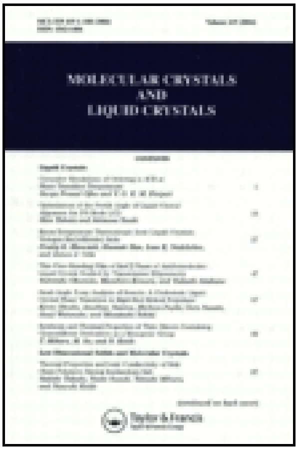

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# Surface Polarization in Interfacial Monolayer and SHG-MDC Spectroscopy

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# SURFACE POLARIZATION IN INTERFACIAL MONOLAYER AND SHG-MDC SPECTROSCOPY

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*Optical Second Harmonic Generation (SHG) and Maxwell displacement current (MDC) spectroscopy for the exploration of organic monolayer film is described. MDC and SHG are ascribed to the surface spontaneous and non-linear polarization of the monolayers due to symmetry breaking, respectively. It is shown that the SHG-MDC measurement can be used for the study of the orientational orders. In order to show the effect of the SHG-MDC spectroscopy, the dielectric polarization of monolayer with $C_\infty$-symmetry is theoretically analyzed with a simple rod-molecule model, and the surface polarization induced in the monolayer is expressed using orientational order parameters. The SHG and MDC generated from mesogenic liquid crystal (LC) monolayers are shown, and discussed based on the developed theory.*

## I. INTRODUCTION

On account of symmetry breaking, organic monolayers on water surface show interesting behaviors as a two-dimensional (2D) system unobserved in 3D bulk materials. Since the discovery of the technique for the formation of floating monomolecular films by Langmuir [1], the physico-chemical properties of monolayers at the air-water interface become a research topic for physicists, chemists and biologists.

Classically, monolayer study was started when the technique of surface pressure-area ($\pi$–A) isotherm measurement was introduced [1]. Since then, step by step, many instruments equipped with $\pi$–A measuring system have been developed. We can see an example of an extensive study on Langmuir monolayers in a review article by Kaganer et al. [2]. However, the physical properties of specific 2D systems have not been discussed yet thorou-ghly from the dielectric physics point of view [3,4]. The knowledge on

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monolayers based upon dielectric physics is essentially in the fields of nano-electronics, soft material electronics, low-dimensional physics, interfacial physics, etc. In order to explore the dielectric property of monolayers on the water surface in association with their 2D textures, obviously, it requires both experimental and theoretical studies. Experimentally, Maxwell-displacement current (MDC) [5] and optical second harmonic generation (SHG) [6] methods are very helpful, because the generation of MDC and SHG coming from surface polarization due to symmetry breaking can be explored. From theoretical side, it is also convenient to discuss the spontaneous polarization leading to the generation of MDC and the nonlinear polarization leading to the SHG at the same time. Therefore, we had carried out some theoretical and experimental studies on monolayer systems based on the MDC-SHG spectroscopy. In this paper, the SHG and MDCs generated from mesogenic liquid crystal (LC) monolayers (4′-*n-octyl*-4-*cyanobiphenyl* (8CB) and *S–citronelloxy–cyanobiphenyl* (*S–CCB*) are examined, and discussed based on the developed theory.

## II. ANALYSIS OF MONOLAYER FILMS

The state of floating monolayers composed of rod-like polar molecules can be expressed by two kinds of order parameters [7], the planar order parameter and the orientational order parameter. The former expresses the molecular configuration describing the positional distribution of the heads of the molecules on the water surface, and the latter expresses the orientational distribution of the rod-like polar molecules normal to the water surface. The orientational order parameter is specially important to specify the surface polarization in monolayers, and the specific properties of the organic monolayers such as spontaneous polarization and nonlinear polarization can be interpreted with these parameters [4]. Therefore, in the development of SHG-MDC spectroscopy, the determination of the orientational order parameters and the establishment for theory of dielectric monolayers are important [4,7]. Generally, we need various kinds of order parameters to express the orientation of molecules [8], but for the case of a monolayer composed of rod-like polar molecules with $C_\infty$-symmetry, the surface polarization of the monolayer is expressed by the orientational order parameters, $S_n$, ($n = 1$,2,and 3), defined as the thermodynamic average of the Legendre polynomials, $P_n(\cos\theta)$ ($n = 1$,2, and 3), of the orientational angles of molecules from the normal direction to the monolayer. It is instructive here to note that material systems composed of rod molecules can be classified using non-zero orientational order parameters $S_n$, ($n = 1$, 2 and 3) (see Fig. 1). Figure 1(a) describes the isotropic bulk materials,

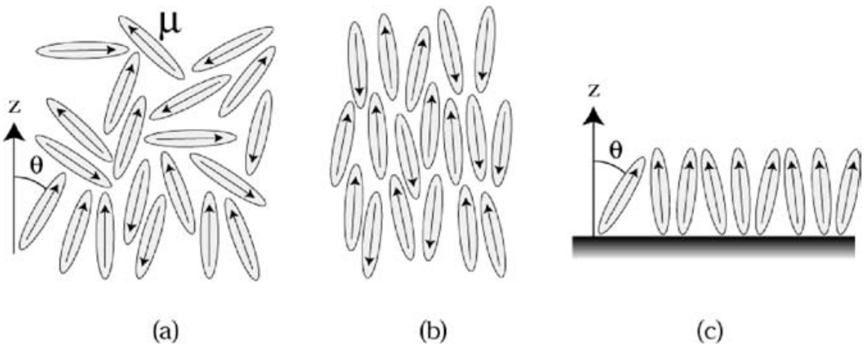


**FIGURE 1** Materials and orientational order parameters. (a) Isotropic bulk materials, (b) Nematic liquid crystals, and (c) Monolayers.

where $S_1 = \langle P_1(\cos\theta)\rangle = \langle\cos\theta\rangle = 0$, $S_2 = \langle P_2(\cos\theta)\rangle = \left\langle\frac{3\cos^2\theta - 1}{2}\right\rangle = 0$, and $S_3 = \langle P_3(\cos\theta)\rangle = \left\langle\frac{5\cos^3\theta - 3\cos\theta}{2}\right\rangle = 0$. Figure 1(b) describes the nematic phase of bulk LCs, where $S_1 = 0$, $S_3 = 0$, but $S_2 \neq 0$. Figure 1(c) describes the monolayer composed of rod molecules, where $S_1$, $S_2$, $S_3 \neq 0$. From Figure 1, we find that the physical properties of nematic LCs can be described using order parameter $S_2$. Thus, Tsvetkov [9,10] first introduced $S_2$ to describe bulk LCs with symmetric structure. Similarly, we may conclude that the physical properties of monolayers can be described using order parameters $S_1$, $S_2$, and $S_3$. Obviously, the specific properties of monolayer systems coming from symmetry breaking are associated with $S_1$ and $S_3$. In the following, we show surface polarization of monolayers, i.e., spontaneous polarization and second order nonlinear polarization can be expressed by non-zero order parameters $S_1$, $S_2$ and $S_3$.

First we consider the simple case that each molecule has a permanent dipole moment $\mu$ along its long axis together with an anisotropic electronic polarizability, i.e., electronic polarizability $\alpha_\parallel$ parallel to the molecular long axis and $\alpha_\perp$ perpendicular to the molecular long axis. Furthermore, the molecule possesses a second-order susceptibility, $\alpha_M^{(2)}$. The water surface and the monolayer film are considered as infinite planes. The coordinate system are chosen in such that the monolayer is parallel to the $xy$ plane and the monolayer normal directs along the positive $z$ axis, as shown in Figure 2. The molecule at the origin is facing the water surface, and tilts with an angle $\theta$ from the normal.

Using the parameters $S_n$ defined earlier, spontaneous polarization of monolayer $\boldsymbol{P}_o$ is expressed as

$$\boldsymbol{P}_0 = N_s \mu S_1 \vec{n}. \tag{1}$$

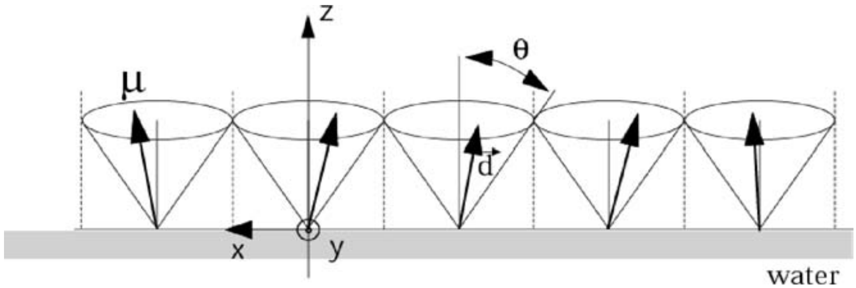


**FIGURE 2** Model of untilting monolayer on the water surface.

In the MDC measurement, MDC generated from monolayers flows in a closed circuit due to the change of $\boldsymbol{P}_o$ whilst the monolayers are compressed, as will be described later. Thus the $S_1$ is determined experimentally by the MDC. Similarly, nonlinear polarization of monolayer $\boldsymbol{P}^{(2)}$ can be expressed using the parameters $S_n$ defined earlier. Nonlinear polarization $\boldsymbol{P}^{(2)} = \vec{P}^N$ is sum of the polarization $\vec{P}^N_{ch}$ associated with the chirality of the monolayer and the polarizations $\vec{P}^N_{ach}$ associated with the nonchirality of the monolayer. The two polarizations are expressed in vector form as [11–13]:

$$\vec{P}^N_{ch} = \frac{1}{2}s_{14}\left[\left(\vec{E}\cdot\vec{n}\right)\left(\vec{F}\times\vec{n}\right) + \left(\vec{F}\cdot\vec{n}\right)\left(\vec{E}\times\vec{n}\right)\right] + \frac{1}{2}a_{14}\left(\vec{E}\times\vec{F}\right) + \frac{1}{2}(a_{36}-a_{14})\vec{n}\cdot\left(\vec{E}\times\vec{F}\right)\vec{n}, \tag{2}$$

$$\vec{P}^N_{ach} = (s_{33}-s_{15}-s_{31})\left(\vec{n}\cdot\vec{E}\right)\left(\vec{n}\cdot\vec{F}\right)\vec{n} + s_{31}\left(\vec{E}\cdot\vec{F}\right)\vec{n} + \frac{1}{2}s_{15}\left[\left(\vec{n}\cdot\vec{F}\right)\vec{E} + \left(\vec{n}\cdot\vec{E}\right)\vec{F}\right] + \frac{1}{2}a_{15}\left(\vec{E}\times\vec{F}\right)\times\vec{n}; \tag{3}$$

where the contracted nonlinear susceptibilities $(S_{ij})$ and $(a_{ij})$ are the function of the order parameters and the nonlinear molecular susceptibilities, and $\vec{E}$ and $\vec{F}$ are the external electric fields. Complete forms of the $(S_{ij})$ and $(a_{ij})$ are given in our previous paper [12], briefly $s_{14}$, $a_{14}$ and $a_{36}$ related to $\vec{P}^N_{ch}$ are only functions of $S_2$, whereas $s_{31}$, $s_{33}$, $s_{15}$ and $a_{15}$ related to $\vec{P}^N_{ach}$ are only functions of $S_1$ and $S_3$.

From the dielectric polarization point of view, the orientational order parameters $S_1$ and $S_3$ are related to the nonlinear polarization associated with the nonchirality of the monolayers, whereas $S_2$ is related to the nonlinear polarization associated with the chirality of the monolayers. In other words, chiral property is not specific for monolayers. In case of monolayers with $C_{\infty v}$-symmetry, where the constituent molecules are achiral, i.e.,

$s_{14} = a_{14} = a_{36} = 0$, the nonlinear electric polarization in SHG ($\vec{E} = \vec{F}$) reduces to [11–13]

$$\vec{P}^N = (s_{33} - s_{31} - s_{15})\left(\vec{n}\cdot\vec{E}\right)^2\vec{n} + s_{31}\left(\vec{E}\cdot\vec{E}\right)\vec{n} + s_{15}\left(\vec{n}\cdot\vec{E}\right)\vec{E}. \quad (4)$$

Thus, the nonlinear dielectric polarization is only a function of the order parameters $S_1$ and $S_3$. Similarly, in case of monolayers with $C_\infty$-symmetry, where the constituent molecules are chiral, i.e., $s_{14} \neq a_{14} \neq a_{36} \neq 0$, the nonlinear electric polarization in SHG ($\vec{E} = \vec{F}$) is given by:

$$\vec{P}^N = s_{14}\left(\vec{E}\cdot\vec{n}\right)\cdot\left(\vec{E}\times\vec{n}\right) + (s_{33} - s_{31} - s_{15})\left(\vec{n}\cdot\vec{E}\right)^2\vec{n} + s_{31}\left(\vec{E}\cdot\vec{E}\right)\vec{n} + s_{15}\left(\vec{n}\cdot\vec{E}\right)\vec{E}. \quad (5)$$

The first term on the right hand side of Eq. (5) is a function of $S_2$, and represents the chiral effect. In other words, the molecular chirality makes a contribution to change the phase of polarization of monolayers.

## III. SHG-MDC MEASUREMENT

Figure 3 shows a schematic diagram of the MDC measurement coupled with SHG measurement. Electrode 1 is suspended in air and is placed parallel to the water surface. Electrode 2 is immersed in the water. These two electrodes (1 and 2) are connected to each other through an electrometer. The induced charge on Electrode 1 changes in accordance with the

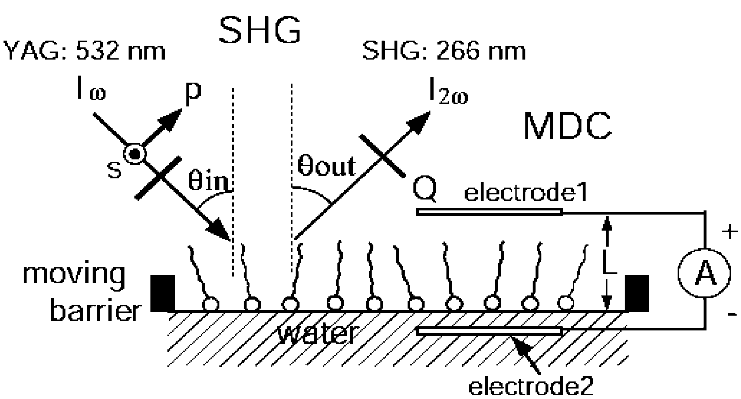


**FIGURE 3** A schematic diagram of experimental setup for MDC and SHG measurements.

orientational motion of the molecules on the water surface and the change of the surface density of the molecules. Thus MDC flows through the closed circuit by monolayer compression with the aid of two moving barriers. The induced charge $Q_1$ on Electrode 1 comes from the spontaneous polarization $P_z$ given by Eq.(1), and it is given as [4]

$$Q_1 = -P_z B/L - C\phi_s, \tag{6}$$

where $B$ is the working area of Electrode 1, $C$ is the capacitance between Electrode 1 and the water surface, $L$ (1 mm in our case) is the distance between Electrode 1 and the water surface, and $\phi_s$ is the surface potential of the water. In the MDC measurement, $Q_1$ changes by monolayer compression, and current $I = dQ_1/dt$ flows through the short circuit. In other words, MDC comes from the change of $P_z$, and $S_1$ can be determined from MDC.

On the other hand, SH light is generated from the monolayer by laser irradiation. The output light is the sum of the $s$- and the $p$- polarized wave. With these, the output light intensity $I_{2\omega}$ is proportional to $\overrightarrow{e_{out}}(2\omega) \cdot \overrightarrow{P^N}$, where $\overrightarrow{e_{out}}(2\omega)$ represents electric field vector of the SH signal after passing through the analyzer. With proper choice of the input and output polarized angles, and the assumption that $\alpha_{3'3'3'}$ is the main contributor, the orientational order parameters, $S_1$ and $S_3$, of monolayers with $C_{\infty v}$-symmetry can be determined experimentally [11]. Similarly, we can determine $S_1$ and $S_3$ of the monolayer even if no single component of the hyperpolarizability does not dominate, since $\overrightarrow{e_{out}}(2\omega) \cdot \overrightarrow{P^N}$ is a function of $S_1$ and $S_3$ [15].

The experimental setup consists of a Langmuir-trough equipped with a two-electrode arrangement for the MDC measurement and the optical measurement arrangement with a Q-switched Nd:YAG laser (wavelength 0.532 μm, pulse duration $<7$ nsec, fundamental pulse rate $\leq 15$ Hz) for the SHG measurement (see Figs. 3 and 4). The rectangular Langmuir-trough (600 mm × 150 mm in length and width, 10 mm in depth) is made of polytetra.fluoroethylene (PTFE) and filled with pure water (resistivity $>17$ MΩ· cm). A transparent silica glass plate is attached to the bottom of the Langmuir-trough for the SHG measurement. For MDC measurement, transparent glass slide coated with Indium-Tin Oxide (ITO) is used as Electrode 1 (45 $cm^2$). Electrode 2 is a gold-wire spiral(1 mm$\phi$ and 500 mm) and is immersed in the water. For SHG measurement, the fundamental light is irradiated onto the monolayer with energy of about 6 mJ at a pulse rate of 2 Hz. The size of the laser spot is about 42 $mm^2$. After spreading a 0.001 mol · $l^{-1}$ chloroform solution of 8CB onto the water surface of the Langmuir-trough as a floating monolayer, the MDC-SHG measurement was carried out with monolayer compression at a speed of 10 mm·$min^{-1}$

($0.056\,\mathrm{nm}^2\,\mathrm{min}^{-1}\,\mathrm{molecule}^{-1}$). The surface pressure of the monolayer was also measured during the monolayer compression by a Wilhelmy plate.

## IV. RESULTS AND DISCUSSIONS

8CB molecule is a rod-like amphiphilic molecule. The alkyl group is hydrophobic, whereas the cyano group is hydrophilic. Both alkyl and cyano groups have permanent dipole moment along the molecular long-axis. It is expected that the permanent dipole moments of these alkyl and cyano groups in 8CB lead to the generation of MDC, whereas the second order nonlinear electronic polarizability of the biphenyl group with alkyl and cyano groups leads to SHG.

It should be noted that the contribution of the permanent dipole moment of the hydrophilic part is diminished owing to the screening effect of the water with a high dielectric constant ($\approx$78) when the hydrophilic part is protruding into the water. As a result, although the dipole moment of the methyl group is very small in comparison with that of the nitorile, the long alkyl chain can also make a contribution to the generation of MDC, in a manner as that appeared in fatty acid monolayers [1,4]. As the MDC and SHG generation is related to the surface polarization of monolayers given by Eq. (1) and Eq. (5), the orientational order parameters $S_1$ and $S_3$ can be determined experimentally by choosing appropriate polarized angles for the SHG detection. Figure 4 shows an example of the determination of order parameters $S_1$, and $S_3$ for 8CB monolayers with $C_{\infty v}$-symmetry. In region 1, $S_1$ and $S_3$ of SHG are very small although the fluctuation is observed owing to the formation of domains and the high sensitivity of the detection system. In region 2, $S_1$ and $S_3$ increase gradually and give the maximum. In region 3, they are nearly constant about 0.5. In contrast, $S_1$ of MDC is nearly zero in region 1, and it increases monotonously in region 2. $S_1$ is about 0.5 in region 3. From these results, it is estimated that molecules lying on a water surface stand up by monolayer compression, with an average tilting angle of about $60^\circ$ in region 2. As mentioned above, using the MDC-SHG measurement, orientational order parameters $S_1$ and $S_3$ that are specific to monolayers can be explored [14,15].

As derived in Eq. (5), the polarization associated with molecular chiral appears in the first term of Eq. (5). This term gives rise to a change of generated SHG signals. Actually, in our experimental setup, the $s$-polarized reflected SH intensity is expected to be,

$$I(2\omega)_s \propto \left|s_{15}\sin\delta\cos\delta - s_{14}\cos^2\delta\cos\theta_{in}\right|^2. \qquad (7)$$

for the monolayer with $C_\infty$ symmetry, where $\theta_{in}$ represents the incident angle and $\delta$ represents the polarized angle. Using chiral monolayers of

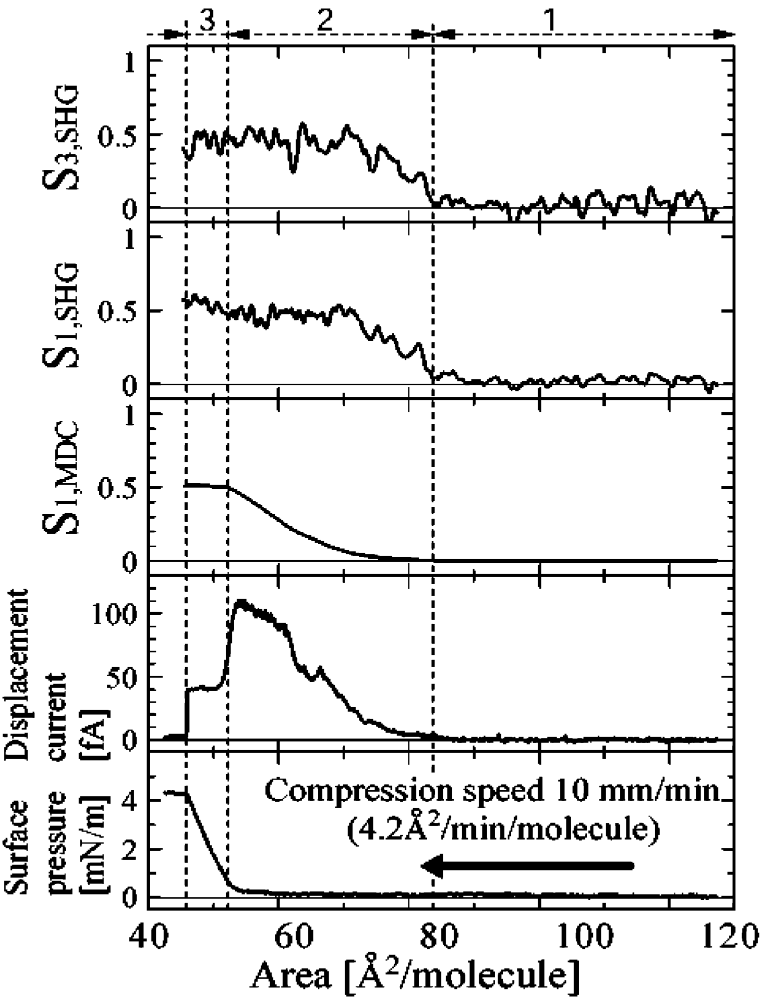


**FIGURE 4** Order parameters of 8CB monolayer determined from the MDC-SHG measurement.



S-CCB, we could show the asymmetric dependence of SHG with respect to the incidence angle $\theta_{in}$ due to non-zero $s_{14}$, i.e., $S_2 \neq 0$, though the ratio $s_{14}/s_{15}$ was very small, and estimated $\approx 1/30$. It should be noted here that from the achiral monolayers of 8CB, an symmetric dependence of SHG generation with respect to the incidence angle $\theta_{in}$ was observed, possibly because $s_{14} = 0$ [16]. As mentioned above, using SHG and MDC measurement, we can explore the specific property of monolayers.

## V. SUMMARY

The dielectric polarization of organic monolayers at the air-water interface has been analyzed. The formula of polarization of organic monolayers is derived and it is expressed using orientational order parameters. It was revealed that Maxwell Displacement Current (MDC) measurement coupled with optical second harmonic generation (SHG) measurement is helpful for the determination of these orientational order parameters. Furthermore, we show that the contribution of chiral property of monolayers can be also examined by using this technique.



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