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The Order Parameters of Some Nematic Liquid Crystals Measured by the Resonance Raman Effect and Its Relevance to the Nematic-Isotropic Phase Transition

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The second and fourth order parameters of nematic MBBA and 5CB have been determined near the nematic-isotropic transition temperatures by means of resonance Raman measurements on β-carotene dissolved as an orientational probe. The limiting behaviour of the second order parameter of MBBA near the transition point has been investigated on the basis of its fluctuation, which is deduced from the 2nd and 4th order parameter values.

1 INTRODUCTION

In recent years, there has been increased activity in the determination of the orientational order parameters of nematic liquid crystals by means of polarized Raman measurements.[1–4] The Raman technique has the merit of providing not only the second ($\overline{P_2^0}$) but also the fourth ($\overline{P_4^0}$) orientational order parameter simultaneously. However, the accuracy of order parameters determined by the Raman technique depends severely on the accurate form of the Raman scattering tensor to be used in analysing the data. Hence, it is

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necessary to know exactly the form of the scattering tensor

$$\alpha\begin{pmatrix} a, & 0, & 0 \\ 0, & b, & 0 \\ 0, & 0, & 1 \end{pmatrix}$$

as well as the orientation of the principal axis relative to the molecular long axis. Since liquid crystal molecules are usually large and complex, the above requirement may scarcely be fulfilled even for a well-defined vibrational mode. In order to avoid the difficulty, it seems advisable to take advantage of the resonance Raman effect (RRE)[5] for which the Raman scattering tensor is determined mostly by a single electronic state responsible for the resonance, and assumes a form

$$\alpha\begin{pmatrix} 0, & 0, & 0 \\ 0, & 0, & 0 \\ 0, & 0, & 1 \end{pmatrix}$$

for a nondegenerate vibrational mode. Here, z is the direction of the transition moment with respect to the resonant electronic state, and may be determined accurately by experiment or theoretical calculation.

Recently, we determined $\overline{P_2^0}$ and $\overline{P_4^0}$ for MBBA with fair accuracy by utilizing the resonance Raman polarization measurement of all-trans β-carotene dissolved in MBBA as an orientational probe.[6]

In the present report, the same type of investigation has been extended with success to the system 5CB and all-trans β-carotene. We are mainly concerned with the orientational behaviour of liquid crystal molecules close to the nematic-isotropic phase transition as revealed by the $\overline{P_2^0}$ and $\overline{P_4^0}$ values thus obtained.

2 RESULTS AND DISCUSSION

Experimental details and the procedure to determine $\overline{P_2^0}$ and $\overline{P_4^0}$ from the resonance Raman depolarization ratios will be described elsewhere.[6,7] The final results are shown in Figure 1 and Table I for MBBA, and Figure 2 and Table II for 5CB. It has been shown that the $\overline{P_2^0}$ values so obtained are in good agreement over a wide temperature range of measurement with those values obtained for neat MBBA and 5CB by various other techniques, such as diamagnetic anisotropy, refractive index etc. However, our $\overline{P_4^0}$ shows a marked difference (near to the transition temperature) from the previous result using neat samples; there $\overline{P_4^0}$ collapses to notably negative values.

TABLE I

Temperature dependence of $\overline{P_2^0}$, $\overline{P_4^0}$, $\overline{P_2^2}$ and σ for MBBA

ΔT	$\overline{P_2^0}$	$\overline{P_4^0}$	$\overline{P_2^2}$	σ
0.5	0.334	0.0037	0.294	1.277
1.0	0.381	0.031	0.325	1.112
2.0	0.446	0.073	0.365	0.914
3.0	0.453	0.046	0.353	0.849
4.0	0.484	0.073	0.376	0.777
5.0	0.493	0.076	0.380	0.750
6.0	0.501	0.079	0.384	0.727
7.0	0.512	0.095	0.395	0.712
8.0	0.531	0.110	0.408	0.669
10.0	0.550	0.130	0.424	0.634
15.0	0.580	0.156	0.446	0.571
20.0	0.606	0.185	0.468	0.525

TABLE II

Temperature dependence of $\overline{P_2^0}$, $\overline{P_4^0}$, $\overline{P_2^2}$ and σ for 5CB

ΔT	$\overline{P_2^0}$	$\overline{P_4^0}$	$\overline{P_2^2}$	σ
0.1	0.295	−0.039	0.2639	1.962
0.2	0.372	−0.020	0.296	1.589
0.3	0.422	−0.002	0.320	1.420
0.5	0.457	0.011	0.336	0.783
0.7	0.480	0.032	0.354	0.730
0.9	0.498	0.046	0.366	0.690
1.1	0.510	0.057	0.375	0.665
1.6	0.527	0.073	0.388	0.630
2.1	0.541	0.087	0.399	0.605
3.1	0.562	0.109	0.417	0.564
4.1	0.573	0.115	0.423	0.115
5.1	0.584	0.126	0.432	0.126

Now, it is known by testing every possibility that the mean field theory of Maier and Saupe or its extended version[8,9] is by no means effective to explain the observed temperature dependence of both order parameters in a unified scheme. On the other hand, it is noted here that the orientational behaviour near the transition point, where the discrepancy between theory and experiment is remarkable, is more properly investigated by dealing with the fluctuation of the second order parameter as follows.

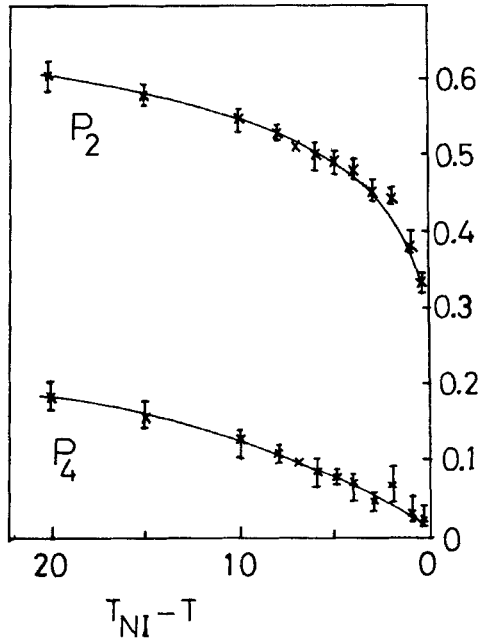

FIGURE 1 Experimental values of the order parameters $\overline{P_2^0}$ and $\overline{P_4^0}$ measured by the RRE of all-trans β-carotene dissolved as a probe in MBBA.

Since P_2^0 and P_4^0 are defined as

$$\overline{P_2^0} = (1/2)(3\ \overline{\cos^2\theta} - 1)$$
$$\overline{P_4^0} = (1/8)(35\ \overline{\cos^4\theta} - 30\ \overline{\cos^2\theta} + 3) \quad (1)$$

the variance of the second order parameter around its equilibrium value, is given by

$$\overline{P_2^2} = (18/35)\overline{P_4^0} + (2/7)\overline{P_2^0} + 1/5 \quad (2)$$

which can be evaluated from the present Raman result. Then, the relative fluctuation is defined as,

$$\sigma = (\overline{P_2^2} - (\overline{P_2^0})^2)^{1/2}/\overline{P_2^0} \quad (3)$$

The values of $\overline{P_2^2}$ and σ are listed in Table I and II for MBBA and 5CB. In Figure 3, σ for MBBA is shown as a function of $\Delta T = T_{NI} - T$ along with the expectation from the mean field theory of Maier and Saupe.[8] The discrepancy is increasingly more remarkable towards the temperature of phase

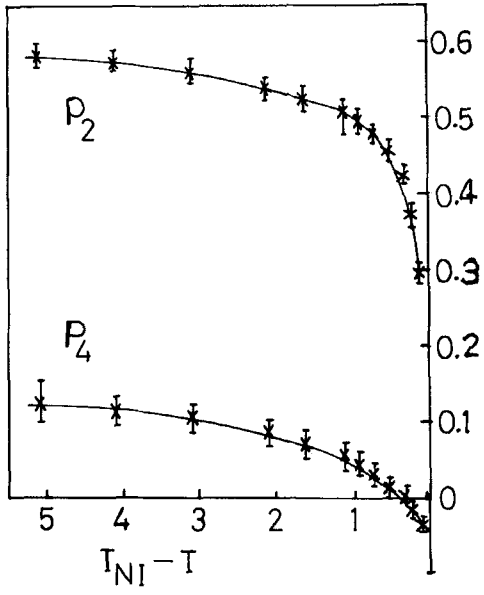

FIGURE 2 Experimental values of the order parameters $\overline{P_2^0}$ and $\overline{P_4^0}$ measured by the RRE of all-trans β-carotene dissolved as a probe in 5CB.

transition $\Delta T = 0$. The experimental σ is well reproduced by the following simple formula,

$$\sigma = \frac{1.096}{(T_{NI} - T)^{-0.236 \pm 0.01}} \tag{4}$$

as evidenced by a linear plot of $\ln \sigma$ against $\ln(T_{NI} - T)$—see Figure 4, approaching infinity towards $T = T_{NI}$. This means that $\overline{P_2^0}$ approaches zero as $T \to T_{NI}$, because the numerator of Eq. (3) remains a finite small quantity even at $T = T_{NI}$. Although a simple extrapolation of the $\overline{P_2^0}$ curve in Figure 1 may give $\overline{P_2^0} = 0.30 \sim 0.33$ at $T = T_{NI}$, the behaviour of σ observed above seems to show more precisely the limiting behaviour $\overline{P_2^0} \to 0$ as $T \to T_{NI}$, suggesting the formula of type $\overline{P_2^0} = A(T_{NI} - T)^{\beta}$ near the transition temperature. On the other hand, $\overline{P_4^0}$ is also estimated to approach zero as $T \to T_{NI}$ in Figure 1. Thus, we have a satisfactory fit with experiment by

$$\begin{aligned} \overline{P_2^0} &= 0.35(T_{NI} - T)^{0.20 \pm 0.02} \\ \overline{P_4^0} &= 0.028(T_{NI} - T)^{0.636} \end{aligned} \tag{5}$$

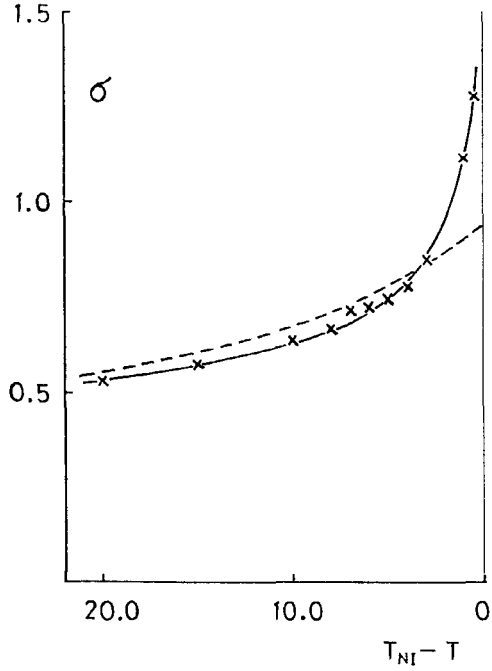

FIGURE 3 Temperature dependence of the relative fluctuation σ of $\overline{P_2^0}$ for MBBA. The solid line represents the experimental σ curve. The dotted line is that expected from Maier–Saupe theory.

The same behaviour, $\overline{P_2^0}$, $\overline{P_4^0} \to 0$ as $T \to T_{NI}$, has been obtained for 5CB.[7] The critical exponent $\beta = 0.20 \pm 0.02$ of $\overline{P_2^0}$ is in good agreement with those obtained for neat MBBA from different sources ($\beta = 0.219, 0.19$) by Haller.[10]

Recently it has been argued by Keyes[11] that the isotropic-nematic phase transition assumes a tricritical nature. In this context, it may be significant to compare the present $\beta = 0.20 \pm 0.02$ with $\beta = 0.25$ given by the mean field theory for the tricritical point and also with $\beta = 0.18 \pm 0.02$ obtained for the tricritical point of $RbCaF_3$.[12]

Finally, let us examine the validity of the scaling relation[13] $\alpha + 2\beta + \gamma = 2$ in the present case. Kim and Ogino recently reported the critical index of specific heat of neat MBBA to be $\alpha = 0.59$ for $T > T_{NI}$ and $\alpha = 0.53$ for $T < T_{NI}$.[14] The critical index, γ, of neat MBBA measured by the Cotton-Mouton effect and the Kerr effect, is known to be $\gamma = 1$ to a good approximation.[15] With these values we have $\alpha + 2\beta + \gamma = 1.93 \sim 1.99$. Thus, we see that the scaling relation $\alpha + 2\beta + \gamma = 2$ is applicable to the nematic-isotropic phase transition of MBBA.

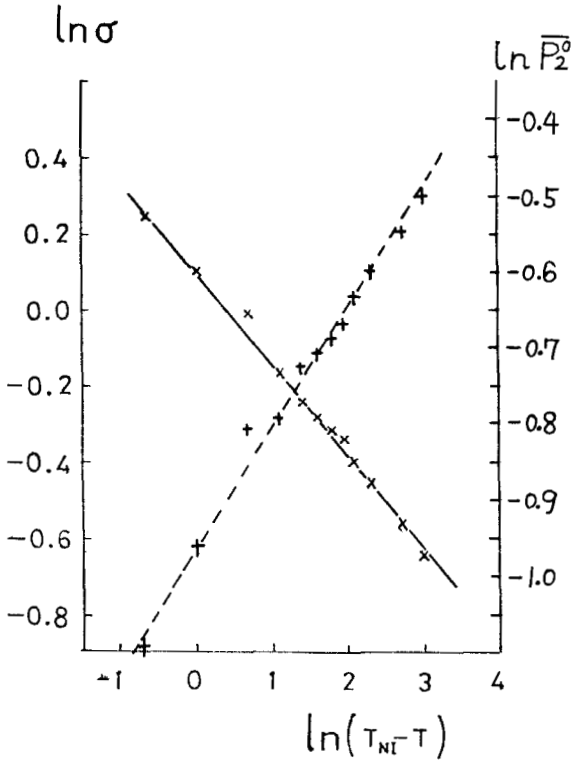

FIGURE 4 Plots of ln σ (solid lines) and ln $\overline{P_2^0}$ (dotted line) against ln($T_{NI} - T$) for MBBA.

The critical behaviour of 5CB has been found to be more complex than MBBA and its analysis is now in progress.

In conclusion, it has been shown that the application of the resonance Raman technique using an appropriate molecule as the orientational microprobe is quite useful for the accurate determination of the second and the fourth order parameters of host nematics. The critical index of $\overline{P_2^0}$ indicates that the NI transition for MBBA is of tricritical nature and within the range of scaling law.

References

1. S. Jen, N. A. Clark, and P. S. Pershan, *J. Chem. Phys.*, **66**, 753 (1977).
2. K. Miyano, *J. Chem. Phys.*, **69**, 4807 (1978).
3. V. F. Shabanov, E. M. Aver'yanov, P. V. Adomenas, and V. P. Spiridonov, *Sov. Phys. JETP.*, **48**, 970 (1978).
4. J. P. Heger, *J. Physique*, **36**, 209 (1975).

5. J. A. Koningstein, *Introduction to the Theory of the Raman effect*, Reidel, Dordrecht, Holland (1972).
6. Y. Nakajima, H. Yoshida, S. Kobinata, and S. Maeda, *J. Phys. Soc. Japan*, **49**, 1140 (1980).
7. H. Yoshida, Y. Nakajima, S. Kobinata, and S. Maeda, to be published.
8. W. Maier and A. Saupe, *Z. Naturforsh.*, **14a**, 882 (1959); **15a**, 287 (1960).
9. R. L. Humphries, P. G. James, and G. R. Luckhurst, *Chem. Soc. Faraday Trans. II*, **68**, 1031 (1972).
10. I. Haller, *Prog. Solid State Chem.*, **10**, 103 (1975).
11. P. H. Keyes, *Phys. Lett.*, **67A**, 132 (1978); *Phys. Rev. Lett.*, **42**, 722 (1979).
12. J. Y. Buzare, J. C. Fayet, W. Berlinger, and K. A. Müller, *Phys. Rev. Lett.*, **42**, 465 (1979).
13. H. E. Stanley, *Introduction to Phase Transition and Critical Phenomena*, Clarendon Press, Oxford (1971).
14. Y. B. Kim and K. Ogino, *Mol. Cryst. Liq. Cryst.*, **53**, 307 (1979).
15. (a) T. W. Stinson and J. D. Lister, *Phys. Rev. Lett.*, **25**, 503 (1970). (b) J. C. Filippini and Y. Poggi, *J. Physique*, **36**, 137 (1975).