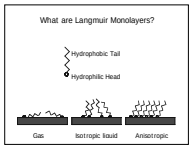
Molecular orientation in Langmuir monolayers studied by surface second harmonic generation

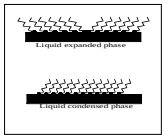
Nan Shen and Eric Mazur

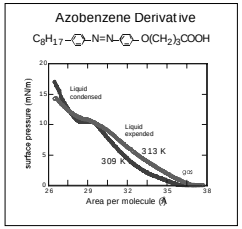
Department of Physics, Harvard University, Cambridge, MA 02138

Introduction

We combined surface second harmonic generation (SHG) with depolarized microscope to study molecular orientation in a smectic-C liquid-crystal Langmuir monolayer at an air/water interface. The molecules under investigation are 4-octyl-4'-(3-carboxytrimenthyleneoxy) azobenzene (8AZ3). Monolayer exhibits a first-order phase transition from liquid expanded (LE) to liquid condensed phase (LC) with increasing surface pressure.

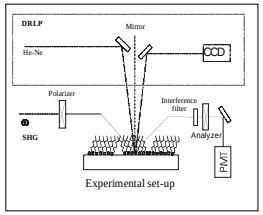






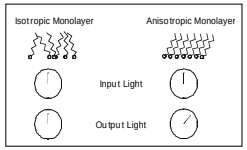
Experimental set-up

A solution of 8AZ3 in chloroform is spread on a subphase of deionized water from a Millipore Milli-Q system. A 800-nm ultrashort laser pulse is incident on the interface at 45° angle. The SHG signal is collected through a interference filter by a photon counting system. A He-Ne laser at nearly normal incident is carefully overlapped on the surface with the 800-nm beam. to image onto a CCD camera.

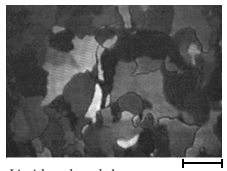


Experimental set-up

Depolarized reflected-light microscope (DRLM)



In the DRLM setup, p-polarized light is incident onto the monolayer almost normal to the surface. The reflected light is imaged through a s-polarized analyzer, which allows visualization of the anisotropy of the monolayer.


Liquid condensed phase

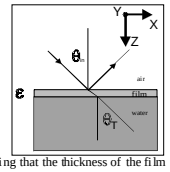
100μm

Liquid expanded phase

When polarized light is incident on an optically anisotropic thin film, the reflection from the film includes information about the dielectric constants and optic-axis directions. Using the Maxwell equation and the 4×4 matrix formalism, we derived the Fresnel formula. We write the Maxwell equation in differential form,

$$\frac{\partial}{\partial z}\Psi = i\frac{\omega}{c}T\Psi \qquad \Psi = \begin{bmatrix} \sqrt{\varepsilon_0}E_x \\ \sqrt{\varepsilon_0}E_y \\ \sqrt{\mu_0}H_y \\ \sqrt{\mu_0}H_x \end{bmatrix}$$

$$T = \begin{bmatrix} -\frac{k_x\varepsilon_{zx}}{k\,\varepsilon_{zz}} & -\frac{k_x\varepsilon_{zy}}{k\,\varepsilon_{zz}} & 0 & 1-\left(\frac{k_x}{k}\right)^2\frac{1}{\varepsilon_{zz}} \\ 0 & 0 & -1 & 0 \\ -\varepsilon_{yy}+\frac{\varepsilon_{yz}\varepsilon_{zy}}{\varepsilon_{zz}} & \left(\frac{k_x}{k}\right)^2 & -\varepsilon_{yz}+\frac{\varepsilon_{yz}^2}{\varepsilon_{zz}} & 0 \\ \varepsilon_{xx}-\frac{\varepsilon_{xz}^2}{\varepsilon_{zz}} & \varepsilon_{xy}-\frac{\varepsilon_{xz}\varepsilon_{zy}}{\varepsilon_{zz}} & 0 & -\frac{k_x}{k}\frac{\varepsilon_{xz}}{\varepsilon_{zz}} \end{bmatrix}$$



Assuming that the thickness of the film $\Delta z \ll \lambda_0$, we can solve the differential equation approximately. For uniaxial monolayers, the DRLM reflectivity at nearly normal incident takes the form

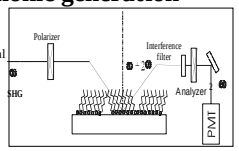
$$I(\alpha) = h_i^2 \sin^2\alpha\cos^2\alpha$$

$$h_i = \delta h_i \frac{\varepsilon_3(\varepsilon_1-\varepsilon_3)}{\varepsilon_3\cos^2\beta+\varepsilon_1\sin^2\beta}\sin^2\beta$$

DRLP image simulation

$$h = \frac{2n\cos\theta_i\cos\theta_t}{(n\cos\theta_t+\cos\theta_i)(n\cos\theta_i+\cos\theta_t)}$$

Surface second-harmonic generation (SHG)



As a second-order nonlinear process, optical SHG is highly surface specific. The polarization relates to the field as

$$P(2\omega) = \chi_{ijk}E_jE_k$$

Under the dipole approximation, χ_{ijk} must vanish in centro-symmetric materials. However, at the interface the inversion symmetry is broken. This allows us to probe surfaces with sub-monolayer sensitivity. Consider a monolayer of molecules with a second-order polarizability α. Assuming local field effects are negligible, the nonlinear susceptibility is given by

$$\chi_{ijk} = N_s\langle G_{ijk}\rangle\alpha_{lmn}$$

where Ns is the density of molecules in the monolayer. If α is dominated by a component along the molecular axis ξ, we can write χ in the simple form

$$\chi_{ijk} = N_s\langle(i\cdot\xi)(j\cdot\xi)(k\cdot\xi)\rangle\alpha_{\xi\xi\xi}$$

If the molecules have a preferred alignment along the x-axis, the symmetry allows six independent and nonvanishing components of χ

$$\chi_{xxx} = N_s\langle\cos^3\theta\rangle$$
$$\chi_{xxy} = \chi_{xyx} = \chi_{yxx} = N_s\langle\cos\theta-\cos^3\theta\rangle = N_s\langle1-\cos^2\phi\rangle$$
$$\chi_{xzz} = \chi_{zxz} = \chi_{zzx} = N_s\langle\cos\theta-\cos^3\theta\rangle = N_s\langle\cos^2\phi\rangle$$
$$\chi_{zzx} = \chi_{zxz} = \chi_{xzz} = N_s\langle\sin\theta-\sin^3\theta\rangle = N_s\langle\cos\phi\rangle$$
$$\chi_{yyx} = \chi_{yxy} = \chi_{xyy} = N_s\langle\cos\theta-\cos^3\theta\rangle = N_s\langle\sin^2\phi\rangle$$
$$\chi_{zzx} = \chi_{zxz} = \chi_{xzz} = N_s\langle\cos\theta-\cos^3\theta\rangle = N_s\langle\sin^2\phi\rangle$$

Consider the general case where the monolayer is sandwiched between air and water. The reflected SHG output is given by

$$S(2\omega) = \frac{32\pi^3\omega\sec^2\theta}{hc^2\varepsilon(2\omega)^{1/2}\varepsilon(\omega)}\left|\chi_{eff}\right|^2 I^2TA$$

where I is the incident laser intensity, T is the laser pulse width, and A is the beam spot size. The effective nonlinear susceptibility χ has the form

$$\chi_{eff} = [\hat{e}(2\omega)\cdot L(2\omega)]\chi^{(2)}:[L(\omega)\cdot\hat{e}(\omega)][L(\omega)\cdot\hat{e}(\omega)]$$

Specifically we have, for the Sin/Sout polarization setup

$$\chi_{eff} = \chi_{zzz}\sin^2\theta L_z(2\omega)L_z^2(\omega) + 3\chi_{xxy}\cos^2\phi\sin\theta L_x(2\omega)L_y^2(\omega)$$

For P_{in}/S_{out},

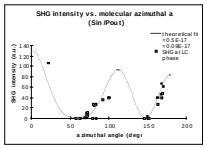
$$\chi_{eff} = \chi_{xxy}(3\sin^2\phi-2\sin\phi)L_x(2\omega)L_y^2(\omega)\cos^2\theta + 3\chi_{xxx}\cos^2\phi\sin\theta L_x(2\omega)L_x^2(\omega)\cos^2\theta + 3\chi_{xxy}\cos^2\theta\sin\theta L_x(2\omega)L_y^2(\omega) + (\chi_{xxx}-\chi_{xyy})\sin2\phi L_x(2\omega)L_x(\omega)L_z(\omega)[-\sin\theta\cos\theta]$$

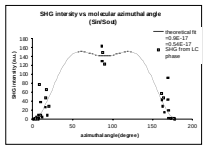
For P_{in}/P_{out}

$$\chi_{eff} = (3\chi_{xxy}\sin^2\theta\cos\theta+\chi_{zzx}\cos^3\theta)L_z(2\omega) L_x^2(\omega)\cos^3\theta + (\chi_{zzz}\cos^2\phi+\chi_{zyy}\sin^2\phi) \{2L_z(2\omega)L_x(\omega)L_x(\omega)[-\cos^2\theta\sin\theta] + L_z(2\omega)L_x^2(\omega)\cos^2\theta\sin\theta\} + \chi_{zzx}\cos\phi[L_z(2\omega)L_x^2(\omega)\sin^2\theta\cos\theta - 2L_z(2\omega)L_x(\omega)L_x(\omega)\sin^2\theta\cos\theta] + 3\chi_{zzx}[L_z(2\omega)L_z^2(\omega)\sin^2\theta$$

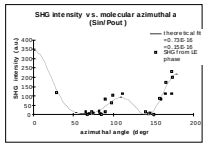
SHG signal depends on molecular azimuthal and tilt angle. DRLP is sensitive to the azimuthal angle of the molecule. Since the 800-nm beam is focused down to ~10 μm, which is on the order of a single domain size, we can measure the SHG from each individual domain. Combined, these two techniques allow determination of molecular orientation.

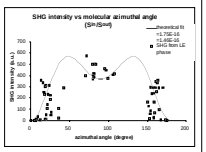
Results





SHG signal from liquid expanded phase





SHG signal from liquid condensed phase

We measure SHG as a function of Φ for different polarization combinations. By fitting the data with the theoretical model, we deduce all nonvanishing components of χ, and then determine the parameters related to molecular orientation.

$$\frac{\langle\sin^3\theta\rangle}{\langle\sin\theta\rangle} = \frac{\chi_{zzz}+\chi_{zyy}}{\chi_{xxx}+\chi_{xyy}+\chi_{zzz}}$$

For 8AZ3, the average tilt angle at the liquid condensed phase is ~65°. For the liquid expanded phase, θ is ~59°.

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Yuka Tabe

Electrotechnical Laboratory, Japan

For a copy of this talk and additional information, see:

http://mazur-www.harvard.edu