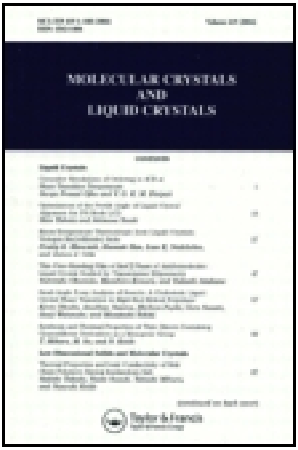

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Pure-Dipolar Nuclear Spin-Lattice Relaxation in Nematic Liquid Crystals†

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A technique is described for exploiting the large nuclear dipole-dipole interactions in nematic liquid crystals to study the details of the spin-lattice relaxation mechanisms, including cross relaxation effects. This technique provides a means for selectively preparing the magnetization in such a way as to enhance the relative contribution of a selected group of spins. Data illustrating this technique are presented for the nematic phase of MBBA. Further, the orientational dependence of the pure-dipolar spin-lattice relaxation time T_{1D} for MBBA is shown to be similar to that of the laboratory frame spin-lattice relaxation time T_1 and markedly different from the orientational dependence of the rotating-frame spin-lattice relaxation time $T_{1\rho}$.

INTRODUCTION

The strong nuclear dipole-dipole interaction present in liquid crystals may be exploited to provide a variety of information about molecular orientation, order, and motions in these systems. For example, nuclear magnetic resonance spectra yield information about the orientation of liquid crystal molecules with respect to the applied magnetic field used in the resonance experiment,[1] while the frequency, temperature, and orientational dependences of both the laboratory-frame and the rotating-frame nuclear spin-lattice relaxation times have been used to probe molecular motions in liquid crystals.[2,3] In this paper we propose a method of exploring the time evolution of the nuclear dipolar order to determine the relative importance of the inter-molecular and intra-molecular contributions to nuclear spin-lattice relaxation in nematic liquid crystals. These techniques should also be

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applicable to the study of other systems exhibiting large dipole-dipole interactions.

PREPARATION OF DIPOLAR ORDER

In a typical magnetic resonance experiment the energy associated with the dipolar ordering arising from the local field is much smaller than the Zeeman energy associated with the coupling of the spins to the external magnetic field. Nonetheless, studies of dipolar order have been very important in a variety of studies, particularly those involving very slow molecular motions. Because the local fields are so small in most systems (e.g. three or four gauss, maximum, for a typical nematic liquid crystal) it is usually impossible to observe dipolar order directly. As a result, several schemes have been developed that take advantage of the much larger Zeeman order and transform this order into observable dipolar order. For example, ultraslow atomic motions have been studied by adiabatic demagnetization in an r.f. field rotating at the Larmor frequency.[4,5] A similar transformation of Zeeman to dipolar order may be accomplished with a sequence of properly phased r.f. pulses. This technique proposed by Jeener and Broekaert[6–8] has been applied to investigate the thermodynamic behaviour of spin systems in solids.[9] It is this latter technique that we propose to apply to the study of liquid crystals.

The Jeener-Broekaert pulse sequence consists of a pair of pulses which prepare the spin system in such a way as to transfer Zeeman order to dipolar order, followed by a third pulse which provides a means of observing the dipolar order produced. The first pulse of the initial pair is a 90° pulse followed at a time τ by a short pulse of precession angle θ phase-shifted by 90° with respect to the first pulse. Following Jeener-Broekaert, this pulse sequence may be donated as a $90^\circ_x - \tau - \theta_y$ sequence. The pulse separation τ is less than the duration of the Zeeman free induction decay. After a delay t which is greater than several times the spin-spin relaxation time T_2, the various components of the spin system will each have reached internal equilibrium, and a third pulse ϕ with the same phase as the initial 90° pulse provides a dipolar echo whose amplitude is a measure of the dipolar order produced. A maximum echo amplitude is obtained for $\theta = \phi = 45°$. Thus, the basic Jeener-Broekaert pulse sequence is $90^\circ_x - \tau - 45^\circ_y - t - 45^\circ_x$. As the dipolar order decays through pure dipolar spin-lattice relaxation in the local field, the Zeeman magnetization also then returns to equilibrium in the external magnetic field. Because of the phase relationship between the pulses, the dipolar echo following the third pulse and a free induction decay due to any Zeeman magnetization at time t are simultaneously observable using two phase-sensitive detectors in quadrature.

Two properties of the signal following the third pulse in a Jeener-Broekaert sequence are of particular importance to its application to the study of liquid crystals. First, the efficiency of the transfer of Zeeman to dipolar order is proportional to the time derivative of the free induction decay at time τ. Second, the echo following the third pulse is the time derivative of a "theoretical" Zeeman free induction decay.[8] To be more specific, in the case of a simple single spin system, the amplitude of the echo (for fixed τ) as a function of t would yield a measure of the pure dipolar relaxation time T_{1D}, while the time integral of the echo would produce a signal proportional to the Zeeman free induction decay.

APPLICATION TO LIQUID CRYSTALS

A rather more complicated situation arises if we consider the dipolar echo produced in an ordered nematic. In order to understand what is observed let us simplify the problem by assuming that there are only two subsets of spins producing the NMR signal, namely those associated with aromatic rings whose para-axes are approximately parallel to the molecular axis and spins associated with alkyl end chains. Further, let us assume that the observed proton NMR spectrum consists only of a motionally averaged center peak at the Larmor frequency ω_0 due to the end-chains and a pair of peaks at $\omega_0 \pm \delta\omega$ arising from the phenyl protons (see Figure 1(a). The Zeeman free induction decay $F(\tau)$ is the Fourier transform[10] of the absorption spectrum, and will be modulated as shown in Figure 1(b). Assuming for simplicity that each group of spins contains equal numbers of spins and that each of the three peaks in the absorption spectrum has the same shape, then the free induction decay will be the sum of two functions (e.g. two Gaussians). Denoting the free induction decay function arising from the Fourier transform of the center peak in the absorption spectrum by $f(\tau)$, then the free induction decay will be given by: $F(\tau) = f(\tau) + f(\tau)\cos(\delta\omega\tau)$. These two components are indicated in Figure 1(c) and (d).

Note that the two components of the free induction decay associated with the two spin sub-systems have different time derivatives. Recalling that the efficiency of transforming Zeeman to dipolar order is proportional to the derivative at time τ of the free induction decay, we see that it is possible to selectively transfer order associated with the end-chains, while relatively suppressing the transfer of order associated with the aromatic rings. In particular, there exist zero derivatives of the free induction decay associated with the latter for times τ at which the derivative of the end-chain free induction decay is non-zero. We may take advantage of this fact to probe several interesting properties of liquid crystals.

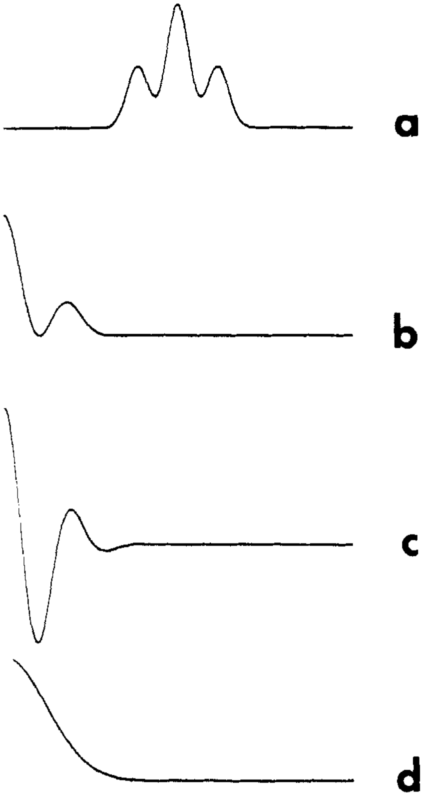

FIGURE 1 Magnetic resonance signals for a model liquid crystal compound with equal numbers of spins on alkyl chains and on aromatic sites. (a) Proton NMR spectrum. (b) Composite free induction decay corresponding to (a) (c) Portion of free induction decay associated with spins on alkyl chain sites. (d) Portion of free induction decay due to spins on aromatic sites. Note that (b) is the normalized sum of (c) and (d), and that (a) is the Fourier transform of (b).

Selective transfer of dipolar order

The proton free induction decay in the nematic phase of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) is rather similar to that for the simple model shown in Figure 1. The MBBA free induction decay shows several crossing points and has several easily observable zeroes in its derivative at τ's near multiples of 60 μsec. In order to test the method described above, dipolar echoes following a Jeener-Broekaert pulse sequence were recorded for a variety of initial pulse separations τ. To minimize the effects of cross relaxation, the delay t between the second and third pulses was kept as short as possible (500–1000 μsec, i.e. several times the spin-spin relaxation time

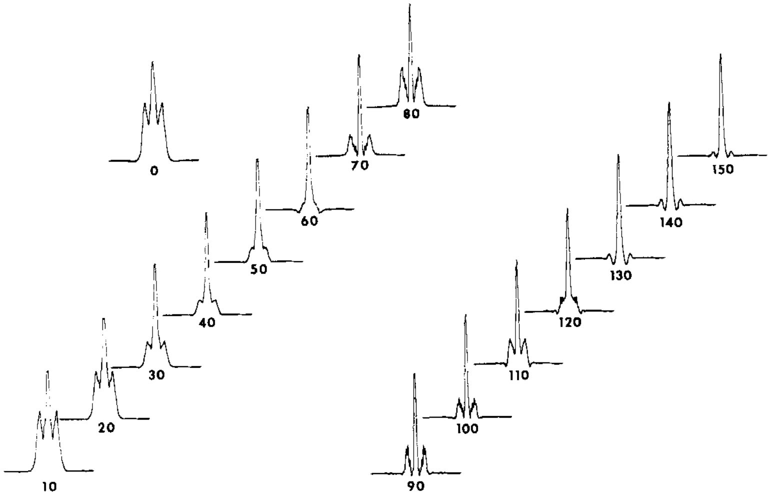

FIGURE 2 Fourier transforms of time integrals of dipolar echoes following a Jeener–Broekaert pulse sequence. Numbers below spectra indicate delay time τ in μsec between first and second pulses (see text). The spectrum labelled 0 is the ordinary NMR spectrum. All data are for MBBA at 23 C.

T_2). The echoes were signal averaged to improve the signal-to-noise ratio and then integrated to produce a free induction decay which was a weighted sum of the Zeeman free induction decays associated with the several spin sub-systems. Following suitable base correction and apodization, these free induction decay signals were Fourier transformed to produce spectra whose components were again weighted sums of the absorption spectra associated with the spin sub-systems. If there were negligible interactions between the spin sub-systems, such component spectra could be observed for selectively isotopically substituted molecules.

The results of these measurements are shown in Figure 2. It is interesting to note that there are minima in the relative intensities of the side peaks for τ's near multiples of $\sim 60\,\mu$sec as expected. Further, it was noted that the sign of the dipolar echo alternated between extrema in the free induction decay, as expected.

Pure dipolar spin-lattice relaxation

If the initial pulse separation time τ is fixed, then the time (t) dependence of the dipolar echo following the third pulse in the Jeener-Broekaert sequence gives a measure of the pure-dipolar spin-lattice relaxation time T_{1D}. If the relaxation mechanisms associated with the spin sub-systems are the same, or, alternatively, if the cross relaxation between them is rapid compared to T_{1D}, then we might assume that the behaviour of T_{1D} would be similar to that of the laboratory frame spin-lattice relaxation time T_1. One should expect to find such behaviour for nematic liquid crystals exhibiting a single exponential T_1. In particular, the orientational dependence of T_{1D} was measured in MBBA at a frequency of 10 MHz. This low frequency (and hence low magnetic field) was used to permit good alignment of the sample by relatively low (4 kV/cm) electric fields. The observed relaxation was exponential within experimental error, and the orientational dependence (Figure 3) was seen to be quite small and similar to that for the orientational dependence of the laboratory-frame spin-lattice relaxation time T_1 and quite different from that of the rotating-frame relaxation time for MBBA.[3]

Cross relaxation effects

If the relaxation rates of the spin sub-systems are not the same and if the cross relaxation between them is not fast compared to these rates, then it should be possible to measure both the different relaxation rates and the cross relaxation. To see that this is the case, consider preparing the spin system in such a way that some feature of the spectrum is dominant (e.g. the center line for $\tau \sim 60\ \mu$sec in MBBA in Figure 2). Then by varying the pulse delay t, it should be possible to monitor the decay of the total dipolar order as well as

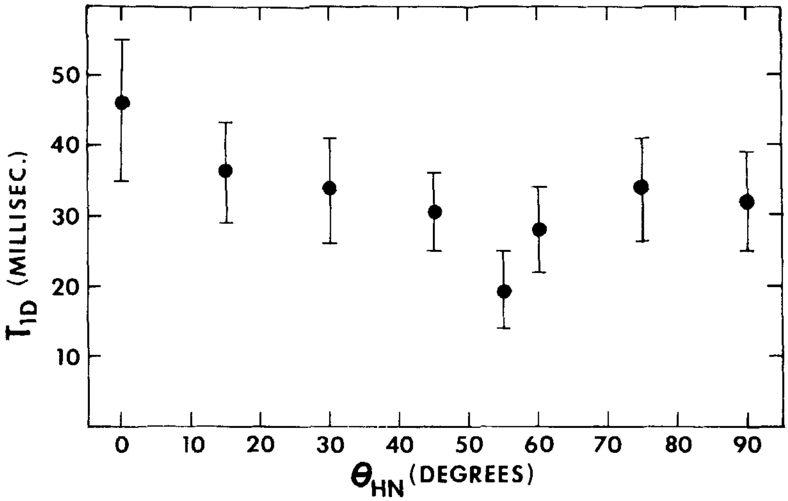

FIGURE 3 Orientational dependence of the proton T_{1D} for MBBA at 10 MHz at a temperature of 23 C. The molecules were oriented with a 5 kHz electric field with an intensity of 4 kV/cm. The angle plotted is that between the applied magnetic field H and the nematic director N.

the redistribution of order via cross relaxation. This requires integrating the dipolar echo, Fourier transforming the resulting free induction decays, and the extracting the relaxation times associated with each peak in the spectrum. Preliminary measurements for *p*-azoxyanisole (PAA) and several of its homologs which show non-exponential spin-lattice relaxation in the laboratory frame indicate that this is feasible. It should be noted that these experiments are difficult and that some care is required to obtain reproducible data.

CONCLUSIONS

In an ordered material such as a nematic liquid crystal which contains several groups of spins exhibiting very different and large nuclear dipole-dipole interactions, it is possible to prepare the spin system in such a way as to enhance the relative contribution to an NMR signal of one spin group with respect to the other(s). This preparation may be exploited to study the spin-lattice relaxation mechanism, including cross relaxation, for such systems. Further applications of these techniques to liquid crystals and other materials are currently underway in our laboratory.

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