PHYSICAL REVIEW E VOLUME 59, NUMBER 4 APRIL 1999

Molecular motion in a smectic liquid crystal showing V-shaped switching as studied by optical second-harmonic generation

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(Received 7 December 1998)

The molecular motion during the V-shaped switching in a homogeneously aligned smectic-C^*-like liquid crystal (LC) cell has been investigated by means of second-harmonic generation (SHG) and SHG interferometry. At normal incidence, SHG intensity profiles were observed as a function of applied electric field for four combinations of input-output polarizations of light. For the analysis of SHG results, the V-shaped switching system was considered as a ferroelectric uniform state with C_2 symmetry (collective model). It was shown that the observed SHG behavior was successfully simulated using the collective model. By using SHG interferometry measurements, it was found that azimuthal rotation of LC molecules is limited within half the cone, where molecules could distribute. Moreover, it was also found that LC molecules undergo counterazimuthal rotation in the upper and lower halves of the LC layer in chevron structure. The stabilization of the uniform molecular alignment was attributed to the escape from the formation of polarization charges and a surface molecular constraint. The mechanism of the collective motion was discussed on the basis of the softening of the system due to the frustration of ferroelectric and antiferroelectric interactions. [S1063-651X(99)51604-8]

PACS number(s): 61.30.−v, 68.45.−v, 64.70.−p, 42.65.Ky

Since the discovery of tristable switching between the antiferroelectric chiral smectic-C_A (S^*_{CA}) phase and the ferroelectric chiral smectic-C (S^*_C) phase [1,2], a large number of investigations on S^*_{CA}, S^*_C, and related subphases in several liquid crystals have been performed to clarify their structure and the origin of their emergence. Among them, the thresholdless and hysteresis free V-shaped switching [3–7] has been highlighted because of its fundamental interest and practical importance for designing liquid crystal (LC) displays [5–7] following the bistable [8], tristable [1], and deformed helix ferroelectric (DHF) switchings [9]. This switching was first speculated to occur in a phase with randomly oriented C directors due to the reduction of the interlayer tilting correlation [3,4]. The dynamic switching behaviors were explained by the random model based on the two-dimensional Langevin function [3,4,10] under a strong influence of an electric field and surface conditions [11–15]. Recently, unexpectedly strong optical second harmonic generation (SHG) signals were observed at normal incidence from the V-shaped switching LC cell [16]. This result seemed to be also explained by the two-dimensional Langevin potential, supporting the random model. More recently, however, we showed that a switching model of the other extreme against the random model, i.e., the highly coherent azimuthal angle rotation model (collective model), is much more appropriate to interpret the V-shaped switching than the random model [17].

In this Rapid Communication, molecular switching behaviors were studied by SHG and its interferometry for the V-shaped switching LCs. The dynamic response was well simulated by the collective model. We will discuss the switching characteristics and mechanism on the basis of SHG interferometry.

The LC used was a three-component mixture used in the original and recent works of the V-shaped switching [3,17]. The phase sequence in thin homogeneous cells was as follows:

AF($\sim$20°) (coexist) ($\sim$43°) S^*_X (64°) S_A (68.5°) Iso,

where AF, S^*_X, S_A, and Iso represent the antiferroelectric, smectic-X^*, smectic-A, and isotropic phases, respectively. The V-shaped switching was observed in the phase designated as S^*_X. Homogeneously aligned cells of about 1.7 μm thick were prepared by sandwiching the mixture between two glass plates with indium tin oxide (ITO) electrodes. The substrates were treated with polyimide and one of the surface was rubbed unidirectionally.

For the SHG measurements, a Q-switched neodymium-doped yttrium aluminum garnet laser (BMI, AL-152SI) producing pulses of 10 ns duration at a repetition rate of 100 Hz was used as a fundamental light (1064 nm) source. The fundamental beam was normally incident onto the homogeneous cell after selecting the polarization of the incident beam. In this study, the states of polarizations of lights are defined as p- and s-polarizations, which are parallel and perpendicular to the smectic layer, respectively. The transmitted SHG output (532 nm) from the sample cell was selected through an interference filter for p- and s-polarizations. The SHG output was detected using a photomultiplier and a boxcar system by applying a triangular wave form at a frequency of 0.1 Hz to the sample cell. Before the SHG measurement, it was confirmed that transmittance vs electric field curves show the typical thresholdless V-shaped switching. All the measurements were performed at 50 °C.

Figure 1 shows the SHG intensity profiles as a function of applied electric field for four input-output polarization combinations, i.e., p-p (p-in/p-out), s-p, p-s, and s-s at normal incidence. As shown in Fig. 1(a), for p-p combination, fairly large SHG signals showing a Λ shape were generated at about zero field during the switching, as already reported [16,17]. For s-p [Fig. 1(b)], the obtained SHG intensity profile is similar to that for p-p except for relatively small signal intensities. On the other hand, for p-s [Fig. 1(c)], the

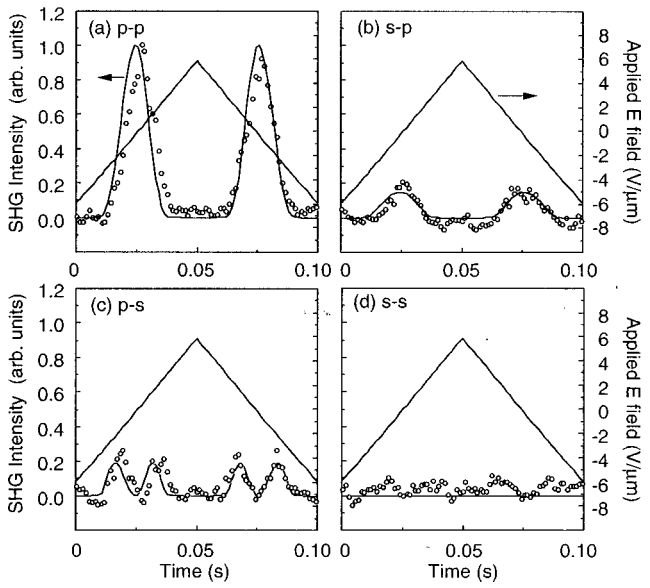

FIG. 1. SHG intensities (circles) observed from a V-shaped switching LC cell for four input-output polarization combinations during the application of triangular wave of 0.1 Hz at 50 °C. Solid curves show the calculated SHG results (see text for details).

intensity profile exhibits two peaks around zero field during the switching. It is noted that relatively small SHG signals were generated for *s*-*s* polarization combination [Fig. 1(d)]. These SHG behaviors are characteristic features of the V-shaped switching because the SHG cannot be observed in normal ferroelectric bistable switching, in which the dipole direction in the field-induced ferroelectric uniform state is perpendicular to the electric field direction of incident light and switches instantaneously to the opposite direction.

For the analysis of obtained SHG intensity profiles, theoretical SHG intensities were calculated for the collective model, where the V-shaped switching system was considered as a ferroelectric uniform state (C_2 symmetry) with an azimuthal dipole orientation of 90° at zero field measured from that in a field-induced ferroelectric state [17]. In this model, the symmetry of LC molecules can be considered as C_2, whose nonzero nonlinear optical (NLO) coefficients are χ_{14}, χ_{16}, χ_{22}, and χ_{23}. The laboratory coordinates are defined as $(\hat{x},\hat{y},\hat{z})$, where $\hat{x}$ is the propagation direction of the fundamental light that is parallel to the direction of an applied electric field, $\hat{z}$ is taken as the projection direction of the smectic layer normal to the substrate, and $\hat{y}$ the direction perpendicular to $\hat{x}$ and $\hat{z}$. With respect to the laboratory coordinates, the major (optic) axes of LC sample coordinates $(\hat{1},\hat{2},\hat{3})$ can be written by $\hat{1}=(-\cos\delta\cos\theta\sin\phi - \sin\delta\sin\theta,\ -\cos\phi\cos\theta,\ -\cos\theta\sin\delta\sin\phi+\cos\delta\sin\theta)$, $\hat{2}=(\cos\delta\cos\phi,\ -\sin\phi,\ \cos\phi\sin\delta)$, $\hat{3}=(-\cos\theta\sin\delta +\cos\delta\sin\phi\sin\theta,\ \cos\phi\sin\theta,\ \cos\delta\cos\theta+\sin\delta\sin\phi\sin\theta)$, where $\hat{3}$ is the unit vector along the LC director, $\hat{2}$ along the dipole, and $\hat{1}$ the unit vector perpendicular to $\hat{2}$ and $\hat{3}$. Here, 2θ is the cone angle, ϕ the azimuthal rotation angle of dipole moment, and δ the layer tilt angle. For input and output lights, unit vectors of *p*- and *s*-polarizations with respect to the sample coordinates are given by $\hat{e}_p=(-\cos\phi\cos\theta,\ -\sin\phi,\ \cos\phi\sin\theta)$, $\hat{e}_S=(-\cos\theta\sin\delta\sin\phi+\cos\delta\sin\theta,\ \cos\phi\sin\delta,\cos\delta\cos\theta+\sin\delta\sin\phi\sin\theta)$. Then, one can describe effective NLO coefficients for polarization combinations as follows:

$$
\begin{aligned}
P_{pp} &= E_0^2\sin\phi[-\chi_{22}\sin^2\phi+3\cos^2\phi(2\chi_{14}\cos\theta\sin\theta \\
&\quad -\chi_{23}\sin^2\theta-\chi_{16}\cos^2\theta)], \\
P_{ps} &= 2E_0^2\cos\phi\sin\phi[\chi_{14}(\cos^2\theta-\sin^2\theta) \\
&\quad +(\chi_{16}-\chi_{23})\cos\theta\sin\theta], \\
P_{sp} &= -E_0^2\sin\phi(\chi_{23}\cos^2\theta+2\chi_{14}\cos\theta\sin\theta+\chi_{16}\sin^2\theta), \\
P_{ss} &= 0.
\end{aligned}
\tag{1}
$$

In these equations, we considered the layer tilt $\delta=0°$ for simplicity. By using the above equations and the field dependence of ϕ obtained from the linear electrooptic measurements mentioned in Ref. [17], one can obtain theoretical SHG intensities from the nonlinear polarizations $[I(2\omega)\propto|P_{ij}|^2]$. Thus, when using the relative values of NLO coefficients as theoretical fitting parameters in Eq. (1), experimental SHG data can be analyzed for combinations of input-output polarizations.

The solid curves in Fig. 1 show the best fitted SHG intensity profiles thus simulated. As shown in the figure, it is clear that the calculated SHG profiles are identically the same as the experimental results. From the theoretical fit, the obtained relative ratio of nonlinear optical coefficients of LC cell was $\chi_{22}:\chi_{14}:\chi_{16}:\chi_{23}=1.00:-0.08:-0.14:0.74$. Thus, it is clear that SHG behaviors of the V-shaped switching LCs can be explained by the collective model (C_2) and that dipole orientation at zero field is parallel to substrate ($\hat{y}$) with azimuthal angle of 90°.

Next, SHG interference measurement [18] was performed to study the LC switching behaviors. A crystal quartz plate was inserted on the optical path. Then, SH waves were generated both from the quartz plate and the sample and interfered to each other. A fused silica plate was located between the quartz plate and the sample cell, and was rotated about the axis parallel to the fused silica plate and perpendicular to the optical path, producing a relative phase change between SH waves from the two sources because of a frequency dispersion of the refractive index of the fused silica plate. In this way, we observed interference fringes. We observed the SHG interference fringes for the different input-output polarization combinations. Figure 2 shows interferograms of SHG peaks obtained by rotating the fused silica plate for positive and negative slopes of applied fields during the switching. As shown in Fig. 2(a), it is obvious that the phase of the SHG fringe is not reversed in the opposite slopes of an applied electric field. It is also confirmed that SHG interferograms of the two SHG peaks for *p*-*s* [Figs. 2(b) and 2(c)] and the single SHG peak for *s*-*p* show the same phases for positive and negative slopes of applied fields. These SHG interference results unambiguously prove that nonlinear polarizations do not change their directional sense by reversing the slope of electric field. This indicates that the azimuthal rotation of dipole moments of LC molecules is limited from 0° to 180° (half a cone) but not 360° during the switching because interference patterns must be out of phases if dipole

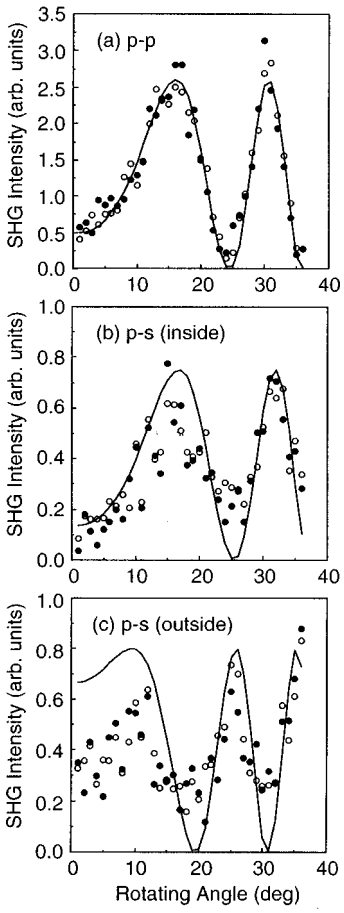

FIG. 2. Interference fringes of SHG peak for p-p (a), inside peak for p-s (b), and outside peak for p-s (c) observed by rotating a fused silica plate during positive (open circles) and negative (closed circles) slopes of an applied electric field. Solid curves show the calculated interference fringes.

moments of LC molecules rotate from 0° to 360° during the switching. Note that, for p-s, the phase of interferogram for inside SHG peaks [Fig. 2(b)] is out of phase to that for outside SHG peaks [Fig. 2(c)] as predicted in the theoretical description in Eq. (1) ($P_{ps} \propto \cos\phi \sin\phi$).

Now the question is why and how molecules choose one half of the cone for the switching. If the smectic layer is of bookshelf type, there is no reason to choose either half of the cone. However, there exists a chevron structure, as it was confirmed using a separate cell by an x-ray analysis. Then molecules can choose one half (actually less than 180°) of the azimuthal angle on the cone, since molecules have a tendency to align themselves parallel to a substrate surface, as illustrated in Fig. 3 ($E=0$). In this geometry, SH waves are generated from upper and lower halves of the chevron layer, but with almost (if we neglect the dispersion of the refractive index) the opposite phase. Therefore, if the volumes of the upper and lower halves of the chevron structure are the same, no SHG would be observed. Actually the absolute SHG intensity depends on each cell made.

Another evidence for this interpretation is provided by the following experiment: We constructed optical geometries so that average directions of (nonlinear) polarization with and without an electric field are almost parallel to the polarization direction of the incident beam by properly choosing

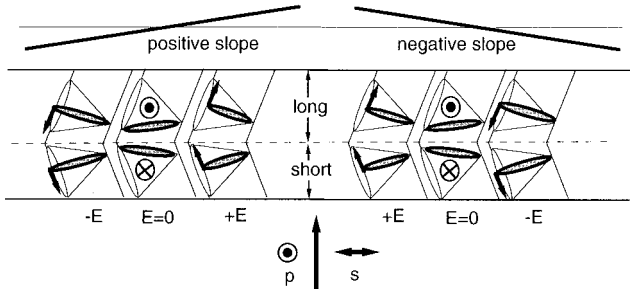

FIG. 3. Illustration of the collective switching model for the V-shaped switching.

the rotation angles about the axes parallel and perpendicular to the cell surface. The SHG measurements were made to compare the SHG intensity in the LC state at zero field with that in the field-induced ferroelectric uniform state. It was found that the SHG intensity from the uniform state at zero field is ten times smaller than that from the field-induced ferroelectric state. This result indicates that the (nonlinear) polarization is considerably cancelled in the state at zero field, though the molecules are well aligned, as suggested by polarized Fourier transform infrared (FT-IR) absorption measurements [17]. This situation is illustrated in Fig. 3: The LC molecules rotate toward the opposite directions in the upper and lower halves of the chevron structure and that the position of the chevron cusp may not be at the center of the cell thickness (asymmetric chevron). One side rubbing may cause an asymmetric influence to the LCs from the surface.

In this way, collective molecular switching occurs, as illustrated in Fig. 3. It is clear that the directional senses of the p-polarized SH light in positive and negative slopes of the field are the same, as experimentally observed. On the other hand, it is also easy to understand that two peaks appear for the s-polarized SHG at positive and negative sides of zero field and have the opposite phases and that the outer (inner) peaks in positive and negative slopes have the same phase, as also observed experimentally. Thus, the simple collective model shown in Fig. 3 satisfies all the experimental results of SHG intensity and SHG interferometry.

Finally, we want to make a comment on the cause and the mechanism of the V-shaped switching. The first important question is why the molecules take the uniform orientation shown in Fig. 3 at zero field. We would like to point out the effect of polarization space charge ρ which is given by $\nabla \cdot \mathbf{P}$ [19–21], where $\mathbf{P}$ is a polarization. It is well known that polar surface interaction stabilizes a twisted state [22], in which a splay deformation of $\mathbf{P}$ exists. Then the polarization space charge is produced. This effect is pronounced when $\mathbf{P}$ becomes large. Hence, molecules tend to form a uniform orientation shown in Fig. 3 ($E=0$) to avoid the production of the polarization charge. The following two facts support this consideration: i.e., the V-shaped switching becomes stable in thinner cells; a highly polar surface such as bare ITO surface gives rise to the twisted state even for the material which shows the V-shaped switching. The nonpolar interaction between surface and molecules forces the molecules align parallel to the surface. This surface constraint also promotes the uniform alignment shown in Fig. 3 ($E=0$).

The next question is why molecules switch collectively. The V-shaped switching occurs in the systems where ferroelectric and antiferroelectric interactions compete and frustration between these structures takes place [14,23]. Since such a frustrated system is very soft and the relaxation time becomes long, molecules change their steady state orientation continuously under the surface constraint and varying field, resulting in the collective motion. The softening of the system may influence the effect of the polarization charge through elastic constant. The details will be discussed elsewhere.

In summary, we observed the molecular motion of the V-shaped switching LCs by monitoring the SHG behaviors. The SHG signals observed at normal incidence were successfully explained using the collective model. Using the SHG interferometry, it was also found that the azimuthal rotation of LC molecules is limited within half the cone. Moreover, it was also found that the LC molecules undergo counter azimuthal rotations in the upper and lower halves of the LC layer in chevron structure. The cause of the uniform alignment at zero field was ascribed to polarization charges and surface constraint. It was speculated that the softening of the system due to the frustration of the ferroelectric and antiferroelectric interactions brings about the collective molecular motion.

We acknowledge Professor A. Fukuda, Professor M. A. Osipov, and Professor N. A. Clark for stimulating discussions. B.P. was supported by the Venture Business Laboratory of TIT.

[1] A. D. L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., Part 2 **27**, L729 (1988).

[2] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., Part 2 **28**, L1265 (1989).

[3] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, and A. Fukuda, J. Mater. Chem. **6**, 71 (1996).

[4] A. Fukuda, *Proceedings of the 15th International Display Research Conference*, Asia Display '95 (Hamamatsu) S6-1 (Society for Information Display, Santa Ana, CA, 1995), p. 61.

[5] T. Tanaka, K. Sakamoto, K. Tada, and J. Ogura, *SID '95 Digest* (Society for Information Display, Santa Ana, CA, 1994), p. 430.

[6] T. Saishu, K. Takatoh, R. Iida, H. Nagata, and Y. Mori, *SID '96 (San Diego) Digest* (Society for Information Display, Santa Ana, CA, 1996), p. 284.

[7] T. Yoshida, T. Tanaka, J. Ogura, H. Wakai, and H. Aoki, *SID '96 (Boston) Digest* (Society for Information Display, Santa Ana, CA, 1997), p. 841.

[8] N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. **36**, 899 (1980).

[9] J. Fünfschilling and M. Schadt, J. Appl. Phys. **66**, 3877 (1989).

[10] A. Fukuda, S. S. Seomun, T. Takahashi, Y. Takanishi, and K. Ishikawa, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **303**, 379 (1997).

[11] S. S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, C. Tanaka, T. Fujiyama, T. Maruyama, and S. Nishiyama, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **303**, 181 (1997).

[12] S. S. Seomun, T. Gouda, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, C. Tanaka, T. Fujiyama, T. Maruyama, and S. Nishiyama, Dig. AM-LCD **96**, 61 (1996).

[13] S. S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **36**, 3586 (1997).

[14] S. S. Seomun, T. Gouda, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Liq. Cryst. **26** 151 (1999).

[15] A. D. L. Chandani, Y. Cui, S. S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Liq. Cryst. **26**, 167 (1999).

[16] S. S. Seomun, B. Park, A. L. D. Chandani, D. S. Hermann, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **37**, L691 (1998).

[17] B. Park, S. S. Seomun, M. Nakata, Y. Takanishi, K. Ishikawa, and H. Takezoe, Jpn. J. Appl. Phys., Part 1 **38**, 1474 (1999).

[18] S.-W. Choi, Y. Kinoshita, B. Park, H. Takezoe, T. Niori, and J. Watanabe, Jpn. J. Appl. Phys. **37**, 3408 (1998).

[19] K. Okano, Jpn. J. Appl. Phys. **25**, L846 (1986).

[20] M. Nakagawa and T. Akahane, J. Phys. Soc. Jpn. **55**, 1516 (1986).

[21] N. A. Clark, T. P. Rieker, and J. E. Maclennan, Ferroelectrics **85**, 79 (1988).

[22] Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **26**, 1 (1987).

[23] E. Gorecka, D. Pociecha, M. Glogarova, and J. Mieczkowski, Phys. Rev. Lett. **81**, 2946 (1998).