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Electric field-induced optical second harmonic generation in nematic liquid crystal 5CB

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Abstract. Electric field-induced second harmonic generation (EFISH) was studied for the liquid crystal 4-cyano-4'-pentylbiphenyl (5CB) (a nematic phase material at room temperature). The intensity of coherent SHG from 5CB cells upon DC electric field was measured for various initial orientations of the liquid crystal. The dependence of the SHG intensity on the pump beam incidence angle was obtained in transmission geometry using sample rotation method. The experimental results (the registered light intensity in the output SHG interference patterns) were theoretically modelled and analyzed.

1. Introduction

The structure and properties of nematic liquid crystals (NLC) are extensively studied for a long time [1]. The NLC molecules are usually highly anisotropic and noncentrosymmetric and possess large hyperpolarizability. However, in the bulk phase, the NLC materials are macroscopically characterized as structures possessing inversion symmetry that prevents the even-order nonlinear optical processes. As a result, although the individual molecular hyperpolarizability of NLC is quite large, the bulk NLCs can not usually produce optical second harmonic generation (SHG) (lowest even-order nonlinear optical process). However, an external electric field (with a magnitude that is high enough) applied to NLC cells can efficiently remove the inversion centre and thus can give a rise of an electric field-induced SHG (EFISH) [2-4]. Valuable information can be obtained by varying the optical phase in EFISH experiments, e.g. by the change of the optical path. In this case, one can observe so called Maker fringes as interference patterns [5].

There are two ways to change the optical path in a NLC cell. The first is the movement of a wedge-formed sample across the incident laser beam (pump beam), usually at normal incidence. The second is the rotation of a plane-parallel sample thus changing the pump beam incidence angle. The former is known as a wedge method. Small value of a wedge angle (~1°) allows one to consider the NLC cell within the laser spotsize as a plane-parallel sample with a variable thickness and, therefore, to use well-known models. This method has been used for the studies of a number of NLCs including

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MBBA, 5CB, 8CB and other cyanobiphenyls, and the temperature dependencies of the SHG intensity, as well as the coherence length, have been obtained [7-8]. However, there was no detailed analysis of the abovementioned Maker fringes.

In the present work, the dependence of EFISH intensity on the pump beam incidence angle is investigated using the rotation of a plane-parallel NLC cell. Experimental data were collected for coherent SHG from 5CB cells as measured in transmission geometry, and are linked to results from theoretical simulations responding to the NLC director orientation.

2. Experimental

The room-temperature nematic liquid crystal *p*-*n*-pentyl-*p*'-cyanobiphenyl (5CB) (from Merck) was used after rectification procedure. The 5CB cells were assembled from two parallel glass plates. The cell gap was fixed with 100 µm-thick copper spacers, also serving as electrodes. The distance between the electrodes was about 2 mm. 5CB cells with either homeotropic or planar alignment, were studied. In the first case, the inner surfaces of the glass plates of the cells were covered with a monolayer of silane in order to orient the liquid crystalline molecules homeotropically. The treatment we have used involves a deposition of silane cross-linked films [9]. For this purpose, 0.1 vol% of ODS-E silane (Chisso, Japan) was dissolved in 9:1 isopropyl alcohol/distilled water, and glass plates were dipped in the solution for several hours. The plates were then rinsed with distilled water and ODS-E was polymerized, keeping it at 110°C for one hour. Planar-oriented 5CB cells were prepared by use of glass plates covered with polyimide that was unidirectionally rubbed. Polyimide films were made by spin coating (at 2000 rpm) of a polyimide precursor 3 wt.% solution (polyimide system ZLI-2650 from Merck in cyclopentanone) onto clean glass after that baking to polymerize and followed by rubbing of the cured film with a filter paper under constant pressure of 100 g. The empty cells with the alignment layers were assembled in parallel rubbing configuration. 5CB in its isotropic phase was capillary filled into the cells, then the samples were cooled slowly to the nematic phase to achieve the desired good alignment of the nematic 5CB, as verified by polarizing microscope (Leitz DMRXP).

The prepared 5CB cells were mounted on a rotational stage driven by step motor. The SHG from the cells was studied in transmission geometry. The coherent SHG signal (highly directed SHG beam) from the 5CB cells was registered by a two-channel experimental set-up with a reference channel. In the experiments, Nd^{3+}:YAG laser was employed as a pump laser source with a wavelength of 1064 nm, pulse duration of 30 ns, and pulse energy of 0.2 mJ. Measurements were performed for both *s*- and *p*-polarization of the pump beam. The *s*-polarized SHG signal was detected as the most intense one. The diameter of the pump laser spot on the sample surface was about 1 mm and special attention has been paid to prevent the contact of the laser beam and metal electrodes. The spectrally filtered output SHG signals (at the wavelength of 532 nm) in the main and reference channels were detected by sensitive photomultipliers and processed by automated data acquisition system. An intensity calibration was carried out using a plate of *y*-cut α-SiO_2 crystal placed into the peak of Maker fringes [2]. The relative units for the measured intensity, used hereafter and given below, are 10^{-6} of the intensity of the calibration signal. SHG from empty cells has been also measured and the observed signal was negligible.

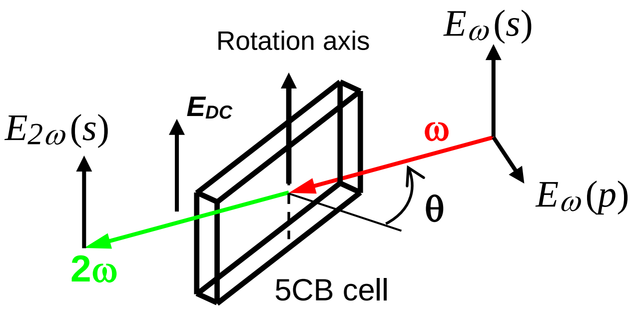

Figure 1. Geometry of the EFISH experiment performed in this work.

In the rotation experiments, the pump incidence angle θ was changed and the dependence of EFISH intensity $I_{2\omega}(\theta)$ was measured (figure 1). The rotation axis was parallel to the film plane and orthogonal to the plane of incidence. The rotation angle was changed in a step of 1°. The source of external direct current (DC) electric field was home-made high-voltage pulse generator, producing 10 μs pulses of 3 kV voltage at flat top region of the pulse and temporally synchronized with the pump laser pulse. As the external electric field was switched off, no SHG signal was detected for all cells. The experiments were carried out at room temperature (ca. 21°C).

3. Results and Discussion

Firstly, the dependencies of SHG intensity $I_{2\omega}(\theta)$ at different (*s* or *p*) polarizations of the pump beam were measured in the case of a glass cell filled with nitrobenzene (isotropic liquid having a large and well established SHG nonlinearity). The results are reported in figure 2. A single-layer model [10] and refraction index data [11] were used in the fitting procedure (generally, the method is described in [12]). The results presented exhibit two interference patterns, depending on the sum and the difference of wave vectors of the pump $\boldsymbol{k}_{\omega}(\theta)$ and SHG $\boldsymbol{k}_{2\omega}(\theta)$ [13]. The first pattern (the main pattern), defining the envelope curve, depends on the difference $\boldsymbol{k}_{2\omega} - 2\boldsymbol{k}_{\omega}$ and is a relatively slow function of θ. The second pattern depends on the sum $\boldsymbol{k}_{2\omega} + 2\boldsymbol{k}_{\omega}$. The amplitude of the second pattern is several times smaller than that of the first one. It should be noted also that the maximum signal for *s*-polarized pump is ~7 times higher than that for the *p*-polarized one.

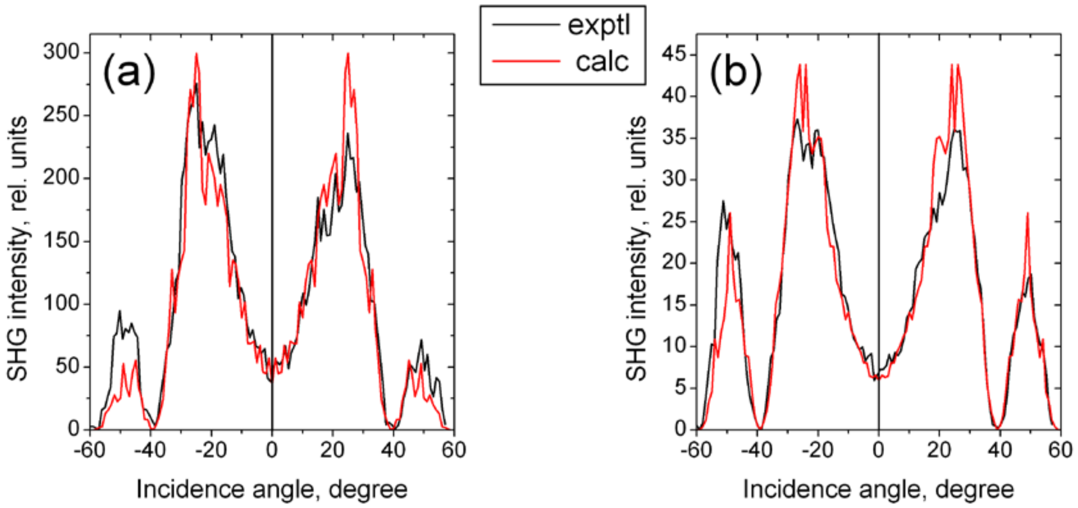

Figure 2. Angular dependence of SHG signal from pure glass cell filled with nitrobenzene: (a) *s*-polarized pump; (b) *p*-polarized pump.

The angular dependencies of SHG signal from a cell covered with polyimide, is presented in figure 3. In this case, the rubbing direction of the cell under study was parallel to the direction of the applied DC electric field. For *s*-polarized pump (figure 3 (a)) the frequency of Maker fringes is similar to that for nitrobenzene reported above, because the same N_e (the extraordinary refractive index) is responsible for both the pump and SHG. When the pump is *p*-polarized (figure 3 (b)), then it is represented with N_o (the ordinary refractive index). The difference between the wavevectors becomes significant and comparable to the wavevector sum. Now the two patterns are indistinguishable. Nevertheless there is qualitative agreement of the calculated and experimental graphs. The interference pattern exhibits an increased frequency of the oscillations and strongly reduced amplitude. The maximal SHG signal for *p*-polarized pump is ~180 times smaller as compared to the *s*-pump experiment.

The case of the same planarly-aligned (by polyimide-coated substrates) cells, but with rubbing orientation perpendicular to the direction of the applied DC electric field, is shown in figure 4. As seen, for *s*-polarized pump a new oscillation process is present. The frequency of this process is ~ 3 times higher than the main frequency and the amplitude is ~ 3 times smaller. The presence of the new process is obvious if one compares the form of the minimum in the figures 2 and 3 to that in figure 4. When the pump was *p*-polarized, then the model failed to simulate all parts of the experimental curve. It was possible to simulate either the central part (*calc2*) or the peripheral one (*calc1*). The optimal thickness values were 87 μm for *calc1* and 35 μm for *calc2*. Also the modulation depth of the experimental oscillations in peripheral parts was not 100% as predicted by the single-layer model. This indicates the failure of the single-layer model in the last case.

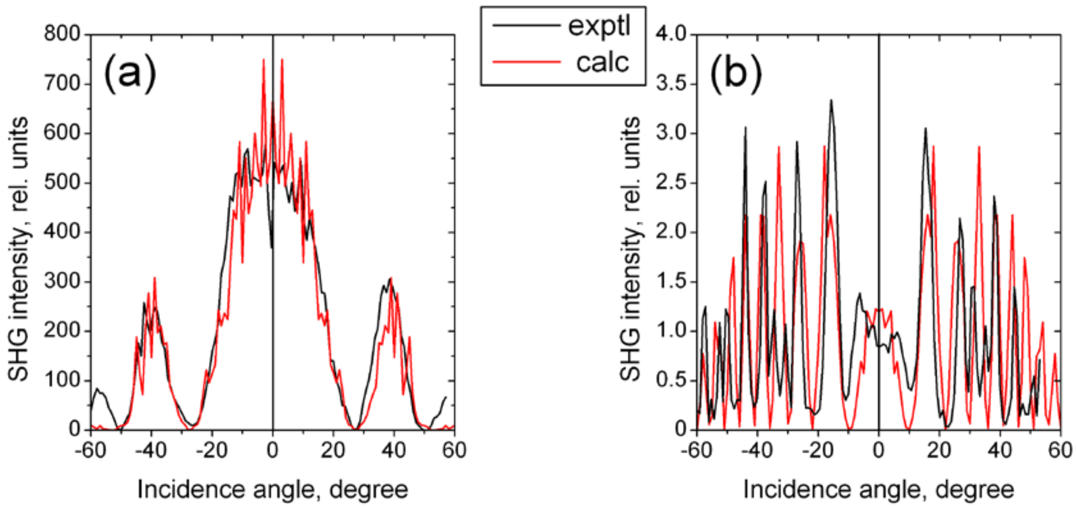

Figure 3. Angular dependencies of SHG signal from a cell covered with polyimide and filled with 5CB; the rubbing direction of the cell is parallel to the direction of the applied DC electric field: (a) *s*-polarized pump; (b) *p*-polarized pump.

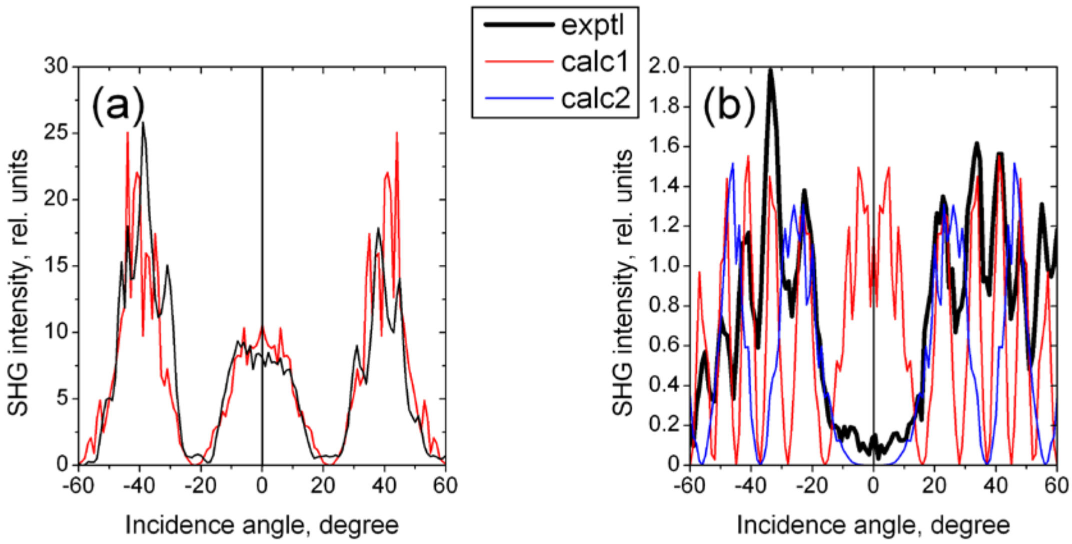

Figure 4. Angular dependencies of SHG signal from a cell covered with polyimide and filled with 5CB; the rubbing direction of the cell is perpendicular to the direction of the applied DC electric field: (a) *s*-polarized pump, (b) *p*-polarized pump.

The results for the homeotropic orientation (inner surfaces of the cell covered with silane) of the 5CB cells are shown in figure 5. For *s*-polarized pump (figure 5 (a)), the new oscillation process was also observed. Actually, within the experimental uncertainty the angular dependencies of SHG signal in this case was close to the one measured by 5CB cells with use of *s*-polarized pump and at crossed directions of the rubbing and the electric field discussed above (recall figure 4 (a)). When the pump was *p*-polarized (figure 5 (b)), then the well known phase synchronism for optical coherent process takes place, resulting in a large increase of the signal for a specific angle, so called phase matching angle. At this angle, the coherent parametric process of SHG through the NLC as a nonlinear optical medium is characterized by enhanced efficiency of the conversion from the input fundamental wave (at the wave frequency ω) to the SHG output. Furthermore, by the phase match the SHG is highly coherent, accompanied with a narrow spatial localization of the SHG beam behind the 5CB cell. Indeed, the SHG output in this case was detected as a highly collinear light beam. The optical phase matching angle is defined only by refractive index values and the wavelength of the pump. The value of this angle calculated from experiment data was in the agreement with the theoretical one. The latter was calculated using known refractive index of 5CB [11] corresponding to homeotropic orientation.

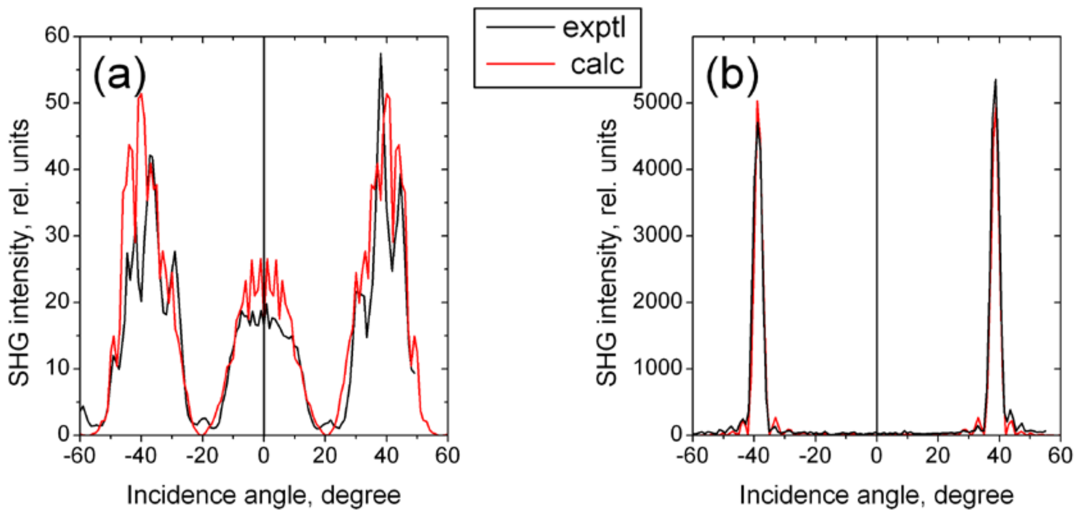

Figure 5. Angular dependencies of SHG signal from a cell covered with silane and filled with 5CB; homeotropic alignment perpendicular to the direction of the applied DC electric field: (a) *s*-polarized pump; (b) *p*-polarized pump.

Possible explanation of the fringe data can be a creation of effectively layered structure in the NLC formed under the high voltage pulses in the case when initial (without field) director orientation is not parallel to the field direction. In the homeotropic samples surface polarizations occur at both silanized (hydrophobic) surfaces due to biphilc asymmetry of 5CB molecule [14]. DC electric field normal to surface polarizations induces a component parallel to itself due to the tilt of surface director (figure 6(a)). On the other hand, in planar samples surface conditions of pretilt angle anchoring for nematic director at both surfaces lead to creation of splay deformation and developing splay flexopolarization in the bulk (figure 6(b)). However this polarization is screened due to space charges. When the electric field is applied it sweeps away the mobile charges allowing the unscreened polarization to interact with the field, and be rotated by it in one case. In most cases then opposite director orientations in upper and lower sublayers take place. The borders of the sublayers are parallel to the glass surfaces and the director orientation within the layers changes from one to another layer, leading to an effective layered structure of the sample. The optical path between these effective layers depends on the

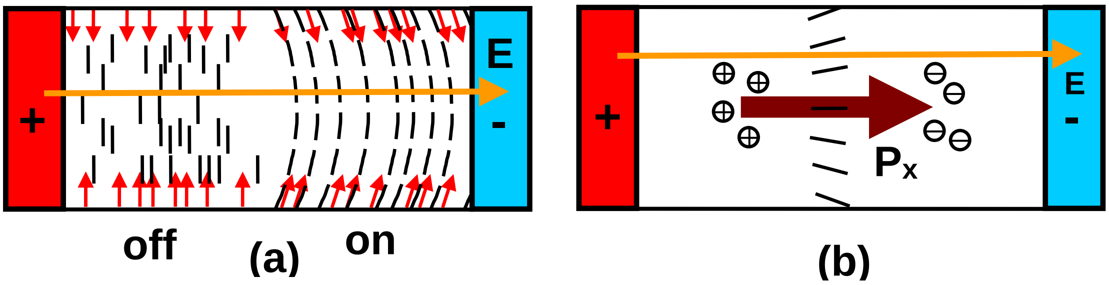

Figure 6. Flexoelectric polarization of plane nematic layers under in-plane electric field **E**: (a) Homeotropic layer. Arrows indicate surface polarization.; (b) Planar layer with free charges. Circles represent ions. The big arrow indicates flexoelectric polarization $\mathbf{P}_x$.

incidence angles. This structure could be responsible for multiple interference observed in SH amplitude modulation. Our experimental results support the conventional view of a liquid crystal (e.g., see figures 6 and 7 in references [1] and [15], respectively. The elucidation of the observed effect of variation of the EFISH intensity and angular distribution of the EFISH excitation (strongly depending on the NLC initial orientation) need further experimental and theoretical research. The efforts in this respect will be continued (work in progress).

4. Conclusions

The effect of external electric field on the coherent optical second harmonic generation in transmission was studied by different initial alignment of nematic liquid crystal (NLC), in particular 5CB. The method of sample rotation demonstrated different EFISH behavior depending on initial director orientation, as well as on the director orientation with respect to the direction of the electric field applied on the examined 5CB cells. Most probably, a layered structure of the liquid crystal under high voltage pulse is responsible for the observed variations in EFISH angular dependence. The EFISH nonlinear optical technique is highly sensitive (also sensitive to the polarization orientation of the incident laser beam) and can be sufficiently applied for optical, structural and director orientation characterization of NLC systems (including NLC mixtures, as well as various micro- and nano-scale composites, like NLC-based polymer-dispersed liquid crystals or NLC doped with nanoparticles).

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