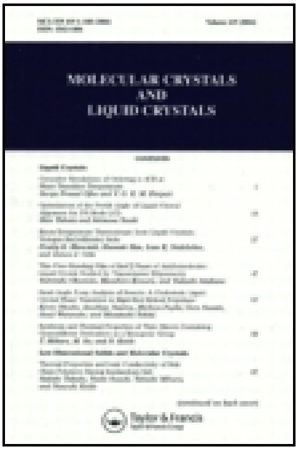

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Inter and Intramolecular Contributions to the Proton Dipolar and Rotating Frame Spin-Lattice Relaxation Times in the Nematic Phase of the Liquid Crystal 5CB-d $_{11}$

J. S. Lewis [a] , E. Tomchuk [a] & E. Bock [b]

[a] Department of Physics, University of Winnipeg, Winnipeg, Manitoba, R3B2E9, Canada

[b] Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

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Inter and Intramolecular Contributions to the Proton Dipolar and Rotating Frame Spin-Lattice Relaxation Times in the Nematic Phase of the Liquid Crystal 5*CB*-d_{11}*

J. S. LEWIS and E. TOMCHUK

Department of Physics, University of Winnipeg, Winnipeg, Manitoba, R3B 2E9, Canada

and

E. BOCK

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

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An isotopic dilution study of the proton dipolar and rotating frame spin-lattice relaxation times (T_{1D} and $T_{1\rho}$) in the nematic liquid crystal 4-cyano-4′-*n*-pentyl-d_{11}-biphenyl (5*CB*-d_{11}) at 13.8 MHz over the nematic phase temperature range was used to separate the intermolecular and intramolecular contributions to the ring proton relaxation rates. This is the first such study to be reported. Combined with our earlier proton study of inter/intra Zeeman spin-lattice relaxation (T_1) in 5*CB*-d_{11}, these data permit a critical study of the soft-mode dynamics in the system. A qualitative explanation of the T_{1D} results is presented, but a complete explanation of the $T_{1\rho}$ results is not possible with existing theory.

INTRODUCTION

The proton relaxation rates R_1, $R_{1\rho}$ and R_{1D} are sums of intermolecular (R_{1r}, $R_{1\rho r}$ and R_{1Dr}) and intramolecular (R_{1a}, $R_{1\rho a}$ and R_{1Da}) contributions. We

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present here a study of the proton T_{1D} ($= 1/R_{1D}$) and $T_{1\rho}$ ($= 1/R_{1\rho}$) relaxation times in the nematic liquid crystal 4-cyano-4′-*n*-pentyl-d_{11}-biphenyl (5*CB*-d_{11}) in solutions of the perdeuterated analogue (5*CB*-d_{19}) at 13.8 MHz over the nematic phase temperature range. These data yield the intermolecular and intramolecular contributions which when combined with our earlier[1] R_{1r} and R_{1a} data for the same molecule permite a study of the soft-mode dynamics[2] of the system and the validity of the approximations used in Reference 2. The existence of additional slow relaxation mechanisms[3] is also considered.

RESULTS AND DISCUSSIONS

All measurements were performed on a Bruker SXP-4-100 MHz spectrometer interfaced with a Nicolet 1180 computer. The various solutions of

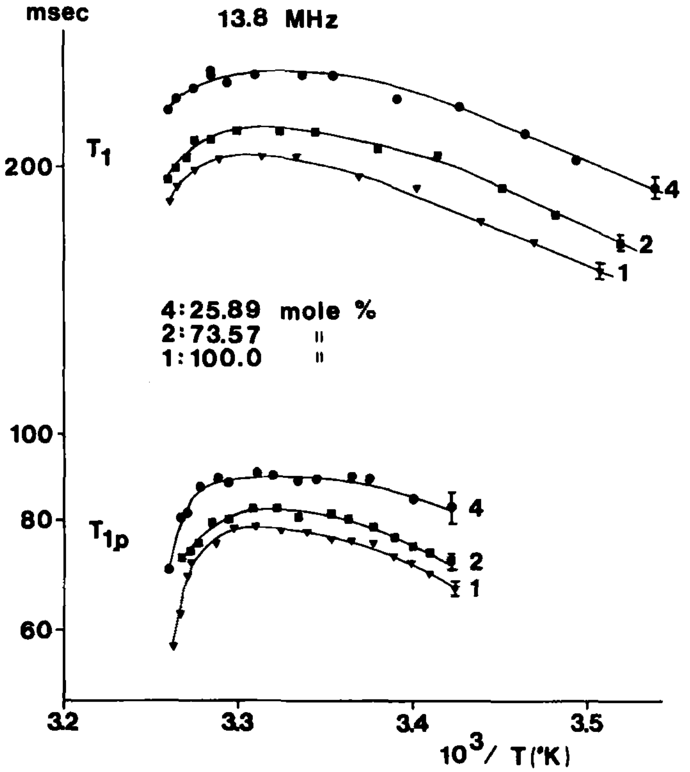

FIGURE 1 Plot of proton Zeeman and rotating frame relaxation times in 5*CB*-d_{11} vs $10^3/T$, *T* in K. The concentrations of 5*CB*-d_{11} in 5*CB*-d_{19} are indicated in the figure.

5CB-d_{11} in *5CB*-d_{19} have different clearing temperatures, and thus we use $T = T_{\text{measured}} - (T_{c,\text{sample}} - T_{c,5CB\text{-}d_{11}})$ where T_c is the clearing temperature. The effect of the deuterons on the proton relaxation was compensated for by the method of Fung *et al.* The T_1 and $T_{1\rho}$ results at 13.8 MHz are given in Figure 1. The separation into intermolecular and intramolecular contributions is given in Figure 2. The solid points are based on the curves of Figure 1, and the open circles on the data points of Figure 1. We use only the former. The frequency dispersion of R_{1a} and R_{1r} are shown in Figure 3. In Ref. 2 it was assumed that in *PAA*-d_6 the ratio R_{1a}/R_{1r} is independent of temperature, that $R_{1\rho} = R_{1\rho a}$, and that $R_{1\rho a}/R_{1\rho r} = \infty$. It is seen from Figure 4 that for *5CB*-d_{11} these assumptions are not valid.

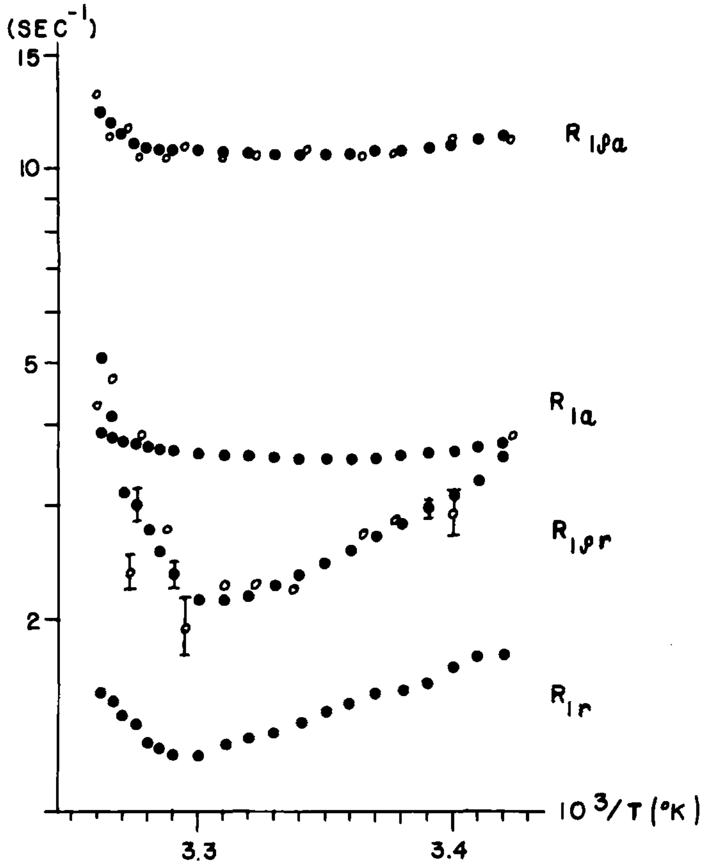

FIGURE 2 Intermolecular and intramolecular contributions to the proton Zeeman and rotating frame relaxation rates vs $10^3/T$, T in K.

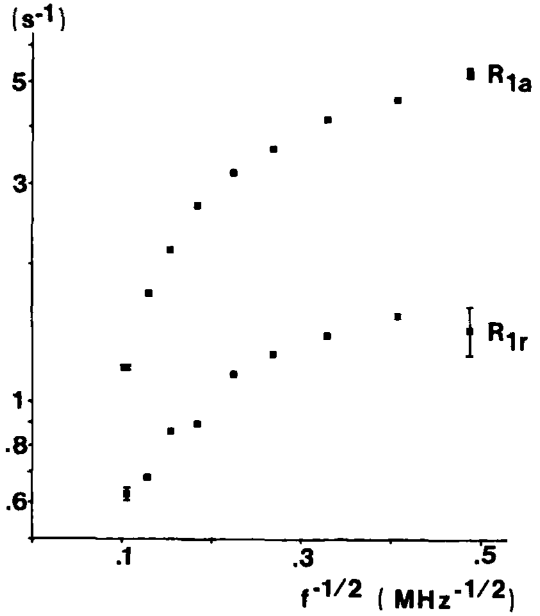

FIGURE 3 Intermolecular and intramolecular contributions to the proton Zeeman relaxation rates vs $f^{-1/2}$, f in MHz at 29°C.

Following Ref. 2, the theories of Freed[5] and Jones[6] yield for a pair of protons the following rates:

$$R_1 = \frac{3}{2}(\gamma^2 h/r^3)^2 \sum (f^{(k)}(\beta))^2 [J_{k1}(\omega_0) + 4J_{k2}(2\omega_0)]$$

$$R_{1\rho} = \frac{3}{2}(\gamma^2 \hbar/r^3)^2 \sum (f^{(k)}(\beta))^2 \left[\frac{5}{2}J_{k1}(\omega_0) + J_{k2}(2\omega_0) + \frac{3}{2}J_{k0}(2\omega_1)\right]$$

where $\beta = 0°$ for the intramolecular rates, $\beta = 90°$ for the intermolecular rates, and where the possible contributions are as follows:

(a) AFS: limited random fluctuations of individual molecules,

$$J_{\mathrm{KM}}^{\mathrm{AFS}}(\omega) = \kappa(K, M)\tau/(1 + \omega^2\tau^2),$$

(b) ODF: 1.r.f. of direction of local order

$$J_{\mathrm{KM}}^{\mathrm{ODF}}(\omega) = (3/4\, 2^{1/2}\pi) S^2 kT(\eta/K^3)^{1/2}\, \delta_{K0}\, \delta_{M\pm1}\omega^{-1/2}$$

(c) OPF: 1.r.f. of direction and magnitude "near" the phase transition,

$$J_{\mathrm{KM}}^{\mathrm{OPF}}(\omega) = \left[\left(\frac{1}{4}2^{1/2}\pi\right)(\kappa(0, M))^2 kT(\nu\tau_0/L^3)^{1/2}\, \delta_{K,0}[1 + (1 + \omega^2\tau_0^2)^{1/2}\right]^{-1/2}$$

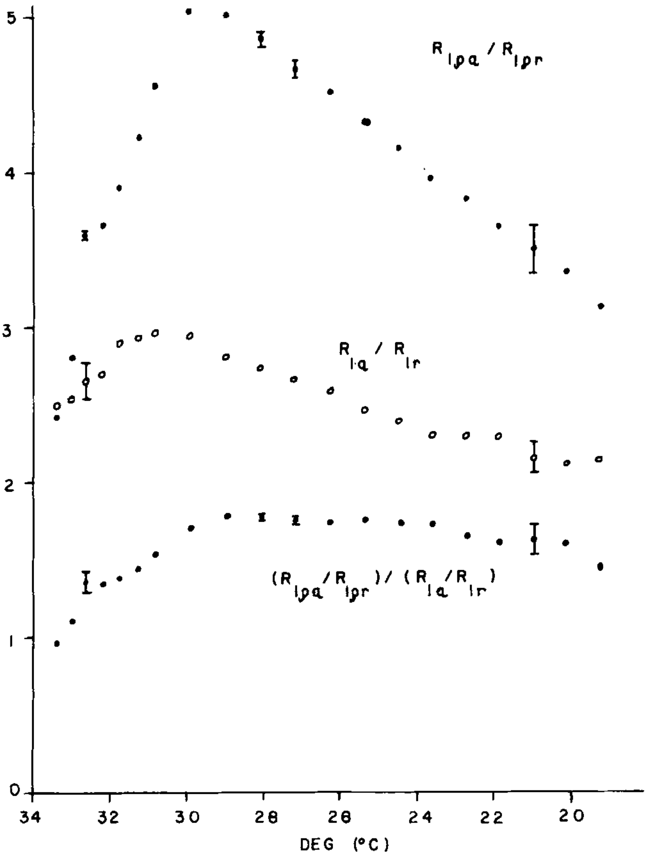

FIGURE 4 Relaxation rate ratios as a function of temperature in °C.

and where τ and τ_0 are correlation times, S is the order parameter, k is Boltzmann's constant, T is the temperature in K, η and ν are viscosities, K and L are elastic constants, and where

$$\kappa(K,M) = \langle D^2_{km} D^{2*}_{km} \rangle - \langle D^2_{00} \rangle \, \delta_{K,0} \, \delta_{M,0}.$$

For the present case

$$J^{\mathrm{OPF}}_{\mathrm{OM}}(\omega) \alpha [\kappa(0,0)]^2 T(\nu\xi/L^2) \qquad \text{for } M = 0 \text{ and } \omega = 2\omega_1,$$

$$J^{\mathrm{OPF}}_{\mathrm{OM}}(\omega) \alpha [\kappa(0,M)]^2 T(\nu/L)^{1/2} \omega^{-1/2} \qquad \text{for } M = 1,2 \quad \text{and } \omega = \omega_0,\ 2\omega_0,$$

where ξ is the coherence length of the nematic OPF. Clearly R_1 does not depend on ξ. The above theory was used to fit the R_{1a} and the R_{1r} results as a function of temperature and frequency. These results at 13.8 MHz are given in Figures 5 and 6. All of the terms in $R_{1\rho a}$ except the term involving J_{00}^{OPF} can be calculated from the terms in R_{1a} and R_{1r}. These results are given in Figures 5 and 6 also.

Let T^* be the supercooling point, T' the superheating point, and T_C the critical point. Lin and Cai[7] use the de Gennes-Landau theory to show that

$$(T' - T_C) = \tfrac{1}{8}(T_C - T^*) \text{ and}$$

$$\xi \sim [(1 - T/T') + \alpha(1 - T/T')^{1/2}]^{-1/2}$$

where $\alpha \equiv (1 - T^*/T')^{1/2}$. To within ~3% the above expression is approximated by

$$\xi \sim (T' - T)^{-2/5}.$$

For $PAA\text{-}d_6$ the expression $\xi \sim (T' - T)^{-\nu}$ with $\nu = \tfrac{1}{2}, \tfrac{2}{5}$, and $\tfrac{2}{3}$ has been used.[2,8] It can be seen from Figure 5 that to explain $R_{1\rho a}$ within the present formalism it would be necessary to have $J_{00}^{\mathrm{OPF}}(2\omega_1)$ essentially independent of temperature, a requirement that appears to be inconsistent with the de Gennes-Landau theory. This suggests either that there is an additional

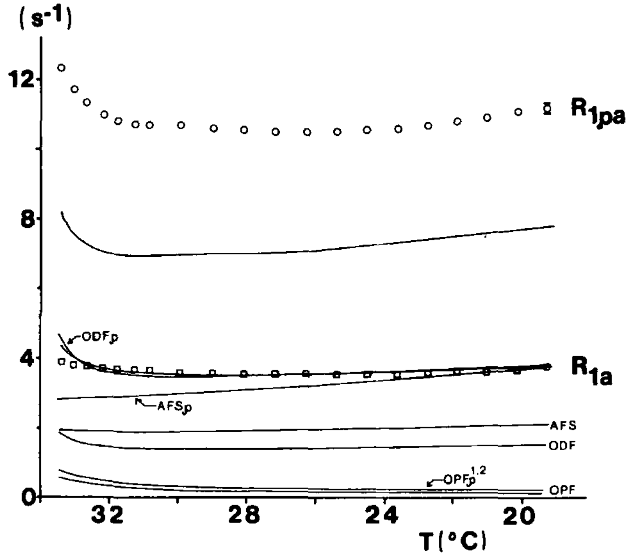

FIGURE 5 Calculated contributions to the intramolecular proton Zeeman and rotating frame relaxation rates as a function of T, T in °C. The subscript ρ refers to rotating frame relaxation contributions and the superscript 1, 2 indicates that for $R_{1\rho a}$ the contribution from $J_{\mathrm{OM}}^{\mathrm{OPF}}(2\omega_1)$ for $M = 0$ is not included. The unlabelled lines are sums of the appropriate terms for R_{1a} (lower line) and $R_{1\rho a}$ (upper line).

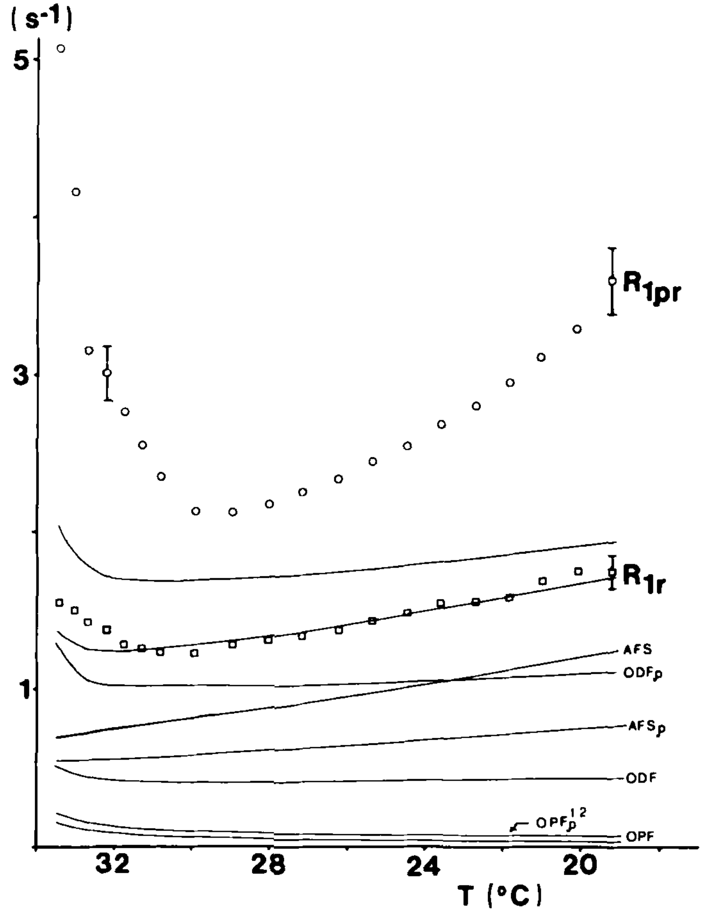

FIGURE 6 Calculated contributions to the intermolecular proton Zeeman and rotating frame relaxation rates as a function of T, T in °C. The subscript ρ refers to rotating frame relaxation contributions and the superscript 1, 2 indicates that for $R_{1\rho r}$ the contribution from $J^{\mathrm{OPF}}_{0M}(2\omega_1)$ for $M = 0$ is not included. The unlabelled lines are the sums of the appropriate terms for R_{1r} (lower line) and $R_{1\rho r}$(upper line).

slow relaxation mechanism[3] or that there is a difficulty with the theory. It can be seen from Figure 6 that to explain $R_{1\rho r}$ it would be necessary to have a very unusual $J^{\mathrm{OPF}}_{00}(2\omega_1)$. It is known[9] that the theory used here is only an approximation for intermolecular relaxation, but to our knowledge the extension of Torrey-type theory[9] to the case of $R_{1\rho}$ and R_{1D} in liquid crystals has not been published.

It is possible[2,8] to study the soft-made dynamics if one notes that the de Gennes-Landau theory is expected to hold only very near the nematic-

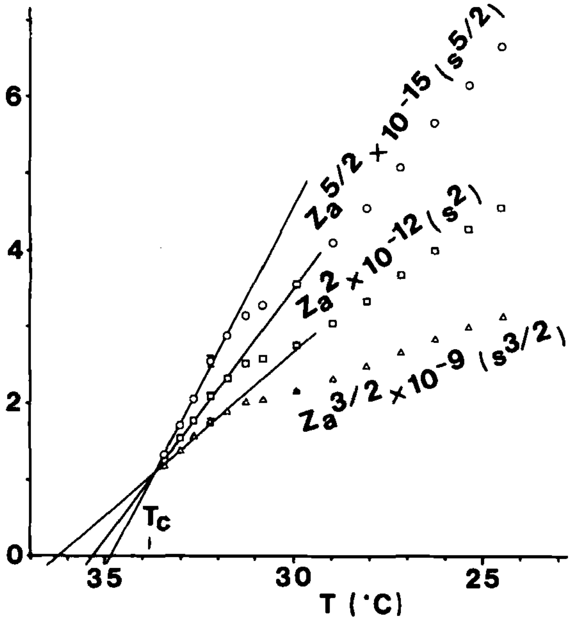

FIGURE 7 Plots of appropriate powers of $Z_a = \kappa(0,0)^2 T'_{1\rho a} \exp(W/T)$ as a function of T, T in °C, where $W = 5960$ K. The straight lines are linear least squares fits in the first 5 points only, and the intercepts give the resulting superheating points.

isotropic transition temperature,[7] and if one assumes that $R^{AFS}_{1\rho a}$ is correct. If we define

$$R'_{1\rho a} = (R_{1\rho a} - R^{AFS}_{1\rho a} - f(S, \langle D^4_{00}\rangle)(R_{1a} - R^{AFS}_{1a})$$

then it can be shown[2,8] that

$$[\kappa(0,0)^2 e^{W/T} T'_{1\rho a}]^{1/\nu} \sim (T' - T),$$

with a similar result for the intermolecular case. These plots are shown in Figures 7 and 8. For the intramolecular case the results compare favorably with these obtained for *PAA*-d_6,[2,8] and in particular give the same trend of T as a function of ν. Unfortunately, the result $(T' - T_C) = 1.03$°C for $\nu = 2/5$ is about three times as large as obtained for *PAA*-d_6, and approximately an order of magnitude larger than the value obtained for 5*CB* by Poggi *et al.*[10,11] For the intermolecular case only the $\nu = 2/3$ result is physically acceptable, as T' must be greater than Tc, and $(T' - T_C) = 0.26$°C appears plausible.

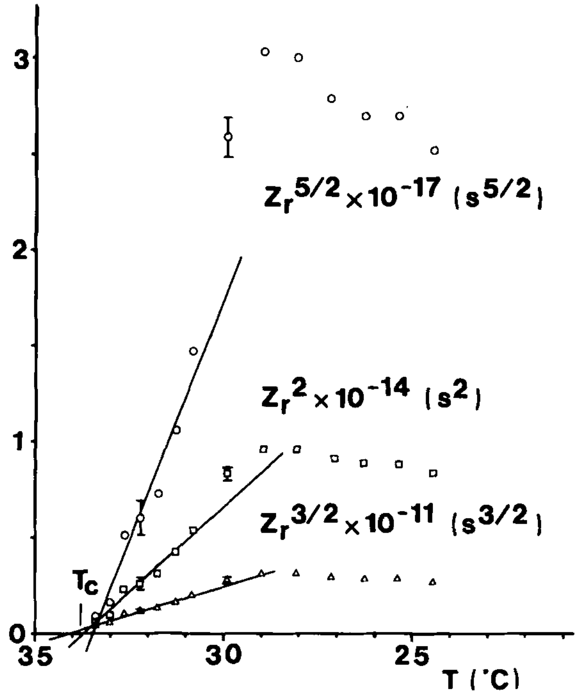

FIGURE 8 Plots of appropriate powers of $Z_r = \kappa(0,0)^2 T'_{1\rho r} \exp(W/T)$ as a function of T, T in °C, where $W = 5960$ K. The straight lines are linear least squares fits to the first 7 points only, and the intercepts give the resulting superheating points.

The T_{1D} data and intra/inter separation are given in Figure 9. For a two spin system the theory of Blicharski[13] suggests that

$$R_{1D} = b\frac{3}{2}(\gamma^2\hbar/r^3)^2 \sum (f^{(k)}(\beta))^2 K_{k1}(\omega_0),$$

where b is a constant. We find that b varies by ~20% over the nematic range, which might indicate a failure in the two-spin approximation. We find $b_a \sim 0.12$ and $b_r \sim 0.09$.

CONCLUSION

The first intermolecular and intramolecular separations of $R_{1\rho a}$ and R_{1D} in a nematic liquid crystal have been performed. The results indicate difficulties in the theory currently available.

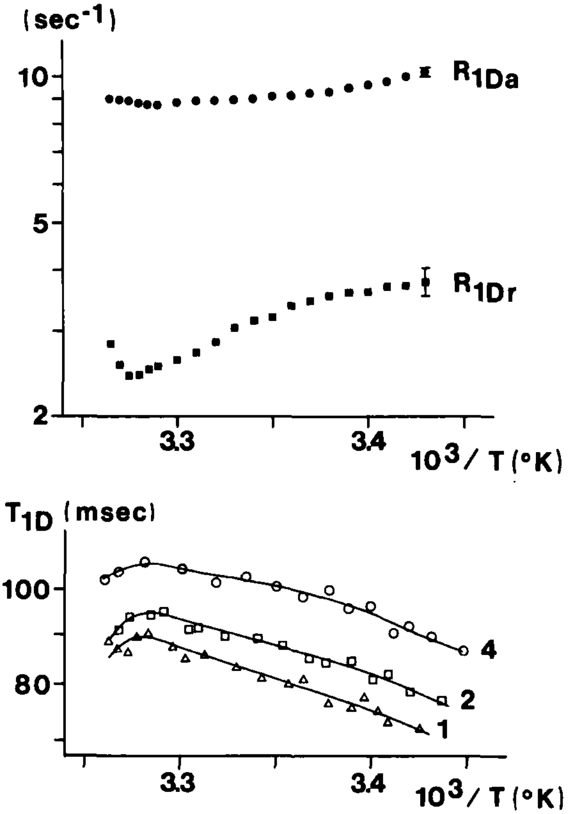

FIGURE 9 Plot of proton dipolar relaxation times and resulting intermolecular and intramolecular contributions to the proton dipolar relaxation rates, all as a function of $10^3/T$, T in K. The numbers on the T_{1D} plots refer to the concentration, as in Figure 1. The results for R_{1Da} and R_{1Dr} are obtained using the smooth curves passing through the T_{1D} data.

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