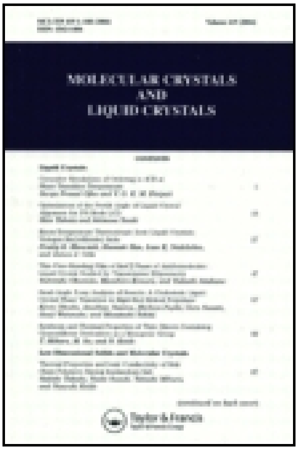

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Atsushi Tojima [a], Ryouhei Hiyoshi [a], Hiroshi Fujimaki [a], Hiroshi Ootake [a], Takaaki Manaka [a] & Mitsumasa Iwamoto [a]

[a] Department of Physical Electronics, Tokyo Institute of Technology, Tokyo, Japan

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STUDY OF ORIENTATIONAL ORDER PARAMETERS OF 4-OCTYL-4′-n-CYANOBIPHENYL LANGMUIR FILMS BY MAXWELL DISPLACEMENT CURRENT MEASUREMENT COUPLED WITH OPTICAL SECOND HARMONIC GENERATION MEASUREMENT

Atsushi Tojima, Ryouhei Hiyoshi, Hiroshi Fujimaki, Hiroshi Ootake, Takaaki Manaka, and Mitsumasa Iwamoto
Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Using Maxwell displacement current (MDC) and optical second harmonic generation (SHG) measurements, the orientational order parameters S_1 and S_3 of 4-octyl-4′-n-cyanobiphenyl (8CB) monolayers on the water surface were determined by monolayer compression.

Keywords: maxwell displacement current; MDC; second harmonic generation; SHG

INTRODUCTION

Organic monolayers on the water surface, Langmuir films show specific electrical and optical properties due to their non-centrosymmetric structure [1], because these properties are dependent on the molecular orientation, monolayer structure and so on. The positional and orientational distributions of molecules in monolayers are key factors to describe the monolayer properties, especially the latter one is important. The orientational distribution of rod-like molecules on the water surface would be independent of azimuthal direction, and only dependent on the polar orientational direction normal to the water surface. This is thus characterized using the orientational order parameters $S_{\mathrm{m}} = \langle P_{\mathrm{m}}(\cos\theta)\rangle$ (m = 1, 2, 3, ...), where P_{m} is the m-th Legendre polynomial, θ represents an angle away from the normal direction to the water surface and $\langle\,\rangle$ represents a thermodynamic average all over molecular directions [2]. Using Maxwell displacement current (MDC) measurement, we can determine the orientational

Address correspondence to Mitsumasa Iwamoto, Dept. of Physical Electronics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

order parameter S_1 in association with spontaneous polarization of monolayers. Similarly, using optical second harmonic generation (SHG) measurement, orientational order parameters S_1 and S_3 in association with second order nonlinear polarization can be determined. The MDC measurement coupled with the SHG measurement will be helpful for better understanding of the polarization properties, i.e., the dielectric properties of monolayers [3–5].

In this study, we examined 4-octyl-4′-n-cyanobiphenyl (8CB) Langmuir films by monolayer compression and determined the orientational order parameters S_1 and S_3.

MDC AND SHG MEASUREMENTS

The dielectric polarization of monolayers on the water surface in the presence of external electric field $\mathbf{E}(\omega)$ is expressed as [6]:

$$\mathbf{P} = \mathbf{P}_0 + \chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} : \mathbf{EE} + \chi^{(3)} : \mathbf{EEE} + \cdots, \tag{1}$$

where $\mathbf{P}_0$ is the spontaneous polarization, $\chi^{(1)}$ is the linear susceptibility and $\chi^{(n)}$ $(n \geq 2)$ is the n-th order nonlinear susceptibility. These polarizations can be specified using orientational order parameters. Let us here consider monolayers with $C_{\infty v}$-symmetry composed of rod-like amphiphilic molecules. Then spontaneous polarization $\mathbf{P}_0$ is given by

$$\mathbf{P}_0 = \mu S_1 N_s \mathbf{n}, \tag{2}$$

where μ is the magnitude of permanent dipole moment along molecular long axis, N_s is the surface density of molecules, and $\mathbf{n}$ is unit vector defined in the direction normal to the water surface toward air. S_1 is the orientational order parameter defined as $S_1 = \langle \cos\theta_m \rangle$, representing the average of all over molecular orientation. Here θ_m is an orientational angle of a molecule from $\mathbf{n}$.

In the MDC measurement, the charge $Q(= -B_s(\mathbf{P}_0 \cdot \mathbf{n})/d_0)$ induced on electrode 1 due to $\mathbf{P}_0$ changes by monolayer compression, and MDC *i(t)* flows through the closed circuit and it is approximately given by [2,3]

$$i(t) = \frac{dQ}{dt} = \frac{\mu B_s N_s}{d_0}\frac{dS_1}{dt} + \frac{\mu B_s S_1}{d_0}\frac{dN_s}{dt}. \tag{3}$$

Here B_s is the working area of electrode 1, d_0 is the distance between electrode 1 and the water surface. Therefore, the orientational order parameter S_1 is determined from the following relation

$$S_1 = \frac{d}{\mu N}\int_0^t i(t)dt, \tag{4}$$

assuming that $S_1 = 0$ before monolayer compression, i.e., molecules lie on the water. As mentioned above, S_1 is estimated by measuring MDC.

On the other hand, the second harmonic (SH) intensity generated from monolayers by irradiating light with a laser beam intensity $I(\omega)$ becomes

$$I(2\omega) = \frac{32\pi^3\omega^2 \sec^2\theta_{in}}{c^3\varepsilon^{1/2}(2\omega)\varepsilon(\omega)}\left|\mathbf{e}^{2\omega}\cdot\chi^{(2)}:\mathbf{e}^{\omega}\mathbf{e}^{\omega}\right|^2 I^2(\omega)$$
$$\propto N_s^2\beta_{z'z'z'}^2|(AS_1+BS_3)|^2 I^2(\omega). \tag{5}$$

with

$$\chi^{(2)} = \begin{pmatrix} 0 & 0 & 0 & 0 & \chi_{xzx} & 0 \\ 0 & 0 & 0 & \chi_{yyz} & 0 & 0 \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{pmatrix}, \tag{6}$$

$$\chi_{zzz} = \frac{1}{5}N_s(2S_3+3S_1)\beta_{z'z'z'}, \tag{7}$$

and

$$\chi_{zxx} = \chi_{zyy} = \chi_{xzx} = \chi_{yyz} = \frac{1}{5}N_s(S_1 - S_3)\beta_{z'z'z'}, \tag{8}$$

using orientational order parameters $S_1 = \langle\cos\theta_s\rangle$ and $S_3 = \langle(5\cos^3\theta_s - 3\cos\theta_s)/2\rangle$, under the assumption that the second order nonlinear molecular polarizability $\beta_{z'z'z'}$ along the molecular long axis is dominant. The subscripts of χ and β are referred to the coordinate in the laboratory frame (x, y, z) and the molecular frame (x′, y′, z′) (see Fig. 1). Here ω is the angular frequency of incident light, θ_{in} is the incident angle, c is the velocity of light, and ε is the dielectric constant of medium. A and B are functions of incident angle θ_{in}, the polarizer angle of incident light δ, those of output SH light γ_R and γ_T (subscripts R and T represent the reflection and transmission, respectively) and the dielectric constants of air, water, monolayers and so on [4]. By choosing appropriate angles δ, γ_R and γ_T, either A or B becomes zero. Therefore the orientational order parameters S_1 and S_3 are determined from reflected and transmitted SH lights, by choosing appropriate angles to be $B = 0$ at the reflected side and to be $A = 0$ at the transmitted side, respectively.

Originally, the parameters S_1 determined by the MDC and SHG measurement should be different. However, if the direction of the permanent dipole moment and the second order nonlinear polarization coincide each other, *i.e.*, in a special case such as a rod-like molecule, both S_1 should be the same.

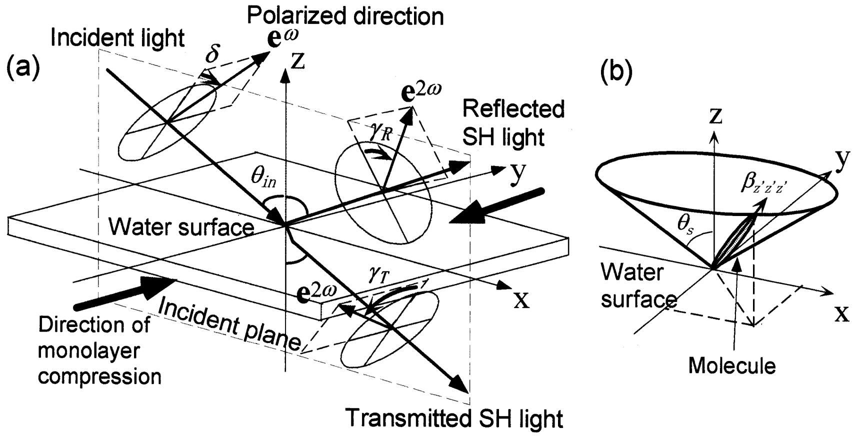

FIGURE 1 A coordinate frame of (a) an experiment setup (b) a monolayer structure for the SHG measurement.

EXPERIMENT

Figure 2 shows an experimental setup of MDC and SHG measurement system. The Langmuir-trough made of polytetrafluoroethylene (PTFE) is filled with pure water (electrical resistivity > 17 MΩ· cm). The monolayer covering area is controlled from 600 mm to 180 mm (150 mm width and 1 mm depth) by moving two barriers. For MDC measurement, two electrodes 1 and 2 connected through an electrometer (Keithley 617) are used. Electrode 1 is a round shape glass slide coated with Indium Tin Oxide (ITO) with a diameter of 76 mm (area of 45.4 cm^2) and it is placed in air to be parallel to the water surface with an air gap of 1 mm. Electrode 2 is a spiral shaped gold wire and it is immersed in the water subphase. For SHG measurement, Q-switched Nd:YAG laser was used as a light source (Continuum Minilite II). In this measurement, the laser power irradiated onto monolayer, wave length, pulse rate and irradiated area were set at about 6 mJ, 532 nm, 2 Hz and about 56 mm^2, respectively. The linearly polarized light by the polarizer (P2) is incident onto a monolayer at an incident angle of $\theta_{in} = 60°$. The reflected and transmitted SH signals are detected by the photomultiplier-tube (PMT) through the filters (F2, F3) and the polarizers (P3). The angles of polarizers were set at $\delta = 34°$, $\gamma_R = 41°$ and $\gamma_T = -68°$ to detect strong SH signals in stable. At these setting conditions we can detect SH signals with components of S_1 at the reflected direction and S_3 at the transmitted direction. The surface pressure - area isotherm is also recorded during monolayer compression.

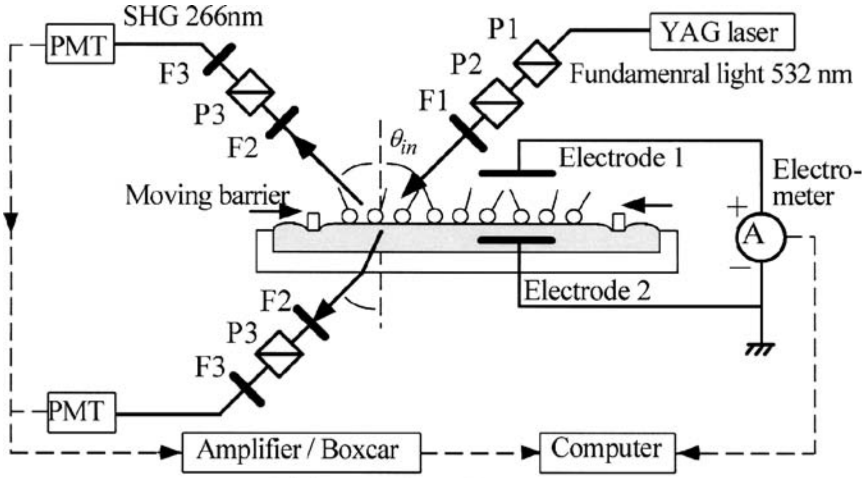

FIGURE 2 An experimental setup of the MDC and SHG measurement system.

In this study, 8CB monolayers were examined. After spreading 120 μL chloroform solution with a density of 1 mmol/1 onto a water surface using a micro-syringe, we kept it for about 10 minutes to evaporate chloroform. The speed of each moving barrier was 10 mm/min during monolayer compression.

RESULTS AND DISCUSSION

Figure 3 shows typical experimental results of the MDC and SHG measurement of 8CB monolayer during compression. The orientational order parameters determined from the MDC and SHG measurement are shown in Figure 4. That is, the orientational order parameter S_1 of MDC ($S_{1,\mathrm{MDC}}$) is calculated by Eq. (4) and the parameters S_1 and S_3 of SHG ($S_{1,\mathrm{SHG}}$ and $S_{3,\mathrm{SHG}}$) are estimated from Eq. (5) as

$$S_j \propto \frac{\sqrt{I(2\omega)}}{N_s} \ (j = 1, 3), \tag{10}$$

assuming the orientational order parameters S_1 and S_3 are about 0.5 at an molecular area of 52 A^2, corresponding to the boundary between region 2 and 3 [4].

In region 1, SHG, MDC and the surface pressure are nearly zero, indicating that molecules lie on the water surface due to the electrostatic

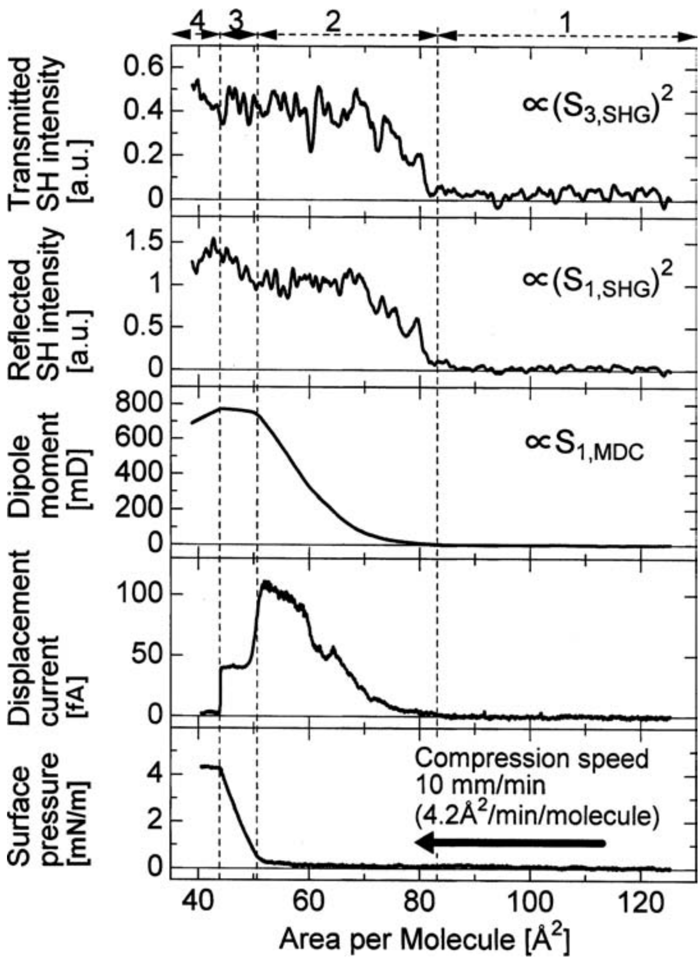

FIGURE 3 Typical experimental results of 8CB monolayer by compression.

attractive Coulomb interaction between molecules and water [2]. The fluctuation of $S_{1,\mathrm{SHG}}$, and $S_{3,\mathrm{SHG}}$ are due to the fluctuation of the SHG signals and can be discarded, *i.e.*, S_1 and S_3 are almost zero in this region.

In region 2, the MDC and SHG signals appear by compression. Fluctuations are observed in the SHG signals and the stability of the SHG signals is not good in comparison with that of the MDC signal. This may be due to the formation of domains and the thermodynamic motion of molecules on the water surface. Furthermore, the irradiated area of the laser beam was 56 mm^2 in the SHG measurement whereas the working area of electrodes was about 45 cm^2 in the MDC measurement. The MDC signal gradually

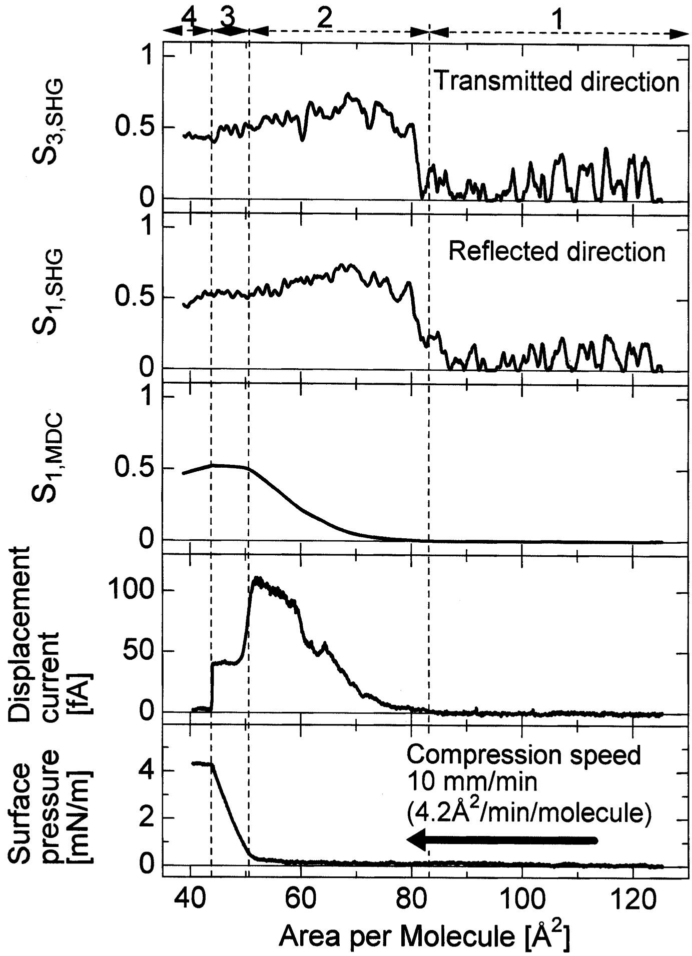

FIGURE 4 Typical orientational order parameters estimated from MDC and SHG measurement, e.g., fig. 3.

increases, whereas the SHG signals increase steeply at the beginning and then remains constant by monolayer compression. In corresponding to these SHG signals, $S_{1,\mathrm{SHG}}$ and $S_{3,\mathrm{SHG}}$ give peaks and then gradually decrease by monolayer compression. It is postulated that monolayers have mosaic domains.

In region 3, the surface pressure increases monotonously. The MDC signal decreases suddenly and then becomes steady. The magnitude of dipole moment m_z and $S_{1,\mathrm{MDC}}$ increase slightly. The reflected SH signal for S_1 component tends to increase whereas the transmitted SH signal for S_3

component seems steady. $S_{1,\mathrm{SHG}}$ and $S_{3,\mathrm{SHG}}$ are nearly constant. As molecules are gradually packed in this region by monolayer compression, the molecular density increases inversely proportional to the molecular area but the orientational change is gradually restricted. Therefore the order parameters do not change by monolayer compression.

In region 4, the surface pressure increase slightly, the MDC signal is nearly zero and the SHG signals seem to remain constant. If multi-layered structure, *e.g.*, 2-layer structure, with molecules which orient in the same director direction toward air is formed, MDC and SHG signals increase in proportion to the square of the density of molecules (see Eqs. (3) and (5)). On the other hand, if alternating layer structure is formed, these signals do not increase due to the cancellation of polarization between the adjacent alternating layers. Our experimental results support the latter one. That is, the deformation from single-layer to alternate 3-layer structure happens during monolayer compression [7].

Finally it should be noted that *s-s* and p-s signals are not detected in the entire range of surface pressures, whereas s-p and p-p signals are generated in ranges 2, 3 and 4. This result supports our analysis in MDC AND SHG MEASUREMENTS where the structure of monolayers is treated as $C_{\infty v}$-symmetry.

CONCLUSION

Using the MDC and SHG measurements, we examined 4-octyl-4′-n-cyanobiphenyl (8CB) monolayers by monolayer compression and determined the orientational order parameters S_1 and S_3. S_1 of SHG and MDC shows similar tendency over the entire range of molecular area.

REFERENCES

[1] Ulman, A. (1995). *Characterization of Organic Thin Films*, (Ed.), Butterworth-Heiman: Boston.
[2] Iwamoto, M. & Wu, C. X. (2001). *The Physical Properties of Organic Monolayers*, World Scientific: Singapore.
[3] Tojima, A., Matsuo, Y., Hiyoshi, R., Manaka, T., Majima, Y., & Iwamoto, M. (2001). *Thin Solid Films*, *393*, 86.
[4] Tojima, A., Manaka, T., & Iwamoto, M. (2003). *Rev. Sci. Instrumn.*, *74*, 2828.
[5] Tojima, A., Manaka, T., & Iwamoto, M. (2001). *J. Chem. Phys.*, *115*, 9010.
[6] Shen, Y. R. (1984). *The Principles of Nonlinear Optics*, Wiley Interscience: New York.
[7] Xue, J., Jung, C. S., & Kim, M. W. (1992). *Phys. Rev. Lett.*, *69*, 474.