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Investigation of Nematic Ordering Using Raman Scattering†‡

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Consider a uniformly oriented nematic liquid crystal sample within which the direction of average molecular alignment is described by a unit vector **n** called the director. While the molecules, on the average, are oriented with their long axes parallel to **n**, at any instant in time a particular molecule may be oriented with its long axis at some angle θ with respect to **n** due to thermal fluctuations. The azimuthal angle ϕ about the director can be shown by symmetry to be unimportant. Thus, the angular distribution function $f(\theta)$ is symmetric about **n** and depends only on the angle θ. With the assumption that **n** and $-$**n** are equivalent physical states of the system, $f(\theta)$ can be expanded in terms of Legendre polynomials in the form(1)

$$f(\cos\theta) = \tfrac{1}{2}S_0P_0(\cos\theta) + 5/2S_2P_2(\cos\theta) + 9/2S_4P_4(\cos\theta) + \ldots \quad (1)$$

with the coefficients S_n defined by

$$S_n = \int_{-1}^{1} P_n(\cos\theta)f(\cos\theta)d(\cos\theta), \quad n = 0, 2, 4\ldots \quad (2)$$

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S_0, S_2 and S_4 can be written explicitly as

$$S_0 = 1 \tag{3a}$$

$$S_2 = \tfrac{1}{2}[3\langle\cos^2\theta\rangle - 1] \tag{3b}$$

$$S_4 = \tfrac{1}{8}[35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3] \tag{3c}$$

where the angular brackets denote the statistical average defined in Eq. (2). For complete order, $\langle\cos^2\theta\rangle = \langle\cos^4\theta\rangle = 1$ so that $S_2 = S_4 = 1$; for complete disorder, $\langle\cos^2\theta\rangle = \frac{1}{3}$ and $\langle\cos^4\theta\rangle = \frac{1}{5}$ so that $S_2 = S_4 = 0$. Any intermediate degree of ordering will correspond to values of S_2 which lie between 0 and 1. The behavior of S_4 for intermediate ordering can be investigated with the aid of the Schwarz inequality.⁽²⁾ It can be shown that $\langle\cos^4\theta\rangle \geq [\langle\cos^2\theta\rangle]^2$ and, consequently, that

$$S_4 \geq \tfrac{1}{18}(35S_2^2 - 10S_2 - 7). \tag{4}$$

From Eq. (4) it is apparent that S_4 can become negative for values of $S_2 \lesssim 0.6$. Raman scattering data can be used to experimentally determine the values of $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$, hence S_2 and S_4, as a function of temperature over the entire nematic range. Furthermore, the ability to measure $\langle\cos^4\theta\rangle$ makes possible for the first time an experimental evaluation of the quantity

$$\psi = \langle\cos^4\theta\rangle - [\langle\cos^2\theta\rangle]^2 \tag{5}$$

which, it will be noted from the inequality above, must always be greater than, or equal to zero. The magnitude of ψ is a measure of the mean square fluctuation in $\cos^2\theta$ and, consequently, is sensitive to the shape of the angular distribution function $f(\theta)$.

The intensity of a Stokes-shifted Raman line polarized in a direction γ, excited by a laser beam polarized in a direction σ, is⁽³,⁴⁾

$$I_{AB}(\gamma) = \frac{2\pi^2(\nu_0 - \nu_{AB})^4 hN}{\mu c^4 \nu_{AB}[1 - \exp(-h\nu_{AB}/kT)]}(\alpha'_{\gamma\sigma})^2_{AB} I_0(\sigma). \tag{6}$$

In deriving Eq. (6), the vibrational part of the molecular wave function has been taken to be that of an harmonic oscillator of frequency ν_{AB} and reduced mass μ; ν_0 is the laser frequency; N is the effective number of molecules illuminated by the laser that can be viewed by the spectrometer; $I_0(\sigma)$ is the intensity of the laser beam polarized in the σ-direction; and $(\alpha'_{\gamma\sigma})_{AB} = (\partial\alpha_{\gamma\sigma}/\partial Q_{AB})$ is the derivative of the $\gamma\sigma$-component of the polarizability tensor with respect to the normal coordinate Q_{AB} at the equilibrium position. For the simplest differential polarizability tensor in the molecular frame of reference, i.e.

$$(\alpha'_{\mathrm{mol}})_{AB} = a \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

it can be shown that, viewed in the laboratory frame, the quantity $(\alpha')^2{}_{AB}$ in Eq. (6) has the form (for the case $\mathbf{n}//z$)

$$\langle(\alpha'_L)^2_{AB}\rangle = a^2 \begin{pmatrix} \frac{3}{8}\langle(1-c^2)^2\rangle & \frac{1}{8}\langle(1-c^2)^2\rangle & \frac{1}{2}\langle(1-c^2)c^2\rangle \\ \frac{1}{8}\langle(1-c^2)^2\rangle & \frac{3}{8}\langle(1-c^2)^2\rangle & \frac{1}{2}\langle(1-c^2)c^2\rangle \\ \frac{1}{2}\langle(1-c^2)c^2\rangle & \frac{1}{2}\langle(1-c^2)c^2\rangle & \langle c^4\rangle \end{pmatrix}$$

where $c \equiv \cos\theta$ (the same angle that appears in the distribution function) and the angular brackets again denote the statistical average defined in Eq. (2). Defining two depolarization ratios with respect to the laboratory frame as

$$\rho_1 = \frac{I_{zx}}{I_{zz}} \tag{7a}$$

and

$$\rho_2 = \frac{I_{xz}}{I_{xx}}, \tag{7b}$$

it is straightforward to show that $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$ can be expressed in the form

$$\langle\cos^2\theta\rangle = \frac{3\rho_2(2\rho_1+1)}{8\rho_1+3\rho_2+12\rho_1\rho_2} \tag{8a}$$

and

$$\langle\cos^4\theta\rangle = \frac{3\rho_2}{8\rho_1+3\rho_2+12\rho_1\rho_2} \tag{8b}$$

provided the laser intensity and temperature are held constant and there is no change in the effective number of scatterers N during the two measurements. The values of S_2 and S_4 then follow directly from substitution of Eqs. (8) into Eqs. (3). The same general formalism is applicable in the case of molecular vibrations having more than one non-zero differential polarizability tensor element so that scattering from various vibrations can be used to determine $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$.

To demonstrate the method, we have made an investigation of the temperature dependence of the molecular ordering in N-(*p*′-methoxybenzylidene)-*p*-*n*-butylaniline (MBBA)/N-(*p*′-butoxybenzylidene-*p*-cyanoaniline (BBCA) mixtures.(5) Polarized light from a cw ion laser (100 mW; 5145 Å, argon or 6471 Å, krypton) was incident normal to an aligned, 75 μm thick layer of the nematic mixture. Alignment of the molecules parallel to the glass cell walls was achieved by a method similar to that described by Janning.(6) Backscattered light (180° scattering geometry), Stokes-shifted by the —C≡N molecular vibration in BBCA (Δv = 2230 cm^{-1}), was collected, analyzed with a Glan-Thompson prism polarizer, passed through a quartz wedge polarization scrambler and finally focused on the entrance slit of a Spex double grating monochromator. The resulting signal was detected by a cooled P.M. tube whose output was processed with standard photon counting electronics.(7) The raw data were corrected for the effects of reflection and refraction at the liquid crystal–glass interface(8) as well as for anisotropy in the radiated power density resulting from the uniaxial symmetry of the sample. Over the reduced temperature range $(T - T_c)/T_c = -0.065$ to -0.0025, S_2 varied between 0.64 and 0.43 while S_4 had values in the range from 0.09 to -0.14, both decreasing monotonically with increasing temperature. ψ was found to increase monotonically from 0.009 to 0.030, jumping discontinuously to its isotropic value at the nematic–isotropic transition temperature.

There are many potential applications of the technique. For example, the order can be probed on a much smaller scale than is possible using previously reported methods, the limitations being (a) how well the incident beam can be focused, and (b) how selectively the scattered light can be collected. One might also be able to study surface alignment using the evanescent field associated with total internal reflection of the incident beam in a prism on whose surface the liquid crystalline sample is placed. In addition, the technique could be used to study the internal structure of the various smectic phases.

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