Spin Relaxation in Nematogens and their Deuterated Derivatives

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I. INTRODUCTION

A brief review of spin relaxation (1) in nematogens is given. The usual problems in this area arise from the lack of a good theoretical model and a spin system in which meaningful measurements and direct comparison with the model can be made. The proton and deuteron spin-lattice relaxation in nematics have been extensively studied both theoretically (2,3) and experimentally (4-8). It is generally agreed that the total proton relaxation rate is the sum of two contributions

$$T_{1\,total}^{-1} = T_{1a}^{-1} + T_{1r}^{-1} \qquad (1)$$

where T_{1a}^{-1} is an intramolecular contribution and T_{1r}^{-1} an intermolecular contribution. They are due to the modulation of the dipolar interactions within a molecule and between different molecules, respectively. The deuteron relaxation rate is governed by the modulation of the electric quadrupole interactions which are almost entirely intramolecular.

Recent theoretical studies (2,3) have shown that the intramolecular relaxation is a sum of three contributions, *viz*, nematic order director fluctuations, $T_{1\,ODF}^{-1}$, angular fluctuations of the long molecular axis about the short molecular axis, $T_{1\,AFS}^{-1}$, and a coupling between the former two contributions to provide a cross-relaxation, T_{1CROSS}^{-1}. Both theories give identical expressions for T_{1ODF}^{-1} and $T_{1\,AFS}^{-1}$, but different expressions for $T_{1\,CROSS}^{-1}$. The cross-relaxation term in the theory of Doane and co-workers (2) is always positive and often the dominant term. It also remains finite even in the isotropic limit where the order parameter S becomes zero. On the other hand, the theory of Freed (3) gives a cross-relaxation term which is negative and dependent on the effect of cutoff. It is often smaller than the other two terms. Furthermore, the cross-relaxation becomes zero when S becomes zero, as one would expect for an isotropic liquid. An earlier spin-lattice relaxation study (6) of the partially deuterated *p*-azoxyanisole (PAA) and *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) met with limited success when Doane's theory was applied, probably due to the improper cross-relaxation term. Here we choose Freed's theory to re-examine some previous proton and deuteron data. Freed has also considered (3) the intramolecular spin relaxation by quasi-critical order parameter fluctuations (OPF) which may become a dominant relaxation mechanism near the isotropic-nematic phase transition at T_c. His theory was used

(9) to search for OPF in a study of proton spin-lattice relaxation time ($T_{1\varrho}$) in the rotating frame.

Although there is general agreement in the literature on the mechanisms giving rise to the intramolecular relaxation, there is disagreement concerning the mechanisms responsible for intermolecular relaxation. Two recent theories (2,10) of spin relaxation by intermolecular interactions were proposed for liquid crystals. Doane and co-workers (2) adapted their expression for intramolecular relaxation to the intermolecular case by assuming that a pair of spins reside on two perfectly parallel rod-like molecules. The dipolar interaction is again modulated by ODF and AFS, but is turned on or off with a characteristic time τ_d, a molecular jump correlation time. As in the intramolecular case, the intermolecular cross-relaxation term is usually large, positive, and finite even in the limit when S goes to zero. Here we ignore the intermolecular cross-relaxation term. The other theory proposed by Zumer and Vilfan (10) is an extension of Torrey's treatment of isotropic self-diffusion in simple liquids to the anisotropic self-diffusion in liquid crystals. The theory assumes an elongated cylindrical shape for the liquid crystal molecules, a certain distribution of spins on the cylindrical surface, and a perfect alignment of the long molecular axis. As each of these two theories assumes that the relaxation mechanisms treated by the other do not exist, it may be that both are responsible for intermolecular spin relaxation (8) in liquid crystals.

II. INTRAMOLECULAR CONTRIBUTION

A. Proton Relaxation

As Freed's theory is applicable to a pair of spin $-\frac{1}{2}$ nuclei, the appropriate spin system for direct comparison with the theoretical model is the phenyl protons of a suitably deuterated nematogen. Two such nematogens are available to us, *viz*; methyl-deuterated PAA (PAA-d_6) and *p*-methoxy-d_3-benzylidene-d_4-*p*-*n*-butyl-d_9-aniline (MBBA-d_{13}). According to Freed, the proton intramolecular relaxation rate in the laboratory frame is

$$T_{1a}^{-1} = T_{1ODF}^{-1} + T_{1\,AFS}^{-1} + T_{1\,CROSS}^{-1} \qquad (2)$$

where

$$T_{1ODF}^{-1} = (9/32\sqrt{2\pi})(\gamma^2\hbar/r^3)^2(1 - 3\cos^2\theta)^2 S^2 \qquad (3)$$
$$kTu(\omega/\omega_c)\Big/K(K/\eta + D)^{1/2}\omega^{1/2}$$

$$T_{1\,AFS}^{-1} = (3/2)(\gamma^2\hbar/r^3)^2\tau_R[1 - S(1 + 3\cos 2\theta)/4] \qquad (4)$$

where the short correlation time limit ($\tau_R \ll 1/\omega$) is assumed.

$$T_{1\,CROSS}^{-1} = -T_{1ODF}^{-1}(2\sqrt{2}/\pi)(\omega\omega^c)^{1/2}\tau_R/u(\omega/\omega_c) \qquad (5)$$

and

$$u(\omega/\omega_c) = 1 - (\tfrac{1}{2}\pi\ln[1 + \sqrt{2}\omega/\omega_c + \omega/\omega_c)/(1 - \sqrt{2}\omega/\omega_c + \omega/\omega_c)]$$
$$-(1/\pi\tan^{-1}[\sqrt{2}\omega/\omega_c/(1 - (\omega/\omega_c)] + \varrho$$

with $\varrho = 0$ if $(\omega/\omega_c) < 1$; $\varrho = 1$ if $(\omega/\omega_c) > 1$. Here $\omega_c/2\pi$ is the critical cutoff frequency which is related to the critical wavelength λ, the average elastic constant K, and the viscosity η as follows

$$\omega_c = K4\pi^2/\lambda^2\eta \qquad (6)$$

In our calculations, we assumed $\lambda = 25$ Å, the approximate molecular length. The other quantities in the above equations are: θ, the angle between r and the long molecular axis M; D, the average diffusion coefficient, and τ_R, the correlation time for molecular reorientation about the short axis.

Since the measured proton relaxation rate is the sum of T_{1a}^{-1} and T_{1r}^{-1}, one must separate them before comparing results with theoretical predictions. This can be achieved reliably by the isotopic dilution technique (11) where one measures the proton relaxation of a partially deuterated molecule in a solution of its perdeuterated analogue, extrapolates the measurements to infinite dilution, and obtains the intramolecular relaxation directly. This was carried out (11) for PAA-d_6 at 120°C. The result is reproduced in Figure 1.

The plot of T_{1a}^{-1} vs $\nu^{-1/2}$ indicates that $\omega\tau_R \ll 1$. Although the cutoff frequency is 1100 MHz ($K = 7.8 \times 10^{-7}$ dynes, $\eta = 7.1 \times 10^{-2}$ poise), $u(\omega/\omega_c)$ is 0.91 and 0.73 at 10 and 100 MHZ, respectively. The experimental data are fitted to Eq. 2 ($D = 3.4 \times 10^{-6}$ cm²/s, $S = 0.5$, $\theta = 10°$). The cross relaxation term is 10% of the AFS contribution, but is comparable in magnitude to the ODF term at 100 MHz and higher frequencies. The ODF contributes only about 24% of the total intramolecular relaxation rate at 60 MHz. The solid curve is drawn for $r = 2.49$ Å and $\tau_R = 1.9 \times 10^{-10}$ s. The deduced value of r compares well with the accepted value of 2.45 Å for a pair of ortho phenyl protons. Dipole-relaxation experiments in PAA at 125°C give

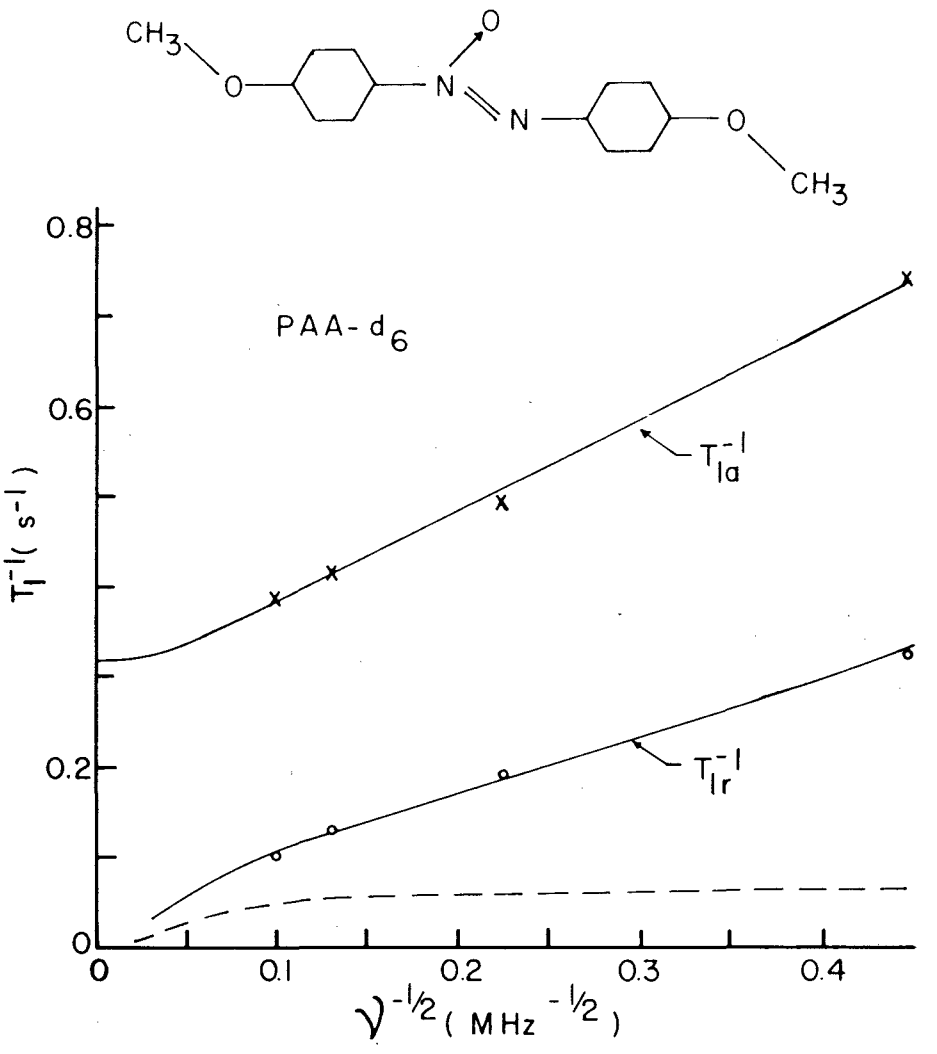

Figure 1. The structure of PAA and proton spin-lattice relaxation rate of PAA-d_6 *vs* inverse square root of the Larmor frequency at 120°C. O and X denote the *inter* molecular and the *intra* molecular contributions, respectively, obtained by Fung *et al* (11). Solid curves denote theoretical plots (see text), and dashed curve is given by the theory of Zumer and Vilfan (10).

two values of υ_D for the rotational motion of the long molecular axis:

$$\tau_{D1} = 2.5 \times 10^{-11} \text{ s and } \tau_{D2} = 4.3 \times 10^{-9} \text{ s. } 3\tau_R$$

is an order of magnitude smaller than τ_{D2} which is for an end-for-end flip of the molecule. This is reasonable because the large angle fluctuations of the long molecular axis about the short axis could occur more frequently. The proton T_{1a}^{-1} has not been measured in MBBA-d_{13} by the isotopic dilution method. However, if τ_R is determined by other means, one can calculate the theoretical intramolecular contribution to the total proton relaxation in MBBA-d_{13}. We will see below that τ_R (Table 1)

Table 1. τ_R **for the Deuterons of Carbon-15 and** υ_{D2} **in MBBA**

T	τ_R*	υ_{D2}**
(K)	(x 10^{-10}s)	(x 10^{08}s)
311	1.1 (1.2)	3
305	1.3 (1.2)	4.8
298	1.7 (1.6)	8.2
289	2.5 (1.7)	19

* The numbers in parentheses were calculated (7) with $\upsilon(\omega/\omega_c) = 1$ and without the cross-relaxation term.

** F. Rondelez and A. Mircea-Roussel, *Mol. Cryst. Liq. Cryst.* **28**, 173 (1974).

can be calculated from the relaxation rate (T_{1Q}^{-1}) of C-15 deuterons (see Figure 3). We chose the deuterons on carbon 15 because this carbon atom is situated more or less on the long molecular axis and it is the motion of the long molecular axis which gives rise to the intramolecular relaxation of the phenyl protons. The theoretical proton T_{1a}^{-1} for MBBA-d_{13} (8) at different frequencies obtained from the calculated values of τ_R is reproduced in Figure 2. The experimental proton T_{1a}^{-1}, when available, would be useful for checking the assumption that the same mechanisms (AFS) which are responsible for the in-

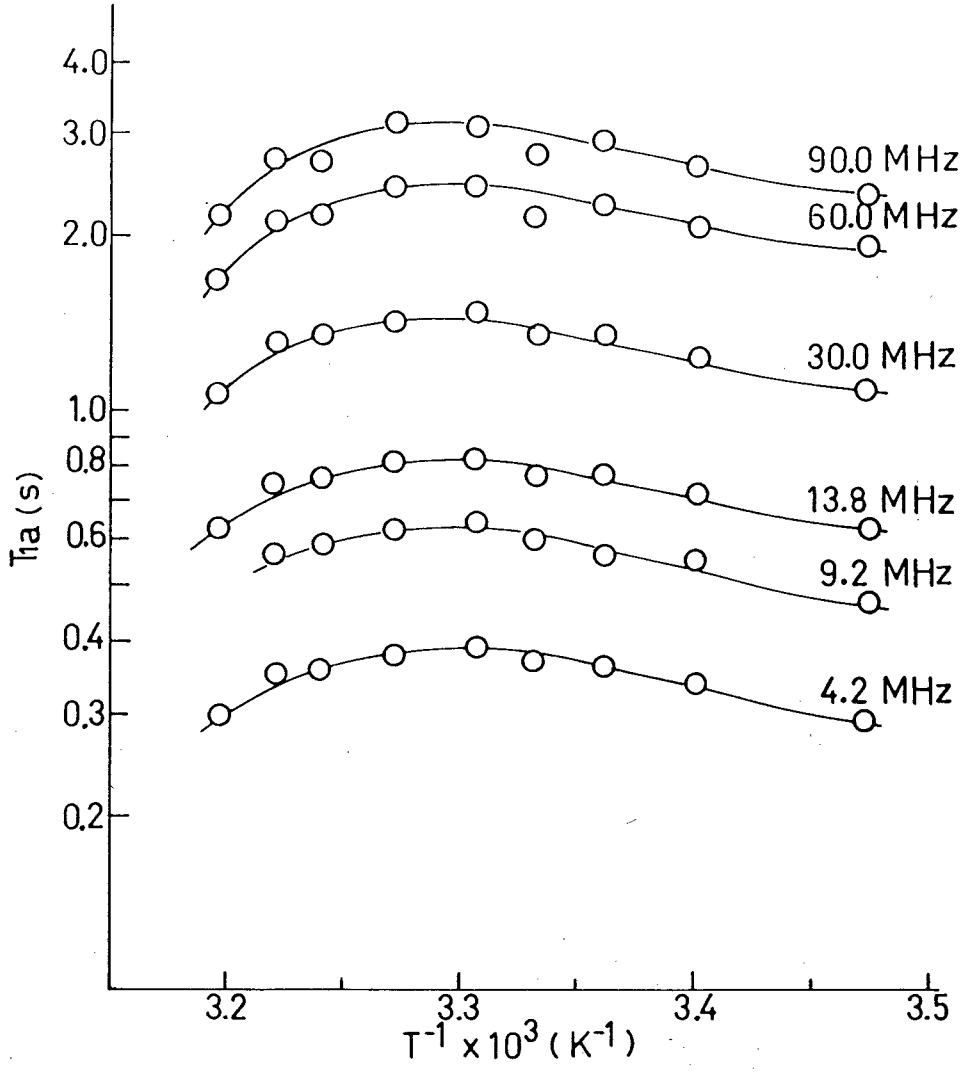

Figure 2. Calculated *intra* molecular proton relaxation time of MBBA-d_{13} at different temperatures and frequencies.

tramolecular relaxation of the phenyl protons are also responsible for relaxing the deuterons on C-15.

B. Deuteron Relaxation

Eqs. 3-5 are also applicable to the deuteron relaxation, except that the factor $\gamma^2 \hbar / r^3$ must be replaced with $e^2qQ/2h$ and the angle θ is now the angle between the C-D bond and M. There are, however, two problems in using Eq. 3 to calculate the ODF contribution for deuterons. The first problem is that the ODF contribution depends on S and on the secondary or asymmetry parameter δ, which is usually small but unknown. The second problem is that the value of the angular function $(1 - 3\cos^2\theta)$ is very sensitive to the choice of θ, especially in the vicinity of $\Theta = 60°$. Fortunately, the quadrupole splitting for deuterons, $\Delta\nu$, depends on δ and Θ in the same way as the ODF contribution. In terms of $\Delta\nu$, the expression for the ODF contribution becomes (7)

$$T_{1ODF}^{-1} = (\Delta\nu)_2 (\pi/2\sqrt{2}) kTu\ (\omega/\omega_c)/K(D + K/\eta)^{1/2}\omega^{1/2} \qquad (7)$$

Deuteron spin-lattice relaxation (T_{1Q}) in ring-deuterated PAA—PAA-d_8—(12) and in ring-deuterated MBBA— MBBA-d_8— (6,13) shows no detectable frequency dependence between 4 and 45 MHz but a strong temperature dependence. The deuterium spectrum of MBBA-d_{13} at 13.81 MHz has the advantage of being well resolved, thus allowing selective deuteron T_{1Q} measurements (7). A typical spectrum with assignment by the structural carbon numbers is given in Figure 3. In addition, the time-averaged quadrupole tensor along the director is readily determined from the spectrum. In accordance with Eq. 7, T_{1ODF}^{-1} was calculated for the C-15 deuterons using their $\Delta\nu$ values (see Figure 4), $\omega_c = 4.8 \times 10^8\ s^{-1}$, and the values for K, D, and η from the literature (14). Subtraction of T_{1ODF}^{-1} from the measured relaxation rate (Figure 4) yielded the sum of the AFS and CROSS terms, from which the value of τ_R (7,8) was finally calculated. In the latter calculation, we use $\theta = 75°$, 170 kHz for the quadrupole coupling constant e^2qQ/h, and the S values of Lee *et al* (14). Some τ_R values at different temperatures are tabulated in Table 1 together with those obtained in (7) in which both $u(\omega/\omega_c)$ and cross-relaxation terms are neglected. The assumptions made in (7) are justified, as seen in Table 1. This is because both the ODF and the cross-relaxation terms for deuterons are small, about 16%, and 1%, respectively, of the AFS contribution for the C-15 deuterons. Also shown in Table 1 are the dielectric relaxation times τ_{D2} for MBBA. $3\tau_R$ is again smaller than υ_{D2} as in PAA, but by two orders of magnitude.

Figure 5 shows the deuteron data (6,13) for MBBA-d_8. We assume again that the τ_R's used above describe the AFS contribution of the phenyl deuterons. The solid line denotes calculations based on the theory of Freed. We used $\Delta\nu = 10.4$ kHz (for peak *b*) (13) at 26°C and 13.8 MHz and $\theta = 58.35°$ to calculate the ODF contribution and $\theta = 58.35°$. This angle is also used to calculate the AFS term with $e^2qQ/h = 187$ kHz. Since the ODF and CROSS terms constitute about 1-2% of the AFS term, T_{1Q} should be almost totally independent of frequency. The discrepancies between theory and experiment in the magnitude of T_{1Q} can be explained by rotation of the ring about its para axis, which produces additional relaxation of phenyl deuterons. As seen in Figure 5, the AFS and ring rotation about the para axis contribute about equally to the observed deuteron relaxation rate in MBBA-d_8. It was noted that the aniline and benzylidene rings reorient at different rates about the para axes (13).

C. Order Parameter Fluctuation

Just below T_c, fluctuations in the magnitude of the nematic order parameter S may be observable by NMR relaxation techniques. When the quasi-critical OPF contribution dominates over the usual ODF contribution near T_c, then T_{1ODF}^{-1} in Eqs. 2 and 5 are replaced by $T_{1\,OPF}^{-1}$ (3). To obtain $T_{1\,CROSS}^{-1}$ in Eq. 5, we have included $u(\omega/\omega_c)$ and $\omega\tau_0 >> 1$ in $T_{1\,OPF}^{-1}$ (see Eq. 8 below) and used $\omega\tau_R << 1$ and $\omega_c\tau_0 << 1$, where $\tau_0 \equiv \nu_N/A$, $A \propto (T\dagger - T)$ in the mean field approximation, and $T\dagger\ (> T_c)$ is the temperature at which a second order isotropic nematic phase transition would occur. While $T_{1\,AFS}^{-1}$ is again given by Eq. 4, Freed (3) has obtained for a spin-½ pair with $r >> M$

$$T_{1\,OPF}^{-1} = (9/8)(\gamma^2\hbar/r^3)^2[kT\nu_N^{1/2}u(\omega/\omega_c)/3\sqrt{2}\pi LN^{3/2}\omega^{1/2}]([x(0,1)]^2 + 2\sqrt{2}[x(0,2)]^2) \qquad (8)$$

and

$$T_{1Q}\,OPF^{-1} = (9/8)(\gamma^2\hbar/r^3)^2\{[kT\nu_N^{1/2}u(\omega/\omega_c)/3\sqrt{2}\pi L_N^{3/2}\omega^{1/2}](5[x(0,1)]^2/2 + [x(0,2)]^2/\sqrt{2}]) + (kT/2\sqrt{2}\varrho)\dagger_N\varepsilon[x(0,0)]^2/L^2_N| \qquad (9)$$

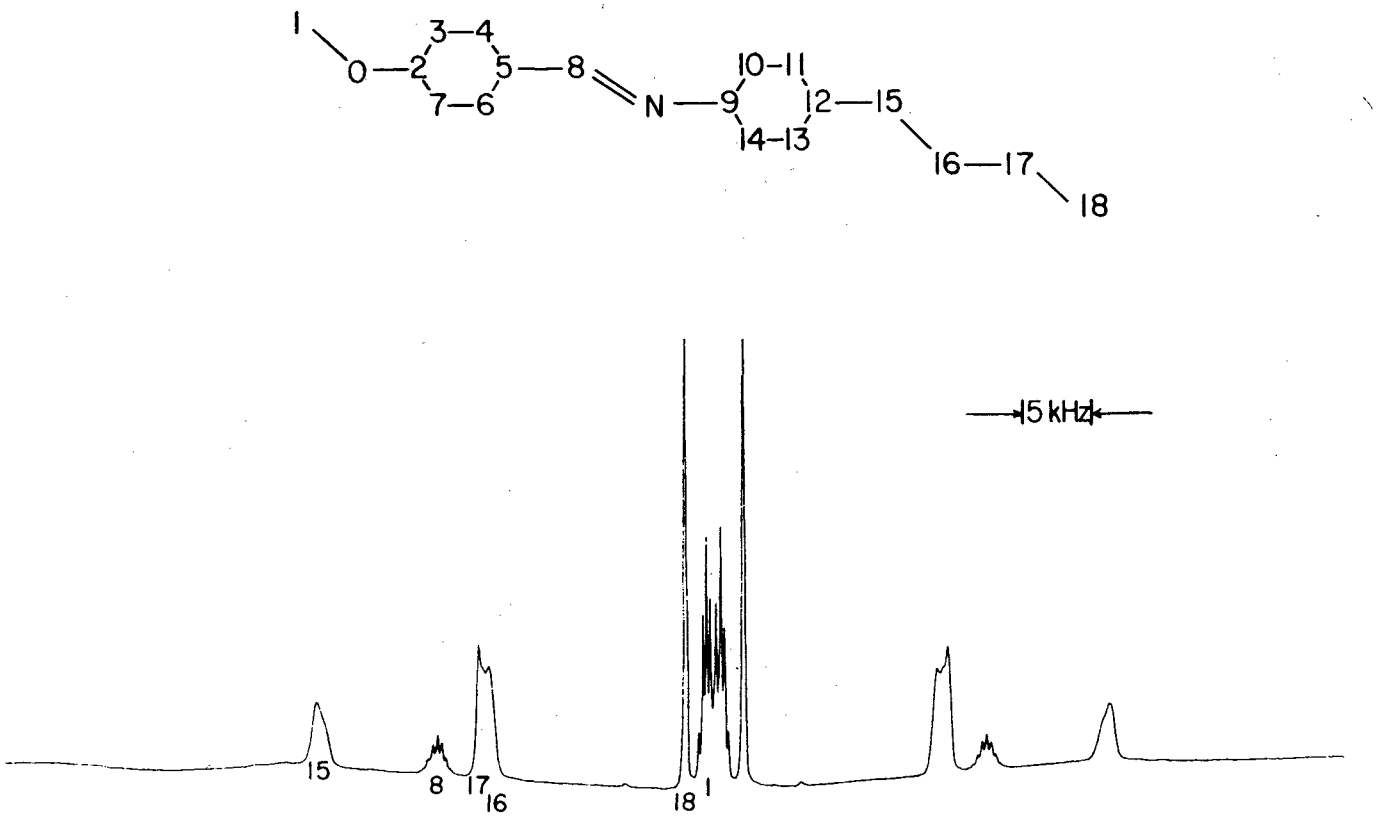

Figure 3. The structure of MBBA and a typical deuterium FFT spectrum of MBBA-d_{13}. The carbon atoms of the methoxy group and the *n*-butyl chain are numbered as 1 and 15-18, respectively. H atoms are omitted for clarity. The doublets in the spectrum are labelled by the carbon atoms.

where $\omega_1 << t'_0 << \omega$ is assumed, ω_1/γ is the rotating field $B1$, and $\xi = (LN/A)^{1/2}$ is the coherence length of the nematic order parameter fluctuations. The coefficients $\kappa(0,M)$ are given (3) as a power series in S in (9), together with definitions of all other symbols. The last term in Eq. 9 comes from the spectral density $J^{(0)}(2\omega_1)$ which is independent of B_1 because $\omega_1\tau << 1$ and acquires a critical dependence on temperature through the coherence length ξ. The quasi-critical OPF can therefore be detect by $J^{(0)}(2\omega_1)$. By combining Eqs. 8 and 9, one obtains

$$T_{1\varrho}^{-1} = T_{1\varrho}\,\mathrm{OPF}^{-1} - f(s)\,T_{1\,OPF}^{-1} =$$

$$(9/8)(\gamma^2\hbar/r^3)^2(kT/2\sqrt{2}\pi)[\kappa(0,0)]^2\nu_N\xi/L_N^2 \qquad (10)$$

where

$$f(S) = [(5/2) + (1 - 5S/4)^2/\sqrt{2}]/[1 + 4(1 - 5S/4)^2/\sqrt{2}]$$

The problem of evaluating $T_{1\varrho}'$ is in obtaining the quantities $T_{1\varrho}$ OPF^1 and $T_{1OPF}{}^1$. In our attempt (9) to search for OPF in PAA-d_6 at ω = 60 MHz, we made the following assumptions: (1) $T_{1\varrho}{}^1 = T_{1\varrho}a^{-1}$; (2) $T_1^{-1} = T_{1a}^{-1} + T_{1r}^{-1} = 1.29\ T_{1a}^{-1}$ for all temperatures and (3) $T_{1a}^{-1} = T_{1\,OPF}^{-1}$ and $T_{1\varrho}a^{-1} = T_{1\varrho}$ OPF^{-1} near T_c. The third assumption may be questionable since it has been shown that $T_{1\,AFS}^{-1}$ at 60 MHz and 120°C makes a significant contribution to the total intramolecular relaxation rate. By analogy to Eq 2, one writes

$$T_{1\varrho}a^{-1} = T_{1\varrho}\,\mathrm{OPF}^{-1}\,[1 - (2\sqrt{2}/\pi)(\omega\omega_c)^{1/2}\tau_R/U(\omega/\omega_c)] + T_{1\varrho\,AFS}^{-1} \qquad (11)$$

where $T_{1\varrho}$ AFS^{-1} = $T_{1\,AFS}^{-1}$ is (1 + 3S/2)used. We will not discuss OPF further because a proper analysis of PAA-d_6 data still awaits further isotopic dilution ex-

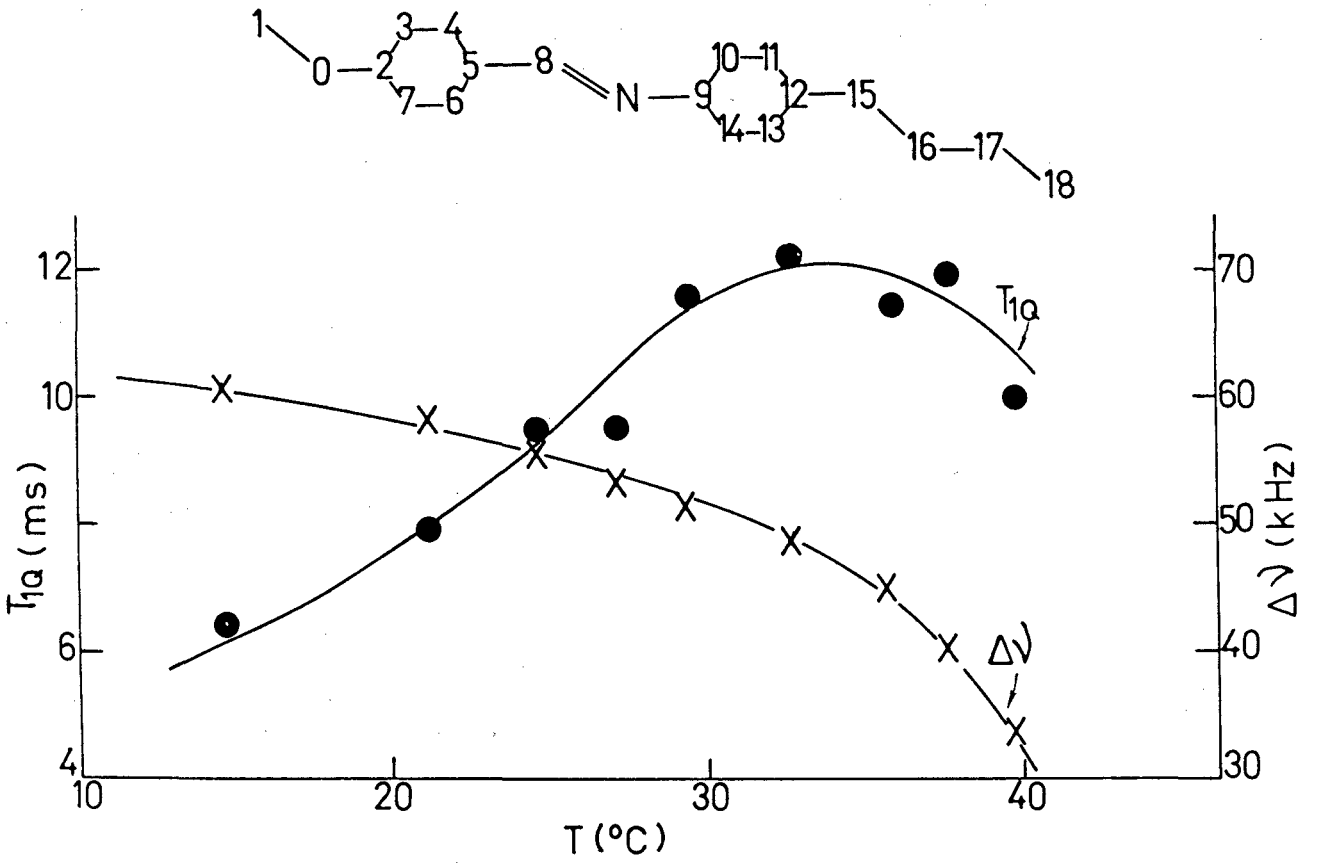

Figure 4. Plot of the deuteron relaxation time, T_{1Q} and deuteron doublet splitting, $\Delta\nu$, for the carbon-15 deuterons *vs* temperature in the nematic phase of MBBA-d_{13}.

periments in this system at temperatures near T_c from which $T_{1_R}^{-1}$ and τ_R are experimentally determined.

III. INTERMOLECULAR INTERACTION

Doane *et al* (2) give the following expression for the intermolecular proton relaxation rate, omitting the cross-relaxation term,

$$T_{1r}^{-1} = (9/4)(\gamma^2\hbar/r^3)^2$$
$$\{[kTS^2u(\omega/\omega_c)/8\sqrt{2}\pi K(D + K/\eta)^{1/2}\omega^{1/2}] +$$
$$(\tau_d/15)[2(1\text{-}S)/(1 + W^2\tau d^2)$$
$$+ (8 + 7S)/(1 + 4\omega^2\tau_d)^2)]\}? \qquad (12)$$

where r is the distance between protons on different molecules, and τ_d is the molecular jump correlation time. The corresponding expression obtained by Zumer and Vilfan (10) is

$$T_{1r}^{-1} = (9/8)(\gamma^4\hbar^2/d^3)n\,\tau Q(\omega\tau, <r_\perp^2>/d^2, D_{||}^\circ/D_\perp^\circ) \qquad (13)$$

where n is the spin density, d the diameter of the rod-like molecules, $<r_\perp^2>$ the mean square molecular jump length, $D_{||}^\circ$ and $D_\perp^\circ$ the self-diffusion coefficients in the direction parallel and perpendicular, respectively, to the direction of the long molecular axis, and $\tau = (<r_\perp^2>/d^2)\tau^\circ$ where τ° is defined by $\tau^\circ = d^2/4D_\perp^\circ$. Q is a dimensionless function which must be calculated numerically. Zumer and Vilfan (10) have calculated Q for the case $d = 5$Å, $D_{||}^\circ/D_\perp^\circ = 2$, for different frequencies and three different values of the ratio $<r_\perp^2>/d^2$, *viz*, 1, 0.1, and 0.01.

In order to test experimentally the theories on the intermolecular proton spin-lattice relaxation, it is necessary to separate the measured relaxation rate into the intra- and intermolecular contributions. As mentioned before, one way of separation is to obtain T_{1a}^{-1} directly by the isotopic dilution technique. The other way is to calculate T_{1a}^{-1} theoretically. For the phenyl protons of MBBA-d_{13}, we chose the latter

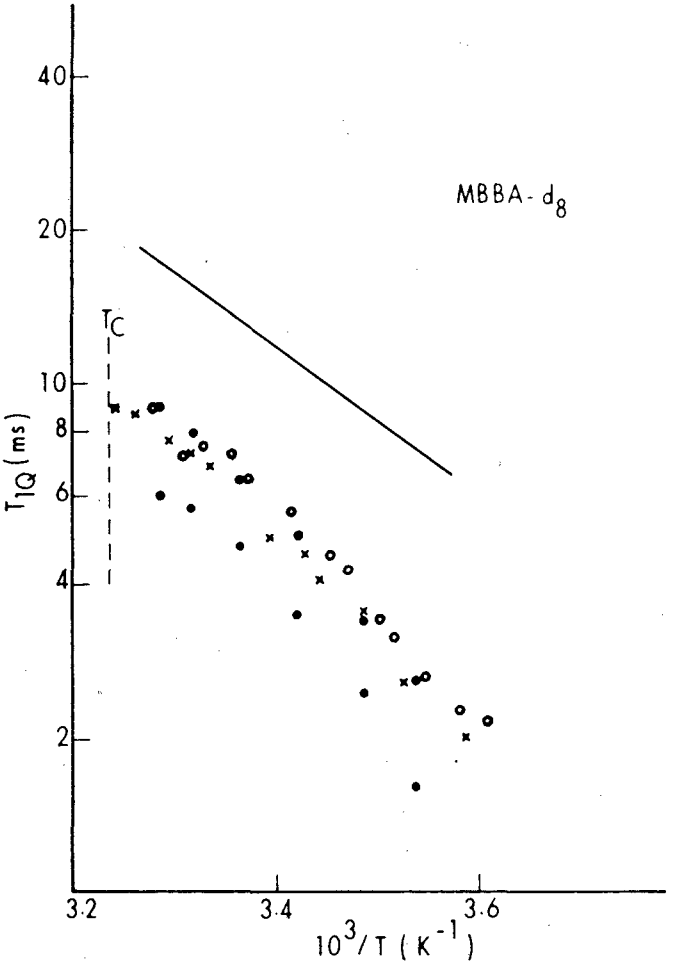

Figure 5. Deuteron spin-lattice relaxation time T_{1Q} of MBBA-d_8 *vs* the inverse of temperature. O and X denote measurements by Visintainer *et al* (6) at 9.21 and 4.5 MHz, respectively, and O denotes measurements by Rutar *et al* at 13.8 MHz. Solid line denotes theoretical plot at 13.8 MHz.

method. The proton T_{1r}^{-1} (Figure 6) was calculated (8) from Eq. 2 using the result in Figure 2 and the measured proton spin-lattice relaxation rate of MBBA-d_{13}. Figure 7 presents typical fits to the "experimental" T_{1r}^{-1} data at 29.2°C based on the above-mentioned theories. The lower curve is a theoretical plot of T_{1r}^{-1} vs $\nu^{1/2}$ using Zumer and Vilfan's theory. We used $n = 0.019/\text{Å}^3$, $d = 5\text{Å}$, $\langle r_\perp{}^2\rangle / d^2 = 0.1$, and $\tau^0 = 3.47 \times 10^{-9}$s. As seen in Figure 7, the agreement between theory and experiment is poor. The solid curve represents a fit to the experimental data using Eq. 12 with the adjustable parameters r and τ_d equal to 2.85 Å and 1.73×10^{-9}s, respectively. We set $u(\omega/\omega_c) = 1$ because the ODF contribution in this case is negligibly small in comparison with the AFS contribution. Now r remains essentially constant in the nematic range while τ_d's at different temperatures produce an activation energy of 4.8 ± 0.4 kcal/mole. This compares favourably with the activation energy for self-diffusion (14) in MBBA found by Hervet *et al*, *viz* 5.8 ± 0.7 kcal/mole for $D_{||}$ and 6.0 ± 0.8 kcal/mole for $D_\perp$. The temperature dependence of T_{1r}^{-1} (Figure 6) at different frequencies can be reproduced quite well by the above τ_d values. It would therefore seem that self diffusion is not the sole intermolecular contribution to the spin relaxation rate in MBBA, and the other relaxation mechanisms must also be present. If one assumes that the expression of Doane *et al* (2) for T_{1r}^{-1} accounts for the ODF and AFS only, and if one further assumes that these fluctuations are not coupled to self-diffusion, then the experimental T_{1r}^{-1} should be analyzed by the sum of Eqs. 12 and 13. Indeed, such an analysis is suggested by the frequency dependence of T_{1r}^{-1} in PAA (Figure 1). The dashed curve in the figure represents a fit with $r = 2.91$ Å, $\tau_d = 1.55 \times 10^{-9}$s, and the self-diffusion contribution given by the lower curve. We note that the r and τ_d do not vary significantly for the two fits, although the latter τ_d values give an activation energy of 6.5 ± 0.3 kcal/mole in closer agreement with that for self-diffusion.

Finally, the experimental T_{1r}^{-1} data of PAA-d_6 (Figure 1) at 120°C can be analyzed in exactly the same manner. In Figure 1, the lower dashed curve represents a plot given by Zumer and Vilfan's theory with $n = 0.02/\text{Å}^3$, $\langle r\perp{}^2\rangle / d^2 = 0\text{-}1$, $d = 5\text{Å}$, and $\tau^\circ = 2.08 \times 10^{-10}$s. In the frequency range examined, self-diffusion are almost frequency independent. Again, the experimental T_{1r}^{-1} data is fitted by the sum of Eqs. 12 and 13. The solid curve represents the theory with $r = 2.2$ Å, $\tau_d = 1.64 \times 10^{-12}$ s, and the self-diffusion given by the dashed curve. In this case, the ODF con-

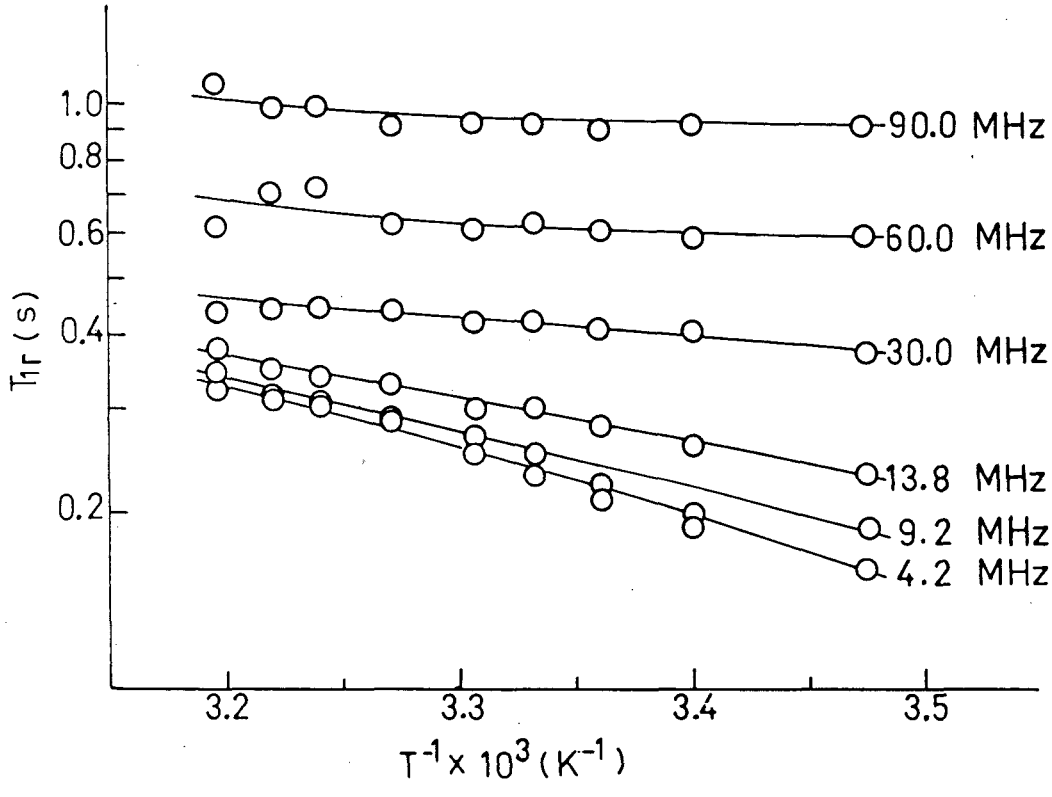

Figure 6. Intermolecular proton relaxation times of MBBA-d_{13} at different temperatures and frequencies.

tribution dominates, and the AFS term is only ·9% of the ODF contribution. Though τ_d is smaller than that estimated from the self-diffusion constant, the fit appears very good indeed.

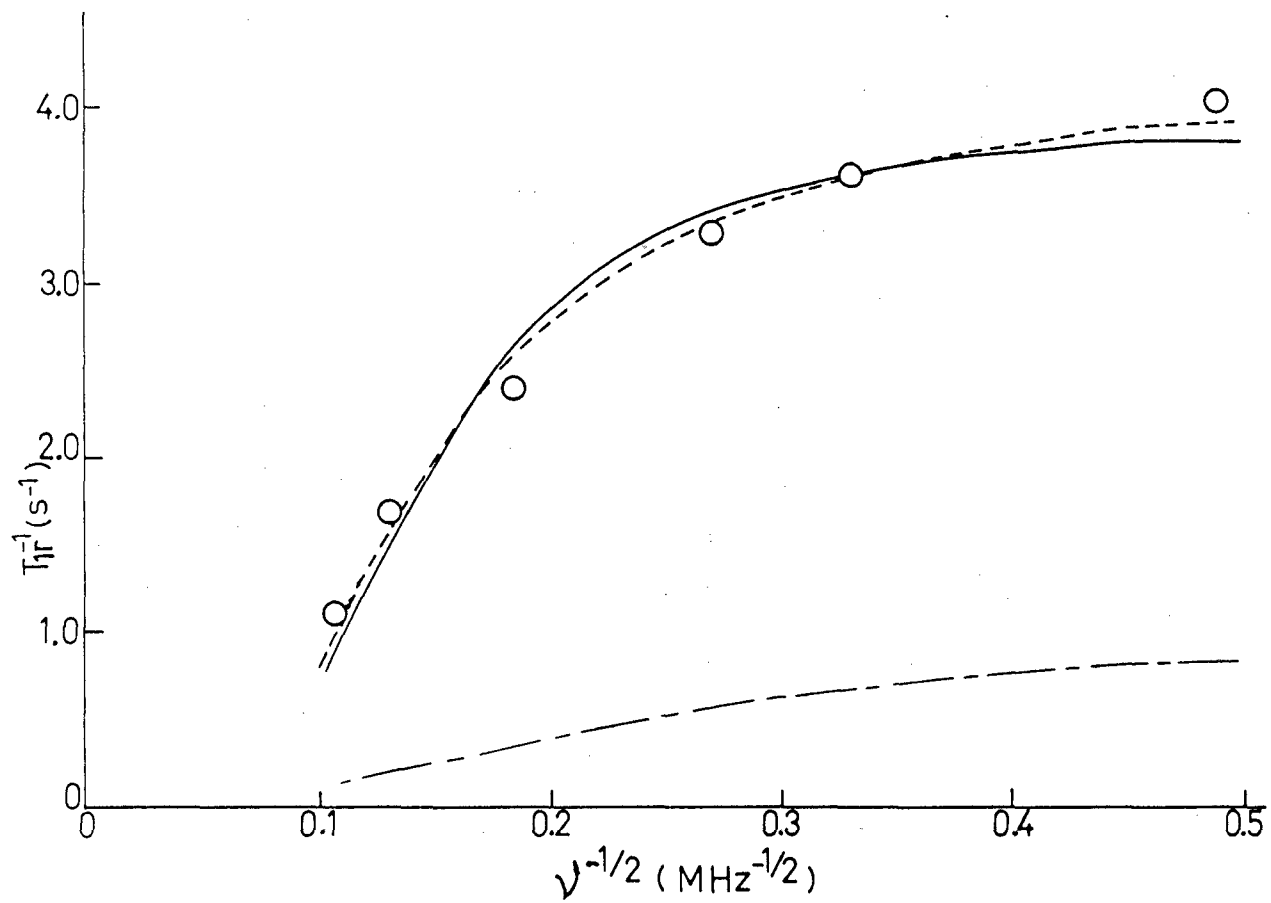

Figure 7. *Plot of the proton* T_{1r}^{-1} *vs* $\nu^{-1/2}$ *for MBBA-*d_{13} *at 29.2°C. The lower curve represents values from the theory of Zumer and Vilfan. Solid and dashed curves denote a fit to the data using, respectively, Doane's theory alone and the theories of both Doane* et al *and Zumer and Vilfan (see text).*

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