refocusing pulse applied in the middle of the evolution period which is illustrated in the demagnetization sequence of Figure 6b. As expected, this variation of the Hahn spin-echo experiment<sup>21</sup> yields decreased line widths



**Figure 6.** Other zero-field experimental field cycles used in the study of liquid crystals. (a) After demagnetization to zero field, dc pulses are used to initiate and terminate the zero-field evolution period  $t_1$ . The zero-field interferogram  $S(t_1)$  is collected after remagnetization to high field. (b) Same field cycle as (a) except that the  $t_1$  period is now divided by a  $180^\circ$  refocusing pulse. This pulse removes the effect of residual field inhomogeneities in the  $z$  direction. (c) Zero-field dc pulse sequence for the production of dipolar order in zero field. The directions of the dc pulsed fields are shown. The sequence  $90^\circ_x - \tau - 45^\circ_y$  takes the initial state of  $I_z$  to one of dipolar and double quantum order in the lab frame. After the delay  $\Delta$ , the  $45^\circ_y$  pulse transforms the state into observable transverse magnetization. Application of a  $90^\circ_x$  pulse and the  $z$  field allows for observation of this evolution as a function of  $t_1$  in high field.



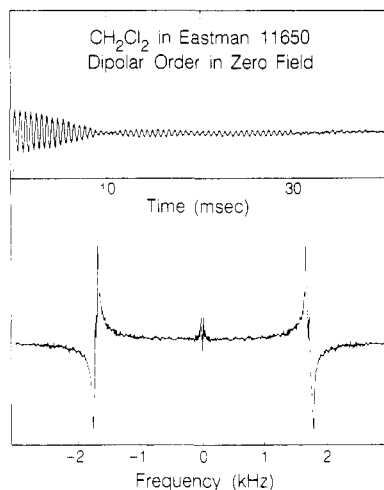
**Figure 7.** Zero-field echo spectrum of  $\text{CH}_2\text{Cl}_2/11650$ . The zero-field spin-echo sequence (Figure 6b) removes the effect of residual fields. Shown is the spectrum with the dc pulse sequence  $90^\circ_y - t_1/2 - 180^\circ_y - t_1/2 - 270^\circ_y$ , where all pulses are applied along the laboratory  $y$  axis. A line width of  $\sim 15$  Hz is obtained. The lines at half the dipolar frequency and zero frequency are artifacts due to dc magnetic field pulse imperfections.

which are measured here as  $\sim 15$  Hz. Lines at half the zero-field frequency appear as artifacts in this echo spectrum and can be accounted for by imperfections in the dc pulses.

**Dipolar and Double Quantum Order in Zero Field.** The zero-field Hamiltonian in the laboratory frame is identical with that of the secular dipolar Hamiltonian in a high-field rotating frame at resonance. With this understanding of the Hamiltonian and behavior of an aligned nematic in zero field, we have attempted application of multiple dc pulse sequences in zero field.

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(21) E. L. Hahn, *Phys. Rev.*, **80**, 580 (1950).



**Figure 8.** Interferogram from the zero-field version of the Jeener–Brokaert<sup>22</sup> experiment using the pulse sequence shown in Figure 6c. The  $\tau$  used in the preparation of dipolar order was 160  $\mu$ s, and the delay  $\Delta$  was chosen to be 20 ms to allow for the decay of any double and single quantum coherences. The sinusoidal appearance of the interferogram,  $S(t_1)$ , is as expected for the conversion by a  $45^\circ_y$  pulse of the dipolar order to observable single quantum coherence. Fourier transformation of the interferogram yields the dispersive zero-field spectrum shown below consisting of lines centered at  $\pm\nu_D$ . The line widths and splittings of the zero-field lines may be attributed to dc pulse imperfections and residual fields.

A zero-field version of the Jeener–Brokaert<sup>22</sup> sequence was performed, but unlike high-field NMR techniques, separate coils were used for each orthogonal pulse direction. By use of the field cycle shown in Figure 6c, the sample was demagnetized to an intermediate field and then suddenly demagnetized to zero field where the pulse sequence  $90^\circ_x - \tau - 45^\circ_y - \Delta - 45^\circ_y - t_1 - 90^\circ_x$  was applied. Immediately after the final  $90^\circ_x$  dc pulse the sample was remagnetized suddenly and the high-field signal recorded as a function of  $t_1$ . The preparation part of the sequence (up until the first  $45^\circ_y$ ) has the effect of creating a density operator given by

$$\rho = \rho_{H_0} + \rho_{DQ} \quad (8)$$

which contains both a dipolar order term and a double quantum term.<sup>23</sup> Methods for the separation of the dipolar order and double quantum terms have been devised for high-field versions of the Jeener–Brokaert experiment,<sup>24</sup> and these phase cycling techniques can in principle be extended to zero field as well. Here the delay  $\Delta$  used in the sequence was chosen to be long enough to allow the double quantum coherence to decay to zero. Accumulation of the high-field magnetization as a function of  $t_1$  yields the interferogram of Figure 8a. As expected, the signal arising from the created dipolar order grows sinusoidally in  $t_1$ . Fourier transformation of the signal produces the spectrum shown in Figure 8b.

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## Conclusions

The molecular order parameter of a  $\text{CH}_2\text{Cl}_2/11650$  nematic liquid crystal sample has been measured in high and zero field and has been found to be the same in both cases and does not differ by more than an experimental error of 2%. Several conclusions can be reached based on the frequencies and intensities in the zero-field spectra, and the apparent dependence of the signal on the dc pulses used. Due to the short duration and relatively low fields used for the dc magnetic field pulses, only the spin states are perturbed and not the spatial ordering of the liquid crystal molecules. Most notably, we observe that the  $\text{CH}_2\text{Cl}_2/11650$  system studied does not disorder in low ( $\leq 200$  G) or zero fields in times on the order of 10–500 ms. The zero-field spectra are indicative of an aligned system and show no change in the order parameter from high field. Experimental evidence<sup>25</sup> suggests that fields of the order of 1 kG need be applied to change the alignment of the molecules in a time on the order of seconds. On that basis nematic liquid crystals may be expected to remain aligned in zero field on relatively long time scales, unless some perturbation such as the application of an appropriately large field causes more rapid reorientation of the sample.

We note as an experimental verification of the stability of the sample under field cycling conditions that no appreciable change was found in the high-field spectrum and order parameter after demagnetization and immediate remagnetization. The possibility of complete disordering and subsequent reordering in the time of the field cycle is ruled out by the results of these zero-field experiments.

In general, demagnetization experiments of nonoriented samples are expected to produce initial conditions other than  $I_z$ . However, due to the unchanged ordering and molecular motions of the  $\text{CH}_2\text{Cl}_2$ /nematic system in the demagnetization experiment, the magnetization remains quantized along the lab  $z$  axis. Thus, demagnetization experiments on the nematic system produce an initial condition no different than that in experiments utilizing an intermediate field to maintain the spin order. Direct current pulses applied along various directions of the laboratory frame may then be successfully used to produce a new spin order. This encourages further applications of composite pulses,<sup>26</sup> decoupling sequences, and other multiple pulse techniques in zero field. Extensions are under way to use zero-field NMR for the study of more complex systems such as smectics, discotics, and lyotropics which do not order uniformly in an applied field. High-field studies of these materials are hindered due to orientational disorder and thus might be usefully studied in zero field.

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