

## Heteronuclear Zero-Field NMR of Liquid Crystals

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Heteronuclear spin systems in solids have previously been studied by zero-field NMR (1, 2). Inequivalent nuclear spins (e.g.,  $^{13}\text{C}$ - $^1\text{H}$ ) behave identically to homonuclear spins (e.g.,  $^1\text{H}$ - $^1\text{H}$ ) except that they can be independently manipulated in high and zero fields (2, 3). In combination with anisotropic liquid crystal solvents, such spin systems often produce interesting and unexpected features in the zero-field NMR spectra. This paper presents the simplest case of an I-S (I =  $^1\text{H}$ , S =  $^{13}\text{C}$ ) spin pair in nematic and smectic liquid crystalline phases, the latter displaying the effects of small asymmetries.

A comparison between the high- and zero-field NMR Hamiltonians illustrates a few of the relevant features of heteronuclear spin systems in zero field. For a  $^{13}\text{C}$ - $^1\text{H}$  pair, the high-field NMR Hamiltonian in a uniaxial phase may be written as

$$\mathcal{H}_{\text{HF}}^0 = -\omega_I I_z - \omega_S S_z - \frac{\gamma_I \gamma_S \hbar \mathbf{S}}{2r^3} (2I_z S_z) (3 \cos^2 \theta - 1) - J I_z S_z, \quad [1]$$

where  $\mathbf{S} = 1/2 \langle 3 \cos^2 \beta - 1 \rangle$  is the order parameter, scaling only the dipolar interaction and describing the relative alignment of the I-S internuclear vector and the liquid crystal director frame (4). The term containing  $\theta$  relates the liquid crystalline director frame to the laboratory frame. A high-field spectrum will show the usual dipolar doublet pattern with a peak separation corresponding to

$$\begin{aligned} \Delta\omega &= 2\mathbf{S}\omega_D + J & \text{for } \Delta\chi > 0, \theta = 0^\circ \\ \Delta\omega &= \mathbf{S}\omega_D - J & \text{for } \Delta\chi < 0, \theta = 90^\circ \end{aligned} \quad [2]$$

and  $\omega_D = \gamma_I \gamma_S \hbar / r^3$ . Thus one can see how liquid crystals with differing magnetic susceptibility anisotropies,  $\Delta\chi$ , can be used to differentiate between the contributions of  $J$  and  $\omega_D$  in the spectra (5).

The high-field Hamiltonian contains only the secular terms of the dipolar and indirect couplings. Since there are no Zeeman energy differences in zero field, the I and S spins

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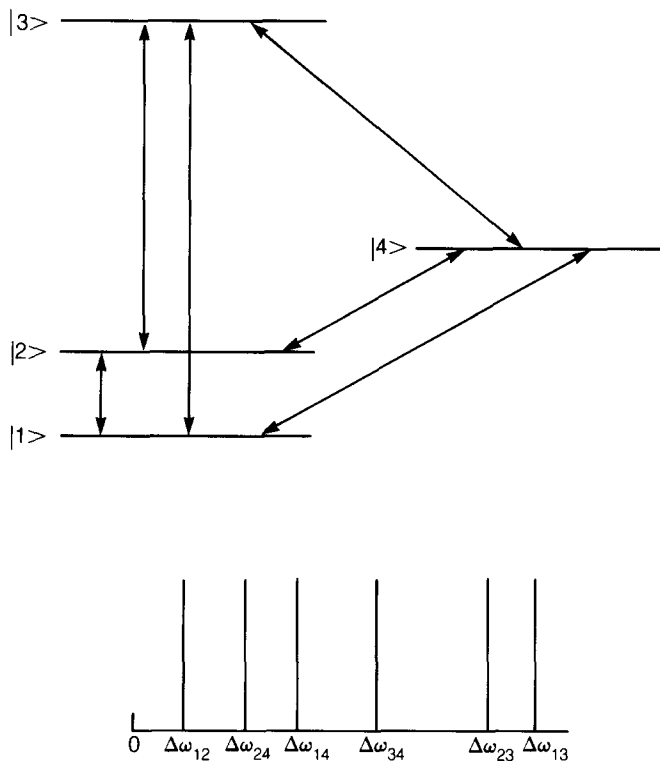


FIG. 1. Zero-field energy levels and allowed zero-field NMR transitions for a pair of I-S spins ( $I = {}^1\text{H}$ ,  $S = {}^{13}\text{C}$ ). The most general scheme with  $\eta \neq 0$  is illustrated based on the Hamiltonian given as Eq. [3] in the text. The eigenstates are linear combinations of the two spin product states and consist of  $|1\rangle = 2^{-1/2}(|\alpha\alpha\rangle + |\beta\beta\rangle)$ ,  $|2\rangle = -i2^{-1/2}(|\alpha\alpha\rangle - |\beta\beta\rangle)$ ,  $|3\rangle = 2^{-1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle)$ , and  $|4\rangle = 2^{-1/2}(|\alpha\beta\rangle - |\beta\alpha\rangle)$ . The energies depend upon the indirect coupling constant,  $J$ , and the dipolar coupling ( $\omega_D = \gamma_I\gamma_S\hbar/r^3$ ) scaled by the liquid crystal order parameter,  $S$ . The asymmetry in the dipolar coupling ( $\eta \neq 0$ ) removes the degeneracy of eigenstates 1 and 2 resulting in six allowed transitions. When  $\eta = 0$ , levels 1 and 2 are degenerate, thus introducing a zero-frequency transition and reducing the total number to four.

are identical with respect to exchange and additional terms in the Hamiltonian become energy conserving. For the general case in zero field, the Hamiltonian is then written as

$$\mathcal{H}_{\text{ZF}} = -\frac{\gamma_I\gamma_S\hbar S}{r^3}(3I_zS_z - \mathbf{I} \cdot \mathbf{S} + \eta(I_xS_x - I_yS_y)) - J\mathbf{I} \cdot \mathbf{S}, \quad [3]$$

where  $x$ ,  $y$ , and  $z$  refer to a molecular-based frame. The full  $J$  coupling (except anisotropic terms) and dipolar coupling, including a possible asymmetry,  $\eta$ , are now included. Truncation of the Hamiltonian by the allowed motions in the liquid crystalline environment retains the same terms as for the homonuclear case (6, 7). The eigenstates, energy levels, and allowed transitions for the Hamiltonian of Eq. [3] are shown in Fig. 1 for the energies given below

$$\begin{aligned}
 E_1 &= -\frac{S\omega_D}{2}(1+\eta) - \frac{J}{4} \\
 E_2 &= -\frac{S\omega_D}{2}(1-\eta) - \frac{J}{4} \\
 E_3 &= S\omega_D - \frac{J}{4} \\
 E_4 &= \frac{3}{4}J.
 \end{aligned}
 \tag{4}$$

Note that, unlike the homonuclear case, transitions are now allowed between the singlet and triplet energy levels (2).

The zero-field NMR spectra of probe molecules, which consisted of two spin homonuclear systems, in several different liquid crystal solvents have previously been reported (6, 7). To detect signal in zero field ( $I$ ), the sample is adiabatically demagnetized to an intermediate field. The sudden removal of this field initiates evolution at the dipolar frequencies if the initial condition does not commute with the zero-field Hamiltonian. The sample is then remagnetized and the signal is detected as a function of time spent in zero field. In order to produce dipolar signal in an aligned nematic with  $\Delta\chi > 0$ , dc field pulses are required (6, 7) to produce a different initial state. This can be attributed to the symmetry of the homonuclear dipolar Hamiltonian in zero field and the initial state of magnetization prepared in high field (i.e., they commute) (6).

In the high temperature limit, the equilibrium initial condition for an I-S spin pair may be written as the reduced laboratory frame density matrix

$$\rho(0) \sim aI_z + bS_z, \tag{5}$$

in which the coefficients  $a$  and  $b$  represent the relative polarizations of I and S spins. If the liquid crystal is aligned with the director axes along the laboratory  $z$  axis ( $\Delta\chi > 0$ ), the molecular and laboratory frames in Eqs. [3] and [5], respectively, are coincident. For  $a = b$ , the commutator is

$$[\rho(0), \mathcal{H}_{ZF}] = 0 \tag{6}$$

and no signal results. This is identical to a homonuclear case, as the I and S spins are indistinguishable spin  $I = 1/2$  nuclei in zero field. Since the coefficient  $a$  is generally not equal to  $b$ , but rather  $b \approx a/4$  for equilibrium polarizations, it can easily be shown that the initial condition for a heteronuclear pair does not commute and evolution will occur.

For other relative orientations of the director and lab frames and values of the coefficients, zero-field evolution is initiated in all situations. The normalized signal can be calculated for an arbitrary orientation of director frame, described by the angles  $\theta$  and  $\phi$  with respect to the laboratory  $z$  axis, from

$$S(t) = \text{Tr}\{RI_zR^{-1}\exp(-i\mathcal{H}_{ZF}t)R(aI_z + bS_z)R^{-1}\exp(i\mathcal{H}_{ZF}t)\} \tag{7}$$

in which the detected operator is  $I_z$  and  $R = \exp(-i\phi I_z)\exp(-i\theta I_y)$ . For any single orientation of director with  $\eta = 0$  this reduces to

$$S(t) = N \left\{ (a+b)\cos^2\theta + (a-b)\sin^2\theta \cos\left(\frac{1}{2}S\omega_D + J\right)t \right. \\ \left. + (a-b)\cos^2\theta \cos(S\omega_D - J)t + (a+b)\sin^2\theta \cos\left(\frac{3}{2}S\omega_D\right)t \right\}, \quad [8]$$

where  $\omega_D = \gamma_I\gamma_S\hbar/r^3$  and  $N$  is a normalization constant. The angular factor depends on a single value of  $\theta$  for a liquid crystal sample which remains uniformly aligned in zero field. For example, nematic liquid crystals with  $\Delta\chi > 0$  will have  $\theta = 0^\circ$  and Eq. [8] becomes

$$S(t) = N \left\{ (a+b) + (a-b)\cos(S\omega_D - J)t \right\}. \quad [9]$$

Similarly, for a nematic liquid crystal with  $\Delta\chi < 0$  the angle of alignment with respect to the laboratory  $z$  axis is  $90^\circ$  and

$$S(t) = N \left\{ (a-b)\cos\left(\frac{1}{2}S\omega_D + J\right)t + (a+b)\cos\left(\frac{3}{2}S\omega_D\right)t \right\}. \quad [10]$$

Experimentally this means that separate transitions of the heteronuclear spin manifold will be selected by the ordering of the liquid crystal matrix. Spectra of  $^{13}\text{CHCl}_3$  in nematic phases with  $\Delta\chi > 0$  and  $\Delta\chi < 0$  are shown in Fig. 2 and demonstrate this effect. The order parameter can be calculated from the spectrum using values of  $J = +0.210$  kHz (8, 9) and  $r = 1.073$  Å (10) yielding values of  $S = 0.115 \pm 0.001$  ( $\Delta\chi > 0$ ) and  $S = 0.083 \pm 0.001$  ( $\Delta\chi < 0$ ) for the two nematics. These values are identical to those calculated from the splittings measured in high field with  $S = 0.115 \pm 0.001$  and  $S = 0.082 \pm 0.001$ , respectively.

Nonaligned samples, such as smectic B (axially symmetric) and E (nonaxially symmetric) (11), have a distribution of director orientations, and describing the signal in these cases requires that Eq. [8] be averaged over the angle  $\theta$ . An axially symmetric heteronuclear dipolar coupling ( $\eta = 0$ ) produces the spectrum shown in Fig. 3 and the signal is given by the normalized expression

$$S(t) = N \left\{ (a+b) + 2(a-b)\cos\left(\frac{1}{2}S\omega_D + J\right)t \right. \\ \left. + (a-b)\cos(S\omega_D - J)t + 2(a+b)\cos\left(\frac{3}{2}S\omega_D\right)t \right\}. \quad [11]$$

Due to the symmetry effects of the liquid crystalline phase, the Hamiltonian may be nonaxially symmetric ( $\eta \neq 0$ ) (11, 12). This asymmetry lifts the degeneracy of the two lowest energy levels and increases the number of peaks in the spectrum such that

$$S(t) = N \left\{ (a+b)\cos(S\omega_D\eta)t + (a-b)\cos\left(\frac{1}{2}S\omega_D(1-\eta) + J\right)t \right. \\ \left. + (a-b)\cos\left(\frac{1}{2}S\omega_D(1+\eta) + J\right)t + (a-b)\cos(S\omega_D - J)t \right. \\ \left. + (a+b)\cos(S\omega_D(3-\eta)/2)t + (a+b)\cos(S\omega_D(3+\eta)/2)t \right\}. \quad [12]$$

The spectrum of a nonaxially symmetric dipolar coupled I-S pair is shown in Fig. 4. This spectrum illustrates the most general form of the heteronuclear dipolar Hamiltonian for two spins as all possible transitions in the singlet-triplet manifold are present.

An interesting result arises when calculating the order parameter for the smectic B and E cases. In order to account for the frequencies in the spectrum, the sign of  $S$

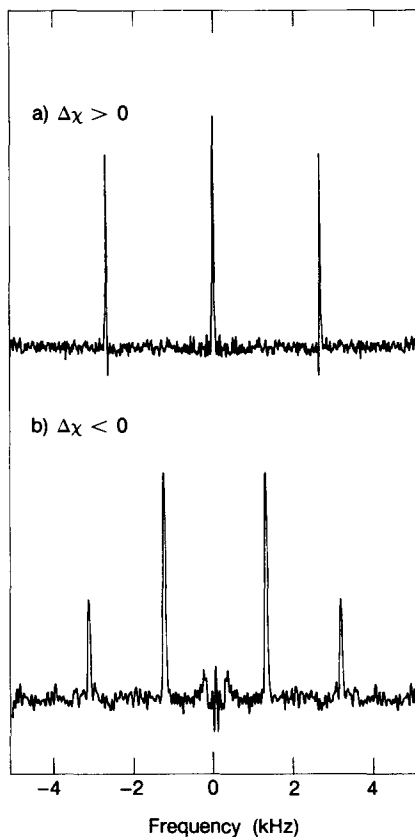


FIG. 2. Zero-field NMR spectra of a  $^{13}\text{C}$ - $^1\text{H}$  pair in nematic liquid crystals. (a)  $^{13}\text{CHCl}_3$  (6 wt%) in EBBA (*p*-ethoxybenzylidene *p*-butylaniline,  $\Delta\chi > 0$ ). Zero-field signal results after the transition to zero field with lines corresponding to  $\Delta\omega_{12}$  and  $\Delta\omega_{34}$  of Fig. 1 and Eq. [9]. The calculated value of the order parameter is  $S = 0.118 \pm 0.001$ . (b)  $^{13}\text{CHCl}_3$  (6 wt%) in ZLI 1167 (a mixture of propyl-, pentyl-, and bicyclohexylcarbonitriles,  $\Delta\chi < 0$ ). The spectrum shows the other possible transitions in the singlet/triplet manifold ( $\Delta\omega_{14} = \Delta\omega_{24}$  and  $\Delta\omega_{13} = \Delta\omega_{23}$  for  $\eta = 0$  in Fig. 1.) The order parameter was found to be  $S = 0.084 \pm 0.001$ .

must be negative for the proper relationship of the dipolar and  $J$  coupling terms. The order parameters for the smectic phases are then  $S = -0.080 \pm 0.001$  and  $S = -0.062 \pm 0.001$  for smectic B and E, respectively, with an asymmetry parameter of  $\eta = 0.186 \pm 0.002$  in the latter. This change in sign is most likely indicative of a different average angle of alignment, either greater or less than the magic angle, between nematic and smectic phases.

Although small solute molecules do not align to a very high degree, as illustrated by the small values of the order parameters, they are still sensitive measures of the ordering and symmetry properties of the liquid crystalline phases. The zero-field NMR spectra of simple heteronuclear spin systems have demonstrated the diversity in appearance of the spectra for different phases and have proved valuable in experiments

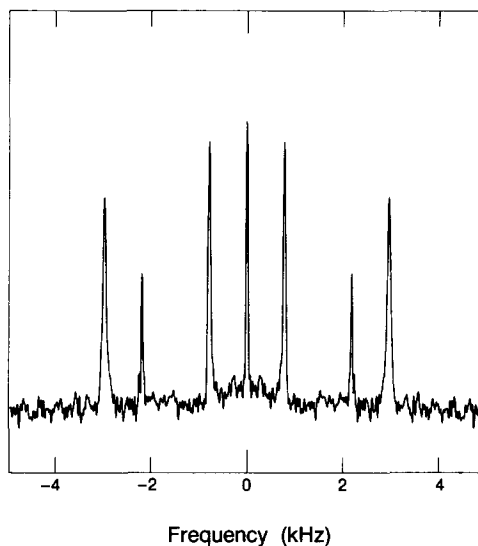


FIG. 3.  $^{13}\text{CHCl}_3$  in smectic B phase liquid crystal ( $\sim 8$  wt% in a 60:40 wt% mixture of 4-*n*-butyloxybenzylidene-4'-*n*-octylaniline and 4-*n*-octyloxycyanobiphenyl). The seven peaks correspond to the transitions with  $\eta = 0$  of  $\Delta\omega_{12}$ ,  $\pm\Delta\omega_{13} = \Delta\omega_{23}$ ,  $\pm\Delta\omega_{34}$ , and  $\pm\Delta\omega_{14} = \Delta\omega_{24}$  between the triplet and singlet energy levels. In order to account for the positions of the peaks in the experimental spectrum the relative sign of  $S$  in Eq. [9] must be changed. The calculated value of  $S$  is found to be  $-0.080 \pm 0.001$ .

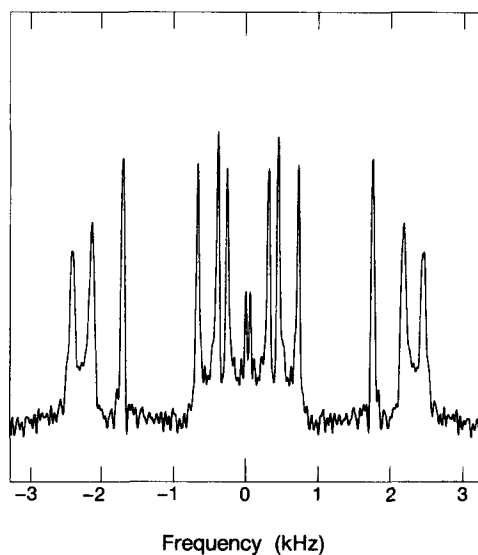


FIG. 4.  $^{13}\text{CHCl}_3$  in smectic E phase liquid crystal ( $\sim 10$  wt% in a 50:50 wt% mixture of 4-*n*-butyloxybenzylidene-4'-*n*-octylaniline and 4-*n*-octyloxycyanobiphenyl) with a nonaxially symmetric dipolar coupling ( $\eta \neq 0$ ). The 12 peaks in the spectrum correspond to all the possible allowed transitions in the singlet/triplet manifold for two spins. The order parameter was found to have a negative value of  $S = -0.063 \pm 0.001$  and an asymmetry parameter of  $\eta = 0.186 \pm 0.002$ .

on isotope selectivity in zero-field NMR with composite pulses (3). In addition, they also demonstrate the sensitivity of the zero-field NMR spectra to the symmetry of the phase (12).

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## REFERENCES

1. D. B. ZAX, A. BIELECKI, K. W. ZILM, A. PINES, AND D. P. WEITEKAMP, *J. Chem. Phys.* **83**, 4877 (1983); A. PINES, Lectures on Pulsed NMR, Proceedings of the 100th Fermi School on Physics (B. Maraviglia, Ed.), in press.
2. D. B. ZAX, A. BIELECKI, K. W. ZILM, AND A. PINES, *Chem. Phys. Lett.* **106**, 550 (1984).
3. A. M. THAYER AND A. PINES, *J. Magn. Reson.* **70**, 518 (1986).
4. P. G. DE GENNES, "The Physics of Liquid Crystals," Clarendon, Oxford, 1974.
5. C. L. KHETRAPAL AND A. C. KUNWAR, *Isr. J. Chem.* **23**, 229 (1983).
6. A. M. THAYER, J. M. MILLAR, M. LUZAR, T. P. JARVIE, AND A. PINES, *J. Phys. Chem.* **90**, 1577 (1986).
7. A. M. THAYER, M. LUZAR, AND A. PINES, *Mol. Phys.*, in press.
8. P. K. BHATTACHARYYA AND B. P. DAILEY, *J. Magn. Reson.* **12**, 36 (1973).
9. J. R. EVERETT, *J. Chem. Soc. Perkin Trans. 2* **7**, 1151 (1984).
10. S. N. GHOSH, R. TRAMBARULO, AND W. GORDY, *J. Chem. Phys.* **31**, 1471 (1959).
11. N. A. VAZ, M. J. VAZ, AND J. W. DOANE, *Phys. Rev. A* **30**, 1008 (1984).
12. M. LUZAR, A. M. THAYER, AND A. PINES, *Liq. Cryst.*, in press.