

Core and chain dynamics in thermotropic liquid crystals

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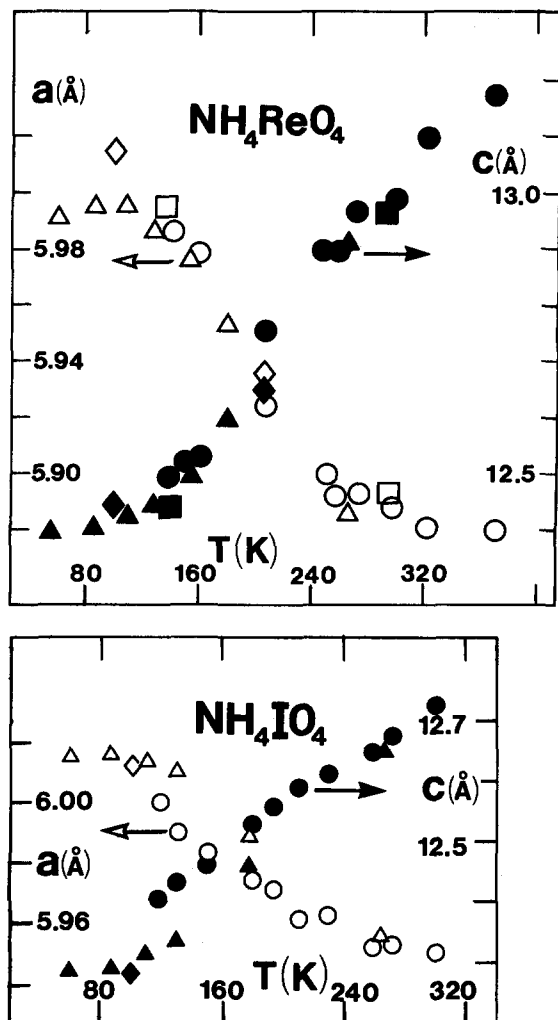


FIG. 1. Lattice constants of NH_4ReO_4 (a) and NH_4IO_4 (b) as a function of temperature. Legend: Open data, a parameter; closed data, c parameter; Δ , this work (single crystal, x-ray); \circ , Brown (Ref. 2) and Segel (Ref. 3) (powder samples, Guinier-Lenne); \diamond , Brown (Ref. 4) (powder sample, neutron); \square , Kruger (Ref. 5) (single crystal, x-ray).

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Core and chain dynamics in thermotropic liquid crystals

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In this note we report a preliminary analysis of 9.2 and 38.4 MHz deuteron spin relaxation data for 4-*n*-butoxybenzylidene-4'-*n*-octylaniline (40.8) with a perdeuterated octyl chain and aniline ring.¹ The spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$ were obtained from measurements of the spin-lattice relaxation rate $R_{1Z} = (3\pi^2/$

$2)(e^2qQ/h)^2[J_1(\omega_0) + 4J_2(2\omega_0)]$ and the decay of quadrupolar order $R_{1Q} = (9\pi^2/2)(e^2qQ/h)^2J_1(\omega_0)$ using modified² Jeener-Broekaert experiments.³ The relaxation behavior of aromatic and aliphatic deuterons differs as illustrated in Fig. 1.

Aromatic deuterons. Motion responsible for the re-

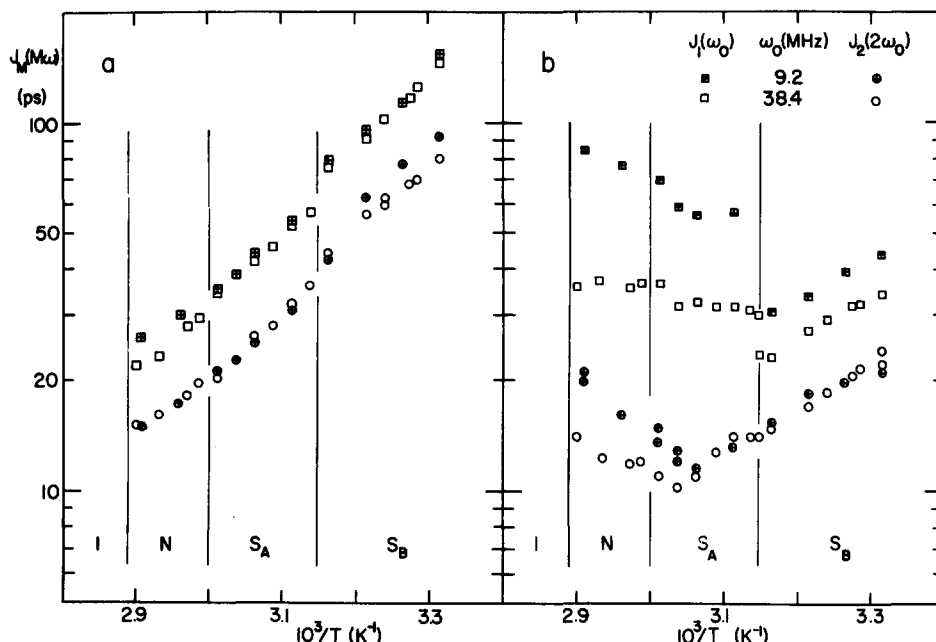


FIG. 1. Temperature dependence of the spectral densities of motion $J_1(\omega_0)$ and $J_2(2\omega_0)$ for (a) aniline deuterons and (b) α -methylene deuterons in liquid crystalline 4-*n*-butoxybenzylidene-4'-*n*-octylaniline (40.8). Transition temperatures for the slightly impure sample are $T_{IN} \sim 75^\circ\text{C}$, $T_{NA} \sim 60^\circ\text{C}$, and $T_{AB} \sim 43^\circ\text{C}$. The spectral densities are normalized such that in an isotropic fluid in the extreme narrowing limit $J_1 = J_2 = \tau_c/5$, where τ_c is the correlation time for the relevant motion.

laxation of the aniline deuterons appears unaffected by the transition from nematic to smectic A (T_{NA}), but a discontinuity in J_1 and J_2 is observed at the smectic A to B phase transition T_{AB} . Both spectral densities are essentially independent of frequency but strong functions of temperature, $\Delta H = 8.0 \pm 0.5$ kcal/mol in all three mesophases. J_1 is seen to be $\sim 50\%$ larger than J_2 throughout the liquid crystalline range, but the high activation enthalpy combined with the absence of an observable frequency dependence for $J_1^{4,5}$ means that director fluctuations^{6,7} cannot be responsible for this observation. In fact, no such contributions are expected considering the orientation of the aromatic C-D bonds near the "magic angle."

Strongly activated relaxation rates were observed previously^{8,9} for aromatic deuterons in nematic MBBA (4-methoxybenzylidene-4'-*n*-butylaniline), and as noted then⁹ for MBBA, the 40.8 data suggest that the aromatic deuterons relax predominantly by fast rotation about the long molecular axis or, possibly, by internal rotation of the aromatic ring. The decrease in the rate of rotation observed at T_{AB} , which mimics an observed discontinuity in the quadrupolar splitting,¹⁰ may then be ascribed to a lower transition state entropy in the more highly ordered S_B phase. A more complete analysis in terms of restricted rotational diffusion^{10,11} of a symmetric top supports this interpretation; in particular, the relative magnitudes of $J_1(\omega_0)$ and $J_2(2\omega_0)$, which are due to the influence of static order on the corresponding correlation functions, can be quantitatively accounted for by such calculations.¹²

Aliphatic deuterons. Figure 1(b) shows results obtained for the α deuterons of 40.8. Plots of $J_1(\omega_0)$ and $J_2(2\omega_0)$ for the other methylene groups are qualitatively similar with J_1 and J_2 both decreasing linearly with $(\Delta\nu)^2$, the square of the quadrupolar splitting. Thus the comments made below are relevant not only for the α

deuterons, but also for methylene groups further removed from the core.

$J_1(\omega_0)$ is more strongly frequency dependent than $J_2(2\omega_0)$ in all three phases,¹³ and a pronounced discontinuity is observed at T_{AB} . In the S_B phase both J_1 and J_2 are linear functions of inverse temperature with $\Delta H = 5\text{--}7$ kcal/mol depending on methylene group, lower than ΔH for the core deuterons. This reduction of ΔH may be associated with the higher order parameters observed for the chain deuterons, which increase the contribution to the relaxation rates from libration about the short axis, a process expected to have lower activation enthalpy.

J_2 is practically continuous at T_{AB} , going through a shallow minimum with increasing temperature in the S_A phase and taking on a weak but distinct frequency dependence just below the T_{NA} transition. J_1 on the other hand, increases gently with increasing temperature, in some cases with a mild discontinuity at T_{NA} . Above T_{AB} , $J_1(9.2)$ is observed to be roughly two times larger than $J_1(38.4)$. Figure 2 shows plots of $J_1(9.2)$ and $J_1(38.4)$ for the four resolved methylene doublets as a function of $(\Delta\nu)^2 \nu_0^{-1/2}$ at four temperatures: 64.5°C (nematic); 58.3 and 48.2°C (both smectic A); and 43.0°C (smectic B data from the A-B biphasic region). At 64.5 and 58.3°C , J_1 scales not only with $(\Delta\nu)^2$, but also with $\nu_0^{-1/2}$, whereas the 38.4 and 9.2 MHz data do not fall on the same straight line at either 48.2°C or at 43.0°C . Since $J_1(\omega_0)$ is also observed to drop sharply at T_{AB} , we conclude that director fluctuations contribute to J_1 at the higher temperatures, as expected in view of known values^{14,15} of elastic constants and viscosities for 40.8.

The decrease in J_2 with decreasing temperature in the nematic phase may be explained by the rapid increase in ordering of the 40.8 molecules in this range. Similar behavior has been observed in other nematic phases of

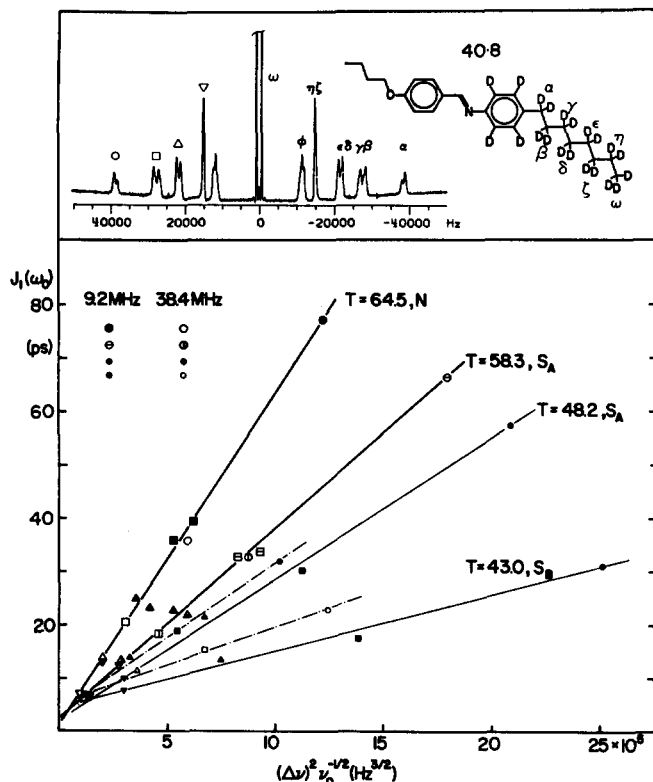


FIG. 2. Dependence of $J_1(\omega_0)$ on $(\Delta\nu)^2 \nu_0^{-1/2}$ for the methylene deuterons in the octyl chain of 40.8. Different symbols denote data at 9.2 and 38.4 MHz for each methylene group as indicated in the accompanying nematic phase spectrum. The linear dependence of J_1 upon $(\Delta\nu)^2 \nu_0^{-1/2}$ for all methylenes at 64.5 (nematic) and 58.3 °C (high temperature end of the S_A phase) is indicated by heavy solid lines. At lower temperatures in the smectic A phase and throughout the smectic B phase, the 38.4 MHz data (stippled lines) fall above the 9.2 MHz data (light solid lines).

liquid crystals with underlying smectic phases.^{16–20} The extent of the drop in J_2 for the chain deuterons varies with carbon number and may be a direct consequence of

the influence of static order on the spectral density functions²⁰ for rotational diffusion, but it is also possible that relatively large angle, coherent fluctuations of the director just below T_{IN} contribute to J_2 . A more quantitative analysis of this problem and other aspects of the 40.8 relaxation data is in progress.

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¹ Detailed synthetic procedures for this material will be published later by M. E. Neubert.

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Unimolecular reactions in condensed phases: Is the turnover in the viscosity dependence of the rate observable?

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Theoretical studies^{1–5} of unimolecular rate processes in condensed phases predict an initial growth of the rate with solvent viscosity at very low viscosity, then a turnover and a decreasing rate with further increase of viscosity. On the experimental side, Hasha *et al.*⁶ have observed this turnover in the rate of ring inversion in cyclohexane solutions. In contrast, such behavior is not observed in

the photochemical isomerization of diphenyl butadiene (DPB) even going in solvent viscosity down to 0.04 cp,⁷ and the results may be fitted to the non-Markovian version^{3,8} of Kramers intermediate and high viscosity regime. Courtney *et al.*⁹ have recently observed that the rate of DPB photoisomerization is approximately the same in room temperature liquid ethane and in an