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Proton-spin thermometry at low fields in liquid crystals*

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The relaxation rate, resulting from the order-director fluctuation, of the dipolar energy of benzene proton-spin pairs in a liquid crystal was calculated. For this mechanism the ratio T_1/T_{1D} is 3. Proton-spin–lattice relaxation times, T_1, T_{1X}, and T_{1D}, as well as the transverse and longitudinal magnetization, were measured in the liquid crystals para-octyloxybenzoic acid and para-azoxyanisole (PAA). Since the spins on one liquid-crystal molecule are isolated from spins on other molecules, each molecule represents an independent small ensemble. Although the macroscopic thermodynamics applies to a large sample of these small ensembles, the spin-temperature concept should only be applied to such systems with care. In both liquid crystals, the spin-relaxation processes were analyzed using the concept of spin temperature. It is shown that in PAA the relaxation of Zeeman energy in the rotating frame is influenced by the proton-to-nitrogen relaxation.

I. INTRODUCTION

Recent research into the nuclear-spin magnetic resonance of liquid crystals[1] has produced many NMR absorption (cw) and spin-lattice relaxation data, particularly at high fields.[2-13] These data are reasonably well understood. However, spin-lattice relaxation at low fields (in the rotating frame) is not understood. An attempt is made in this paper to study the relaxation phenomena in nematics at low fields.

The main difficulty encountered was the extent of applicability of the concept of spin temperature[14] in such systems. In most liquid crystals, the molecules undergo very fast translational diffusion, thus effectively isolating the spins on one molecule from other molecules. The spins on individual molecules are isolated from spins on other molecules during heat flow from the spins to the lattice at low fields. Each molecule is therefore an independent small ensemble. Although the macroscopic thermodynamics applies to a large sample of these small ensembles, the establishment of internal semiequilibrium does depend on the size of the small ensembles; that is, on the number of spins in one molecule. Consequently, the spin-temperature concept should only be applied to such systems with care.

Spin-lattice relaxation at low fields and the applicability of the spin-temperature concept was studied in the liquid crystals para-octyloxybenzoic acid (POBA), Fig. 1(a), and para-azoxyanisole (PAA), Fig. 1(b). In POBA the spin-temperature concept does apply, since the fast dissociation of the dimer and the association of molecules for the equilibrium between spins on different molecules, and the spin-lattice relaxation time in low fields are much larger than the spin-spin–lattice relaxation time (T_2). On the other hand, in PAA, where the translational diffusion is fast, although $T_{1\rho}$ is some three orders of magnitude larger than T_2, the spin temperature should be established in a way typical for a small system. In addition, in PAA the spin coupling within one molecule may be too weak for proper establishment of the spin temperature.

The relaxation in low fields was studied in the smectic and nematic phases of POBA and in the nematic phase of PAA. The relaxation time of the dipolar reservoir (T_{1D}) resulting from the order-director fluctuations was calculated for the proton pairs on benzene rings. In the case of PAA, the nitrogen spins had to be considered in order to explain the low-field relaxation. In particular, the value of T_{1D} at high fields, as measured by the Jenner-Broekaert[15,16] method, and the apparent value of T_{1D}, as analyzed from the low-field experiments, are different. This difference is explained by proton-spin relaxation via N^{14} spins.

II. CALCULATION OF RELAXATION TIMES RESULTING FROM THE ORDER-DIRECTOR FLUCTUATIONS

Compounds which exhibit a nematic liquid-crystal phase are usually composed of long (~20 Å) organic molecules [Figs. 1(a) and 1(b)]. In the nematic phase, these long molecules tend to align with one another, yet each molecule is free to translate and rotate around its long axis.[1] That is, the nematic phase shows orientational order; the direction of preferred orientation is designated by the equilibrium order director $\vec{n}_0$. In a typical nematic, the molecules in a given region are tipped nearly randomly by as much as 30° from the axis given by $\vec{n}_0$. In the presence of a strong magnetic field $\vec{H}_0$, the equilibrium order director will lie nearly parallel to $\vec{H}_0$. As a result of thermal fluctuations, the instantaneous order director will not be $\vec{n}_0$ but rather

$$\vec{n}(\vec{r}, t) = \vec{n}_0 + \delta\vec{n}(\vec{r}, t) .$$

The fluctuations $\delta\vec{n}(\vec{r}, t)$ are quite effective in relaxing spins. This theory was originally presented by Pincus.[2] The calculation of the spin-lattice relaxation rate (T_1^{-1}) and of the spin-lattice relaxation rate along the rotating frame field (T_{1X}^{-1}) is known from a previous work.[2,4] The calculation of the dipolar relaxation rate (T_{1D}^{-1}) resulting from the order-director fluctuations is presented here.

The relaxation rates derived below are those for the weak collision limit. That is, the correlation time of the fluctuations τ is much less than T_2, and the time-dependent part of the spin Hamiltonian is a small perturbation.

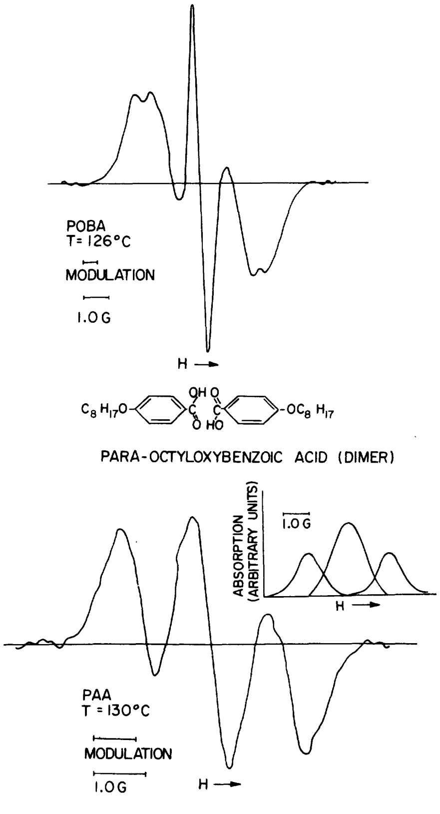

FIG. 1. Typical experimental first derivative of absorption spectrum of (a) nematic POBA at 126 °C and (b) of nematic PAA at 130 °C. The insert shows the integrated absorption spectrum of nematic PAA at 123 °C separated approximately into three components. The central line is due to the CH_3 protons while the outer lines are due to the ring-proton pairs.

In a high magnetic field, the spin Hamiltonian of a nuclear-spin system with only dipole-dipole interactions may be written as

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_D^0 + \mathcal{H}_1(t) ,$$

where $\mathcal{H}_Z$ is the Zeeman term and $\mathcal{H}_D^0$ is the secular part of the dipole-dipole interaction. That is, $\mathcal{H}_D^0$ is that part of the total dipolar Hamiltonian $\mathcal{H}_D$ which commutes with $\mathcal{H}_Z$, and $\mathcal{H}_1(t)$ is a time-dependent perturbation which describes the interaction of the spin system with the lattice.

Then in the second order the spin-lattice relaxation rate is given by[14]

$$\frac{1}{T_1} = \frac{\mathrm{tr}\{\int_0^\infty \langle [\mathcal{H}_Z, \mathcal{H}_1(t)][\mathcal{H}_1^*(t-\tau), \mathcal{H}_Z]\rangle_{\mathrm{av}}\, d\tau\}}{\mathrm{tr}\{\mathcal{H}_Z^2\}} , \tag{1}$$

and the dipolar relaxation rate by

$$\frac{1}{T_{1D}} = \frac{\mathrm{tr}\{\int_0^\infty \langle [\mathcal{H}_D^0, \mathcal{H}_1(t)][\mathcal{H}_1^*(t-\tau), \mathcal{H}_D^0]_{\mathrm{av}}\, d\tau\}}{\mathrm{tr}\{\mathcal{H}_D^{02}\}} , \tag{2}$$

where

$$\mathcal{H}_1^*(t-\tau) = e^{-i(\mathcal{H}_Z + \mathcal{H}_D^0)\tau}\, \mathcal{H}_1(t-\tau) e^{i(\mathcal{H}_Z + \mathcal{H}_D^0)\tau}$$
$$= e^{-i\mathcal{H}_Z\tau} \mathcal{H}_1(t-\tau) e^{i\mathcal{H}_Z\tau} .$$

This is allowed since $\mathcal{H}_D^0 \ll \mathcal{H}_Z$. Similarly, in the rotating reference frame for $\omega_1\tau \ll 1$, the relaxation rate along the field H_1 is given by

$$\frac{1}{T_{1X}} = \frac{\mathrm{tr}\{\int_0^\infty \langle [\mathcal{H}_X, \mathcal{H}(t)][\mathcal{H}_1^*(t-\tau), \mathcal{H}_X]\rangle_{\mathrm{av}}\, d\tau\}}{\mathrm{tr}\{\mathcal{H}_X^2\}} , \tag{3}$$

where $\mathcal{H}_X$ is the Zeeman Hamiltonian in the rotating frame. The symbol $\langle\ \rangle_{\mathrm{av}}$ represents the time average.

In the present case, since the relaxation is due to dipolar modulation, $\mathcal{H}_D$ itself is time dependent. Therefore it is possible to expand $\mathcal{H}_D$ as

$$\mathcal{H}_D = \langle \mathcal{H}_D^0 \rangle_{\mathrm{av}} + \delta\mathcal{H}_D(t) ,$$

where $\langle \mathcal{H}_D^0 \rangle_{\mathrm{av}}$ is independent of time and $\delta\mathcal{H}_D(t)$ is time dependent; $\delta\mathcal{H}_D(t)$ corresponds to $\mathcal{H}_1(t)$. For simplicity, $\langle \mathcal{H}_D^0 \rangle_{\mathrm{av}}$ will be written as $\mathcal{H}_D^0$.

For the isolated proton pairs on the benzene rings present in most liquid crystals, the dipolar Hamiltonian may be written in terms of the instantaneous order director. The order-director fluctuations of the form proposed by Pincus can be expressed by

$$\vec{\mathrm{n}}(\vec{\mathrm{r}}, t) = [n_0 + \delta n_z(t)]\hat{k} + \delta n_x(t)\hat{\imath} + \delta n_y(t)\hat{\jmath}\,.$$

Neglecting terms of order δn^2, it follows that

$$\mathcal{H}_D^0 = \omega_D(1 - 3n_0^2)[I_1^Z I_2^Z - \tfrac{1}{4}(I_1^+ I_2^- + I_1^- I_2^+)]$$

and

$$\begin{aligned}\delta\mathcal{H}_D(t) = {}& -6\omega_D n_0 \delta n_z [I_1^Z I_2^Z - \tfrac{1}{4}(I_1^+ I_2^- + I_1^- I_2^+)] \\ & - \tfrac{3}{2}\omega_D n_0 [\delta n_x - i\delta n_y)(I_1^+ I_2^Z + I_1^Z I_2^+) \\ & + (\delta n_x + i\delta n_y)(I_1^- I_2^Z + I_1^Z I_2^-)]\end{aligned}$$

with $\omega_D = \gamma^2\hbar/r^3$. Now

$$\int_0^\infty \langle [\mathcal{H}_Z, \mathcal{H}_1(t)][\mathcal{H}_1^*(t-\tau), \mathcal{H}_Z]\rangle_{\mathrm{av}}\, d\tau$$

may be written as

$$\sum_{\substack{\mu, m\\ \lambda, n}} [\mathcal{H}_Z, V_\mu^m][V_\mu^{\dagger n}, \mathcal{H}_Z] \int_0^\infty \langle f_\mu(t) f_\lambda^*(t-\tau)\rangle_{\mathrm{av}}\, e^{in\omega\tau}\, d\tau\,,$$

where

$$\delta\mathcal{H}_D(t) = \sum_{\mu, m} f_\mu(t) V_\mu^m\,,$$

and V_μ^m is chosen such that

$$[I_Z, V_\mu^m] = m V_\mu^m\,.$$

For fluctuations in the order director we have

$$f_X = -\tfrac{3}{2}\omega_D n_0 \delta n_x\,, \quad V_X^{(1)} = I_1^+ I_2^Z + I_1^Z I_2^+\,,$$

$$V_X^{(-1)} = I_1^- I_2^Z + I_1^Z I_2^-\,, \quad f_Y = \tfrac{3}{2} i\omega_D n_0 \delta n_y\,,$$

$$V_Y^{(1)} = I_1^+ I_2^Z + I_1^Z I_2^+\,, \quad V_Y^{(-1)} = I_1^- I_2^Z + I_1^Z I_2^-\,,$$

$$f_Z = -\omega_D 6 n_0 \delta n_z\,, \quad V_Z^0 = I_1^Z I_2^Z - \tfrac{1}{4}(I_1^+ I_2^- + I_1^- I_2^+)\,.$$

Note that $V_\mu^{\dagger m} = V_\mu^{-m}$. The substitution of these results in Eq. (1) produces

$$\begin{aligned}\frac{1}{T_1} = {}& \frac{1}{\mathrm{tr}(I_Z^2)} (\tfrac{3}{2} n_0 \omega_D)^2 \left(\int_{-\infty}^{+\infty} \langle \delta n_x(t) \delta n_x(t-\tau)\rangle_{\mathrm{av}}\, e^{-i\omega_0\tau}\, d\tau + \int_{-\infty}^{+\infty} \langle \delta n_y(t)\delta n_y(t-\tau)\rangle_{\mathrm{av}}\, e^{-i\omega_0\tau}\, d\tau \right) \\ & \times \mathrm{tr}\{(I_1^+ I_2^Z + I_2^+ I_1^Z)(I_1^- I_2^Z + I_2^- I_1^Z)\} \\ = {}& (\tfrac{3}{2} n_0 \omega_D)^2 J(\omega_0) \frac{[\mathrm{tr}\{I_1^+ I_2^Z I_1^- I_2^Z\} + \mathrm{tr}\{I_1^+ I_2^Z I_2^- I_1^Z\} + \mathrm{tr}\{I_2^+ I_1^Z I_1^- I_2^Z\} + \mathrm{tr}\{I_2^+ I_1^Z I_2^- I_1^Z\}]}{[\mathrm{tr}\{I_1^{Z2}\} + 2\,\mathrm{tr}\{I_1^Z I_2^Z\} + \mathrm{tr}\{I_2^{Z2}\}]}\,,\end{aligned}$$

where ω_0 is the resonance frequency and

$$J(\omega_0) = \int_{-\infty}^{+\infty} \langle \delta n_x(t)\delta n_x(t-\tau) + \delta n_y(t)\delta n_y(t-\tau)\rangle_{\mathrm{av}}\, e^{-i\omega_0\tau}\, d\tau\,.$$

For $I = \frac{1}{2}$

$$\mathrm{tr}\{I_1^+ I_2^Z I_1^- I_2^Z\} = \mathrm{tr}\{I_2^+ I_1^Z I_2^- I_1^Z\} = \tfrac{1}{4}\,, \quad \mathrm{tr}\{I_1^{Z2}\} = \tfrac{1}{2}$$

and

$$\mathrm{tr}\{I_1^+ I_2^Z I_2^- I_1^Z\} = \mathrm{tr}\{I_2^+ I_1^Z I_1^- I_2^Z\} = \mathrm{tr}\{I_1^Z I_2^Z\} = 0\,.$$

If these values are substituted in the previous expression we get

$$1/T_1 = \tfrac{9}{8} n_0^2 \omega_D^2 J(\omega_0)\,. \tag{4}$$

Similarly

$$\begin{aligned}\frac{1}{T_{1D}} = {}& \sum_{\substack{\mu, m\\ \lambda, n}} \frac{\mathrm{tr}\{[\mathcal{H}_D^0, V_\mu^m][V_\lambda^{\dagger n}, \mathcal{H}_D^0]\} \int_0^\infty \langle f_\mu(t) f_\lambda^*(t-\tau)\rangle_{\mathrm{av}}\, e^{in\omega_0\tau}\, d\tau}{\mathrm{tr}\{\mathcal{H}_D^{02}\}} \\ = {}& \tfrac{9}{4} n_0^2 \omega_D^4 (1 - 3n_0^2)\, \mathrm{tr}\{I_1^+ I_2^Z I_2^Z + I_2^+ I_1^Z I_1^Z + \tfrac{1}{2} I_1^Z I_2^Z I_2^+ + \tfrac{1}{2} I_1^+ I_1^Z I_2^Z + \tfrac{1}{4} I_2^+ I_2^- I_1^+ + \tfrac{1}{4} I_1^- I_1^+ I_2^+) \\ & \times (I_1^- I_2^Z I_2^Z + I_2^- I_1^Z I_1^Z + \tfrac{1}{2} I_1^- I_1^Z I_2^Z + \tfrac{1}{4} I_1^- I_2^- I_2^+ + \tfrac{1}{4} I_1^+ I_1^- I_2^- + \tfrac{1}{2} I_1^Z I_2^Z I_2^-)\} J(\omega_0) / \tfrac{3}{8}\, \omega_D^2 (1 - 3n_0^2)\,.\end{aligned}$$

After this multiplication is performed, 12 nonzero traces remain for $I = \frac{1}{2}$. These traces total $\frac{9}{16}$. Thus

$$1/T_{1D} = \tfrac{27}{8} n_0^2 \omega_D^2 J(\omega_0)\,. \tag{5}$$

In the limit that terms of order δn^2 cannot be ignored, terms $V^{(2)} = I_1^+ I_2^+$ and $V^{(-2)} = I_1^- I_2^-$ must be considered. However, since

$$\mathrm{tr}\{[\mathcal{H}_D^0, V^{(2)}][V^{(-2)}, \mathcal{H}_D^0]\} \equiv 0\,,$$

these terms do not contribute to T_{1D} (but they contribute to T_{1X} and T_1). Because of this, the form of T_{1D}^{-1} is exact in the limit where benzene ring proton pairs are truly isolated.

For T_{1X}, the procedure is the same, except that the Hamiltonian is first transformed into the rotating frame. Then the $(V_\mu^m)_{\rm rot}$ are chosen such that

$$[I_X, (V_\mu^m)_{\rm rot}] = mI_X \,,$$

$$\delta\mathcal{H}_D(t)_{\rm rot} = \sum_{\mu,\, m} f_\mu^{\rm rot}(t)(V_\mu^m)_{\rm rot} \,.$$

The final result is

$$1/T_{1X} = \tfrac{45}{16} n_0^2 \omega_D^2 J(\omega_0) \,. \qquad (6)$$

Thus, one may calculate the ratios

$$T_1/T_{1X} = \tfrac{5}{2} \,, \qquad (7)$$

$$T_1/T_{1D} = 3 \,, \qquad (8)$$

and

$$T_{1X}/T_{1D} = \tfrac{6}{5} \,. \qquad (9)$$

This shows that the temperature dependences of T_{1X}, T_1, and T_{1D} from order-director fluctuations are identical in the limit where we may ignore terms of order δn^2 in $\delta\mathcal{H}_D(t)$.

III. THE THERMOMETRIC EQUATION

Several experiments are analyzed using the thermometric equation. This equation gives the spin-lattice relaxation in the rotating frame as the weighted average of T_{1Z}^{-1}, T_{1X}^{-1}, and T_{1D}^{-1}, considering the magnitudes of the corresponding specific heats[14, 15]

$$(h^2 + H_1^2 + H_L'^2)T_{1\rho}^{-1} = h^2 T_{1Z}^{-1} + H_1^2 T_{1X}^{-1} + H_L'^2 T_{1D}^{-1} \,, \qquad (10)$$

where H_L' is the local field in the rotating frame defined by $H_L'^2 = \mathrm{tr}\{\mathcal{H}_D^{02}\}/\mathrm{tr}\{M_Z^2\}$. Also T_{1Z} is given by an expression identical to that for T_1 except that ω_0 must be replaced by ω, the rotating-frame angular frequency. This usually makes no difference since the off-field $h = H_0 - H$ is much smaller than H_0.

Equation (10) was derived assuming that the Zeeman system and the dipolar system have a common spin temperature. This will only be the case when the energy-level separation in the Zeeman system at low fields is comparable with that of the dipolar system. Equation (10) is therefore expected to hold for $3H_L' \gtrsim H_1 \gtrsim H_L'$. Since, in the liquid crystals, H_L' is approximately 1 G, no coupling between the Zeeman and dipolar reservoirs is expected above $H_{\rm eff} \sim 5$ G. Furthermore, if at exact resonance the field H_1 is gradually increased above H_L', then at some considerably larger value, $H_1 > H_L'$, the spins will become quantized along the field H_1.[17] This "second secularization," where $\mathcal{H}_D^0$ splits into $\mathcal{H}_D^{00}$ (proportional to $3I_{X1}I_{X2} - \vec{I}_1 \cdot \vec{I}_2$) plus $\mathcal{H}_D^{0n}$, thus decreases the dipolar specific heat to $\frac{1}{4}$ of its value at low H_1, since now the local field $H_L'' = \mathrm{tr}\{\mathcal{H}_D^{002}\}/\mathrm{tr}\{M_Z^2\}$ equals $\frac{1}{2}H_L'$ only. This will happen when the dipolar and Zeeman energies are already almost decoupled, thus effectively speeding up the decoupling process. Experimentally it was not possible to differentiate between the decoupling and the second secularization (see, for example, Fig. 2).

IV. EXPERIMENT

The liquid crystal POBA was obtained commercially from Frinton Laboratories and was used without any purification, while the PAA sample was obtained zone-refined from Princeton Organics. Both samples were sealed in glass under vacuum.

The proton cw absorption experiments were performed with a homemade marginal oscillator operating at 30 MHz. Typical derivative signals of both liquid crystals, measured with a 3-sec time constant in the middle of their nematic regions, are shown in Figs. 1(a) and 1(b). From these absorption lines, the second moments M_2 were calculated, and the local field in the rotating frame, $H_L' = (M_2/3)^{1/2}$, was evaluated for POBA. At 126°C, H_L' of POBA is 1.00 ± 0.08 G and does not vary throughout the nematic phase. Its value in the smectic phase is the same. PAA may have a slightly temperature-dependent H_L'. Its value, which was determined by a pulse experiment (see the Appendix), is 0.82 ± 0.10 G at 123 °C, and 0.75 ±0.10 at 132 °C. It should be mentioned that it is not correct to use the relation $H_L'^2 = \frac{1}{3}M_2$ when two spin species are present.[14] In particular, if the second spin is larger than $\frac{1}{2}$, the relation may be quite complicated.

The relaxation time of the dipolar energy was

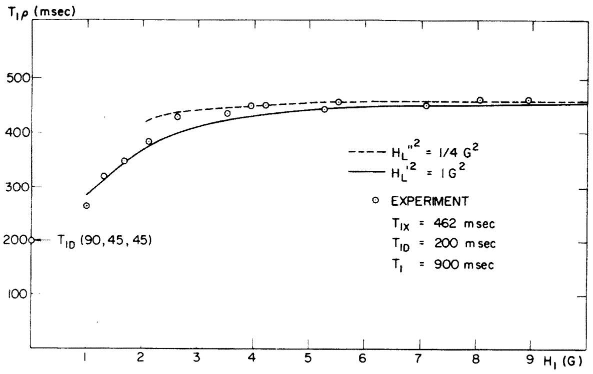

FIG. 2. $T_{1\rho}$ as a function of H_1^2 in nematic POBA at 126 °C. Each value quoted is accurate to within 5%. The value (200 msec) at $H_1 = 0$ is T_{1D} obtained by the Jenner-Broekaert method. The calculated curves were obtained using Eq. (11) and modified Eq. (11) (see text).

measured directly by means of the 90°-45°-45° pulse sequence of Jeener and Broekaert[16] (JB) on a Bruker pulse spectrometer with phase-sensitive detection at 30 MHz. The $T_{1\rho}$ measurements were made on a Spin Lock Electronics single-coil coherent spectrometer at 33 MHz. Rotating fields between 0.5 and 12 G were used. The phase detection was employed.

The dependence of $T_{1\rho}$ on the strength of the rotating field H_1 at exact resonance is shown for POBA in Fig. 2. The data at low H_1 for both liquid crystals are shown in Fig. 3. The results are for the nematic phase. The "saturation" of $T_{1\rho}$ at fields above 5 G can be seen clearly for POBA in Fig. 2. The behavior of $T_{1\rho}$ in the smectic phase of POBA is very similar to its behavior in the nematic phase. The high-H_1 relaxation of PAA is shown in Fig. 10.

The temperature dependence of T_1 and of T_{1D}, together with $T_{1\rho}$ taken at $H_1 = 6 \pm 0.3$ G of POBA and of PAA are shown in Figs. 4 and 5, respectively. As we can see, all relaxation times depend similarly on temperature in both liquid crystals. Such a behavior is suggested by Eqs. (7)-(9). It is worth noting that in POBA, $T_{1\rho}$ extrapolated to zero H_1 is equal to T_{1D} as determined by the JB method (Fig. 3). On the other hand, in PAA the extrapolated $T_{1\rho}$ and T_{1D} determined at the high field by the JB method are not equal (Fig. 3). The difference is quite substantial. We will use the notation $T_{1\rho}(0)$ for the apparent T_{1D} extrapolated from $T_{1\rho}$ field dependence. For example, in PAA at 124 °C, $T_{1\rho}(0)$ equals 290 ± 30 msec, while T_{1D} is 410 ± 20 msec (Fig. 3). That this results from

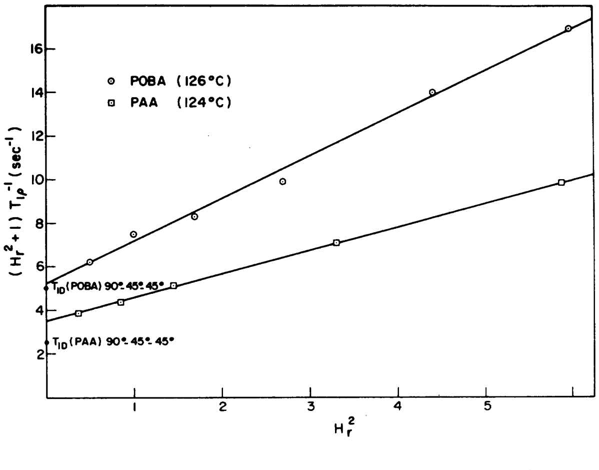

FIG. 3. Strong-coupling relaxation for POBA and PAA at small rotating fields (0.7 < H_1 < 2.5 G). For POBA the extrapolated value $T_{1\rho}^{-1}$ (at $H_1 = 0$) is equal (within experimental accuracy) to T_{1D}^{-1} measured by the JB method. For PAA the extrapolated value is larger (by ~ 30%) than the T_{1D}^{-1} rate measured by the JB method.

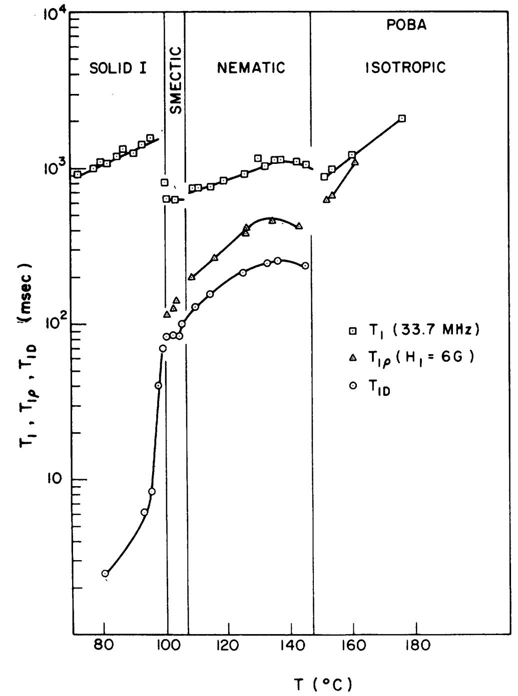

FIG. 4. T_1, $T_{1\rho}$, and T_{1D} in the smectic, nematic, and isotropic phases of POBA. The precision is better than 5%.

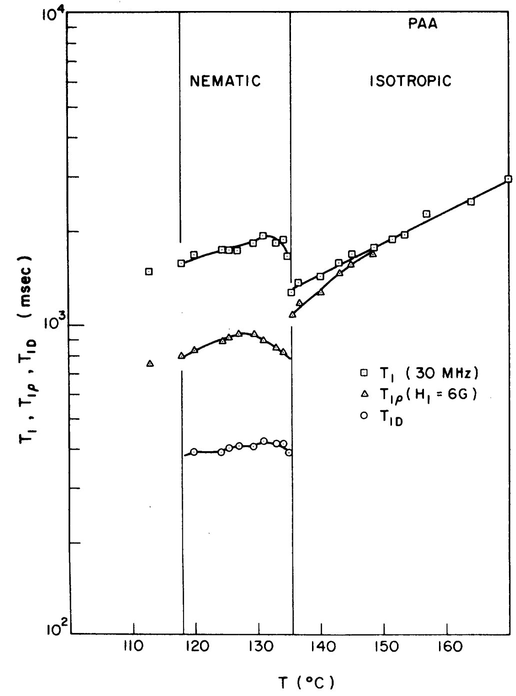

FIG. 5. T_1, $T_{1\rho}$, and T_{1D} in the nematic and isotropic phases of PAA. The precision is better than 5%.

some unknown experimental aberration seems unlikely, since this difference was observed in the nematic phase on several different PAA samples measured with three different spectrometers.

$T_{1\rho}$ was also determined at an effective field H_{eff} of 10.4 ± 0.3 G, that is, at $H_1 = 3.0 \pm 0.2$ G, and 10 ± 0.2 G off-resonance. In this experiment the magnetization growth along the large field H_0 was measured by adding a 90° reading pulse several T_2 after the spin-locking pulse. The result is shown in Fig. 6 and explained in Sec. V E.

The resonance condition was determined accurately (± 0.1 G) by applying a rf pulse of a few gauss and several seconds long. In Fig. 7 such a determination is shown. There the value of M_X measured after a 2.8 ± 0.2 G field pulse of 3.1 sec duration is shown as a function of the off-field h. The experimental M_X values are shown together with the calculated behavior. This point will be discussed in Secs. V B and V E.

The temperature dependence of the ratios T_1/T_{1D} and T_1/T_{1X} for POBA and PAA are plotted in Figs. 8 and 9, respectively.

V. RESULTS AND DISCUSSION

A. Spin-temperature concept

Both liquid crystals studied have T_1 and $T_{1\rho}$ some three orders of magnitude longer than T_2. Thus, the spin-spin equilibrium appears to be established quickly compared to the spin-lattice equilibrium. This process in POBA is believed to be uniform throughout the sample; that is, the equilibrium is established quickly among different spin groups on a particular molecule, as well as among neighboring molecules. This is possible because the translational diffusion is slow[18]; consequently, the intermolecular interactions provide for the heat flow between the molecules. Another possibility is the rapid exchange of monomers which form the liquid-crystal molecule (dimer).[19] The protons on a given monomer are exchanged in a time interval of one T_1 between many dimers. In this way they come into thermal contact with spins on many different molecules.[20] In PAA, the intermolecular interactions are averaged out because of fast translational diffusion.[21] As a result, the PAA molecules are isolated one from another. In addition, the interproton couplings between the CH_3 groups and the spin pairs on the benzene ring on one PAA molecule may be too weak to allow the establishment of a common spin temperature, as we now show.

The criteria for the existence of a spin temperature different from the lattice temperature are[14] that (a) the time required to establish internal equilibrium (this time is loosely characterized by T_2) must be much shorter than the time required to establish equilibrium with the lattice (T_1 or $T_{1\rho}$); (b) an energy-conserving mechanism must be present which allows a redistribution of populations (that is, the density matrix must be able to evolve to a Boltzmann form under the constraint of conservation of energy); (c) the total energy of the spin system (in the absence of spin-lattice relaxation) is the only constant of the motion.

Before the validity of these conditions in the liquid crystal PAA were examined, we checked to see whether the spin-temperature concept could be rejected on the basis of a nonexponential decay of the magnetization in either of the transient experiments. Such nonexponentiality was not observed. We also checked for a variation in T_1 with distance from the 90° pulse. The free-induc-

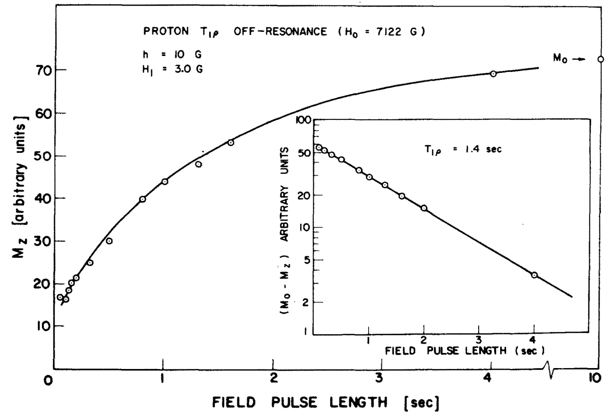

FIG. 6. Analysis of experimental $T_{1\rho}$ measured 10 G off-resonance.

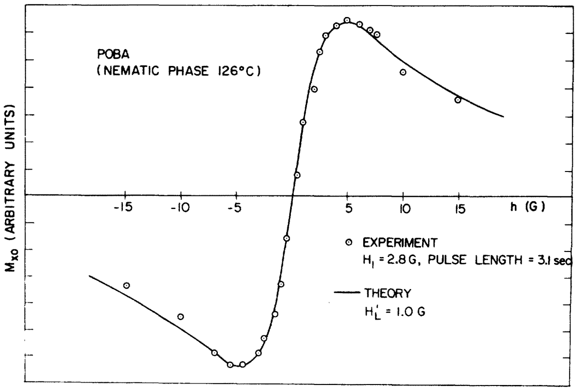

FIG. 7. Variation of M_{X0} as a function of the off-field h. The pulse of $H_1 = 2.8$ G was 3.1 sec long. The full line shows the calculated variation (equation in the text). Readings are accurate within ±8%.

tion decay (FID) was sampled 30 and 140 μsec after the 90° pulse. At 120 °C the results of measurements at 35 MHz are: T_1(30 μsec) = 1.56 sec and T_1(140 μsec) = 1.52 sec. At 131 °C the values are: T_1(30 μsec) = 1.50 sec and T_1(140 μsec) = 1.48 sec. Although ten measurements were taken at each setting, the resulting T_1 difference is not conclusive since the accuracy of measured T_1 was ±2%.

The insert in Fig. 1(b) shows the absorption signal for nematic PAA decomposed into three absorption lines. The outer lines are attributed to the isolated proton pairs located on the benzene rings. The central peak comes from the protons of the CH_3 groups which reorient very quickly around their C_3 axis, as well as around the long molecular axis. Since the absorption lines from the protons in the two distinct environments are noncoincident, the contribution of the CH_3 protons to the free-induction decay will be different than the contribution of the benzene-ring protons. The variation in T_1 along FID would therefore indicate that T_1 (CH_3) is different from T_1 (benzene-proton pairs).

If a T_1 of the order of 1 sec is attributed to the benzene-ring protons, there remain two possibilities for T_1 of the CH_3 protons. The first possibility is that the CH_3 protons are essentially isolated from the ring protons and relax independently. Since the possible variation of T_1 is less than 2%, the T_1 of the CH_3 would also have to be of the order of 1 sec. This is most unlikely. In the solid, near the solid-to-nematic phase transition, τ_3, the correlation time for C_3 reorientation, was already too short for effective relaxation. That is, since $\omega_0^2\tau_3^2 \ll 1$ we have $T_1^{-1} \propto \tau_3$. In the nematic phase, it is expected that τ_3 will be even shorter. Thus, in the nematic phase we would expect $(T_1)^{-1} < 0.1\ \text{sec}^{-1}$. Certainly there remains the diffusion, which is quite effective, but not effective enough, and will be discussed in Sec. V D. The second possibility is that CH_3 protons relax via the benzene protons. The time constant which characterizes the energy flow between the CH_3 protons and the benzene-ring protons must be of the same order as T_1 (ring protons) or shorter for a T_1 difference to be discernible. If this transfer took much longer than T_1 (ring proton), obvious nonexponentiality would be present.

If $T_1(CH_3) \neq T_1$(benzene-proton pairs), then the nematic PAA could not be described rigorously by the spin-temperature concept at high fields. The failure to observe such a difference with significant accuracy indicates that the temperature of the CH_3-proton spins is at least approximately equal to the temperature of the benzene-ring-proton spins. Such a difference was also not observed in POBA. However, in POBA, only $\frac{8}{44}$ of the protons are on the benzene rings, and such a small difference would be difficult to observe experimentally.

An attempt was made to detect such a variation in T_{1D} of PAA with the 90°-45°-45° pulse technique. In this sequence, the first 90°-45° pulse pair transfers order from the Zeeman to the dipolar system. The second 45° pulse is a read pulse that samples the order present in the dipolar system. T_{1D} is then measured by varying the spacing between the two 45° pulses while keeping the 90°-45° pulse spacing τ constant. It can be shown[15,16] that the amount of order transferred to the dipolar system is proportional to $[dG(t)/dt]_{t=\tau}$, where $G(t)$ is the free-induction-decay shape. Thus, by varying τ, the amount of order that is transferred

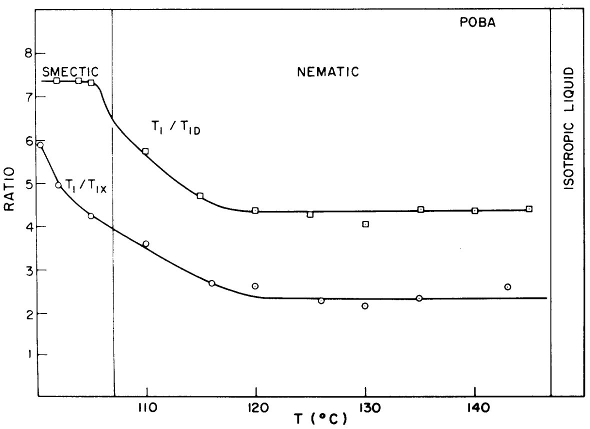

FIG. 8. Temperature dependence of T_1/T_{1D} and T_1/T_{1X} for POBA. The calculated ratios for the ODF relaxation of benzene pairs are 3 and 2.5, respectively.

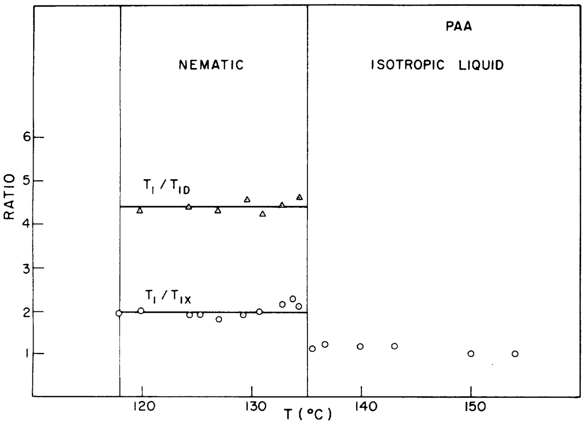

FIG. 9. Temperature dependence of T_1/T_{1D} and T_1/T_{1X} for PAA. The value for T_{1X} taken at $H_1 = 6$ G, contains a small cross relaxation (N^{14} to H) effect.

to each of the two dipolar systems—the CH_3 system and the proton-pair system—is varied. This is because the two contributions to the free-induction decay will not have the same slope everywhere. Experimentally, no detectable variation in T_{1D} was found. This indicates that $T_{1D}(CH_3) = T_{1D}$(benzene-proton pairs). It must then be concluded that the time constant which characterizes the energy flow between the two dipolar systems *must be shorter* than T_{1D} (410 msec). This may be explained by the fact that, in nematic PAA, the possible breakdown of the spin temperature could be connected with all three requirements for its establishment. Condition (c) is the most flexible of these requirements. In many cases, parts of the total Hamiltonian commute with the Zeeman Hamiltonian, for example, $[\mathcal{H}_D^0, \mathcal{H}_Z] = 0$. But $[\mathcal{H}_D^0, \mathcal{H}_D^n] \neq 0$ and $[\mathcal{H}_Z, \mathcal{H}_D^n] \neq 0$. Thus, if it were not for $\mathcal{H}_D^n$, both $\langle \mathcal{H}_D^0 \rangle$ and $\langle \mathcal{H}_Z \rangle$ would separately be constants of the motion. The presence of $\mathcal{H}_D^n$, however, couples these two reservoirs so that they come to equilibrium at a common temperature. In a high field, however, this coupling is so weak that it is permissible to talk about independent spin temperature for the Zeeman and dipolar energy reservoirs.

In PAA the coupling between the ring-proton spins and the CH_3 proton spins is too strong for their respective temperatures to be considered as independent, yet it may not be strong enough for the establishment of a common temperature. It is possible that the Zeeman spin temperature exhibits a small spin-temperature gradient across the molecule. The absence of such a "gradient" in the dipolar temperature is related to condition (b). Since the energy levels in the two dipolar systems are essentially coincident, a redistribution of population within the dipolar system is not hampered by energy considerations. Such may not be the case for the two Zeeman systems (CH_3 and benzene protons) at high fields.

The separated absorption spectrum (Fig. 1) shows that there is only a small overlap of the central CH_3 peak and either of the pair spectrum peaks. The major mechanism for an exchange of energy between these two Zeeman systems is a spin flip-flop involving one spin in each system. Thus, of the possible mutual spin flips, all but a few percent are forbidden by the conservation of energy. Therefore, if we assume that the transfer time at high fields is about equal to T_1 (1 sec), then, for the dipolar reservoir, the transfer time should be shorter by one order of magnitude (100 msec). Thus, complete internal equilibrium between the Zeeman systems should not be expected until after a time of the order of seconds and, for the dipolar systems, not until after a time of the order of hundreds of milliseconds. In spite of the fact that $T_2 \ll T_1$, internal equilibrium may not be established quickly enough for the rigorous application of the spin-temperature concept.

In view of the above discussion, if the transfer time were shorter than T_1, the order-director fluctuation contribution to T_1 would be related to the experimental T_1 as follows:

$$\frac{1}{T_1}\,(\text{expt}) = \frac{8}{44}\,\frac{1}{T_1}\,(\text{ring protons}) + \frac{36}{44}\,\frac{1}{T_1}\,(CH_2,\ CH_3,\ \text{and H})$$

for POBA and

$$\frac{1}{T_1}\,(\text{expt}) = \frac{8}{14}\,\frac{1}{T_1}\,(\text{ring protons}) + \frac{6}{14}\,\frac{1}{T_1}\,(CH_3)$$

for PAA.

Considering that the possible T_1 difference is <2%, we shall freely use the concept of spin temperature in the analysis of experimental data.

B. Spin thermometry

When applying the spin-temperature concept in the rotating frame at rotating fields where equilibrium between the Zeeman and dipolar energy reservoirs exists, $H_1 \sim H_L'$, the thermometric equation (10) at exact resonance reads

$$(H_1^2 + H_L'^2)T_1^{-1} = H_1^2 T_{1X}^{-1} + H_L'^2 T_{1D}^{-1}\,. \tag{11}$$

In Fig. 2 we see that the contact between the Zeeman and dipolar energy reservoirs in POBA breaks down above $H_1 \gtrsim 4H_L'$. That is, the field dependence of $T_{1\rho}$ is governed by Eq. (11) only in a limited range of H_1 near H_L'. A steeper increase of $T_{1\rho}$, between 2 and 4 G, than predicted by (11), the solid line in Fig. 2, is interpreted as the effect of breaking the contact and possibly of second secularization. The dotted line is the calculated behavior considering the second secularization. At higher fields ($H_1 > 5H_L'$), the contact between the two reservoirs does not exist and $T_{1\rho}$ becomes T_{1X}. In the case of POBA an upper limit exists as H_1 increases. The rate T_{1X}^{-1}, obtained as the upper limit of $T_{1\rho}^{-1}$, is then used to analyze for T_{1D}^{-1} [Eq. (11)]. It is encouraging that in POBA the "zero H_1 limit" of $T_{1\rho}$, $T_{1\rho}(0)$, is equal to T_{1D} measured independently by the JB method (see Fig. 3).

A similar approach fails in PAA (Fig. 3), where it was found that $T_{1\rho}(0) \neq T_{1D}$. In the nematic phase of PAA, T_{1D} measured by the three-pulse sequence was independent of temperature and equal to 410 ± 20 msec. On the other hand, $T_{1\rho}(0)$ is only 290 ± 30 msec at 124 °C. This discrepancy is explained by relaxation via N^{14} spins, following a discussion of relaxation mechanisms in POBA. In addition to this difference, the H_1 field dependence of $T_{1\rho}$ in PAA does not appear to have an upper limit at high H_1. This implies that, when the contact with the dipolar reservoir is lost, $T_{1\rho}$ remains slightly field dependent. Since H_L' is only 0.8 G, this happens around $H_1 \sim 3$ G. This field dependence of $T_{1\rho}^{-1}$ is explained by relaxation via N^{14} spins in Sec. V D, where the relaxation mechanisms in PAA are discussed.

It follows from Eq. (10) that, to determine $T_{1\rho}(0)$ from the H_1 dependence of $T_{1\rho}$, it is necessary to know the "off-field" accurately or, preferably, to perform the experiment at exact resonance. Resonance may be determined quite accurately (±0.1 G) by measuring the equilibrium spin temperature in the rotating frame.

Spin-temperature theory predicts that, in the rotating frame, the inverse spin temperature β_ρ is related to the inverse lattice temperature β_L through the relation[14]

$$\beta_\rho = \beta_L h H_0 / (h^2 + \lambda H_1^2 + \delta H_L'^2) , \tag{12}$$

where

$$\lambda = T_{1Z}/T_{1X} \quad \text{and} \quad \delta = T_{1Z}/T_{1D} .$$

The transverse magnetization after a rf pulse of strength H_1, which is long compared to T_{1Z}, will thus be given by

$$M_{X0} = M_0 h H_1 / (h^2 + \lambda H_1^2 + \delta H_L'^2) . \tag{12a}$$

Thus, at exact resonance, $h = 0$ and $M_{X0} = 0$. Figure 7 shows M_{X0} of POBA as a function of h for a 2.8-G-field pulse 3.1 sec long. It should be noted that Eq. (12) is valid only if $H_{\text{eff}} < 3H_L'$. Since H_1 is already 2.8 G, Eq. (12a) reduces to

$$M_{X0} = M_0 h H_1 / (h^2 + 2.3 H_1^2) \tag{12b}$$

for $h > 2$ G. The dependence of M_{X0} on h is in qualitative agreement with Eq. (12b). Similar data on PAA are discussed in Sec. V E.

C. Relaxation in POBA

The order-director fluctuations (ODF) relax the eight phenyl protons on a POBA molecule in a manner discussed by Pincus.[2] Since the molecular axis reorientation reduces the CH_3 and CH_2 local fields considerably, their ODF relaxation is not as strong as for the phenyl protons. (For this reason the ODF relaxation of these proton groups should be considered separately. Due to the lack of information, we shall treat them as one group in our model.) A crude estimate for the ODF relaxation in POBA should be the value found for PAA, which is ~1 sec[11] at high fields in the middle of the nematic phase. The total relaxation rate measured at high fields in POBA is equal to $1.1 \pm 0.1\ \text{sec}^{-1}$ at 126 °C. From this we conclude that ODF relaxation in POBA may be a contributing mechanism. The measured rate in POBA, however, shows no frequency dependence in the range 17–33 MHz, which is different from the observed $\omega_0^{-1/2}$ dependence in PAA.[9,11] It should be noted that, since the POBA dimer is considerably longer than the PAA molecule, the hydrodynamic limit is reached for POBA at smaller q than in PAA. As a result, Lubensky's hydrodynamic integral, which gives the frequency dependence, is considerably smaller for POBA than for PAA.[11,8] Because of this, the relaxation in POBA should be carefully examined.

The total rate of high fields can be approximately written as a sum of an ODF relaxation rate and an unknown (white spectrum) relaxation R_Z:

$$T_1^{-1} = R_{\text{ODF}} + R_Z . \tag{13a}$$

If the protons are separated into a phenyl group (b) and a (CH_2, CH_3) group (m), Eq. (13a) becomes

$$T_1^{-1} = \tfrac{8}{44} R_{\text{ODF}}(\text{b}) + \tfrac{36}{44} R_{\text{ODF}}(m) + R_Z . \tag{13b}$$

A similar equation can be written for the Zeeman relaxation rate in the rotating frame. If it is assumed that all the protons in POBA have $(T_1/T_{1X})_{\text{ODF}}$ equal to 2.5 [Eq. (7)], and that a white spectrum relaxation has (T_1/T_{1X}) equal to 1, we obtain

$$T_{1X}^{-1} = 2.5 R_{\text{ODF}} + R_Z \tag{14a}$$

or, if the protons are regrouped, and the T_1/T_{1X} of 2.5 is taken for the phenyl protons only,

$$T_{1X}^{-1} = 2.5 \tfrac{8}{44} R_{\text{ODF}}(b) + a \tfrac{36}{44} R_{\text{ODF}}(m) + R_Z , \tag{14b}$$

where a is an unknown constant ($1 < a < 2.5$).

Before proceeding with a similar analysis of T_{1D}^{-1}, we should note that in POBA the experimental ratio T_1/T_{1X} is larger than 2.5 in the low-temperature part of the nematic phase (Fig. 8). Consequently, the relaxation mechanisms introduced above cannot explain the experiment. A third mechanism, which is too slow to relax the Zeeman reservoir at high fields ($\omega_0 \tau \gg 1$) but fast enough to relax the Zeeman reservoir at low fields (thus independent of H_1, $\omega_1 \tau \ll 1$), has to be introduced.[22] Equation (14a) becomes

$$T_{1X}^{-1} = 2.5 R_{\text{ODF}} + R_Z + R_S . \tag{14c}$$

In a similar way, the relaxation rate of the dipolar reservoir can be analyzed. If the following assumptions are made: $T_{1Z}/T_{1D} = 3$ for all protons relaxed by ODF; the ratio for the white mechanism is 2; and the ratio for the slow mode is labeled

c, we obtain

$$T_{1D}^{-1}=3R_{\text{ODF}}+2R_Z+cR_S. \tag{15a}$$

If the protons are grouped, Eq. (15a) becomes

$$T_{1D}^{-1}=W_B3R_{\text{ODF}}(b)+(1-W_B)dR_{\text{ODF}}(m)+2R_Z+cR_S, \tag{15b}$$

where W_B is the dipolar weight of the phenyl group, $W_B=\frac{8}{44}M_2(b)/M_2(\text{POBA})$, and d is an unknown constant, $2<d<3$.

Equations (13a), (14c), and (15a), with the constant c equal to 2, were solved for R_{ODF}, R_Z, and R_S at four temperatures in the nematic phase (Table I). It should be mentioned that the constant c has to be larger than 1.5 to keep all the relaxation rates positive. The constant c is, in general, limited between 1 and 2, with $c=2$ for a high-field white process ($\omega_0\tau\ll 1$) and $c=1$ for a low-field white process which is not far from the extremum ($\omega_1\tau<1$).

The results given in Table I should be considered as illustrative. All processes show only mild temperature dependence and R_{ODF} is likely to be (through the order parameter) most temperature dependent.

D. Relaxation in PAA

Equation (11) can be written in the following form:

$$(1+H_r^2)T_{1\rho}^{-1}=H_r^2T_{1X}^{-1}+T_{1D}^{-1},$$

if the reduced field $H_r^2=H_1^2/H_L'^2$ is introduced. A plot of the above equation for POBA and PAA is shown in Fig. 3. For PAA the intercept $T_{1\rho}^{-1}(0)$ is explained by proton relaxation via N^{14} spins. For such a mechanism, the contributions to the Zeeman relaxation will be given by[23]

$$(1/T_{1X})_{\text{N-H}}=\tfrac{4}{14}M_2(\text{N-H})/H_1^2T_1(\text{N}) \tag{16}$$

in the limit $\gamma_1^2H_1^2T_1(\text{N})^2\gg 1$. The second moment M_2(N-H) is equal to

$$M_2(\text{N-H})=\frac{S(S+1)}{3\gamma_I^2}\sum_{k'}\frac{\gamma_I^2\gamma_S^2\hbar^2}{r_{jk'}^6}(1-3\cos^2\theta_{jk'})^2,$$

where γ_I is the proton gyromagnetic ratio, γ_S is the nitrogen gyromagnetic ratio, $S=1$ (nitrogen spin), and T_1(N) is the T_1 for nitrogen. Since $T_1(N)\sim 2\times 10^{-4}$ sec, the condition $\gamma_I^2H_1^2T_1^2(N)\gg 1$ was always satisfied in our experiments.[24] The factor $\frac{4}{14}$ arises from the fact that only 4 (first neighbors to nitrogen) of 14 proton spins are relaxed by this mechanism. Since in PAA the quadrupole splitting of the N^{14} NMR absorption lines is ~1000 G, Eq. (16) is valid to a good approximation.

Then, at exact resonance, for $H_1\sim H_L'$

$$(H_1^2+H_L'^2)\frac{1}{T_{1\rho}}=H_1^2\left(\frac{1}{T_{1X}}\right)_{\text{H-H}}+H_1^2\frac{4}{14}\frac{M_2(\text{N-H})}{H_1^2T_1(\text{N})}+H_L'^2\frac{1}{T_{1D}}. \tag{17}$$

Thus at small H_r up to ~3 at exact resonance, a plot of $(H_r^2+1)/T_{1\rho}$ vs H_r^2, which is obtained by dividing (17) by $H_L'^2$, will have an intercept of

$$\frac{1}{T_{1\rho}(0)}=\frac{1}{T_{1D}}+\frac{4}{14}\frac{M_2(\text{N-H})}{H_L'^2T_1(\text{N})}. \tag{18}$$

The slope is the proton-proton Zeeman relaxation T_{1X}^{-1}. This slope (Fig. 3) equals 1.1 sec^{-1}. At high fields Eq. (17) is replaced by

$$\frac{1}{T_{1\rho}}=\left(\frac{1}{T_{1X}}\right)_{\text{H-H}}+\frac{4}{14}\frac{M_2(\text{N-H})}{T_1(\text{N})}\frac{1}{H_1^2}. \tag{19}$$

It follows that at high H_1 fields ($H_1\gg H_L'$) the effect of proton-to-nitrogen relaxation can be obtained

TABLE I. POBA and PAA: Spin-lattice relaxation rates at 33.7 MHz in the nematic phase (in sec^{-1}).

T(°C)	T_1^{-1}(expt.)	R_{ODF}(calc.)	R_Z(calc.)	T_{1X}^{-1}(expt.)	R_S(calc.)	T_{1D}^{-1}(expt.)
POBA data						
110	1.35 ± 0.06	0.9	0.4	4.8 ± 0.3	2.0	7.7 ± 0.4
120	1.19 ± 0.06	0.6	0.6	3.2 ± 0.2	1.1	5.3 ± 0.3
130	0.95 ± 0.05	0.2	0.8	2.3 ± 0.2	1.1	4.3 ± 0.2
140	0.91 ± 0.05	0.2	0 7	2.2 ± 0.2	1.0	4.0 ± 0.2
PAA data						
120	0.60 ± 0.04	0.7	0.2	1.2 ± 0.1	0 3	2.6 ± 0.1
125	0 58 ± 0.04	0.6	0.2	1.1 ± 0.1	0.4	2.5 ± 0.1
130	0.53 ± 0.04	0.7	0.1	1.1 ± 0.1	0.3	2.4 ± 0.1
134	0.54 ± 0.05	0.8	0.1	1.2 ± 0.1	0.1	2.4 ± 0.1

from the slope of a $T_{1\rho}^{-1}$-vs-H_1^{-2} diagram (Fig. 10). The proton relaxation $(T_{1X}^{-1})_{\text{H-H}}$ is then the intercept. We note that the intercept and slope roles are reversed in a high-H_1 plot compared with a low-H_1 plot. It should be noted that if relaxation times are long, the high-field regime may not be accessible because of heating problems. In Eq. (18) the first term is the dipolar rate, which was measured by the JB method and found to be temperature independent, $T_{1D}^{-1} = 2.5 \pm 0.2\ \text{sec}^{-1}$. The experimental $T_{1\rho}^{-1}(0)$ is $3.5 \pm 0.3\ \text{sec}^{-1}$. With these data at 124 °C the ratio $\frac{4}{14} M_2(\text{N-H})/H_L'^2 T_1(\text{N})$ is found to be 1 sec^{-1}. If the calculated second moment of $(1 \pm 0.5) \times 10^{-3}\ \text{G}^2$ and the experimental $H_L'^2$ and $T_1(\text{N})$ (see Ref. 24) are used, the ratio is found to be $2.1 \pm 0.5\ \text{sec}^{-1}$, in fair agreement with the experimentally derived value of 1 sec^{-1}.

In conclusion we observe that an agreement exists between the low-H_1 experiment (strong coupling, Fig. 3) and the high-H_1 experiment (Zeeman and dipolar energies not coupled, Fig. 10). These data show that the proton rotating-frame Zeeman reservoir is relaxed partially via nitrogen. The magnitude of this coupling is very small, though, and can be neglected at larger fields H_1; e.g., at $H_1 = 3$ G the proton-to-nitrogen rate at 124 °C is only

$$\left(\frac{1}{T_{1X}}\right)_{\text{N-H}} = \frac{4}{14}\frac{M_2(\text{N-H})}{H_1^2 T_1(\text{N})} = (0.16 \pm 0.08)\ \text{sec}^{-1}.$$

For this reason, in analyzing the relaxation rates, including T_{1X}^{-1}, at larger H_1 the proton-to-nitrogen relaxation can be neglected.

In analogy to the approach in analyzing POBA rates, and assuming that to a good approximation the CH_3 intragroup rate is negligible, we have

$$T_1^{-1} = \tfrac{4}{7} R_{\text{ODF}} + R_Z\,, \tag{20}$$

and for the Zeeman rotating-frame rate at larger H_1

$$T_{1X}^{-1} = \tfrac{4}{7} 2.5 R_{\text{ODF}} + R_Z\,. \tag{21a}$$

The dipolar relaxation is then

$$T_{1D}^{-1} = W_B 3 R_{\text{ODF}} + 2R_Z\,, \tag{22a}$$

where $W_B \sim 0.88$ is the weight of benzene protons. It is equal to $\frac{4}{7}[M_2(b)/M_2(\text{PAA})]$. To obtain a consistent solution of Eqs. (20)–(22a), we have to introduce a slow relaxation rate R_S in Eq. (21a) and c times R_S in Eq. (22a), in analogy to POBA. The Eqs. (21a) and (22a) thus read

$$T_{1X}^{-1} = \tfrac{4}{7} 2.5 R_{\text{ODF}} + R_Z + R_S \tag{21b}$$

and

$$T_{1D}^{-1} = W_B 3 R_{\text{ODF}} + 2R_Z + cR_S\,. \tag{22b}$$

Since only three unknowns can be determined from Eqs. (20), (21b), and (22b), we set c equal to 2. The results are given in Table I. The advantage of the PAA example is that data on partially deuterated samples of PAA (CD_3) are also available.[10,13] The comparison has been made with the T_1 data obtained at 56 and 24 MHz. The proton relaxation rate is in both cases temperature independent and equals 0.83 sec^{-1} at 24 MHz and 0.62 sec^{-1} at 56 MHz.[10] This would imply that all the temperature dependence is due to the intra- and inter-molecular relaxation of the CH_3 group.

Considering the frequency dependence[8] is $A\omega^{-1/2} + B$, we interpolated the experimental rates of deuterated sample PAA (CD_3) evaluated at 24 and 56 MHz to 33 MHz and obtained 0.77 sec^{-1}. For such a molecule, formula (20) would read

$$T_1^{-1} = R_{\text{ODF}} + R_Z\,,$$

where R_{ODF} should be about the same as for a PAA (CH_3) molecule, but R_Z is considerably smaller. Approximating R_Z by half the value obtained from the PAA (CH_3) results, the following rate is obtained:

$$T_1^{-1} = \langle R_{\text{ODF}} \rangle_{120,125,130} + \tfrac{1}{2}\langle R_Z \rangle_{120-130}\,,$$

$$T_1^{-1} = 0.68 + \tfrac{1}{2}(0.18) = 0.77\ \text{sec}^{-1}.$$

The good agreement, which is no doubt accidental, indicates that the values of rates analyzed from the three relaxation rates are reasonably good.

E. Off-resonance experiments in PAA

$T_{1\rho}$ was also measured off-resonance as a further check on Eq. (10). $T_{1\rho}$ may be measured off-resonance by the conventional spin-locking technique (a 90° pulse followed by a variable-length phase-shifted-90° field pulse). However, the equilibrium magnetization in the rotating frame is nonzero if $h \neq 0$. Thus at exact resonance,

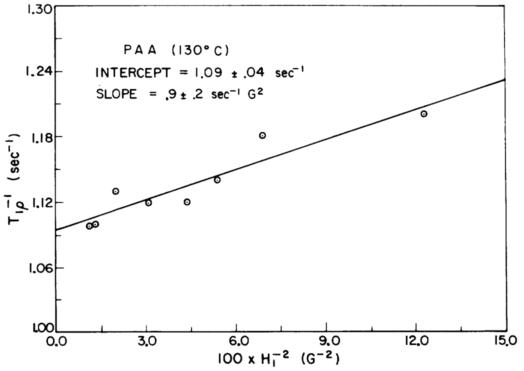

FIG. 10. Proton-relaxation rate in the rotating frame at high H_1 fields ($H_1 \gg H_L'$) at exact resonance for PAA in the nematic phase at 130 °C.

$$\frac{dM_X}{dt} = -\frac{1}{T_{1\rho}} M_X ,$$

while off-resonance

$$\frac{dM_X}{dt} = \frac{1}{T_{1\rho}} (M_{X0} - M_X) ,$$

where M_{X0} is given by Eq. (12a). When the effects of proton relaxation via the nitrogen spins are considered, Eq. (12a) has to be modified by substituting

$$\frac{1}{T_{1X}} = \left(\frac{1}{T_{1X}}\right)_{\text{H-H}} + \frac{4}{14} \frac{M_2(\text{N-H})}{(H_1^2 + h^2) T_1(\text{N})} .$$

Then for large effective fields, Eq. (12a) becomes for PAA

$$M_{X0} = M_0 h H_1 \left(h^2 + \frac{T_{1Z}}{T_{1X}} H_1^2 + \frac{4}{14} \frac{T_{1Z} M_2(\text{N-H})}{T_1(\text{N})} \right)^{-1} .$$

It should be noted, however, that for $H_1 > 1$ the cross term is much smaller than the rotating-frame Zeeman term; e.g., at H_1 of 3 G the term H_1^2/T_{1X} is ~9, while the term $\frac{4}{14} M_2(\text{N-H})/T_1(\text{N})$ is only ~1. When $h > H_1$, greater sensitivity (more signal) is obtained by measuring M_Z rather than M_X. The measurement of M_Z is accomplished by the addition of a 90° "read pulse" at a time approximately $5T_2$ after the field pulse.[16] M_Z will obey

$$\frac{dM_Z}{dt} = \frac{1}{T_{1\rho}} (M_{Z0} - M_Z) ,$$

where

$$M_{Z0} = M_0 h^2 \left(h^2 + \lambda H_1^2 + \frac{4}{14} \frac{T_{1Z} M_2(\text{N-H})}{T_1(\text{N})} \right)^{-1}$$

when $H_{\text{eff}} > H_L'$.

$T_{1\rho}$ measured off-resonance did behave qualitatively as expected, increasing from T_{1X} at resonance ($H_r^2 \gg 1$) to T_{1Z} far from resonance.

VI. CONCLUSIONS

The reported study of proton-spin relaxation in the nematics POBA and PAA at low fields has shown that the spin-temperature concept must be applied to liquid crystals with care. In both POBA and PAA, it was observed that the semiequilibrium between spins on one molecule appears to be established properly. That is, the CH_3 protons and the ring protons appear to have the same spin temperature. We believe that the application of the spin-temperature concept is a reasonable approximation.

The dipolar relaxation rate for the relaxation mechanism introduced by Pincus of benzene-proton pairs in a liquid crystal was calculated. The ratios $T_1/T_{1D} = 3$ and $T_{1X}/T_{1D} = \frac{6}{5}$ were determined.

The relaxation rates T_1^{-1}, T_{1X}^{-1}, and T_{1D}^{-1} were analyzed in POBA and PAA. In both materials a qualitative understanding of the experimental data was reached when it was assumed that a small ($R_S \sim 0.3$ sec^{-1}) slow molecular mechanism relaxes the dipolar energy reservoir and the Zeeman energy reservoir in the rotating frame. In PAA, where the relaxation in the rotating frame is influenced by a proton-to-nitrogen relaxation, care was taken to properly separate the proton-to-nitrogen rate from the measured rate. This was made possible by the use of the spin-temperature concept in the rotating frame.

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APPENDIX

The dependence of M_x on the strength of the rotating field H_1 and on the local field H_L' in the case of a spin-locking pulse sequence can be derived starting from the equations given in Goldman's book.[14]

If a system is initially in equilibrium, the density matrix can be expressed as

$$\sigma_i = 1 - \beta_i \mathcal{H}_i .$$

Now if the system undergoes a sudden change (in a time $t \ll T_2$), the Hamiltonian will change but the density matrix will not change. The system will approach a new equilibrium with an inverse temperature

$$\beta_f = -\text{Tr}(\sigma_i \mathcal{H}_f)/\text{Tr}\mathcal{H}_f^2 .$$

Initially, the Hamiltonian is given by

$$\mathcal{H} = \omega_0 I_z + \mathcal{H}_D .$$

This Hamiltonian is not changed by the 90° pulse. After a field H_1 has been applied in the x direction, the Hamiltonian becomes

$$\mathcal{H} = \omega_1 I_x + \mathcal{H}_D' .$$

The effect of the 90° pulse can be expressed as

$$\sigma_i = R(\theta)(1 - \beta_L \omega_0 I_z) R^\dagger(\theta) = 1 - \beta_L \omega_0 I_x ,$$

where $R(\theta)$ is the transformation operator and $(1 - \beta_L \omega_0 I_z)$ is the initial density matrix.

After a field pulse, β evolves to

$$\beta_f = \frac{\beta_i \, \text{Tr} M_x^2 H_0 H_1 / \text{Tr} M_z^2}{H_i^2 \, \text{Tr} M_x^2 / \text{Tr} M_z^2 + \text{Tr} \mathcal{H}_D'^2 / \text{Tr} M_z^2} .$$

This can be further simplified by introducing

$$\mathrm{Tr}M_x^2/\mathrm{Tr}M_z^2=1 \quad \text{and} \quad \mathrm{Tr}\mathcal{H}_D'^2/\mathrm{Tr}M_z^2=H_L'^2 ;$$

therefore

$$\beta_f=\beta_i H_0 H_1/(H_1^2+H_L'^2) .$$

Now since $\beta_f H_1 \propto M_x$ and $\beta_L H_0 \propto M_0$, it follows that

$$M_x=M_0 H_1^2/(H_1^2+H_L'^2) .$$

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