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Frequency Dependence of Proton Spin-Lattice Relaxation in MBBA and PAA

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The frequency dependence of proton T_1 in the nematic phase of MBBA and PAA is reinterpreted taking into account the rotational diffusion mechanism of relaxation. The rotational correlation times for the partially oriented molecules, evaluated with the aid of dieletric relaxation data, allow us to explain the different behaviour of the two compounds.

I INTRODUCTION

Nuclear spin relaxation provides an almost unique tool for studying the various aspects of the molecular dynamics in liquid crystalline phases,[1] and it has been the object of several investigations in the last few years. In particular, the dependence of the longitudinal proton relaxation times upon Larmor frequency has been extensively studied for the two nematics dimethoxy-azoxybenzene (PAA) and *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA). In the first case, measurements have been performed in the frequency range 1.5–100 MHz;[2] in the latter, investigations have been extended up to 270 MHz.[3] Moreover, a complete set of data on PAA isotopically diluted in the perdeutero analog is now available .[4]

The experiments show for the two systems a different relaxation behaviour. PAA exhibits an inverse square root dependence upon frequency, which is expected when collective fluctuations of the mesophase constitute the dominant relaxation mechanism.[1] On the contrary, the frequency dependence of T_1 in MBBA does not appear to follow any simple law. An attempt has been made to justify this result by introducing in the theoretical model of the collective oscillations a finite cut-off of the wavelengths at the level of the molecular dimensions,[5] but it has proved to be unsuccessful and an alternative explanation[3] has been proposed, based only on *inter*-molecular dipolar interactions modulated by translational diffusion. This conclusion, however, is not free from criticism. Firstly, it disagrees with the well-established results on the relaxation mechanisms operating in PAA. In second place, there are no reasons to ignore contributions to the relaxation from *intra*-molecular dipolar interactions modulated by rotational diffusion. In fact, we shall show that the differences in the relaxation behaviour of PAA and MBBA disappear, if the effects of the rotational diffusion are properly taken into account.

II ROTATIONAL DIFFUSION

Molecular reorientations in uniaxial liquid crystals can be described by a diffusion equation which incorporates an orienting pseudo-potential V_N.[6] In the first approximation, V_N has the form $\lambda P_2(\cos\beta)$, where β is the angle between the long molecular axis and the optical axis of the mesophase, and P_2 is a Legendre polynomial. For any given degree of order $S = \langle P_2(\cos\beta)\rangle$ the potential strength λ is determined so that the diffusion equation can be solved, and the correlation functions for the rotational diffusion calculated:

$$g^l_{mn}(t) = \langle D^l_{mn}(0) D^{l*}_{mn}(t)\rangle - |\langle D^l_{mn}\rangle|^2 \tag{1}$$

D^l_{mn} being the Wigner matrix elements which bring the laboratory axis system into the molecular reference frame. *Intra*-molecular dipole interactions are modulated by rotational diffusion, and their contribution to the relaxation rate of the ring protons in MBBA or PAA is given by:[7]

$$T^{-1}_{1_d}(\omega_0) = \tfrac{3}{2}\omega_d^2[j_{10}(\omega_0) + 4j_{20}(2\omega_0)] \tag{2}$$

where $\omega_d = \hbar\gamma^2_H/r^3_{HH}$

$$j_{mn}(\omega) = \int_0^\infty g^2_{mn}(t)\cos\omega t\,\mathrm{d}t \tag{3}$$

Only spectral density functions $j_{mn}(\omega)$ with $n = 0$ appear in Eq. (2) because the *inter*-nuclear vector r_{HH} is parallel to the long molecular axis. The correlation function $g^2_{mn}(t)$ are calculated to be a sum of decreasing exponentials, nevertheless it can be shown that, if $(m, n) \neq (1, 1)$, $g^2_{mn}(t)$ is well approximated by a single exponential decay:[8]

$$g^2_{mn}(t) \simeq \langle |D^2_{mn}|^2\rangle \exp(-\alpha^2_{mn} D_\perp t) - |\langle D^2_{mn}\rangle|^2 \tag{4}$$

where α^l_{mn} is the eigenvalue of the diffusion equation which in the isotropic limit ($S = 0$) reduces to $l(l+1) + (D_\parallel/D_\perp - 1)n^2$; $D_\parallel$ and $D_\perp$ are the rotational diffusion tensor components. Eq. (2) then becomes:

$$T^{-1}_{1_d}(\omega_0) = \tfrac{3}{2}\omega_d^2 D_\perp \sum_{k=1,2} \frac{k^2\langle|D^2_{k0}|^2\rangle\alpha^2_{k0}}{(\alpha^2_{k0}D_\perp)^2 + k^2\omega_0^2} \tag{5}$$

T_{1_d} is frequency dependent, unless the extreme narrowing condition ($\omega_0 \ll \alpha_{m0}^2 D_\perp$) holds.

III RESULTS AND DISCUSSION

a) PAA

The measurements performed in PAA at 393°K[4] show clearly that in the 5–100 MHz range both *intra*- and *inter*-molecular contributions are linear functions of $\omega_0^{-1/2}$. A least square fit for the *intra*-molecular term gives:

$$T_{1_a}^{-1} = A\omega_0^{-1/2} + B, \qquad A = 2.51 \cdot 10^3\ \mathrm{sec}^{-3/2}, \qquad B = 0.28\ \mathrm{sec}^{-1}. \tag{6}$$

The linear dependence upon $\omega_0^{-1/2}$ follows from the thermal fluctuation theory,[1] and B can be ascribed to the zero-frequency limit of $T_{1_d}^{-1}(\omega_0)$. Since the degree of order is known, all the quantities in Eq. (5) can be computed as indicated above,[9] and the value of $D_\perp = 7.3 \cdot 10^8\ \mathrm{sec}^{-1}$ is obtained. This result can be compared with dielectric relaxation data. The dispersion of the dielectric permittivity is related to the molecular electric dipole correlation function, i.e. to $g_{mn}^1(t)$,[6b] and the relaxation time for the lowest frequency dispersion in the nematic mesophase is given by

$$\tau_{\mathrm{diel}}^{-1} = \alpha_{00}^1 D_\perp \tag{7}$$

Since the experimental value of τ_{diel} at 398°K is $4.3 \cdot 10^{-9}$ sec,[10] from the calculated value of α_{00}^1,[11] we obtain $D_\perp = 7.7 \cdot 10^8\ \mathrm{sec}^{-1}$.

These values of $D_\perp$, obtained from different techniques, agree quite well and their magnitude allows us to apply the extreme narrowing limit in Eq. (5) for PAA. In fact we ought to look for a frequency dependence in PAA at frequencies as high as 300 MHz.

TABLE I

Values of $D_\perp$, γ_1, $\sigma_\perp$ and S for PAA and MBBA

	PAA	MBBA	
T(°K)	398	296	305
$D_\perp(10^7\ \mathrm{sec}^{-1})$	77	3.9[a]	5.6[b]
γ_1(cpoise)	6.3[c]	101[c]	56[c]
$\sigma_\perp(\mathrm{Å}^3)$	190	300	300
$S = \langle P_2 \rangle$	0.53[d]	0.61[e]	0.53[e]

[a] Ref. 13.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 16.
[e] Ref. 17.

b) MBBA

MBBA is extremely viscous so we expect that diffusion coefficient be greater than PAA and the extreme narrowing condition not to hold. The values of $D_\perp$ obtained from dielectric relaxation data are reported in the table and a comparison between PAA and MBBA can be made. It has been suggested[12] that the diffusion tensor component $D_\perp$ is given by

$$D_\perp = kT/8\pi\sigma_\perp k_\perp \gamma_1 \tag{8}$$

where $\sigma_\perp$ is related to molecular dimensions, $k_\perp$ is determined by the orienting potential and should be nearly equal to 1, and γ_1 is the rotational viscosity coefficient. We have calculated $\sigma_\perp$ by taking the molecular semiaxes lengths as 9 Å and 3 Å for PAA, 11 Å and 3 Å for MBBA. When the values of $T, \gamma_1, \sigma_\perp$ for the same degree of orientational order are inserted in Eq. (8), we obtain $D_{\mathrm{PAA}}/D_{\mathrm{MBBA}} = 18$, in reasonable agreement with the value obtained from dielectric relaxation data, which is about 14.

The T_1 measurements on MBBA[3] are performed at 291°K ($S = 0.63$); unfortunately no dielectric relaxation data are available for temperatures lower than 296°K, however we can estimate $D_\perp \simeq 3.5 \cdot 10^7\ \mathrm{sec}^{-1}$ at this temperature. This value confirms that the rotational diffusion contribution to proton relaxation rate in MBBA becomes frequency dependent for frequencies higher than 20 MHz. When the calculated values of $T_{1_d}^{-1}(\omega_0)$ are subtracted to the experimental points, the residual relaxation rate $T_{1_r}^{-1}$ can

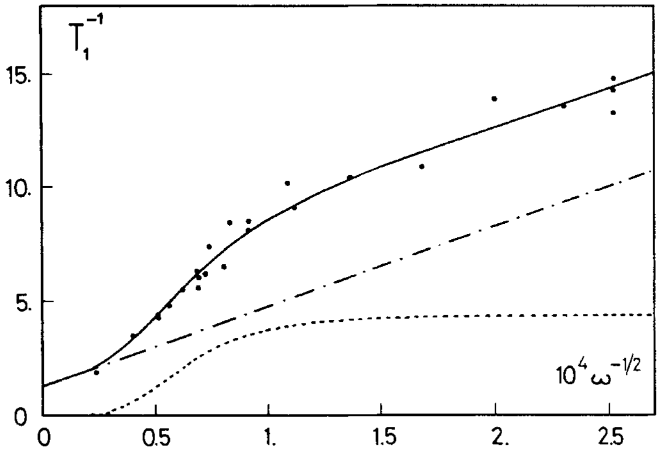

FIGURE 1 Frequency dependence of $T_{1_H}^{-1}$ in MBBA as function of $\omega_0^{-1/2}$. Dotted line: calculated contribution from rotational diffusion. Full line: total relaxation rate (experimental points are taken from Ref. 3. Dashed line: residual contributions.

be fitted quite well by a straight line given by:

$$T_{1_r}^{-1} = A'\omega_0^{-1/2} + B', \quad A' = 3.46 \cdot 10^4 \text{ sec}^{-3/2}, \quad B' = 1.36 \text{ sec}^{-1}. \quad (9)$$

This result is reported in the figure, where the experimental points are taken from Ref. 3, and the dotted curve shows the frequency dependence of the contribution arising from the rotational diffusion mechanism. The residual contribution $T_{1_r}^{-1}$ (dashed line) and the total calculated relaxation rate (full line) are also plotted.

CONCLUSIONS

The introduction of rotational diffusion as a source of spin relaxation through the modulation of the ring-proton dipole interaction brings to the conclusion that the relaxation behaviour of PAA and MBBA are indeed not very dissimilar. Because of the higher viscosity and the larger molecular dimensions of MBBA, this particular relaxation mechanism exhibits its own frequency dependence, in contrast with PAA. When this is subtracted from the experimental relaxation rate, the residual contributions appear to have the same frequency dependence as in PAA. This implies that in MBBA all the relaxation effects resulting from *inter*-molecular interactions have the same frequency dependence of those coming from director oscillations, as found in PAA.[4] This conclusion, however, is rather surprising. In fact, calculations based on different translational diffusion models[18] show that it is unlikely to obtain such a peculiar frequency dependence of $T_{1_{\text{inter}}}$ in a wide range of frequencies. We may point out some arguments which need, to be verified, more experimental data on isotopically substituted MBBA (as done for PAA) and further theoretical investigation:

i) The existing data on proton relaxation in MBBA do not allow us to discriminate between ring and side-chain protons. The relative importance of the various relaxation effects is undoubtedly different for the various sets of protons, and so their frequency dependence. In this case, the analysis of the experimental data might be misleading. This view is supported by the appearance of the constant term B' in Eq. (9), which is hard to justify theoretically.

ii) The current models of translational diffusion, which neglect the anisotropies of the motions and of the molecular shape, are clearly inadequate in describing *inter*-molecular relaxation effects in liquid crystals. In addition, *inter*-molecular relaxation terms resulting from director fluctuations could be taken into account, and give rise to the same $\omega_0^{-1/2}$ frequency dependence of the corresponding *intra*-molecular terms.[19]

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References

1. P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford U. P., London (1974).
2. M. Vilfan, R. Blinc, and J. W. Doane, *Solid State Comm.*, **11**, 1073 (1972).
3. R. Blinc, M. Vilfan, and V. Rutar, *Solid State Comm.*, **17**, 171 (1975).
4. B. M. Fung, C. G. Wade, and R. D. Orwell, *J. Chem. Phys.*, **64**, 148 (1976).
5. J. W. Doane, C. E. Tarr, and M. A. Nickerson, *Phys. Rev. Letters*, **33**, 620 (1974).
6. a) P. L. Nordio, G. Rigatti, and U. Segre, *J. Chem. Phys.*, **56**, 2117 (1972); b) *Mol. Phys.*, **25**, 129 (1973).
7. P. L. Nordio and U. Segre, *Gazz. Chim. Ital.*, **106**, 431 (1976).
8. P. L. Nordio and U. Segre, *Chem. Phys.*, **11**, 57 (1975).
9. At 393°K the degree of order is $S = 0.56$, corresponding to $\lambda = -2.7$; from this value we compute: $\alpha_{10}^2 = 7.4$, $\alpha_{20}^2 = 9.8$, $\langle |D_{10}^2|^2 \rangle = 0.21$, $\langle |D_{20}^2|^2 \rangle = 0.06$.
10. A. J. Martin, G. Meier, and A. Saupe, *Faraday Symp.*, **5**, 119 (1971).
11. At 398°K we have: $S = 0.53$, $\lambda = -2.5$, $\alpha_{00}^1 = 0.30$.
12. G. R. Luckhurst and R. N. Yeates, *Chem. Phys. Lett.*, **38**, 551 (1976).
13. F. Rondalez and A. Mircea-Roussel, *Mol. Cryst. Liquid Cryst.*, **28**, 173 (1974).
14. V. K. Agarwal and A. H. Price, *J. Chem. Soc. Faraday Trans.*, II, **70**, 188 (1974).
15. S. Meiboom and R. C. Hewitt, *Phys. Rev. Letters*, **30**, 261 (1973).
16. J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).
17. S. Jen, N. A. Clark, P. S. Pershan, and E. B. Priestly, *Phys. Rev. Letters*, **31**, 1552 (1973).
18. H. C. Torrey, *Phys. Rev.*, **92**, 962 (1953); Y. Ayant, E. Belorizky, J. Alizon, and J. Gallice, *J. Phys.* (Paris), **36**, 991 (1975); L.-P. Hwang and J. H. Freed, *J. Chem. Phys.*, **63**, 4017 (1975).
19. M. J. Stephen and J. P. Straley, *Rev. Mod. Phys.*, **46**, 617 (1974).