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Time-resolved measurements of the dynamics of the photoinduced smectic-C_α^*–smectic-A transition

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We present the study of the dynamics of the recently reported photoinduced smectic-C_α^*–smectic-A transition. High resolution time-resolved dielectric dispersion measurements carried out during the photoisomerization process demonstrate that the magnitude of the uv intensity mimics the role played by temperature in determining the behavior of the soft mode relaxation. We also show that the uv intensity dependence of the soft mode relaxation frequency f_R in the photoinduced smectic-A phase can be described with a functional form similar to that derived for the temperature dependence of f_R and compare the experimentally determined critical exponent with the theoretically predicted for the Ising and three-dimensional XY universality classes. Our study illustrates an interesting feature, namely, the magnitude of light intensity can be treated like a thermodynamic variable such as temperature and pressure to study phase transitions in general.

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I. INTRODUCTION

Owing to many promising features for practical applications, the phenomenon of reversible photoinduced shape transformation of chromophoric molecules, such as azobenzenes, has been extensively studied [1]. The phenomenon is all the more interesting when associated with mesogenic properties of liquid crystals [2–6], the underlying principle of which is briefly outlined below. In the absence of uv radiation, the azobenzene molecules exist in their energetically more stable E (also known as *trans*) configuration, which has a rodlike form and thus supports the formation of liquid crystalline phases. Upon illumination with uv light (∼360 nm wavelength, corresponding to the π-π^* band of the azo group), a shape transformation takes place to the Z (or *cis*) form. The Z form due to its bent shape results in the destabilization of liquid crystalline phases or, more specifically, in the lowering of the phase transition temperatures. The reverse transformation can be brought about by illuminating with visible light (∼420 nm, corresponding to the n-π^* band). This latter change can also occur spontaneously in the ''dark'' by a process known as thermal back relaxation. All these features provide a new tool to study phase transitions in which the transformation takes place isothermally, but is photocontrolled. Photoinduced effects have been well studied in systems exhibiting nematic-isotropic [2,6,7] and smectic-C^*–smectic-A [8,9] transitions. Very recently, we reported [10] a reentrant nematic–smectic-A transition induced by light (Notice that in this case, contrary to all earlier observations, the photoinduced phase is more ordered.) The discovery in 1989 of the antiferroelectric chiral smectic-C (Sm-C_A^*) phase [11] led to intense activity in the field and resulted in the identification of the other variants of the previously discovered ferroelectric chiral smectic-C (Sm-C^*) phase. One of these variants is the smectic-C_α^* (Sm-C_α^*) phase. This phase has an incommensurate short helical pitch structure [12]. We have recently reported [13] the photoinduced effects on the Sm-A to Sm-C_α^* phase transition. In this paper, we describe results of the dynamics of this phenomenon and demonstrate that the magnitude of the uv intensity mimics the role played by temperature in determining the behavior of the soft mode relaxation. The results have been analyzed in terms of the theoretical predictions for the Ising and three-dimensional (3D) XY models.

II. EXPERIMENT

The liquid crystalline host material is 4-1-(methylheptyloxycarbonyl) phenyl 4′-octyloxy biphenyl-4-carboxylate (well known [14] as MHPOBC), a chiral material exhibiting the following sequence of phase transitions:

$$\text{Iso-Sm-}A\text{–Sm-}C_\alpha^*\text{–Sm-}C^*\text{-Sm-}C\gamma^*\text{–Sm-}C_A^*\text{-crystal.}$$

The guest, uv-active dopant compound p-(p-ethoxyphenylazo)phenyl hexanoate (C_6H_{13}-COO-ϕ-N$=$N-ϕ-OC_2H_5, where ϕ indicates a phenyl ring), hereafter referred to as EPH, is from Eastman Organic Chemicals and is liquid crystalline exhibiting a nematic mesophase. All the results described in this paper have been obtained on a mixture of 4.99 wt % of EPH in MHPOBC. This mixture exhibits a Sm-A–Sm-C_α^* transition at 105.8 °C. The presence of the Sm-C_α^* phase was established by polarizing microscopic observations and from the current response of the sample to applied electric fields. The uv apparatus used for inducing photoisomerization is described in an earlier publication [10]. Briefly, the uv radiation from an intensity stabilized uv source with a fiber-optic guide (Hamamatsu L7212-01, Japan) was used along with a uv bandpass filter (UG 11, Newport). An additional IR-block filter was inserted just before the sample to prevent any effects of heat radiation from the uv source. The actual power I_{uv} of the radiation passing through the filter combination falling on the sample was measured with a uv power meter (Hamamatsu, C6080-03) kept in the sample position.

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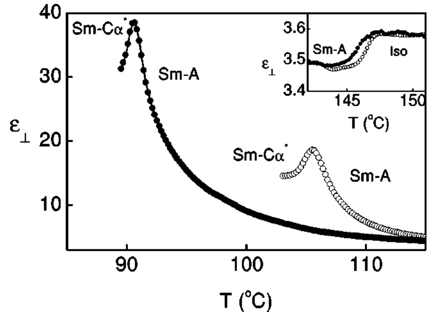

FIG. 1. Temperature dependence of the dielectric constant at 1 kHz in the vicinity of the Sm-A–Sm-C_α^* transition. The open circles represent the data collected in the absence of uv radiation and the filled circles represent the data obtained by illuminating the sample with a uv radiation of 9.9 mW/cm^2 magnitude. The peak point in both the traces signifies the transition point. Notice that upon uv illumination the peak value of the dielectric constant doubles and the transition temperature shifts by ~15 °C. Data near the Iso-Sm-A transition, presented in the inset and showing only about 0.5 °C shift in the transition temperature upon uv illumination, rule out any significant influence of the local heating effects.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the low frequency dielectric constant $\epsilon_\perp$ without and with an uv illumination of 9.9 mW/cm^2 magnitude. The dielectric constant increases from both the sides on approaching the Sm-A–Sm-C_α^* transition and reaches a maximum at T_c, the transition temperature. Such a feature has been attributed [13,14] to the presence of the soft mode associated with the tilt fluctuations. The behavior with and without uv appears qualitatively the same, but there are quantitative differences. In the presence of uv, (a) the transition temperature decreases by ~15 °C and (b) there is nearly a twofold increase in the maximum value (i.e., the value at T_c) of $\epsilon_\perp$. The first feature is quite common in the area of photoinduced phase transitions [2,6,7], although in the present case, the magnitude is somewhat large considering the fact that the transition is between layered phases. It may perhaps be argued that the reason for the shift in the transition temperature is due to local heating effects caused by the uv radiation. As mentioned earlier, we took precautionary steps to reduce (or eliminate) such a possible effect by introducing an IR-block filter between the sample and the uv source. As a further proof of the fact that local heating effects are unimportant in these experiments, we have shown in the inset of Fig. 1 the data of $\epsilon_\perp$ in the vicinity of the isotropic–smectic-A transition. Notice that the shift in the transition temperature caused by the uv light is only 0.5 °C. If the shift is caused due to local heating effects, this puts an upper limit to such a shift. Since the shift seen for the Sm-A–Sm-C_α^* transition is about 30 times higher than this value, it must be due to the photoisomerization related effect and not due to local heating. A possible cause for the second feature, namely, in the presence of the uv illumination the value of $\epsilon_\perp$ at T_c increases by a factor of 2, could be due the reported large increase in the dipole moment of the azobenzene molecules as a result of *trans-cis* isomerization [15]. But in our previous paper [13], we have shown that, based on the value of the dipole moment obtained from molecular modeling and the fact that the concentration of the photoactive compound is quite small, this feature being the cause for the increase in $\epsilon_\perp$ can be ruled out. In fact, our analysis led us to conclude that the observed behavior is caused by the slower dynamics of the system in the presence of the uv radiation.

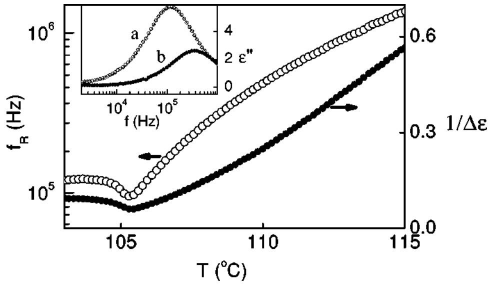

FIG. 2. Temperature dependence of the relaxation frequency f_R and the inverse dielectric strength $1/\Delta\epsilon$ of the soft mode across the Sm-A–Sm-C_α^* transition, in the absence of uv radiation. Inset: representative dielectric dispersion (ϵ'' vs f) scans in the (a) Sm-C_α^* and (b) Sm-A phases. The solid line is a fit of the data to the Havriliak-Negami expression.

Typical scans of ϵ'' vs frequency (ϵ'' is the imaginary part of the dielectric constant) obtained in the Sm-A and Sm-C_α^* phases are shown in the inset of Fig. 2. To extract the relaxation frequency f_R and the dielectric strength $\Delta\epsilon$, the data were fit to the Havriliak-Negami expression [16]. At all temperatures we found that the profiles were close to the ideal Debye type of relaxation. The temperature dependence of f_R and the inverse dielectric strength $1/\Delta\epsilon$ obtained in the absence of the uv radiation is shown in Fig. 2. Both f_R and $1/\Delta\epsilon$ decrease on approaching the transition from both low and high temperature sides. This feature is also established in the literature (see, e.g., Ref. [14]) and is caused by the softening of the relaxation mode connected with the fluctuations of the amplitude part of the tilt order parameter.

Figure 3 shows representative dielectric dispersion scans taken at a temperature (T_{c-1}) °C in the absence of uv light ($t=0$ s) and at $t=10$, 14, 19, 24, and 196 s time intervals after turning it on. It is seen that for the $t=10$ s scan, the relaxation frequency (the peak point frequency in each of the profiles) is lower compared to that for the scan taken without uv light, while for $t \geqslant 14$ s it is higher. As we saw earlier, this is exactly the behavior obtained in the absence of uv light, but by varying the temperature between the scans. It must be emphasized that when the radiation is turned off, the system recovers the original peak. As was done for the temperature-dependent measurements, ϵ'' vs frequency data were fit to the Havriliak-Negami expression [16]. At all uv intensities used in this study, we found that the profiles were close to the ideal Debye type of relaxation.

The temporal variation of f_R and $\Delta\epsilon$ upon illuminating the sample with a uv radiation of intensity $I_{uv}=9.9$ mW/cm^2 is shown in Fig. 4. This plot shows in detail the qualitative trend seen in Fig. 3, viz., upon turning the radiation on f_R decreases and $\Delta\epsilon$ increases at the initial stages of the photoinduced effect, but subsequently a reverse

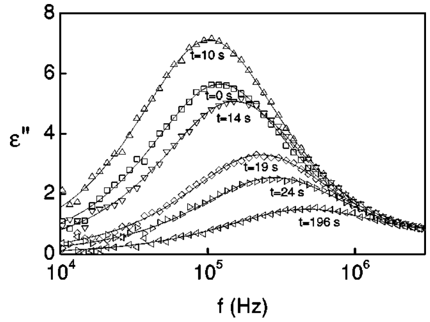

FIG. 3. ϵ'' vs f scans taken in the Sm-C_α^* phase (1 °C below the transition), obtained before ($t=0$ s) and at $t=10,\ 14,\ 19,\ 24$, and 196 s after the uv illumination is turned on. Notice that on uv illumination (9.9 mW/cm^2), initially the relaxation frequency f_R (frequency corresponding to the peak point of the profiles) shifts to a lower value ($t=10$ s scan) and then to higher values, reaching a limiting value for longer time scales. The solid lines indicate the fit of the data to the Havriliak-Negami expression. Even for the data obtained at $t=196$ s, the error bar on the different fit parameters is less than 8%.

trend is seen. It is observed that this overall change takes place in about 1 min before attaining the photostationary state. When the radiation is switched off, the reverse phenomenon takes place and most important the system recovers the original values that existed before uv irradiation. Figure 5(a) shows the time dependence of f_R when I_{uv}, magnitude of the uv intensity is changed. [For the sake of clarity, the time regions close to the photoinduced transition are shown on an enlarged scaled in Fig. 5(b).] Similarly, Fig. 6(a) [and Fig. 6(b) on enlarged scale] shows the time dependence $\Delta\epsilon$ when I_{uv} is changed. Notice that the variaition of f_R with time is not the same at all uv intensities. At lower intensities ($I_{uv} \leqslant I_c$; I_c being a certain critical intensity), the value of f_R decreases [Figs. 5(a) and 5(b)] and $\Delta\epsilon$ increases [Figs. 6(a) and 6(b)] monotonically with time after the uv light is turned on. For $I_{uv} > I_c$, f_R decreases ($\Delta\epsilon$ increases) immediately after turning the radiation on, but reverses its trend after a certain time interval; the time at which the reversal is seen decreases as I_{uv} increases. Comparing this data with the temperature dependence of these parameters (Fig. 2), we can conclude that such a reversal in the trend signifies that the Sm-A-Sm-C_α^* transition has taken place, albeit photoinduced and isothermal. Hence, we can say that I_c, the critical intensity to bring about the phase transition lies in the range of 1.0–1.5 mW/cm^2. It is also seen that as the uv intensity increases, the time at which the transition takes place becomes shorter. This is to be expected since the sample response becomes faster (shorter response time) when the uv intensity is higher. The recovery transition shows the opposite behavior; the higher the uv intensity, longer is the recovery period. This is again expected since the magnitude of the shift in the transition temperature as well as the change in the order parameter would be more for higher uv intensity and thus, the viscosity-dominated spontaneous recovery needs a longer period. In Fig. 7, we plot f_s and $1/\Delta\epsilon_s$, the saturated values of the relaxation frequency and the inverse dielectric strength obtained upon uv illumination (i.e., in the photostationary state), as a function of the uv intensity. Notice the striking similarity between this diagram (i.e., Fig. 7) and Fig. 2, which shows the temperature dependence of the two relaxation parameters. This suggests that the uv intensity mimics the role played by temperature. More specifically, we want to suggest that illuminating with uv intensity is like imposing a disordering field, as opposed to application of electric and magnetic fields, which are considered as ordering fields. In fact, we have recently described the photoinduced nematic-isotropic transition in the framework of a random field model

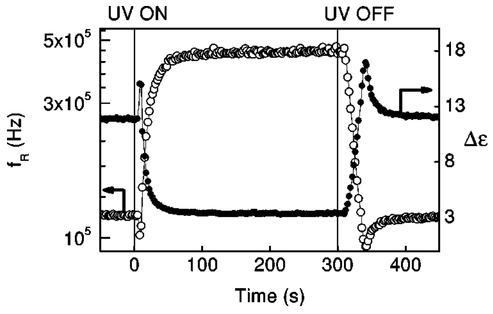

FIG. 4. Time-resolved variation of (○) the relaxation frequency f_R, and (●) the dielectric strength $\Delta\epsilon$ when the uv radiation (of magnitude 9.9 mW/cm^2) is turned on and subsequently off. Initially, f_R decreases ($\Delta\epsilon$ increases) but then increases (decreases) to reach saturation. When the uv illumination is turned off, the features are reversed as a function of time.

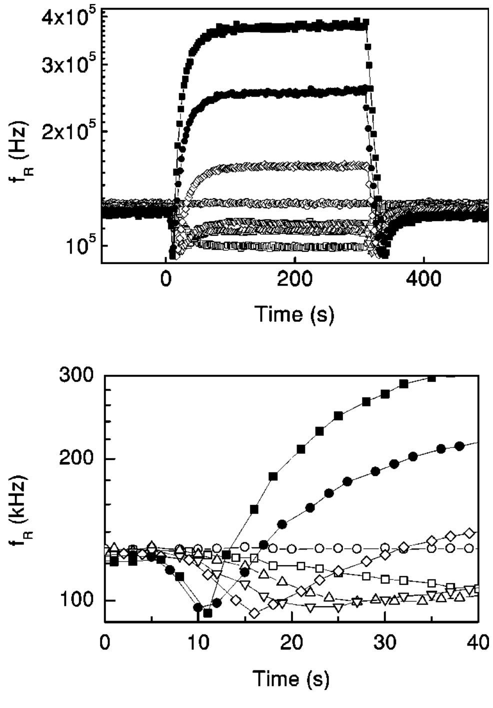

FIG. 5. (a) Plot showing the effect of the magnitude of the uv illumination on the temporal behavior of f_R. The data in the vicinity of the uv-light-on sequence on an enlarged scale is shown in (b). The different symbols stand for different levels of uv intensity, viz., circle for $I_{uv}=0$; open square for $I_{uv}=1$ mW; triangle up for $I_{uv}=1.5$ mW; triangle down for $I_{uv}=1.8$ mW; diamond for $I_{uv}=3.2$ mW; filled circle for $I_{uv}=5.5$ mW; filled square for $I_{uv}=8$ mW.

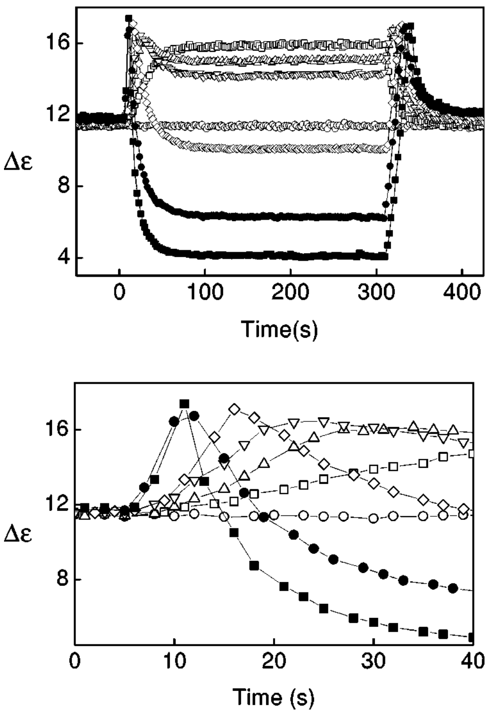

FIG. 6. (a) Plot showing the effect of the magnitude of the uv illumination on the temporal behavior of $\Delta\epsilon$. (b) shows the data in the vicinity of the uv-light-on sequence on an enlarged scale. Symbols carry the same meaning as in Fig. 5.

where uv light plays the role of a disordering field [17].

According to symmetry arguments, the Sm-A–Sm-C (or Sm-C^*) transition belongs to the 3D XY universality class [18]. However, experiments find that generally this transition can be well described by an extended mean field model that includes a sixth-order term of the tilt order parameter [19]. In contrast, high resolution specific heat measurements [20] near the Sm-A–Sm-C_α^* transition reveal critical fluctuation effects, characteristic of the 3D XY model. By including corrections-to-scaling terms in the fitting expression, Ema *et al.* [20] were able to show that the specific heat data are consistent with exponent α values expected for the XY model. As stated earlier, the soft mode is associated with the order parameter fluctuations (in this case tilt fluctuations). Therefore, the pretransitional critical behavior of the relaxation frequency and dielectric strength of this mode are governed by the susceptibility exponent γ. Hence, borrowing the expressions used for the temperature dependence of these parameters near the Sm-A–Sm-C^* transition [21], we can write $f_R \propto (T-T_c)^\gamma$ and $1/\Delta\epsilon \propto (T-T_c)^\gamma$. As already seen, I_{uv}, the magnitude of the UV intensity plays the role of temperature. Therefore, we introduce the following expressions:

$$f_s = \text{const} + A_1^{\pm}(I_{uv} - I_c)^\gamma, \tag{1}$$

$$1/\Delta\epsilon_s = \text{const} + A_2^{\pm}(I_{uv} - I_c)^\gamma. \tag{2}$$

Here, $A_1^{\pm}$ and $A_2^{\pm}$ represent the amplitudes above and below I_c, the critical intensity to induce the isothermal transition. The critical exponent γ is the same as the exponent that describes the behavior of the temperature-dependent susceptibility near a critical point, and having a value of 1.24 for the Ising model and 1.316 for the 3D XY model [22]. The solid lines in Fig. 7 show that the expressions (1) and (2) describe the data well and yields $\gamma = 1.23 \pm 0.04$, which within error bar is in agreement with the theoretically predicted value for the Ising model. But let us recall that the analysis of the specific heat data using correction-to-scaling terms seemed to favor the XY model, although it could not unambiguously preclude the possibility of describing the data with the Ising model [20]. In fact, we feel that one cannot rule out the third possiblity of the measured exponent being an effective one due to the crossover from mean field ($\gamma = 1$) to 3D XY ($\gamma = 1.316$) regimes. Analysis of our results get complicated also by the fact that there is no *a priori* rule to say that the photoinduced isothermal transition should behave the same way as a thermal transition. More experiments are necessary to clarify the matter.

In summary, we have performed time-resolved dielectric dispersion measurements during the photoinduced isothermal Sm-A to Sm-C_α^* transition. We have demonstrated that the magnitude of the uv intensity mimics the role played by temperature in determining the behavior of the soft mode relaxation. Quantitative analysis of the time-dependent relaxation parameters have been done and discussed in terms of the theoretical predictions for the different universality classes.

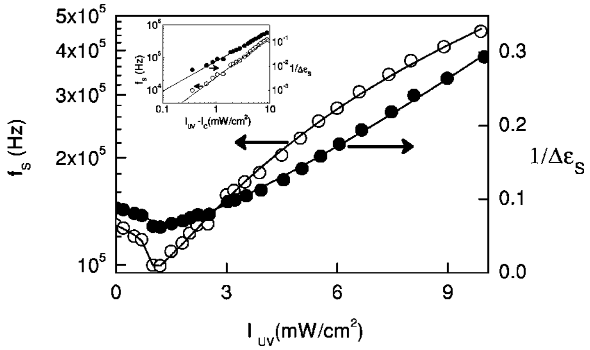

FIG. 7. uv intensity dependence of (○) f_s and (●) $1/\Delta\epsilon_s$, the saturated values of the relaxation frequency and the dielectric strength, respectively. The solid lines show the fit done to Eqs. (1) and (2), which yields $\gamma = 1.23 \pm 0.04$ and a critical intensity I_c value of 1.2 ± 0.1 mW/cm^2. The inset shows the same data plotted on a double logarithmic scale after subtracting the constant part [the first term on the right-hand side of Eqs. (1) and (2)] obtained from the fitting. The fitting shown as a straight line with $\gamma = 1.23 \pm 0.04$ as the slope, clearly demonstrates the power law nature of the behavior.

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