Relaxation time of molecular rotation about its long axis in the smectic-*A* phase of ferroelectric and antiferroelectric liquid crystals as observed by picosecond optical Kerr effect

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We have studied the molecular rotational motion about its long axis in ferroelectric chiral smectic-*C* (Sm-*C**) and antiferroelectric chiral smectic-C_a (Sm-C_A^*) liquid crystals and observed a few tens of picosecond relaxation time. Previously reported results using degenerate four-wave mixing with 25-ps pump pulses [Lalanne *et al.*, Phys. Rev. A **44**, 6632 (1991)] claimed to show a critical slowing down in the temperature region more than 0.1 °C above the Sm-*A*–Sm-*C** phase transition. Our measurements of the optical Kerr effect with 130-fs pump pulses do not show any critical slowing down in the corresponding temperature region above the phase transition from Sm-*A* to Sm-*C** or Sm-C_A^*. The result may indicate that the laser-induced molecular reorientation with $\tau \sim 10^{-11}$ s scarcely couples with the tilt angle and the polarization. A possibility has been discussed that a slower rotational motion with $\tau \gtrsim 10^{-10}$ s plays a primary role for the emergence of ferroelectricity and/or antiferroelectricity. [S1063-651X(97)07002-5]

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I. INTRODUCTION

Ferroelectricity in the chiral smectic-*C* phase (Sm-*C**) of liquid crystals [1] results from the interaction of the molecule with its monoclinic symmetry environment. The molecule does not rotate freely about its long axis so that the chiral part preferentially orients in a polar way; the preferential orientation is caused by a secondary effect of Sm-*C* ordering, but not by the permanent dipole-dipole interaction [2,3]. Antiferroelectricity in the chiral smectic-C_A phase (Sm-C_A^*) [4,5], on the other hand, has been ascribed to the intermolecular interaction due to the permanent dipole moments attached to the molecules [5–8]. In either case, the biased or hindered rotation about the long molecular axis plays an important role for the emergence of ferroelectricity and antiferroelectricity in liquid crystals. The purpose of this paper is to observe as directly as possible the molecular rotational motion about its long axis. In particular, we are interested in whether the rotational motion critically slows down in the smectic-*A* phase (Sm-*A*) as the temperature approaches the Sm-*A*–Sm-*C** or Sm-*A*–Sm-C_A^* transition.

The most direct, though static, microscopic proof for biasing or hindrance was given by Kim *et al.* [9], Miyachi *et al.* [8], and Jang *et al.* [10]; the polarized infrared (ir) spectroscopy indicated that carbonyl rotation in the chiral and core parts of ferroelectric and antiferroelectric liquid crystals is biased or hindered in Sm-*C** and Sm-C_A^*. As for its dynamical aspect, Lalanne *et al.* [11–14] observed the relaxation time, 20 ps or longer, of the individual molecular rotational motion about the long axis in a Merck mixture, ZLI-3488, by the degenerate four-wave mixing (DFWM) technique using 25-ps pump pulses; the relaxation time was concluded to critically slow down in Sm-*A* as the temperature approaches the phase transition to Sm-*C**. They also confirmed that the critical slowing down does not occur in an achiral compound synthesized by themselves. O'Brien *et al.* [15] studied the rotational dynamics in the 50 ps to 1 ns range by the optical Kerr effect (OKE) technique using 55-ps pump pulses; the relaxation consisted of two components, which were associated separately with individual (fast) and collective (slow) molecular rotations, in Sm-*A* of both chiral and achiral liquid crystals. They concluded that there is no detectable critical slowing down in either of these rotations.

The diffusive (thermal) reorientation of small molecules in simple liquids such as CS_2, $CHCl_3$, and CH_2Cl_2 has the relaxation time on the order of 2 ps, which may be proportional to the square root of the molecular moment of inertia $I^{1/2}$ [16]. Consequently, the 55-ps pump pulses O'Brien *et al.* used may not be short enough to observe the individual molecular rotational dynamics. Even the 25-ps pump pulses Lalanne *et al.* used may be too long to obtain any signal due to the reorientation of 4-(1-methylheptyloxycarbonyl)phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC), a prototype antiferroelectric liquid crystal (see the molecular structure shown in Table I) [14]. We used subpicosecond pump pulses and successfully measured the relaxation time of molecular rotation about its long axis in Sm-*A* of four compounds including ferroelectric and antiferroelectric liquid crystals. In particular, we tried to observe the critical slowing down; we could not detect it, however, in the temperature region more than 0.1 °C above the phase transition from Sm-*A* to Sm-*C** or Sm-C_A^*, where Lalanne *et al.* reported its observation in ZLI-3488.

II. EXPERIMENT

Samples used are octylcyanobiphenyl (8CB), MHPOBC, 4-(1-methylheptyloxycarbonyl)phenyl-4'-octylcarboxybiphenyl-4-carboxylate (MHPOCBC), and 2-(4-(6-methyloctyloxy)phenyl)-5-octylpyrimidine (HS-98), of which structural formulas and phase sequences in the cooling processes are summarized in Table I. Partial racemization simplifies the phase sequence of MHPOBC and MHPOCBC [5]. Homeotropically aligned sandwich cells of 100 μm thickness were prepared using polyester film spacers and quartz substrates coated with silane surfactant (Toray Dow Corning Silicone, AY43-021). The relaxation time was mea-

TABLE I. Samples used in this paper.

8CB
NC—⬡—⬡—C_8H_{17}
Iso. $\underset{40°C}{\longleftrightarrow}$ N $\underset{32.5°C}{\longleftrightarrow}$ Sm-A

MHPOBC (32.6% ee.)
$C_8H_{17}O$—⬡—⬡—CO—⬡—CO—CH—C_6H_{13} (with CH_3 and O, O groups, * marked)
Iso. $\underset{148°C}{\longleftrightarrow}$ Sm-A $\underset{120°C}{\longleftrightarrow}$ Sm-C* $\longleftrightarrow$ Sm-C_A*

MHPOCBC (36.8% ee.)
C_8H_{17}—CO—⬡—⬡—CO—⬡—CO—CH—C_6H_{13} (with CH_3 and O, O, O groups, * marked)
Iso. $\underset{148°C}{\longleftrightarrow}$ Sm-A $\underset{99°C}{\longleftrightarrow}$ Sm-C_A*

HS-98P
$H_{17}C_8$—⬡(N,N)—⬡—O—C_5H_{10}—CH—C_2H_5 (with CH_3, * marked)
Iso. $\underset{56°C}{\longleftrightarrow}$ Sm-A $\underset{47°C}{\longleftrightarrow}$ Sm-C*

FIG. 2. Normalized OKE signal vs delay time in two standard liquids CS_2 and CCl_4 observed at RT.

sured by the OKE, using a subpicosecond self-mode-locked Ti:sapphire laser [Coherent, MIRA-basic: 790 nm, 500 mW, 76 MHz, 130 fs, 200 fs autocorrelation time (hence 6.6 nJ/pulse and 50 kW peak power) and approximately 100-μm-inner-diam spot size at the sample cell]. Figure 1 illustrates the optical setup. An intense linearly polarized optical pump pulse induces reorientation around the molecular long axes. The reorientation can be observed as birefringence by using a frequency-doubled probe pulse; the frequency doubling is very effective in reducing the background level due to the scattering of the intense pump pulse. The intensity ratio between the weak probe and strong pump pulses was about 0.05. By delaying the probe pulse with respect to the pump pulse, the induced birefringence was obtained as a function of the delay time.

We used a polarization heterodyne method to enhance the sensitivity [15,16]. The Kerr constant $B(\omega_{pr}, \omega_{pu})$ is defined by the relation

$$\delta = 2\pi \Delta n(\omega_{pr})l/\lambda_{pr} = 2\pi l B(\omega_{pr}, \omega_{pu})|E(\omega_{pu})|^2. \quad (1)$$
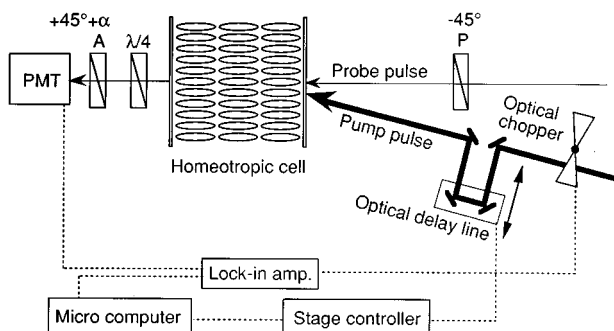

FIG. 1. Optical setup for measuring OKE. Since the probe pulse had a longer optical path actually, the delay time adjustment was made in the pump pulse.
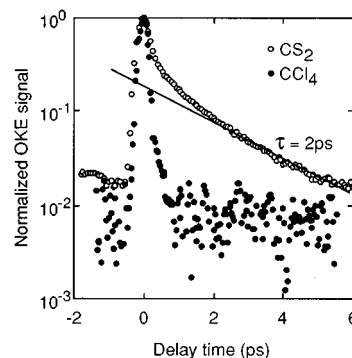
Here δ is the phase shift (2π times the path difference in fractions of the wavelength of the probe pulse λ_{pr}), $\Delta n(\omega_{pr})$ the difference in the refractive indices parallel and normal to the applied pump field $|E(\omega_{pu})|$, and l the path length. If we consider the conventional OKE signal $I_S(\omega_{pr})$ as arising from an electric field $E_S(\omega_{pr})$ by the sample, the use of a local oscillator field $E_{LO}(\omega_{pr})$ results in a detector signal proportional to

$$I_{LO} + I_S + I_B + (n/2)(E_S^* E_{LO} + E_{LO}^* E_S). \quad (2)$$

Here I_{LO} is the local oscillator intensity, I_S the conventional homodyne OKE signal intensity, I_B the intensity due to any background radiation, and $(n/2)(E_S^* E_{LO} + E_{LO}^* E_S)$ the heterodyne term. The local oscillator is adjusted to make the heterodyne term much greater than I_S, but not to saturate the dynamic range of a lock-in amplifier. To determine the Sm-A–Sm-C^* or Sm-A–Sm-C_A^* phase transition temperature, we monitored the transmitted light intensity due to the birefringence and/or the optical rotatory power when shielding the pump pulse.

To assess the quality of our OKE measurements, we observed two standard liquids. Figure 2 shows the temporal decaying profile of the laser induced biaxiality, i.e., the time-resolved OKE signal, in carbon disulfide (CS_2) and tetrachloromethane (CCl_4). Since CCl_4 possesses an isotropic polarizability, all relaxations associated with orientational motion are absent. The signal is rather symmetrical as seen in Fig. 2. It is dominated by an instantaneous response that closely follows the laser pulse autocorrelation and is attributable to the purely electric hyperpolarizability. We could not observe oscillations arising from intramolecular normal mode vibrations coherently excited by the laser pulse [16].

The OKE signal in less symmetrical CS_2 also has a prominent contribution from the electronic hyperpolarizability near zero delay, but exhibits a complicated temporal profile at positive time delay. The profile has been decomposed into three components: (i) a diffusive reorientation component, which accounts for the OKE intensity at probe delays greater than 1.5 ps; (ii) an intermediate component with exponential time constant in the range 400–600 fs; and (iii) an ultrafast component with $\tau < 170$ fs [16]. Since the pump pulse was 130 fs, we could not distinguish the ultrafast component from the instantaneous response due to the electronic hyperpolarizability. The components (i) and (ii) are clearly seen in Fig. 2. In order to show the stray light level clearly, the raw
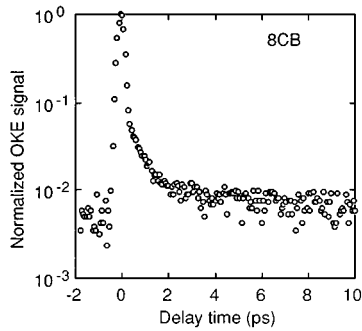
FIG. 3. Normalized OKE signal vs delay time at 22 °C (Sm-*A*) in 8CB.

data were plotted logarithmically after proper normalization; we will keep using this logarithmic plotting in the following. The relative background level naturally depends on the sample cell quality critically. It also depends on the electronic hyperpolarizability because of the normalization; the electronic instantaneous response is much smaller in CS_2 and CCl_4 than in liquid crystals with phenyl rings. The relaxation time was obtained by fitting the data to $\exp(-t/\tau)$ after subtracting the background.

III. RESULTS

The individual rotational relaxation time in Sm-*A* has been successfully observed by Lalanne *et al.* only in four materials: ZLI-3488, 8CB, and two home-synthesized compounds; among these four, only ZLI-3488 is ferroelectric and the others are paraelectric [11–14]. Since ZLI-3488 was not available, however, we first studied 8CB and confirmed the result of Lalanne *et al.* Figure 3 illustrates the OKE signal.

Following the instantaneous electronic response, there exist at least three components in the profile at positive time delay. By comparing the profile in 8CB with that in CS_2 and by taking account of the difference in the moment of inertia between them, the component with the slowest relaxation time, approximately 20 ps in Sm-*A*, can be assigned to the diffusive relaxation of the individual molecular rotational motion. The relaxation time in Sm-*A* obtained in the present study agrees rather well with the value of 35 ps in Sm-*A* reported by Lalanne, Buchert, and Kielich [13]. They did not directly obtain this value from the temporal profile, but estimated it by observing the intensity of the backward wave in DFWM with their pump pulse of 25 ps.

Figure 4 shows the OKE signals for MHPOBC and MHPOCBC, together with the transmitted light intensity when shielding the pump pulse. The phase transitions Sm-*A*–Sm-*C** in MHPOBC and Sm-*A*–Sm-C_A^* in MHPOCBC are not of second order [17]; hence the transitions are easily determined from the transmitted light intensity when shielding the pump light pulse. The OKE signals were measured as a function of temperature. Two of them, obtained at 0.1 °C and 1.1 °C above the phase transition, temperatures are illustrated in Figs. 4(a) and 4(b). Both of the signals at positive time delay contain at least three components in addition to the instantaneous response due to the electronic hyperpolarizability. The fastest component manifests itself as the asymmetry of the peak at zero delay, the slowest one decays with a time constant ~16 ps, and the third component is the intermediate one with a time constant of 1 ps or less. The slowest component must represent the diffusive relaxation of the individual molecular rotational motion. No critical slowing down was observed in the temperature region more than 0.1 °C above the phase transition
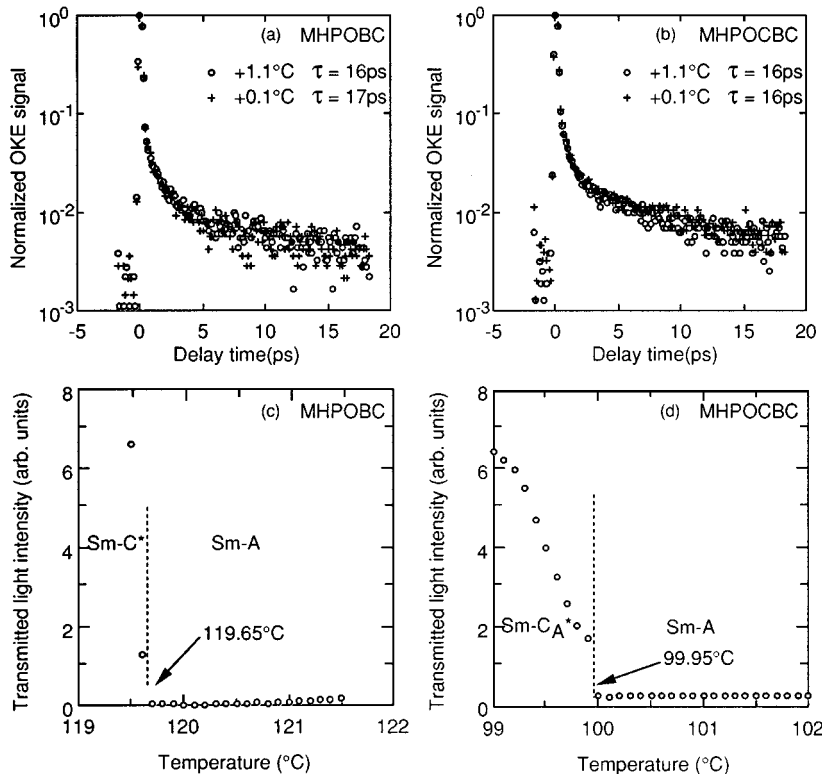

FIG. 4. Normalized OKE signal vs delay time observed at 0.1 °C and 1.1 °C above (a) the Sm-*A*–Sm-*C** phase transition temperature in MHPOBC and (b) the Sm-*A*–Sm-C_A^* phase transition temperature in MHPOCBC, and transmitted light intensity when shielding the pump pulse in (c) MHPOBC and (d) MHPOCBC.
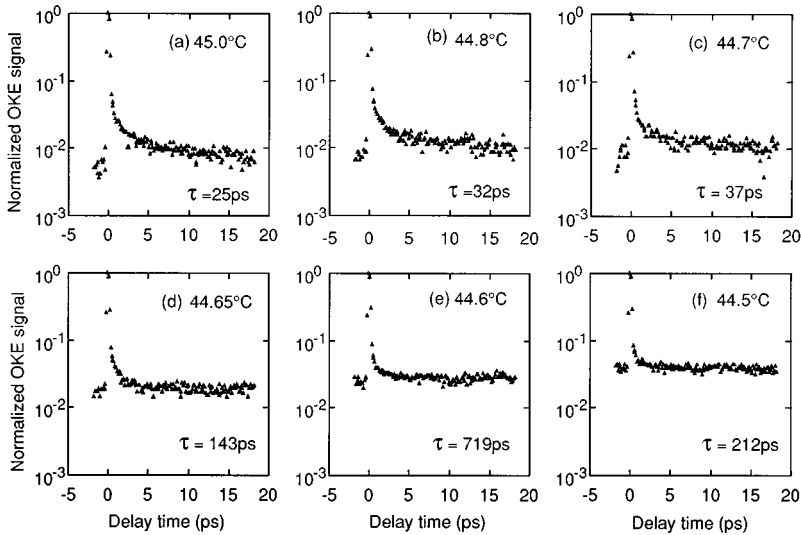
FIG. 5. Normalized OKE signal vs delay time observed at several temperatures above and below the Sm-A–Sm-C^* phase transition temperature in HS-98P. The monitored transmitted light when shielding the pump pulse indicates that the phase transition occurs at a temperature slightly higher than 44.65 °C.

even in MHPOBC, where the spontaneous polarization is as large as 1 mC m^{-2} or more; O'Brien *et al.* [15] pointed out that the critical slowing down may easily be observed in a compound with a large spontaneous polarization.

Figure 5 illustrates the temperature variation of the OKE signals in HS-98P. As in 8CB, MHPOBC, and MHPOCBC, multiple components exist at positive time delay. The Sm-A–Sm-C^* phase transition is of almost second order; the monitored transmitted light does not increase abruptly in HS-98P, unlike in MHPOBC and MHPOCBC, but clearly shows that the phase transition occurs at a temperature slightly higher than 44.65 °C. Moreover, the temperature variation of the OKE signals clearly indicates the occurrence of the phase transition by themselves; the stray light level becomes almost one order of magnitude higher due to an increase in scattering. Since the phase transition is of almost second order, we were able to obtain the temporal decaying profiles even in Sm-C^* at least in the temperature region close to Sm-A. Note that the polarization heterodyne technique is effective even when the medium becomes biaxial as long as the detecting system has a sufficient dynamic range and is not saturated.

As is often the case, an increase in the stray light level apparently slows down the OKE signal. The stray light at 45.0 °C is about 0.5% of the instantaneous response peak, as seen in Fig. 5. Even this low level of stray light affects the relaxation time of the slowest component rather seriously. We obtain $\tau=25$ ps if we neglect the stray light and analyze the raw data by using $\exp(-t/\tau)$, while we obtain $\tau=10$ ps if we similarly analyze the data after subtracting the 0.5% stray light level. In order to see how the increased stray light level causes an apparent effect, we artificially added to the data at 45.0 °C the stray light in amounts 0.0%, 0.5%, 1.5%, and 4.5% of the instantaneous peak and obtained the corresponding decay profiles given in Fig. 6. In this way we can conclude that the critical slowing down does not occur in the temperature region more than 0.1 °C above the phase transition from Sm-A to Sm-C^* even when it is of second order.

IV. DISCUSSION

As described in Sec. I, the rotational motion of the carbonyl group near the chiral part of ferroelectric and antiferro-

electric liquid crystals is biased or hindered in Sm-C^* and Sm-C_A^* [8–10]. Since the carbonyl group is resonant with the core part, both of them are rotating with nearly the same relaxation time as $\tau \sim 10^{-11}$ s, obtained in Sec. III. Our assignment appears to be supported by Leadbetter, Richardson, and Frost [18]; they obtained a similar relaxation time for the diffusive rotational motion of the rigid molecular core in Sm-A by neutron scattering. Contrary to the previous observation by Lalanne *et al.* [11–14], the relaxation time did not show any critical slowing down. The absence of a critical slowing down indicates that the couplings of the laser-induced molecular reorientation with the tilt angle and the polarization are weak [15]. The rotational motion with $\tau \sim 10^{-11}$ s is not primarily responsible for the ferroelectricity and/or antiferroelectricity. We think that the result of Lalanne *et al.* [11–14] is wrong.

Because of the complex molecular structure of liquid crystals, however, it is still possible that a slower rotational motion with $\tau > 10^{-10}$ s plays an important role. In fact, rotational motions with $10^{-8} > \tau > 10^{-10}$ s have been revealed by dielectric spectroscopy in several other compounds [19–21]; their details remain to be studied in future. Particularly in MHPOBC, Jin *et al.* [22] recently showed that the chiral alkyl chain projects obliquely from the rigid core even in Sm-A of MHPOBC and the angle between them is more than
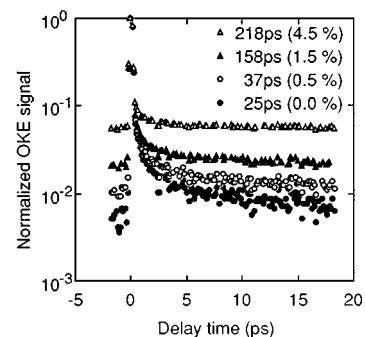

FIG. 6. Effect of scattering on apparent relaxation time. We artificially added the stray light in the amount of 0.0%, 0.5%, 1.5%, and 4.5% of the instantaneous peak to the data at 45.0 °C shown in Fig. 5.

the magic angle, 54.7°. Such a bent molecular structure in the crystal phase has already been reported by Hori and Endo [23]. Considering the uniaxial macroscopic symmetry of Sm-*A*, the chiral alkyl chain must be precessing about the rigid core long axis; the relaxation time ought to be slow because the obliquely projecting chiral chain has a large moment of inertia. When they measured ^{13}C spin-lattice relaxation times, Nakai noticed a possible collective character of the chiral chain precessional motion [24]. The existence of a collective mode in Sm-C^* or Sm-C_A^* has been suggested by OKE [15] and dielectric spectroscopy [20,25,26]. More investigations, in particular, based on ir and NMR spectroscopic techniques, will be necessary to understand the origin of ferroelectricity and antiferroelectricity in connection with the rotational motions: intramolecular, individual, and collective.

ACKNOWLEDGMENTS

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