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PROTON SPIN-LATTICE RELAXATION IN LIQUID CRYSTALS*

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Measurements of spin-lattice relaxation in nematic and smectic liquid crystals are contrasted to recent theoretical predictions for T_1 in these phases.

The unusual thermal behavior of the molecules in nematic liquid crystals has been known for some time and has aroused the interest of several investigators.[1] Only recently, however, has it been recognized that this motion has an influence on the spin-lattice relaxation time T_1. Weger and Cabane[2] reported an unusual frequency dependence of $\nu^{1/2}$ for T_1 in the nematic phase for p-azoxyanisole (PAA). Pincus[3] was able to account for this dependence by considering the dipole interaction between two nuclear spins modulated by small fluctuations in the nematic order. These calculations were later extended by Blinc et al.[4] to include magnetic field effects on the thermal fluctuations. These calculations gave a linear frequency dependence for T_1 which seemed to agree with their measurements of spin-lattice relaxation in the rotating frame $T_{1\rho}$. This result would not, in general, be expected since the influence of magnetic fields of moderate strength on thermal fluctuations is believed[3] to be negligible and has been observed to be small in the case of birefringence studies.[1]

In this paper we present measurements of T_1 versus temperature, frequency, and molecular orientation in PAA and 4, 4′-bis-(heptyloxy)azoxybenzene (HAB). The results are discussed in terms of the above theories and the inadequacies of these theories are pointed out.

The nematic liquid-crystalline state is distinguished from the normal liquid state in that the rodlike molecules on the average align parallel to some preferred direction. In moderate magnetic fields the direction of preferred orientation is established by the direction of the field. The mean orientation of a rigid molecule relative to its preferred direction must in general be described by a tensor quantity. The elongated molecules typical of most nematic systems, however, possess a pseudoaxial symmetry and the order is adequately described by the scalar $S = \frac{1}{2}\langle 3\cos^2\xi - 1\rangle$, where ξ is the angle between the long axis of the molecule and its preferred direction of alignment, and where the brackets indicate a time average. This value of S has been observed to vary from 0.7 to 0.3 as the liquid crystal is heated through the nematic range. The thermal fluctuations in the orientation of the molecule are therefore quite large, ~20 to 40°, throughout the nematic range. It is this nematic order which is responsible for the contrasting behavior in the thermal motion of the molecules observed in nematic liquid crystals to that observed in normal liquids. As an example, dielectric relaxation studies[5] show a dispersion in the radio frequency region which has been interpreted in terms of the motions of the long axis of the molecules about their preferred direction of alignment. Another classic example of the unusual thermal behavior is the strong scattering of

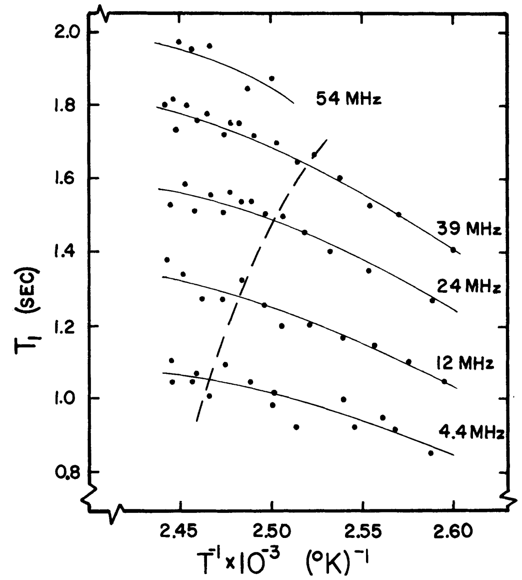

FIG. 1. Temperature dependence of spin-lattice relaxation in *p*-azoxyanisole at frequencies 4.4, 12, 24, 39, and 54 MHz. The solid lines are traces through the experimental points to distinguish those corresponding to each frequency. The dashed line is the predicted temperature dependence fitted to T_1 at $\nu = 24$ MHz and $T^{-1} = 2.50 \times 10^{-3}$/°K.

light from nematic liquids.[6] Theoretical treatments of the problems have varied depending upon the observations to be explained. Calculations of spin-lattice relaxation have been based on the continuum[7] theory. This theory assumes that the direction of molecular orientation varies continuously throughout the nematic liquid. The free energy resulting from deviation in this direction can be calculated in terms of deformation constants. The spectrum of the thermal fluctuations based upon this model have been calculated.

An application of the theoretical treatments to spin-lattice relaxation is nontrivial. Estimates have been made by calculating the fluctuating magnetic dipole-dipole interaction between two nuclear spins. In particular, Pincus[3] has shown that an estimate to the problem can be made if one chooses as a model a nearly perfectly ordered liquid crystal, $S \sim 1$, in which the long axis exhibits small fluctuations about its preferred direction of orientation. Based upon a description of these fluctuations in terms of the continuum model, Pincus calculated T_1 for the case where the internuclear vector is parallel to the molecular axis and hence to the magnetic field. In this case Pincus obtains

$$T_1^{-1} = \omega_D^2 (kT/K)[\omega(D + K/\eta)]^{-1/2}, \tag{1}$$

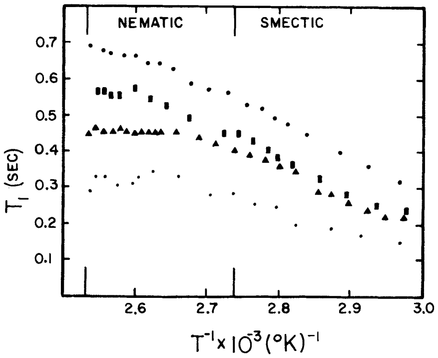

FIG. 2. Spin-lattice relaxation in 4,4′-bis-(heptyloxy)azoxybenzene versus reciprocal temperature at the following frequencies: 39 MHz (large dots), 24 MHz (rectangles), 12 MHz (triangles), and 4 MHz (small dots).

where ω_D^2 is a constant depending upon the strength of the spin-spin interaction, T the absolute temperature, k the Boltzmann constant, K the elastic deformation constant, ω the Larmor precession frequency, D the diffusion constant, and η the viscosity.

Measured values of T_1 plotted versus reciprocal temperature are shown in Fig. 1 for PAA and in Fig. 2 for HAB. The measurements were made with a Bruker model No. B-KR-322S variable-frequency pulsed NMR system. The data were obtained by employing repeated 180°-90° pulse sequences. The samples were prepared from recrystallized compounds and degassed by repeated freezing and melting under vacuum, then sealed in evacuated glass containers. The sample of HAB was further purified by zone refining. Temperatures were measured by a thermocouple immersed in the liquid crystal.

A feature of the curves in Fig. 1 is that they do not at all follow the temperature dependence predicted by Eq. (1). The elastic deformation constant is known to depend upon the degree of molecular order. This dependence has been measured[8] and found to vary as S^2. For the case where diffusion effects are small or when $D \ll K/\eta$, Eq. (1) predicts T_1 to vary as $S^3/T\eta^{1/2}$. The temperature dependence of S and η for PAA can be found in the literature.[1,9] The variation in η is seen to be small relative to that of S^3. These values show Eq. (1) to be an increasing function with reciprocal temperature as is shown by the dashed line in Fig. 1. An improvement is made by considering diffusion to be the most effective term in Eq. (1); however, the agreement is still poor. The character of T_1 in HAB in Fig. 2 is seen to be the same as that in PAA. There is seen to be no measurable change in T_1 as the sample goes from the nematic to the smectic phase. This result is not expected if the value of T_1 is to depend on the deformation constants as it does in Eq. (1).

Orientational studies yield results which are even more disturbing. Measurements of T_1 were made versus the angle between the preferred direction of molecular alignment and the magnetic field. These were made in the smectic phase of HAB. In the case of HAB the preferred axis of orientation aligns parallel to the magnetic field in the nematic phase. As the temperature is lowered and the sample goes into the smectic phase, the preferred direction is maintained while a planar structure is formed characteristic of the smectic *C* classification. While in this phase the preferred direction is "frozen" in and can be altered relative to the magnetic field by rotating the sample.[10] This can be observed by measuring the transverse relaxation time at various sample orientations. The induction decay following a 90° pulse is not a simple exponential since the absorption line shows a complicated structure. The initial part of the decay, however, approximates an exponential with a time constant T_2' proportional to the reciprocal linewidth. As expected,[11] T_2' was found to vary approximately as $|3\cos^2\theta_0 - 1|^{-1}$, where θ_0 is the angle between the preferred axis of orientation and the direction of magnetic field. Such a variation of T_2' was not observed in the nematic phase since θ_0 could not be varied. While in the smectic phase, T_1 was measured at various orientations and its value was not found to vary outside its experimental uncertainty. This result is also not expected if rotational fluctuations in the dipole-dipole interactions are responsible for T_1.[3]

The frequency dependence of T_1 is illustrated in Fig. 3 where T_1 in PAA at 124°C is plotted versus frequency. The solid line shows a variation of $\nu^{1/2}$ as predicted by Eq. (1). The agreement is remarkable, but may be fortuitous in view of the observations above.

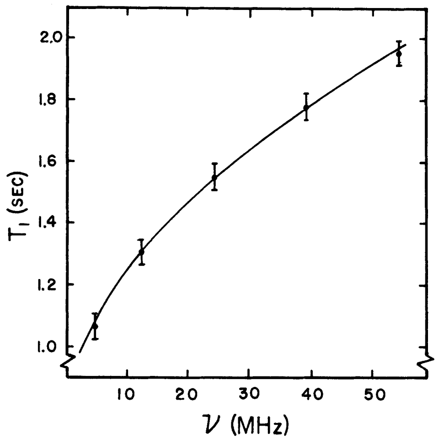

FIG. 3. Frequency dependence of spin-lattice relaxation in *p*-azoxyanisole at 124°C. Solid line is the predicted $\nu^{1/2}$ dependence fitted to the measured values of T_1 at frequencies 12 and 24 MHz.

The results of this work indicate that a development based upon a nearly perfectly ordered molecule exhibiting small fluctuations about its preferred orientation may be too drastic an approximation for the calculation of T_1. The fact that no orientational dependence of T_1 was observed indicates that spin-lattice relaxation may be an intermolecular process rather than an intramolecular one. At any rate, as pointed out by Pincus, the theoretical treatment of T_1 as described here should only be considered an estimate. It cannot be used to infer properties of the liquid-crystalline state.

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