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Second-Harmonic Generation in Chiral Liquid Crystals

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Second-Harmonic Generation in Chiral Liquid Crystals

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Second-Harmonic Generation (SHG) occurs under special circumstances in chiral liquid crystals, such as Ferroelectric Liquid Crystals and, induced by an external electric field, in Short-Pitch Cholesteric Liquid Crystals. Previously, SHG in FLCs has been studied mainly for the application potential of FLCs as a promising NLO-material. However, with the discovery in the last three years of novel electro-optic effects and liquid crystalline phases – *i.e.*, the high-contrast, analog "V-shaped switching" found to occur in so-called "thresholdless antiferroelectric" liquid crystals; and liquid crystals consisting of bow-shaped molecules - the emphasis is shifting towards SHG becoming a standard tool of investigation in liquid crystal research. In this context symmetry, manifestations of chirality as well as analysis and interpretation issues become more important than ever before.

Keywords: Second-harmonic generation; chirality; ferroelectric liquid crystal; cholesteric liquid crystal; nonlinear optics; "thresholdless antiferroelectricity"

INTRODUCTION

Second-Harmonic Generation (SHG) in Ferroelectric Liquid Crystals (FLC) has been extensively studied over the past two decades [1-34], with a considerable intensification of the research effort in the beginning of the nineties when the first step towards optimization of the second-order optical nonlinearity was taken by Walba et al [6] through carefully controlled stereochemistry. The main motivation of research in SHG of FLCs has thus been the search for novel materials to be used in

applications. In this context, a number of different FLC materials concepts were tried, such as FLC-mixtures [9, 17-22], FLC-metallomesogens [23, 24], FLC side-chain polymers (FLCP) [25, 26], and the development of a polar, FLC-based photopolymer (PLCP, *pyroelectric liquid crystalline polymer*) for NLO-applications [9, 27-34].

Apart from FLCs and related polymers with a spontaneous polar order, electric field-induced SHG has also been used in connection with short-pitch cholesteric liquid crystals [35-37] (the flexoelectrooptic effect) as well as with SmA* liquid crystals [38] (electroclinic effect) and with antiferroelectric liquid crystals [31, 39].

The last three years of liquid-crystal research have seen a very exciting development, due to the discoveries of novel electro-optic effects and liquid-crystalline phases, *i.e.*, the high-contrast, analog "V-shaped" electro-optic switching [40-49] found to occur in certain chiral smectic liquid crystals, often referred to as "thresholdless antiferroelectricity" [40-46], as well as smectic liquid crystals consisting of achiral bow-shaped molecules, forming chiral phase structures [50-51]. SHG has been used as an investigative tool in the former [52-54] as well as in the latter case [55-59].

Thus, the emphasis now seems to be shifting towards SHG becoming a standard tool of investigation in contemporary liquid-crystal research. In the following I shall give some examples of SHG, all concerning liquid crystals consisting of chiral molecules†.

SECOND-HARMONIC GENERATION AND SYMMETRY

Bulk Second-Harmonic Generation (SHG) is a nonlinear optical phenomenon which occurs only in noncentrosymmetric media. It is characterized by the second-order nonlinear optical susceptibility tensor, $\chi^{(2)}_{ijk}$, defined through Eq. (1a) below [60]. Macroscopically, the polarization induced in a nonlinear optical medium by an optical electric field is given by

$$P_i = \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \ldots\ldots \qquad (1a)$$

where the subscripts refer to the lab frame. Microscopically, the dipole moment induced in a molecule by an optical electric field is

$$p_\xi = \alpha_{\xi\upsilon} E_\upsilon + \beta_{\xi\upsilon\zeta} E_\upsilon E_\zeta + \gamma_{\xi\upsilon\zeta\sigma} E_\upsilon E_\zeta E_\sigma + \ldots\ldots \qquad (1b)$$

† I hence do not include the achiral bow-shaped molecules in the present treatment. For SHG in these liquid crystals, see the excellent work reported in refs. [55-59])

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where the new subscripts refer to the molecular frame. The macroscopic nonlinear optical susceptibility and the microscopic hyperpolarizability β are interrelated as

$$\chi^{(2)} = N\langle\beta\rangle \tag{2}$$

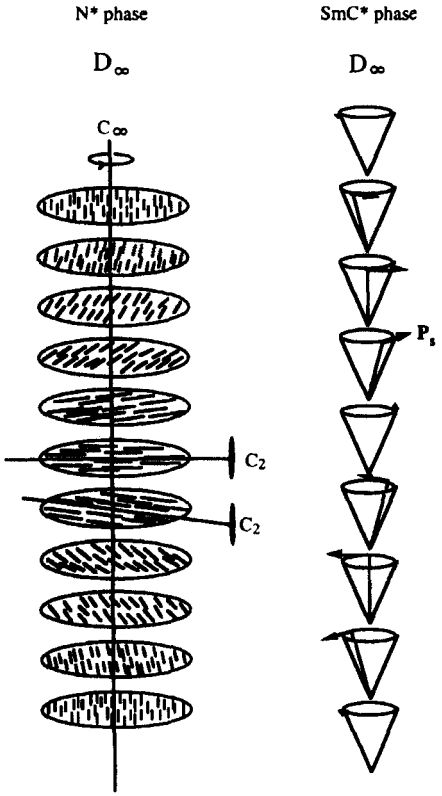

FIGURE 1 The bulk N* and SmC* phases have D_∞ symmetry.

where N is the number density of NLO-chromophores in the macroscopic volume and where the brackets denote the average over a distribution function which, for a bulk sample, is the Boltzmann

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distribution. In order to have $\langle\beta\rangle \neq 0$ the medium must have dipolar order[†].

Liquid crystals are generally orientationally ordered materials, but *without* dipolar order. The local anisotropy axis, the director, has quadrupolar symmetry in the sense that the lowest multipole moment that does not vanish along the director is the quadrupole moment. The natural question that then arises is whether SHG in liquid crystals would at all be possible within the electric dipole approximation.

One can begin by making the molecules that make up the liquid crystalline phase chiral. In this way, one has assured the non-centrosymmetry. The N*, SmA* and bulk SmC* phases are all examples of this. However, the symmetry of these phases is D_∞, which is still too high to allow any nonvanishing macroscopic polar axis. See Figure 1. Consequently, no SHG can be observed in these phases in their bulk state without any external influences.

The local symmetry of the SmC* phase, however, is C_2, which is sufficiently low to allow any physical property with polar symmetry along the local C_2-axis, perpendicular to the tilt plane[††]. Under certain circumstances (surface stabilization in thin cells, SSFLC-cells) this can be transferred to the whole medium, which then acquires a macroscopic polar symmetry [62]. In order for the polar axis to stay in a fixed direction, an electric field might be applied. Such a field is not necessary if the surface stabilization is perfect.

SHG IN FERROELECTRIC LIQUID CRYSTALS

SHG in FLCs was from the beginning measured in a homeotropic geometry in order to get phase matching conditions [3-5, 7, 8]. In this case, an electric field must be applied in the plane of the LC-cell to unwind the helix and line up the director uniformly. However, it is also possible to use the planar-aligned, surface-stabilized cell geometry, in which, ideally at least, a field would not have to be applied. The advantage of being able to use the more conventional, planar-aligned cells is the greater ease of fabrication, and electro-optic as well as nonlinear optical properties can easily be checked on the same sample. In this cell geometry, however, it is in general not possible to obtain phase-matching conditions but it is possible to come close because the cell thickness (~2 μm) is usually well below the coherence length for the FLC (~10-15

[†] This is true within the electric dipole approximation. In general, also higher-order multipolar components of the molecular hyperpolarizability exist and may be optimized through materials design [61].

[††] A medium may have the same or lower, but never higher symmetry than any of its physical properties (*Neumann Principle*).

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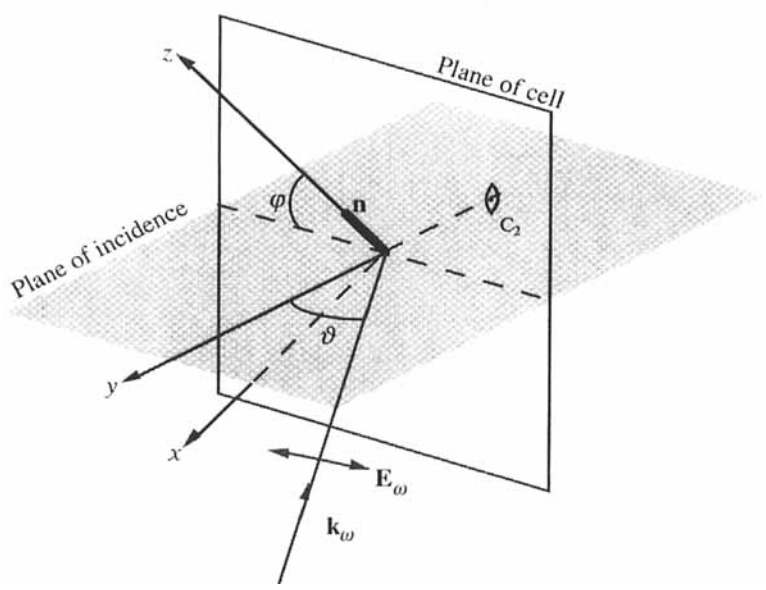

FIGURE 2 Definition of the SHG measurement geometry for a planar-aligned, SSFLC-cell.

μm). This allows the $\chi^{(2)}_{ijk}$-tensor elements of the (unwound) SmC* phase to be analyzed in the planar geometry [9-16].

The measurement geometry is depicted in Figure 2, where the beam of the fundamental frequency is incident at an angle on the FLC-cell, with the optic axis in the plane of the cell. The angle ϑ is the (external) angle of incidence on the cell and φ is the azimuthal angle as measured between the plane of incidence (shaded in Figure 2) and the optic axis (the director in the case of SSFLC). By measuring the SHG-intensity generated by the FLC-cell as a function of ϑ and φ the various elements of the $\chi^{(2)}_{ijk}$-tensor can be evaluated. A typical result of such a measurement is shown in Figure 3.

The C_2-symmetry of the unwound SmC* phase can readily be seen from the azimuthal data in Figure 3. The data of the angle of incidence are taken with the optic axis either in the plane of incidence or perpendicular to it. In this way, the $\chi^{(2)}_{ijk}$ tensor elements can be found according to:

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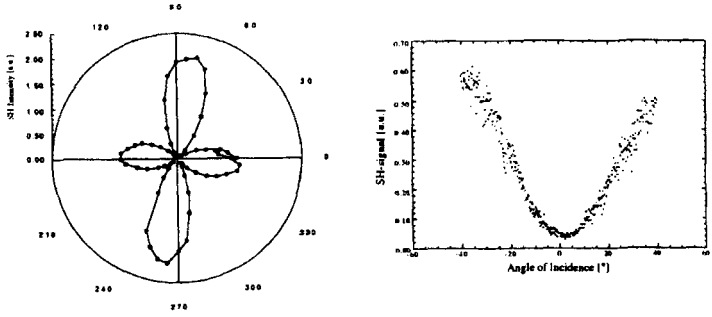

FIGURE 3 SHG from an FLC (**A2c** [9, 29-30]) as a function of azimuthal angle (left) and angle of incidence (right). From the azimuthal data, the C_2-symmetry of the phase is evident.

$$\chi^{(2)}_{\text{eff}}(ooo) = \chi^{(2)}_{yxx}\left(\cos^2\theta_\omega \sin\theta_{2\omega} + 2\cos\theta_\omega \cos\theta_{2\omega} \sin\theta_\omega\right) + \chi^{(2)}_{yyy}\left(\sin^2\theta_\omega \sin\theta_{2\omega}\right)$$
$$\chi^{(2)}_{\text{eff}}(eee) = \chi^{(2)}_{yzz}\left(\cos^2\theta_\omega \sin\theta_{2\omega} + 2\cos\theta_\omega \cos\theta_{2\omega} \sin\theta_\omega\right) + \chi^{(2)}_{yyy}\left(\sin^2\theta_\omega \sin\theta_{2\omega}\right)$$
$$\chi^{(2)}_{\text{eff}}(ooe) = -\chi^{(2)}_{xyz} \sin 2\theta_{2\omega}$$
$$\chi^{(2)}_{\text{eff}}(eeo) = \chi^{(2)}_{xyz} \sin 2\theta_{2\omega} \tag{3}$$

SHG IN SHORT PITCH CHOLESTERICS

The cholesteric or chiral nematic phase, although being noncentrosymmetric, does not show any second-harmonic generation. However, under very special circumstances, a flexoelectric polarization can be induced by an externally applied electric field in a cholesteric with short pitch, leading to a very large electro-optic effect termed "flexoelectrooptic effect" [63-68]. The flexoelectric polarization is related to splay and bend deformations of the director field of the liquid crystal. The electric field and thus the flexoelectric polarization reduce the symmetry of the phase from D_∞ to C_2.

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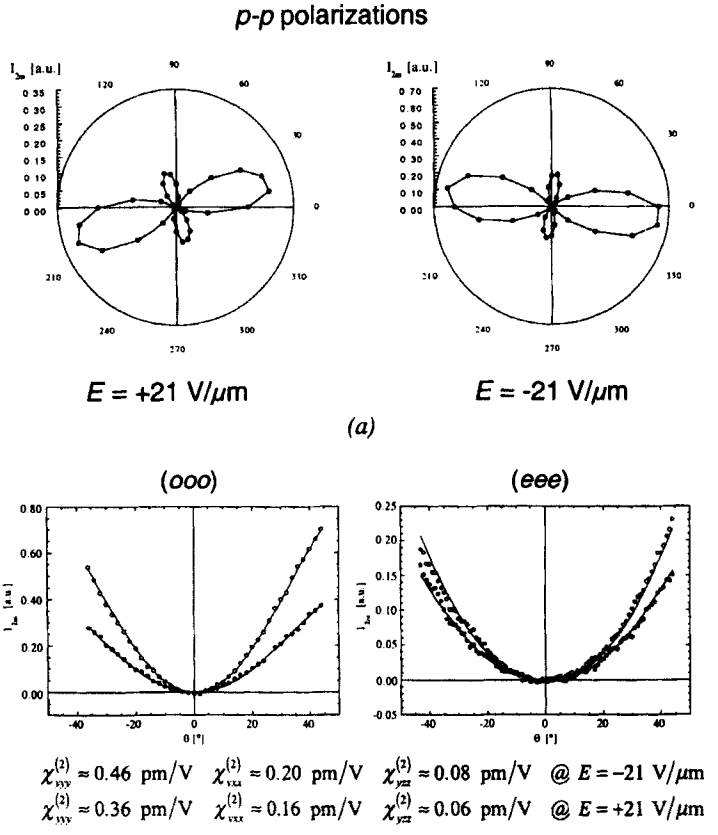

FIGURE 4 *a)* SHG-intensity as function of azimuthal angle, at an oblique angle of incidence for a positive and negative applied electric field, respectively. *b)* SHG-intensity as function of the angle of incidence for two different azimuthal directions, along the large lobes (*ooo*) and along the small lobes (*eee*).

In the flexoelectrooptic effect the helix axis of the cholesteric liquid crystal is aligned uniformly in the plane of a thin (~2 μm) LC-cell (the so-called *Uniform-Lying Helix*, or *ULH*-geometry). The pitch being short with respect to the wavelength of light, the helix axis acts as a macroscopic optic axis. By applying an electric field across

the cell, the molecules everywhere along the helix axis are rotated around the electric-field vector through an angle proportional to the electric field strength. This leads macroscopically to a field-induced deviation of the optic axis through the same angle, which depends linearly on the applied electric field.

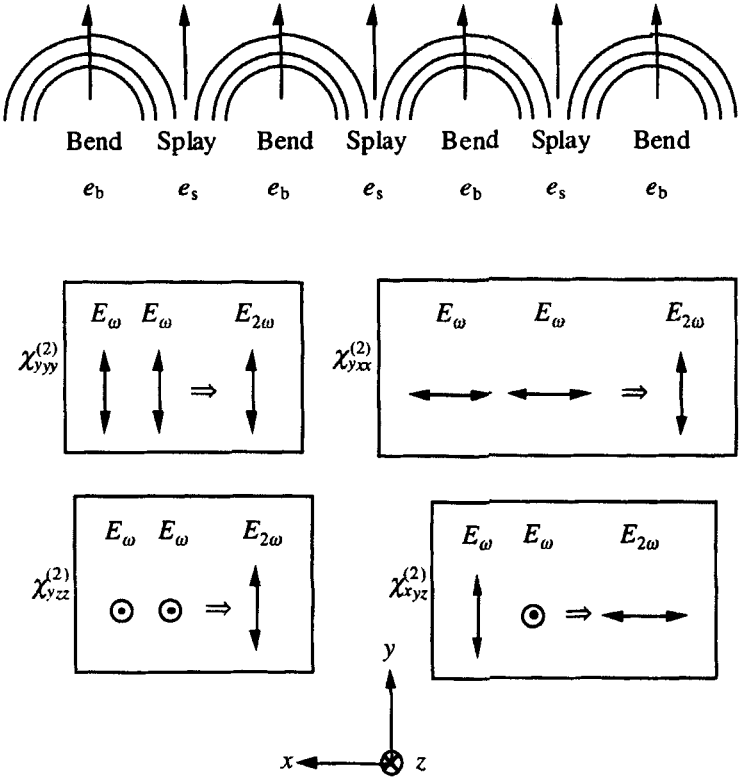

FIGURE 5 The relation between the second-order nonlinear optical tensor components and the flexoelectric coefficients for splay and bend deformations in the periodic structure of the Bouligand plane.

From an optical point of view, a cholesteric ULH-cell is thus equivalent to an SSFLC-cell. Therefore, the same kind of SHG-measurement and the same kind of analysis as in the planar FLC-case can be applied in the case of a short-pitch cholesteric. A typical example of

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this is shown in Figure 4, where the azimuthal data directly show the electric-field-induced C_2-symmetry. Moreover, analyzing the incidence-angle data according to Eqs. (3) above, the values of the second-order nonlinear optical tensor elements are found to be quite high (up to 0.4 pm/V @ 21 V/μm applied field) considering that a material that was never intended for second-order nonlinear optics was used in this experiment.

The polar symmetry of the flexoelectrooptic effect can be evidenced if we imagine making a cut perpendicular to the field-induced direction of the optic axis: what we see then is a periodic splay-bend deformation pattern of the director profile, sometimes also called Bouligand plane from the work of Y. Bouligand, who, among others, studied cholesteric structures in biological materials such as insect and crab cuticle and dinoflagellate chromosomes [69]. The elements of the second-order nonlinear optical tensor can thus be perceived to relate to this periodic splay-bend pattern, and therefore, in turn, also to the flexoelectric coefficients for splay and bend, respectively. This is schematically depicted in Figure 5.

SHG IN "THRESHOLDLESS ANTIFERROELECTRICITY"

The analog, high-contrast electro-optic "V-shaped" switching (shown schematically in Figure 6) which under certain circumstances is observed from planar-aligned cells of chiral tilted smectic liquid crystals was first observed in materials possessing antiferroelectric as well as ferroelectric phases, which led to the denomination "thresholdless antiferroelectricity" or "TLAF" [40-46]. The TLAF-effect was thought to be brought about by a decrease of the correlation between the tilt directions from one

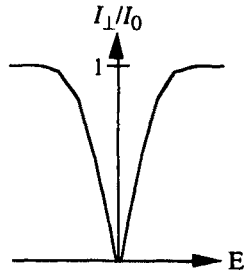

FIGURE 6 A schematic picture of the analog, high-contrast electro-optic "V-shaped" switching from a sample between crossed polarizers, with the sample oriented such that the smectic layer normal be parallel to one of the polarizers.

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smectic layer to the other, the inter-layer tilt correlation, thus resulting in a "Random SmC* phase". Ever since, an intense research effort has gone on to elucidate the origin of the electro-optic effect and the nature of the new phase – if at all a new phase [43-49]. Here, SHG can serve as a powerful investigative tool, in that it allows a direct observation of the polar order in the sample.

In ref. [52], SHG was used to investigate the nature of the so-called "TLAF" for the first time. In that work, dynamic SHG-measurements (as function of a time-varying applied electric field) were reported on the same three-component mixture which had been used in the original work [41]. The three components of this mixture are for short denoted MC579:MC513:MC514, and have the composition 40:40:20. It will in the following be referred to as the "Tokyo T3-mixture". The dynamic SHG-measurements were preceded by static SHG-measurements (applied dc-field) on one of the components of this mixture, the one denoted MC514. Those SHG-measurements are shown in Figure 7. It was the "strange" behavior of these measurements that led

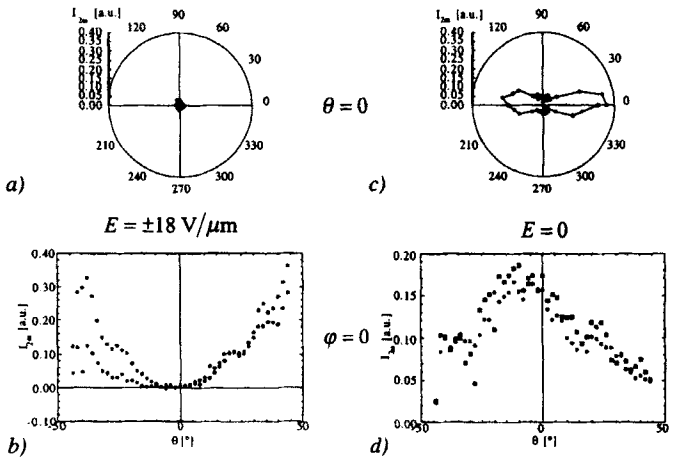

FIGURE 7 The first SHG-measurements on a "TLAF" liquid crystal from MC514, one of the components of the T3-mixture, under static conditions and *p-p* polarizations. *a)* SHG as function of azimuthal angle at normal incidence, with a dc electric field applied. *b)* SHG as function of angle of incidence with a dc electric field applied. *c)* SHG as function of azimuthal angle at normal incidence, *without* electric field. *d)* SHG as function of angle of incidence *without* electric field.

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to the further investigations on the whole three-component mixture, as reported in ref. [52]. As long as the field was applied (Figures 7a and 7b) the cell behaved in a "normal" way, *i.e.*, in accordance with what was explained in the preceding sections for FLCs and short-pitch cholesterics (note that Figure 7a is for *normal* incidence – hence, the SHG-signal is zero for all azimuthal angles). As soon as the external field was turned off, remaining at normal incidence, a significant SHG-signal was observed. The azimuthal angular dependence of this signal, at normal incidence, is shown in Figure 7c. The behavior is clearly different from the case of FLC and N* as shown in Figures 3 and 4. Finally, the dependence of the signal on the angle of incidence, still without field, is also fundamentally different from the case shown in Figures 3, 4 and 7b: the curve in fact now seems to be inverted, with the maximum signal being close to normal incidence.

What this SHG-experiment proves is that without electric field there is a polar axis *in the plane* of the cell, while with an electric field applied there is a polar axis *perpendicular* to the plane of the cell as in the case of FLC and N* described above. Thus, there is always a spontaneous polarization present in the sample. Nevertheless, the dynamic SHG-measurements published in ref. [52] were at the time interpreted to agree with the opposite interpretation, namely that of the random SmC* model. The random model implies an isotropic distribution of polarization vectors and therefore cannot give rise to a net, spontaneous polarization. In this case, no SHG would have been observed at all, contrary to the experimental findings.

In fact, further SHG-experiments performed by the Tokyo group, along with a number of other experiments, have led to the random model being abandoned [53, 54]. For the interpretation of SHG-data a C_2-axis in the plane of the cell was used to re-derive the equations for the second-order nonlinear optical polarization (of the same type as Eqs. (3) above) for this new geometry. In refs. [53, 54] it was concluded that the molecules move collectively during switching, not randomly; however, the origin of the collective motion was still interpreted to arise from a frustration between antiferroelectricity and ferroelectricity and, moreover, the possibility of twisted states was excluded.

In the mean-time, the Boulder and Göteborg groups have carried out a series of other experiments on the Tokyo T3-mixture [47-49]. The conclusions drawn are that it is a polarization-stabilized twisted SmC*-structure which is what gives rise to the electro-optic V-shaped switching. In other words, the "new phase" is *not* new, it is simply an ordinary SmC*-phase. In a cell with polar surface interactions a twisted structure is stabilized, such that the polar vector varies through the cell as a splay-bend deformation, see Figure 8a. The splay in $\mathbf{P}$ gives rise to a polarization-charge density $\rho_p = -\nabla \cdot \mathbf{P}$ and thereby an additional electrostatic energy density $\sim (\nabla \cdot \mathbf{P})^2$. For high values of the spontaneous polarization this electrostatic energy becomes significant.

Minimizing the sum of elastic and electrostatic energy it is found that the polarization charge self-interaction leads to a stiffening effect, stabilizing a thick slab of uniform orientation in the middle of the cell, with the twist confined to thin surface regions near the cell walls. See Figure 8b. The depth of the twisted region is given by the polarization coherence length, $\xi_P = \sqrt{K\varepsilon/P^2}$ (SI-units), where K is the elastic constant in the one-constant approximation [47-49]. The stiffened, uniform bulk at zero field gives good extinction between crossed polarizers (see Figure 6).

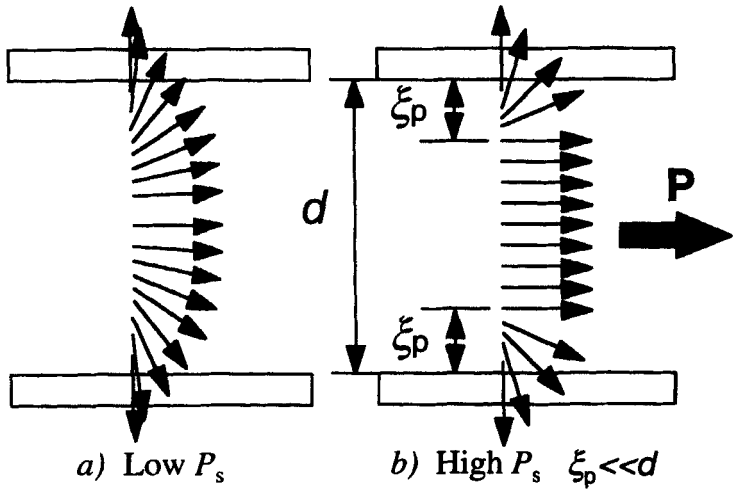

FIGURE 8 A twisted SmC* structure in a cell with polar surface interactions. *a)* In a low-P_s SmC*, the splay of the P_s-field extends through the entire cell thickness. *b)* In a high-P_s SmC* the splay of the P_s-field, and thus the twist of the director field, is confined to thin surface regions, while the bulk of the cell is uniform, due to polarization-charge self-interaction.

In the original SHG-experiment [52] on the T3-mixture a simulation of the dynamic SHG-response was made, using a two-dimensional Langevin model in accordance with a random phase. If analyzed correctly, however, the use of this potential gives an identically zero SHG-signal, as would be expected from a random model. However, it is possible to analyze the experimental dynamic SHG-result

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in ref. [52] using the same analysis by adding a term to the potential that describes the twisted SmC*-structure.

The y-axis is along the C_2-axis, in the plane of the cell. The ξ-axis is along the transverse molecular dipole moment and thus perpendicular to the tilt plane. The angle between y and ξ is denoted ψ, such that $y \cdot \xi = \cos\psi$. From experiment we have: $\psi = 0$ when $E = 0$ and $\psi = \pi/2$ when $E \neq 0$. A potential satisfying these conditions is:

$$U(\psi) = -A\cos\psi - pE\sin\psi \tag{4}$$

The second-order NLO susceptibility for this geometry is defined by $P_y^{(2)} = \chi_{yyy}^{(2)} E_y^{\omega} E_y^{\omega}$ and is in terms of its order parameter related to the corresponding first hyperpolarizability along the ξ-axis as

$$\chi_{yyy}^{(2)} = N\beta_{\xi\xi\xi}\left\langle (y\cdot\xi)(y\cdot\xi)(y\cdot\xi)\right\rangle = N\beta_{\xi\xi\xi}\left\langle \cos^3\psi\right\rangle \tag{5}$$

The distribution function is given by the Boltzmann distribution, such that the order parameter is obtained by:

$$\left\langle \cos^3\psi\right\rangle = \frac{\int_0^{2\pi} \cos^3\psi \cdot e^{-U(\psi)/kT}}{\int_0^{2\pi} e^{-U(\psi)/kT}} \tag{6}$$

The SHG-intensity $I_{2\omega}^{(ooo)} \propto \left|\chi_{yyy}^{(2)}\right|^2 \propto \left|\left\langle \cos^3\psi\right\rangle\right|^2$ as calculated from Eqs. (4)-(6) is plotted in Figure 9 in the time domain (applying a triangle-wave electric field) for the case $A/kT = 1$. The result has a very close resemblance to the experimental result as reported in Figure 2a of ref. [52].

The parameter A in Eq. (4) is connected to the polarization along the y-axis, in the plane of the LC-cell. The twisted structure for high spontaneous polarization results in a large nonlinear optical polarization along the y-axis and a small ξ_P compared to the cell thickness. The parameter A is therefore related to the depth of the twisted region near the surfaces as $A \sim (\xi_P)^{-1}$.

The SHG-behavior can thus be analyzed in terms of the polarization-stabilized twisted SmC* structure. Thus, SHG confirms that the phase is nothing but an ordinary SmC*-phase. In fact, in [47-49] it was also confirmed experimentally that V-shaped electro-optic switching

could be obtained in cells with polar surface interactions (surface electroclinic effect) using another material, W415, which is a high-P_S chiral smectic C liquid crystal *lacking* any antiferroelectric phase. Thus, "thresholdless antiferroelectricity" is a misleading concept, since the effect occurs in the absence of antiferroelectricity.

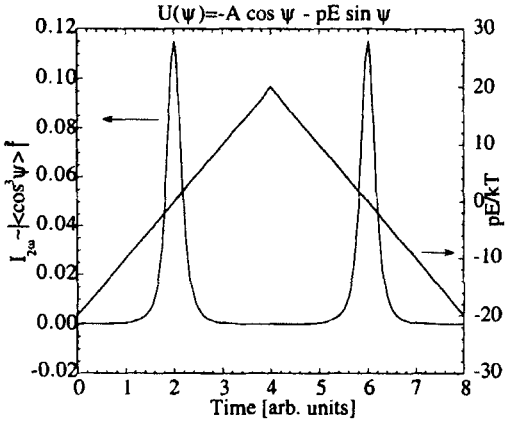

FIGURE 9 The calculated SHG-intensity as function of electric field in the time domain, for a twisted SmC*-structure. The calculated behavior has a close resemblance to that observed experimentally [52].

CONCLUSIONS

- Second-harmonic generation occurs in various chiral liquid crystal phases, either spontaneously or induced by an electric field.
- SHG serves as a powerful investigative tool sensitive to the polar order in these phases, and is enjoying an increased usage in contemporary liquid-crystal research.
- SHG has recently been used to investigate the Flexoelectrooptic Effect in short-pitch cholesteric liquid crystals.
- SHG has recently been used to investigate "V-Shaped Switching" in chiral smectics, and is shown to be consistent with a twisted SmC*-structure with a stiffened, uniform bulk resulting from polarization-charge self-interaction.

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