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Symmetry of Orientational Order Fluctuations about the Nematic-Isotropic Phase Transition: An ESR Study*

K. V. S. Rao, J. S. Hwang, and J. H. Freed
Department of Chemistry, Cornell University, Ithaca, New York 14853
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The ESR relaxation of a weakly aligned spin probe dissolved in N-[*p*-methoxybenzylidine]-*p*-butylaniline has been studied near T_c, the isotropic-nematic transition. Spin relaxation due to critical orientational fluctuations is observed on either side of T_c and is characterized by a symmetry about T_c that is rather well explained by simple Landau–de Gennes mean-field theory for the weak first-order transition.

Orientational order fluctuations have been studied above the nematic-isotropic phase transition (T_c) by light scattering[1,2] and NMR techniques[3,4] in particular and have been successfully interpreted in terms of the Landau–de Gennes theory,[5,6] which treats the transition as almost second order. Such mean-field theories predict that critical fluctuations should also be observed as T_c is approached from below. However, light-scattering and NMR observations in the nematic phase are usually found to be dominated by fluctuations in the nematic director, and no serious attempts appear to have been made to study order fluctuations below T_c. In this Letter, we report an ESR study of spin relaxation of a weakly ordered spin probe (PD-tempone) dissolved in N-[*p*-methoxybenzylidine]-*p*-butylaniline (MBBA) both above and below T_c. It appears to confirm the essential symmetry of order fluctuations about T_c as predicted by simple mean-field theory, modified for the weak first-order nature of the nematic-isotropic transition.

The experiments were performed with $5\times10^{-4}M$ solutions of the nitroxide spin probe PD-tempone[7,8] dissolved in singly distilled MBBA. The sample reported here had $T_c = 41.4$°C compared to 42–43°C for pure solvent. ESR spectra were obtained at 9.2 GHz with a Varian E-12 spectrometer using a thermostated Be-Cu vessel containing a slow-wave helix.[7a] The temperature of the system can be controlled to within ± 0.01°C. The temperature of the fluid surrounding the vessel containing the sample could be measured to within ± 0.05°C with a Cu-Constantan thermocouple or to within ± 0.01°C with a Pt resistance thermometer.[7b] The degassed sample is either sealed in a capillary tube of the same length as the helix, or is in a sealed Teflon container.[7a]

We show in Fig. 1 typical ESR spectra in the coexistence region of the isotropic and nematic phases. Such a coexistence region is due to small amounts of impurity and has been reported in a few light-scattering studies.[2] (The small quantity of spin probe is expected to be only a minor impurity affecting the coexistence.) We observe two sets of overlapping spectra in the range T_c ± 0.2°C as a result of the spin probe dissolved in

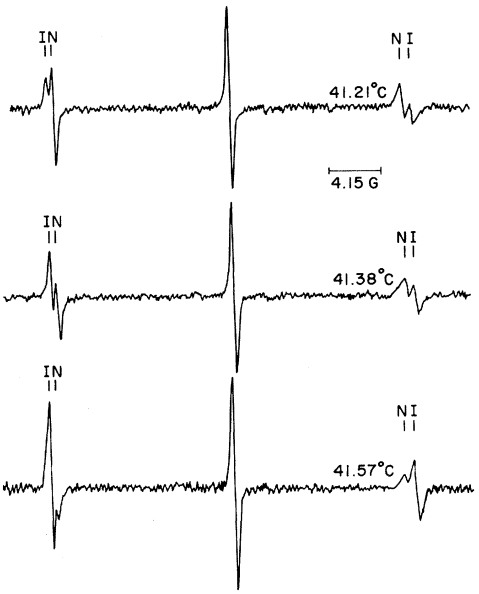

FIG. 1. ESR spectra of PD-tempone in MBBA near T_c = 41.4°C. The three main lines are due to the hyperfine splitting from a single ^{14}N nucleus. The peaks marked *I* and *N* correspond to isotropic and nematic phases, respectively.

the two phases as shown in Fig. 1. The small shift of the nematic lines may be interpreted in terms of an order parameter for the probe $S^{(p)}$ of -0.039, -0.046, and -0.056 at $T=41.10$, 39.91, and 36.67°C, respectively.[8] We have used the known characteristics of the phase diagram[9] to determine the range of the coexistence region from results like those of Fig. 1, which display the changes in relative concentration with temperature. Although the coexistence region had the extent $T_c \pm 0.6$°C, it was found that negligible linewidth correction was required as long as the spectrum from only one phase was distinguishable.

The experimental derivative linewidths δ (in gauss) were corrected for the small inhomogeneous broadening,[8,10] and were then fitted by the usual expression: $\delta = A + BM + CM^2$, where M is the ^{14}N nuclear-spin z-component quantum number. The parameters B and C measured away from T_c are directly related to the rotational correlation time, τ_R, for the overall tumbling motion of the spin probe as shown in previous work.[8,10] Our results for B and C versus T are shown in Fig. 2. One can clearly see from this figure that the values of B and C at the phase transition are anomalous.[11,12] They appear to diverge as T_c is approached from either side.

It is possible to extract the anomalous contributions to B and C (i.e., ΔB and ΔC) by first subtracting out the main contributions to B and C (or B_0 and C_0) which are proportional to τ_R. One extrapolates the values for B and C away from T_c into the phase transition region using a linear extrapolation of $\ln B$ and $\ln C$ versus $1/T$.[7,8,10] The B_0 and C_0 are interpreted for the isotropic[10] and nematic phases[8] to yield values near $T_c = 41.4$°C of $\tau_R = 6.8\times10^{-11}$ sec (42°C) and 8.0×10^{-11} sec (40°C) or nearly the same results. The motion of the spin probe, even when under the orienting potential of the nematic phase (which is included in the analysis), has been shown to be described by an isotropic rotational diffusion coefficient,[7a,8] and the activation energies obtained are about 6.7 and 9.6 kcal/mol for the isotropic and nematic phases.

The ΔB and ΔC values obtained are displayed in Fig. 3, as log-log plots of $1/\Delta B$ and $1/\Delta C$ versus $T - T^*$ (isotropic phase) and $T\dagger - T$ (nematic phase), where T^* and $T\dagger$ are experimentally estimated quantities shortly to be associated with the "apparent" second-order phase transition temperature. These results were fitted by nonlinear least squares by the relations

$$\Delta B \text{ or } \Delta C = k(T - T^*)^{\gamma}, \quad \text{isotropic phase,} \quad (1a)$$

and

$$\Delta B \text{ or } \Delta C = k(T\dagger - T)^{\gamma}, \quad \text{nematic phase,} \quad (1b)$$

to yield values of k, γ, and T^* or $T\dagger$. The results are shown in Table I with standard deviations. These results are characterized by the

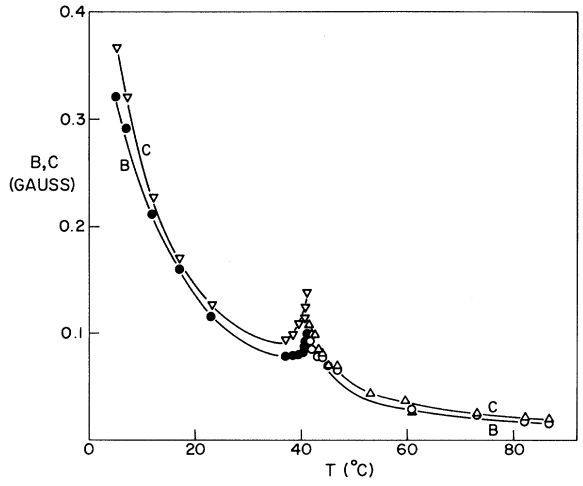

FIG. 2. Variation of B and C values with temperature. The points ● and ▽ are B and C, respectively, in the nematic phase; ○ and △ are B and C, respectively, in the isotropic phase.

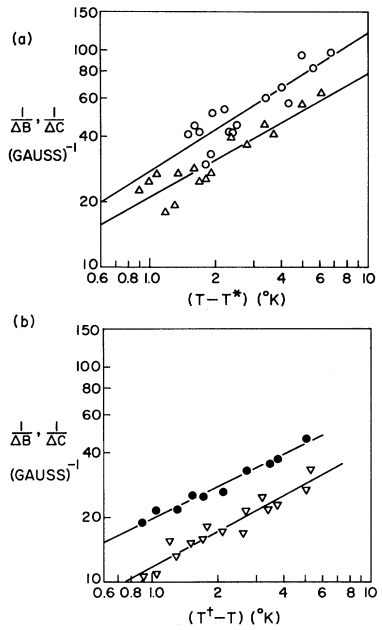

FIG. 3. (a) Variation of $(\Delta B)^{-1}$ (○) and $(\Delta C)^{-1}$ (△) with $T - T^*$ in the isotropic phase. (b) Variation of $(\Delta B)^{-1}$ (●) and $(\Delta C)^{-1}$ (▽) with $T\dagger - T$ in the nematic phase.

TABLE I. Results of experimental fit by Eqs. (1).[a]

	γ	10^2k	T^* or $T\dagger$ (°C)
Isotropic phase			
ΔB (in G)	-0.6 ± 0.2	3.6 ± 2 (2.6 ± 0.7)	$40.0 \pm 1.5°$ ($40.5 \pm 0.6°$)
ΔC (in G)	-0.43 ± 0.1	3.5 ± 0.5 (4.1 ± 0.3)	$40.9 \pm 0.3°$ ($40.6 \pm 0.1°$)
Nematic phase			
ΔB (in G)	-0.5 ± 0.1	5.2 ± 1 (± 0.4)	$42.1 \pm 0.6°$ ($\pm 0.35°$)
ΔC (in G)	-0.5 ± 0.16	7.6 ± 2 (± 0.8)	$41.8 \pm 0.5°$ ($\pm 0.3°$)

[a]Values in parentheses are for γ fixed at $-\frac{1}{2}$.

facts that (1) in *all cases* $\gamma = -\frac{1}{2}$; (2) T^* is about 1°C *below* T_c, while $T\dagger$ is about 0.5°C *above* T_c; and (3) the values of k for B and C are comparable in both the isotropic and nematic phases, although a little greater in the latter.

We now compare these results with Landau–de Gennes theory in its simplest form. The free energy near the phase transition is expanded as a function of the order parameter Q (neglecting its tensorial features)[1,5,6,13]:

$$F = F_0 + \tfrac{1}{2}\tilde{A}Q^2 - \tfrac{1}{3}\tilde{B}Q^3 + \tfrac{1}{4}\tilde{C}Q^4 + \tfrac{1}{2}\int L(\nabla Q)^2 d^3r, \quad (2)$$

where F_0 is the orientation-independent part, $\tilde{A} = a(T - T^*)$, while $\tilde{B}$, $\tilde{C}$, and L are only slowly varying with T, and L is a force constant for distortions. Minimizing F with respect to Q (but neglecting L) gives the nematic value $Q_N = (\tilde{B}/2\tilde{C}) \times [1 + (1 - 4\tilde{A}\tilde{C}/\tilde{B}^2)^{1/2}]$. The phase transition occurs at T_c such that $\tilde{A} = a(T_c - T^*) = 2\tilde{B}^2/9\tilde{C}$ and $Q_N = 2\tilde{B}/3\tilde{C}$. Small fluctuations are studied by Fourier analysis of Eq. (2), and to lowest order $F = F_0 + \frac{1}{2}V\sum_q(\tilde{A} + Lq^2)|Q_q|^2$. The linear response relaxation due to frictional forces is given by [5,6,3] $dQ/dt = -\nu^{-1}\partial F/\partial Q_q = -\tau_q^{-1}Q_q$, where $\xi^{+2} \equiv L/a(T - T^*)$ is the coherence length of the order fluctuations, $\tau_q^{-1} = L(\xi^{-2} + q^2)/\nu$, and ν is a viscosity. In the nematic phase, the fluctuations are about the equilibrium value F_N which is obtained by substituting Q_N for Q in Eq. (2). Then we obtain $F = F_N + \frac{1}{2}V\sum_q(\bar{A} + L_N q^2)|\Delta Q_q|^2$ to lowest order in ΔQ, where ΔQ_q is the Fourier transformation of $\Delta Q \equiv Q - Q_N$, and $\bar{A} \equiv \tilde{A} - 2BQ_N + 3CQ_N^2$. In the limit of small $\tilde{A}$ (i.e., $a|T - T^*| < a|T_c - T^*|$) one may expand the expression for Q_N to obtain $\bar{A} \approx 3a(T\dagger - T)$, where $T\dagger = T_c + \frac{1}{2}(T_c - T^*)$. The nematic relaxation equation becomes $-\nu^{-1}\partial F/\partial \Delta Q_q = -L_N(\bar{\xi}^{-2} + q^2)\Delta Q_q/\nu_N$, where $\bar{\xi}^2 \equiv L_N/\bar{A} \approx L_N/3a(T\dagger - T)$, if A is small enough.[14]

The analysis of ESR relaxation and linewidths due to the fluctuations is somewhat similar to that for NMR.[3,4] The results one obtains[8,13] are (neglecting the high-frequency nonsecular terms)

$$\Delta B \approx 5B_0\tau_R^{-1}K_{0,0}(0), \quad (3a)$$

$$\Delta C \approx C_0\tau_R^{-1}[8K_{0,0}(0) - 3K_{0,1}(\omega_a)], \quad (3b)$$

where

$$K_{0,M}(\omega) = \frac{kT\nu\xi(S^{(p)})^2}{\sqrt{2}\,4\pi L^2(S^{(s)})^2}\left\{1 + \left[1 + \left(\frac{\omega}{\omega_\xi}\right)^2\right]^{1/2}\right\}^{-1/2}. \quad (4)$$

B_0 and C_0 in Eqs. (3) are for the isotropic phase, $\omega_\xi \equiv L/\nu\xi^2$, and ω_a is the pseudo-secular frequency corresponding to nuclear spin-flips.[13] Below T_c, one replaces ξ everywhere by $\bar{\xi}$. Here $S^{(s)}$ and $S^{(p)}$ are the molecular order parameters for the solvent and probe just below T_c. Equations (3) and (4) were obtained by further assuming that the fluctuations in Q are small, by taking the principal molecular axis for ordering to correspond to the main hyperfine tensor principal axis for the nitroxide probe,[8] by neglecting anisotropies in ξ, τ_R, etc., and by neglecting translational diffusion. The main point to note is that for $\omega = 0$ (the secular terms) we have $K_{0,M}(0) \propto \xi$ or $\bar{\xi}$ (however for ω_a it is not expected that $\omega_a/\omega_\xi < 1$), and this serves to explain our observations. That is, we have $\xi \propto (T - T^*)^{-1/2}$ and $\bar{\xi} \propto (T\dagger - T)^{-1/2}$, which is consistent with Fig. 3 showing $\gamma = -\frac{1}{2}$ (cf. Table I). Then with $T_c - T^* \approx 1°$, we predict $T\dagger \approx T_c + 0.5°$ as observed.[14] We now estimate the value of $\Delta B/B_0 = k(T - T^*)^\gamma/B_0$ from Eqs. (3a) and (4) using the Stinson-Litster[1] values of $L_1/a = 1.45 \times 10^{-12}$ cm^2 °C, $a = 6.2 \times 10^9$ erg/cm^3 °C, and $\nu = 0.3$ P (at 42°C) for the isotropic phase. One obtains the prediction $\Delta B/B_0 \approx 0.52/(T - T^*)^{1/2} = 0.52$ at $T - T^* = 1°$, which may be compared with the experimental value at 41.5°C of $\Delta B/B_0 = 0.50$. This agreement is much better than one should expect from such a rough estimate. It does confirm that the effects we see are indeed of the correct order. One finds that $C_0/B_0 \cong 1$ as expected for an iso-

tropic τ_R. Then Eqs. (3) predict $\Delta C/\Delta B = \frac{8}{5}$, if $K_{0,1}(\omega_a) \ll K_{0,0}(0)$, or 1 if $r \equiv K_{0,1}(\omega_a)/K_{0,0}(0) = 1$. The experimental result above T_c (for fixed γ, cf. Table I) is 1.6 but rather uncertain. One estimates from Eq. (4) with $\omega_a = 1.32 \times 10^8$ sec^{-1}, $T - T^* \sim 1°$, and the values above, a ratio of 1.53.

Simple application of Eqs. (3) and (4) to the nematic results leads to the prediction that the values of k should be of comparable order in both phases, as is indeed observed. However, it would predict nematic values to be smaller by about $\sqrt{3}$,[14] although they appear to be larger by about this amount. The possibility exists that the quantities L and ν are changing discontinuously at the weak first-order transition (e.g., one might expand $L_N \approx L + L'Q_N$) and/or the very simple mean-field theory used here for the nematic-phase spin relaxation is not completely adequate [e.g., one might need higher-order terms in Q in Eq. (2)], although it successfully predicts the other observed features.

In our previous work with PD-tempone in nematic solvents away from T_c,[7a,8] we have shown that there are no observable relaxation contributions from fluctuations in the nematic director, and this is consistent with prediction because of the weak ordering of this probe. However, in this present study the effects of the orientational fluctuations are indeed expected, since they are associated with a critical-type divergence.

In summary, our ESR observations about the isotropic-nematic phase transition display a symmetry for spin relaxation due to critical fluctuations, and the characteristic features are predicted rather well by simple mean-field theory. Also, a motional-narrowing spin-relaxation theory is in basic agreement with the observations, contrary to previous suggestions that the τ_q are too slow for averaging the large anisotropic ESR interactions. The success of the theory is attributed in part to the fact that the qth mode relaxes only a very small fraction of such interactions, and there are many such modes.[13]

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[13]J. H. Freed, to be published. One can show that $K_{00}(\omega)$ of Eq. (4) refers to Q_{zz}, and $K_{01}(\omega)$ to $Q_{xz} \pm iQ_{yz}$.

[14]Actually our nematic data cover the range $-4°\text{K} \leq T - T^* \leq 0.7°\text{K}$, so that the lowest-order expansion in $\bar{A}$ is not really valid. However, one finds from the complete expression that $\bar{A}$ is very well represented over this range by $\bar{A} = 2.7a(T\dagger - T)$, with $T\dagger = T_c + 0.6(T_c - T^*)$ when $T_c - T^* \sim 1°$.