Dynamic Polarized Infrared Spectroscopy of Electric Field-Induced Molecular Reorientation in a Chiral Smectic-*A* Liquid Crystal

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We report transient molecular orientation and conformation changes accompanying the electric field-induced soft mode molecular tilt in a chiral smectic-*A* liquid crystal. We exhibit directly the loss of uniaxial molecular symmetry with field-induced tilt, showing that the molecular tails are less tilted with respect to the layer normal than the cores, and during switching reach their equilibrium orientation later than the cores. We also find evidence for a collective mode of rotation about the molecular long axis.

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The rod-shaped molecules which form liquid crystal phases typically have a number of internal chemical bonds about which there are multiple isomeric states, leading to an equilibrium population of many possible molecular conformations. In equilibrium the shape and local environment of each conformation determines its statistical distribution of orientations which must reflect the overall symmetry of the phase [1,2]. In this Letter we report the use of polarized infrared (IR) spectroscopy and polar absorbance patterns (PAP's) [3] to visualize directly the symmetry of the molecular environment in the smectic-*A* and -*C* phases, and to study the dynamics of molecular orientation and/or conformation change during large-scale externally induced change accompanying electro-optic switching. The study of these shape and orientation distributions in equilibrium and during molecular motion is a virtually unexplored area of liquid crystal science, but potentially a very rich one, since it offers a new window into the molecular-level behavior influencing macroscopic dynamic properties, complementing the study of equilibrium conformational statistics via magnetic resonance [4]. Several recent papers indicate that vibrational spectroscopy will be useful as a probe of liquid crystal reorientation dynamics [5–7].

Experiments were carried out at $T = 25$ °C on monodomains of the chiral smectic-*A* (SA) phase of the compound W317 [8] contained in visible-infrared transparent capacitors, with the smectic layers normal to the capacitor plates (bookshelf geometry [9,10]). With zero applied field the smectic-*A* molecular director $\mathbf{n}$ is along the normal to the layers $\mathbf{z}$ and in the plane of the plates. Application of an electric field $\mathbf{E}$ produces the electroclinic effect [10,11], generating a field-induced smectic-*C* (SC) phase via a chiral rotation of $\mathbf{n}$ about $\mathbf{E}$, i.e., a rotation with $\mathbf{n}$ in the plane of the plates. We use dynamic step-scan molecular vibrational spectroscopy [12] to probe features of the molecular shape and orientation dynamics during this rotation.

In systems of uniaxial symmetry (i.e., nematics and smectics *A*), simple dichroic ratio measurements can yield whatever information IR absorption can provide on molecular organization. However, upon a transition to lower symmetry, such as that of the monoclinic field-induced (electroclinic) or temperature-induced SC phase, dichroism changes may arise from either (or both) director reorientation or symmetry change. Unraveling these requires measurement of absorbance over a continuous range of polarizer orientations and analysis of the resulting overall pattern of absorbance vs polarization orientation. We show that one can distinguish conformational from orientational effects in the dynamic behavior, finding in the present experiments, for example, that the molecular tails are less tilted than the cores in the electroclinic SA structure.

The key parameter governing the observability of nonequilibrium effects is $\Omega = \Delta\theta/\Delta t$, the externally induced angular velocity of $\mathbf{n}$, where $\Delta\theta$ is the induced reorientation of $\mathbf{n}$ and Δt is the switching time. We expect the local return to equilibrium to be governed by several characteristic relaxation times τ, and that nonequilibrium effects will appear for $\Omega\tau \gtrsim 1$. The electric field-induced switching of chiral SA phases is thus of particular interest in this connection because of their large values of Ω. W317 has the electronegative polar substituent —NO_2 on a core ring ortho to the chiral tail to give high ferroelectric polarization and fast electroclinic switching. Spectroscopy was carried out using a JEOL dynamic polarized FTIR microspectrometer (JIR-6500 system) imaging 50–100 μm square × 1.5–2 μm thick smectic monodomains aligned between IR and visible light transparent ITO coated CaF_2 plates by oblique SiO evaporation on the plates [13]. Square wave excitation with peak-to-peak amplitudes of 160 V produced director reorientation between ±18° with respect to the layer normal in response times of 10–20 μsec, as determined via the rotation of the visible light optic axes. This

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corresponds to $\Omega \sim 6 \times 10^4$ rad/sec, a high value for liquid crystals.

Spectra obtained vs θ, the angle between the IR polarization and smectic layer normal **z**, were measured over a 180° range in θ at intervals in θ of 10°, and were characterized by the vibrational absorbance bands typical for liquid crystals. Peak absorbance $A(\theta)$ was then determined and polar plotted for each of the principal IR bands, and the overall polar absorbance pattern of $A(\theta)$ for the different bands was analyzed. Figure 1 shows the W317 PAP with $E = 0$. Also shown are the assignments of the bands along with their corresponding groups and absorption dipole orientation, indicated by the open arrows, and angle β relative to the core axis. This PAP exhibits $C2mm$ symmetry about $\theta = 0$, with the mirror lines along the layer normal **z** ($\theta = 0$) and the layer direction ($\theta = 90°$), as expected for a SA bookshelf monodomain, because of the uniaxial SA symmetry resulting from isotropic averaging of orientations about $\mathbf{n} = \mathbf{z}$.

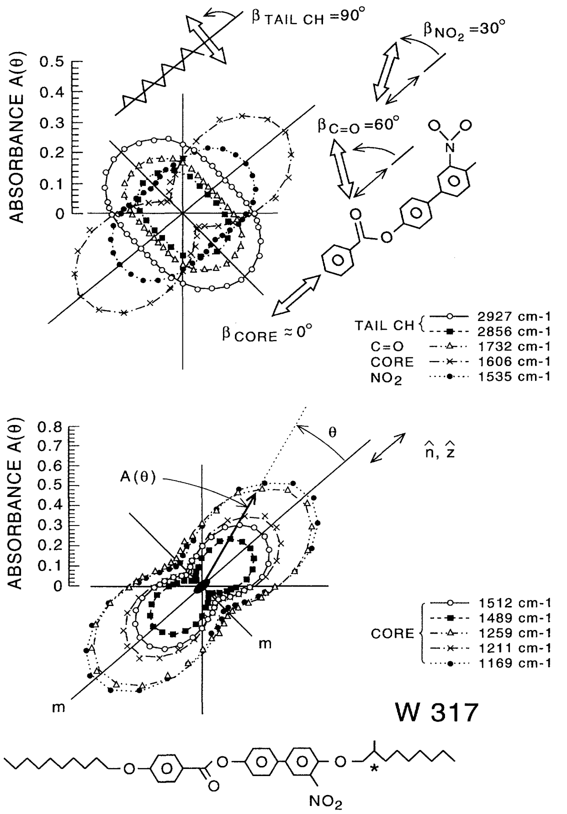

FIG. 1. Polar plot of the absorbance $A(\theta)$ of the principal IR bands of W317 in a smectic-A monodomain with zero electric field applied ($T = 35$ °C). The band assignments are indicated, and orientations of the corresponding absorption dipoles are indicated by the open arrows (⇔). This PAP exhibits $2mm$ symmetry with a mirror line along the director **n** (layer normal **z**), a result of the smectic-A uniaxial symmetry.

If we consider a vibrational mode X having an absorption dipole $\mathbf{P}_X$ oriented at a fixed angle β_X relative to the molecular long axis **M**, which is in turn oriented at an angle ψ to the mean orientation **n**, then, for the isotropic averaging of the angle γ giving the orientation of $\mathbf{P}_X$ about **M** and then of **M** about **n** in the SA phase, the net orientational order parameter $S_{\text{net}} = P_2(\cos\beta)S$, where P_2 is the Legendre polynomial of order 2, and $S = \langle P_2(\cos\psi)\rangle$ is the long axis order parameter about **n**. The dichroic ratio $R(S,\beta) = A(0)/A(90) = [1 + 2P_2(\cos\beta)S]/[1 - P_2(\cos\beta)S]$ [14]. For W317, we take **M** to be the axis of the biphenyl moiety in the core.

The most general form of $A(\theta)$ for a given band in the smectic-A or -C phase is

$$A(\theta \mid \theta_0) = -\ln\{\cos^2(\theta - \theta_0)10^{-A(\theta_0)} + \sin^2(\theta - \theta_0)10^{-A(\theta_0+90°)}\},$$

exhibiting $C2mm$ symmetry with the mirror lines in the θ_0 and $\theta_0 + 90°$ directions. The fits by $A(\theta \mid \theta_0)$, indicated for each band by a line in Fig. 1, are good and, importantly, yield accurate values of θ_0. For the SA phase we find $|\theta_0| < 0.7°(\text{mod } 90°)$ for all bands. The mode assignments of the observed bands were made using standard tables [15]. The absorption dipoles of the core phenyl vibrations bands (1211,1489,1606 cm^{-1}) exhibited the largest values of R ($R_{1211} = 4.7, R_{1489} = 6.7, R_{1606} = 6.6$). Assuming for the largest of these that $\mathbf{P}_{1489}$ is along **M** ($\beta_{1489} = 0$) yields the *minimum* estimate for the nematic order parameter, $S = \langle P_2(\cos\psi)\rangle_{1489} = 0.66$, indicating that the sample is well aligned. It is interesting to note that all of the bands clearly identifiable as coming from core phenyl vibrations have relatively large dichroic ratios, indicating that these absorption dipoles are generally along **n**. The Raman polarizabilities in other liquid crystals exhibit similar behavior [16].

The C=O (1732 cm^{-1}) and NO_2 groups (1535 cm^{-1}) have absorption dipoles oriented nominally at $\beta_{C=O} \sim 60°$ and $\beta_{NO_2} \sim 30°$ from **M**, as indicated in Fig. 1. The observed dichroic ratios $R_{1732} = 0.55$ and $R_{1535} = 1.93$ combined with $R(S = 0.66, \beta)$ above for isotropic averaging yield $\beta_{C=O} \sim 66°$ and $\beta_{NO_2} \sim 40°$, in reasonable agreement with these expectations, indicating that deviations from isotropic averaging about **M** are probably small in the SA phase. The tail *CH* vibrations (2927, 2856 cm^{-1}) are polarized normal to the all-trans chain axis, but exhibit dichroic ratios near 1 because of the disorder in the tail chains.

Figure 2 shows the effect of applying an electric field and displays the temporal evolution of the W317 PAP's during a transient rotation of **n** induced by switching the field from −45–+45 V/μm at $t = 0$. While each band has the $C2mm$ symmetry form of $A(\theta \mid \theta_0)$, the *overall* structure of these PAP's exhibits the lower $C2$ symmetry required by the monoclinic field-induced SC structure resulting from the tilt of **n**. For example, it is clear by inspection that the core bands have rotated

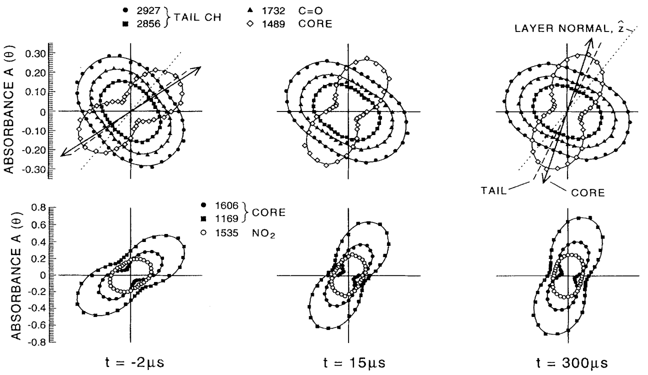

FIG. 2. Polar absorbance patterns $A(\theta, t)$ before and during the dynamic response of the W317 cell of Fig. 1 to an applied voltage step, from -80 to $+80$ V at $t = 0$. The electroclinic rotation of the molecules is evident from the core bands (lower row). The solid lines are fits by $A(\theta \mid \theta_0)$ given in the text. The symmetry reduction accompanying applied electric field is evident in the upper row, which shows that the net rotation of the core and tail during switching is through different net angles. The solid and dashed lines indicate the mean orientations $\theta_0(t)$ of the core and tail groups, respectively, with the core θ_0 rotating through 36° and the tail θ_0 rotating through 27°.

through a larger angle than the tail bands, indicating that in equilibrium under applied field the tails are less tilted than the cores relative to the layer normal **z** (dotted line). After reorientation, *the dichroic ratio for the individual bands is nearly that for* $E = 0$, indicating that the induced anisotropy in molecular orientation about the long axis is small. We quantify the field-induced reorientation by fitting the bands to $A(\theta \mid \theta_0)$, extracting for each band its mean orientation $\theta_0(t)$. The fitted $A(\theta \mid \theta_0)$ are plotted as PAP's in Fig. 2, and $\theta_0(t)_{\text{core}}$ (dashed line) and $\theta_0(t)_{\text{tail}}$ (arrowed line) at $t = -2$ and 300 μsec are indicated, showing clearly the larger tilt of the cores and the overall $C2$ symmetry of the patterns.

The resulting $\theta_0(t)$ data for W317 are shown on two time scales in Figs. 3(a) and 3(b), which also plot the same data as fractional reorientation $f(t)$ vs t, where $f(t) = [\theta_0(t) - \theta_0(-2\ \mu\text{sec})]/[\theta_0(300\ \mu\text{sec}) - \theta_0(-2\ \mu\text{sec})]$. The core vibrations move together with a net change in θ_0 of $\Delta\theta_0(t)_{\text{core}} = 36°$. Visible light measurement of the optic axis rotation yields an electroclinic reorientation of $\Delta\theta_{\text{vis}} = 37°$, in agreement with this result. On the other hand, for the tail vibrations $\Delta\theta_0(t)_{\text{tail}} = 27°$, a much smaller reorientation results. The $f(t)$ data for W317 show that just after field switching the tail reorientation rate is smaller than that of the core, with $\theta_0(t)_{\text{tail}}$ going from being smaller than $\theta_0(t)_{\text{core}}$ to being larger than $\theta_0(t)_{\text{core}}$ in the first 5 μsec after the field switching.

The C=O and NO$_2$ reorientations are particularly interesting. The C=O bands *overshoot* in $f(t)$, eventually reorienting through $\Delta\theta_0(t)_{\text{C=O}} = 29°$, a smaller angle than that of the core. The NO$_2$ reorientation finishes with $\Delta\theta_0(t)_{\text{NO}_2} = 42°$, a larger angle than that of the core. Because of the rigid connection of these groups to the core, such differences in $\Delta\theta_0(t)$ and the apparent

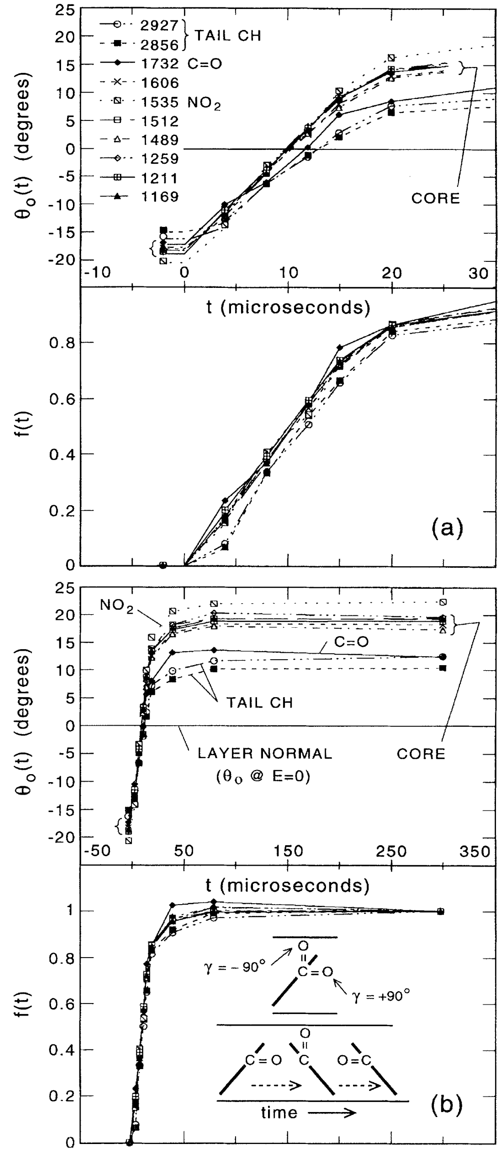

FIG. 3. Time dependence of the mean orientation $\theta_0(t)$ of the principal bands in W317 at (a) short and (b) long time scales. Also shown is $f(t)$, the fractional change of $\theta_0(t)$. The mean smaller tilt of the tails and the C=O vibration relative to the layer normal ($\theta_0 = 0$) is evident. (a) An initial lag in the dynamic response of $\theta_0(t)_{\text{tail}}$ and (b) all of the groups with dichroism sensitive to the orientation distribution around the long axis (tails, C=O, NO$_2$) have a rather long equilibration time, suggestive of a collective process of reorientation about the long molecular axis. The inset shows the extremes $\gamma = 90°$ and $\gamma = -90°$ of C=O orientation about the molecular long axis and a two-stage reorientation process that would yield a transient overshoot in the apparent C=O orientation. The $\gamma = 90°$ orientation is preferred in the steady state $\langle \sin\gamma \rangle = 0.025$.

time lag relative to the core must arise as a result of the anisotropy of orientations about **n**, as indicated in the inset of Fig. 3(b). Considering the C═O, its smaller $\Delta\theta_0$ indicates that, in the steady state, orientation $\gamma = 90°$ of the C═O about **n** is of higher probability than orientation $\gamma = -90°$. For $\beta_{\mathrm{C=O}} \sim 60°$ and $\Delta\theta_0(t)_{\mathrm{core}} = 36°$, fitting the apparent C═O rotation of $\Delta\theta_0(t)_{\mathrm{C=O}} = 29°$ yields $\langle \sin\gamma \rangle \approx 0.025$ [17], indicating that the orientational bias about the long molecular axis is indeed small. The $\Delta\theta_0(t)_{\mathrm{C=O}}$ overshoot upon field switching indicates that the process of equilibration to the new steady state involves two steps: first, a director reorientation which leaves a nonequilibrium orientation distribution about the long axis, followed by equilibration about the long axis. The latter process appears to be relatively slow, taking ~ 100 μsec, suggesting that is a collective process.

To conclude, this study demonstrates that, by using the overall structure of the functional dependence of IR absorbance vs polarization for the principal vibrational bands of liquid crystal forming molecules, one can obtain new information on molecular shape and conformation in their liquid crystal phases.

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