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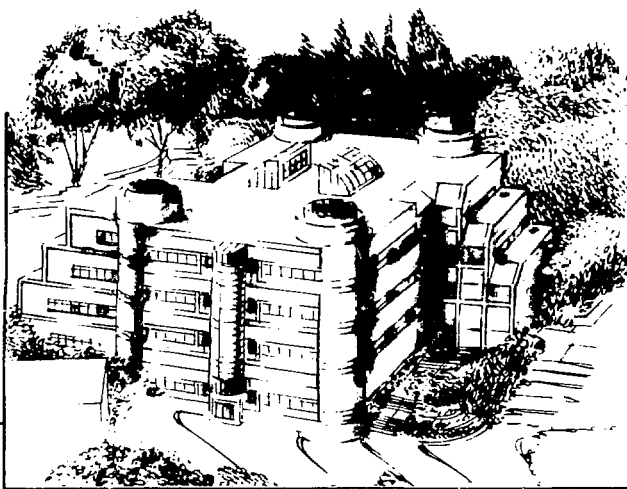# CAM _REPORT_

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**OPTICAL SECOND HARMONIC GENERATION
FROM LANGMUIR-TYPE MOLECULAR MONOLAYERS**

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Optical second harmonic generation from Langmuir-type molecular monolayers

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ABSTRACT

A single molecular layer is generally sufficient to produce observable optical second harmonic generation (SHG). Furthermore, the selection rules governing this process make the SHG from a single monolayer often stronger than that from the medium supporting the monolayer. We have studied SHG from various Langmuir-type monolayers (i.e. monolayers spread on a water surface) in the following contexts:
(1) Study of chemical reactions (e.g. polymerization) and two-dimensional phase transitions in molecular monolayers on water.
(2) Development of a new technique to evaluate optical nonlinear coefficients of organic molecules, and their relationship to the molecular structure.

1. INTRODUCTION

Insoluble molecular monolayers at liquid-gas or liquid-liquid interfaces have been the subject of numerous studies in many fields of basic and applied research. They are rather ideal for studying two-dimensional phase transitions[1] and as model systems for biological membranes. Polymerizable monolayers have been employed as ultrathin coatings in microlithography[2] and microelectronics.[3] Potential applications of organic molecules with very large optical nonlinear coefficients for optoelectronic devices[4] have set off intense efforts in finding such materials and to incorporate them in Langmuir-Blodgett type structures or thin polymeric films.

In all these cases, characterization of the structure and/or optical nonlinearity of the molecular monolayer is essential in order to understand its properties and to be able to custom design new materials and structures. For this purpose analytical tools are needed that are able to detect, nondestructively, a monolayer or less at the surface of a substrate. Though there has been some recent progress in infrared[5] and x-ray diffraction[6] analysis there is a clear need for additional experimental techniques for the study of molecular adsorbates at interfaces.

In this paper we will demonstrate how we can use optical second harmonic generation (SHG) to study the structure, optical nonlinearities and polymerization of Langmuir films of organic molecules. All the materials studied are spreadable on a water surface, which has the advantage of a low background SHG level and an easily controllable surface density of adsorbate molecules.

The effectiveness of SHG as a surface probe stems from the fact that in the electric dipole approximation SHG is forbidden in centrosymmetric media but necessarily allowed at a symmetry breaking interface or surface.[7] As an optical probe it has the advantage of a high spectral and time resolution and of being applicable to any interface accessible by light.

Second harmonic generation arises from the induced nonlinear polarization $\vec{P}(2\omega)$ given by

$$\vec{P}(2\omega) = \overleftrightarrow{\chi}^{(2)} \vec{E}(\omega) \vec{E}(\omega), \tag{1}$$

where $\overleftrightarrow{\chi}^{(2)}$ is a second order nonlinear susceptibility and $\vec{E}(\omega)$ the incident laser field. The surface nonlinear susceptibility $\overleftrightarrow{\chi}_s$ which is responsible for the SHG at an interface generally reflects the properties of the surface layer and can be written as

$$\overleftrightarrow{\chi}_s^{(2)} = \overleftrightarrow{\chi}_w^{(2)} + \overleftrightarrow{\chi}_m^{(2)} + \overleftrightarrow{\chi}_{int}^{(2)}, \tag{2}$$

where $\overleftrightarrow{\chi}_w^{(2)}$ and $\overleftrightarrow{\chi}_m^{(2)}$ are the susceptibilities of the substrate (here water) and adsorbate monolayer, respectively, and $\overleftrightarrow{\chi}_{int}^{(2)}$ includes any perturbational interaction between them. Although zero under the electric dipole approximation, a weak quadrupole effect causes $\overleftrightarrow{\chi}_w^{(2)}$ to be non-zero. For adsorbates of moderate nonlinearity the SHG signal from an adsorbate covered surface far exceeds that of the bare surface, and in those cases we may approximate $\overleftrightarrow{\chi}_s^{(2)} = \overleftrightarrow{\chi}_m^{(2)}$. When $\overleftrightarrow{\chi}_m^{(2)}$ is small, the substrate background cannot be neglected and in order to subtract it, one has to know the phase difference between $\overleftrightarrow{\chi}_s^{(2)}$ and $\overleftrightarrow{\chi}_m^{(2)}$. This was obtained by interference of both the bare and covered substrate signals with that from a

quartz plate excited by the same pump beam. In the present case we have neglected any interaction, i.e. $\overleftrightarrow{\chi}^{(2)}_{int} = 0$.

For a surface density of adsorbates N_s and neglecting local field corrections, $\overleftrightarrow{\chi}^{(2)}_m$ can be written as

$$\chi^{(2)}_{m,ijk} = N_s \langle T^{\lambda\mu\nu}_{ijk}\rangle\alpha^{(2)}_{\lambda\mu\nu} , \tag{3}$$

where $T^{\lambda\mu\nu}_{ijk}$ describes the coordinate transformation between the molecular (ζ,η,ξ) system and the lab (x,y,z) system, $\overleftrightarrow{\alpha}^{(2)}$ is the molecular nonlinear polarizability and the angular brackets $\langle \ \rangle$ denote an average over all molecular orientations.

The SH intensity generated from a monolayer covered surface in the reflected direction in air is given by[8]

$$I(2\omega) = \frac{32\pi^3\omega^2}{c^3\varepsilon(\omega)\varepsilon^{1/2}(2\omega)} \ |\vec{e}_{2\omega} \cdot \overleftrightarrow{\chi}^{(2)}_S\vec{e}_\omega\vec{e}_\omega|^2 I^2(\omega) , \tag{4}$$

where $\vec{e}_\Omega = \overleftrightarrow{L}_\Omega\hat{e}_\Omega$, with $\hat{e}_\Omega$ denoting the unit polarization vector of the field at frequency Ω and $\overleftrightarrow{L}_\Omega$ the Fresnel factor for the field, and $I(\omega)$ the laser intensity. From Eqs. (3) and (4) we see that from the SH measurements we can deduce $\chi^{(2)}_{m,ijk}$ and $\chi^{(2)}_{m,ijk}$ and in that way obtain information about the molecular orientation (via $\overleftrightarrow{T}$) and $\overleftrightarrow{\alpha}^{(2)}$. Thus, in case of a chemical reaction resulting in a change in $\overleftrightarrow{\alpha}^{(2)}$ we can monitor this reaction in situ. Unfortunately, $\overleftrightarrow{T}$ can be quite complicated for a general molecular structure, and quantitative results might be hard to obtain. However, when $\overleftrightarrow{\alpha}^{(2)}$ is dominated by a single component $\alpha^{(2)}_{\xi\xi\xi}$ along the molecular ξ-axis and the latter is randomly distributed around the surface normal, the situation is greatly simplified. For the nonvanishing components of $\overleftrightarrow{\chi}^{(2)}_m$ one can then write:[9]

$$\chi^{(2)}_{m,zzz} = N_s\langle\cos^3\theta\rangle\alpha^{(2)}_{\xi\xi\xi} \tag{5}$$

$$\chi^{(2)}_{m,zii} = \chi^{(2)}_{m,izi} = \chi^{(2)}_{m,iiz} = 1/2N_s\langle\sin^2\theta \cos\theta\rangle\alpha^{(2)}_{\xi\xi\xi} \qquad i = x,y$$

where θ is the polar angle between $\hat{\xi}$ and the surface normal $\hat{z}$. For an orientationally ordered Langmuir film the orientational distribution is expected to sharply peak in a certain direction. Approximating the distribution by a δ-function we can then find a value of θ from the ratio of $\chi^{(2)}_{m,zzz}$ and $\chi^{(2)}_{m,zii}$.[10] Consequently, from the absolute value of $\chi^{(2)}_{m,zzz}$ (measured against a standard reference) the polarizability $\alpha^{(2)}_{\xi\xi\xi}$ can be obtained.[11,12]

We have applied this technique to study the change in molecular orientation at a two-dimensional phase transition,[13] to obtain the second-order nonlinearities of a series of organic molecules[11,12] and to study the polymerization of a monolayer of monomers.[14] All the monolayers were prepared by spreading solutions of the molecules on a Langmuir trough made out of glass. A moveable barrier controls the surface density of the molecules and a platinum float (Wilhelmy plate) attached to a balance measures the surface tension. For the SHG measurements we used the frequency doubled output of a Q-switched Nd:YAG laser at 532 nm as the pump beam. The surface SH signal was calibrated against the SH signal from a thin quartz plate with a bulk nonlinearity $\chi^{(2)}_{xxx} = 2.2 \times 10^{-9}$ esu.[15] Figure 1 shows a schematic picture of the experimental apparatus. With the input and output polarizers we select different $\overleftrightarrow{\chi}^{(2)}_s$ components, whereas the color filters ensure that we only observe the SH signal from the water-air interface of interest.

2. RESULTS AND DISCUSSION

Figure 2 shows the measured surface pressure, π, as a function of the surface area per molecule, A, for a monolayer of pentadecanoic acid (PDA) on a pH $= 2$ water substrate at various temperatures.[13] The sharp kink in the middle of each π-A curve signals the onset of the transition between the so-called liquid-expanded (LE) and liquid-condensed (LC) phases. Though observed and intensively studied in many similar systems, the nature of the LE-LC transition is still controversial. Experimental data are almost exclusively limited to π-A measurements and for their interpretation various assumptions about the molecular orientation are made but have never been checked experimentally. Figure 3 shows the results of our orientational measurements for PDA at 25°C as obtained from the SHG data. In the LE phase, θ rapidly increases with increasing density N_s until the LE-LC transition is reached, whereafter it changes more slowly and linearly with N_s. Here, θ refers to the angle between the surface normal and the polar C-OH bond, which appears to make the dominant contribution to the SHG from this molecule. Intuitively, one expects this polar bond to align normal to the water (and hence the molecular chains would tilt away from the surface normal) as indeed is observed at lower densities where θ approaches 0°. When N_s increases, the steric interaction between the hydrocarbon chains of neighboring molecules tends to align them towards, and hence forcing the C-OH orientation away from, the surface normal. At $N_s = 3.1 \times 10^{14}$ cm^{-2} a phase transition to an oriented liquid occurs. By measuring θ just below the LE-LC transition (in the LE phase) we found $\theta = 45° \pm 3°$ for
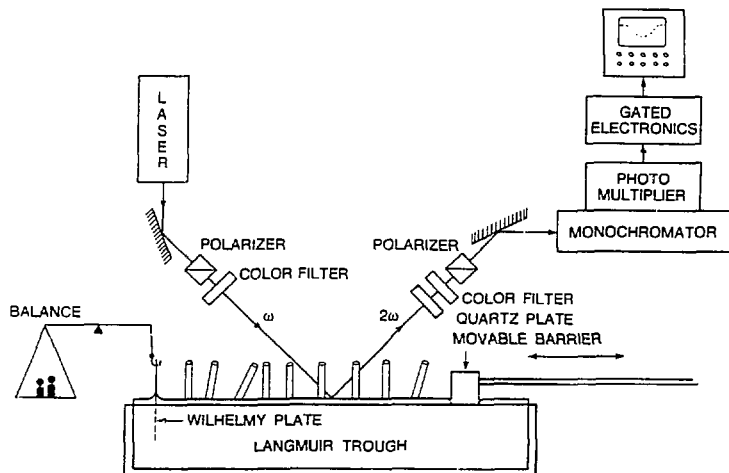
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Figure 1. Schematic picture of the experimental apparatus to observe SHG from monolayers on a water surface.

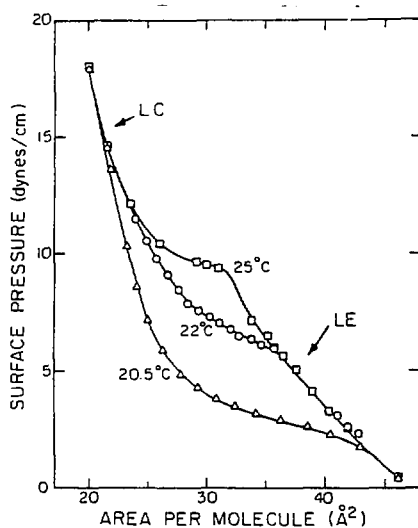
Figure 2. Surface pressure of PDA as a function of the area per molecule on a water surface of pH = 2 for various temperatures.
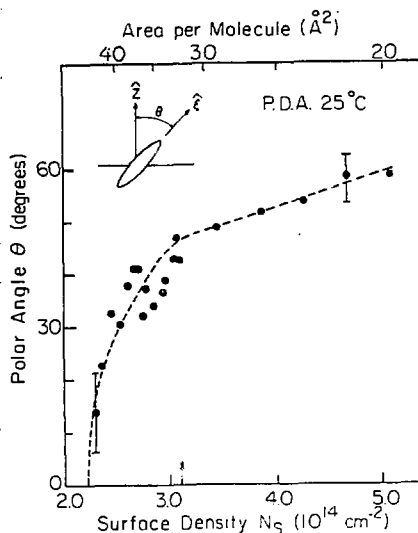
Figure 3. Tilt angle θ between the molecular axis and the surface normal as a function of the surface density of PDA on water at 25°C. The dashed line is an extrapolation through the data points.

3

all temperatures, though the transition point itself is very temperature dependent (see Fig. 2).

To measure $\bar{\alpha}^{(2)}$ of molecules, one usually relies on SHG measurements from powders[16] or dc electric field induced SHG (EFISH) from molecules in a liquid.[17] The problem with the first method is that one has to know the crystal structure and powder size distribution. With EFISH one actually measures an effective third-order nonlinear susceptibility, and to obtain $\bar{\alpha}^{(2)}$, a knowledge of solvent-solute interactions and local fields is essential. We recently introduced an alternative method by measuring SHG from an orientationally ordered monolayer on a water surface.[11] This works well for amphiphilic molecules, i.e. molecules with one hydrophobic and one hydrophilic part, and has the advantage of an easily controllable surface density of molecules and a low background. We have applied the technique on a number of cyanobiphenyl molecules $C_nH_{2n+1}(C_6H_4)_2CN$ (nCB, n = 8,9,10,12), several derivatives of this cyanobiphenyl structure, and a number of fatty acids $C_nH_{2n+1}COOH$ (nFA, n = 14,17,22). All the molecules used formed stable monolayers which were monitored by the SHG signal and the surface tension measurements and additionally checked by solubility tests.

Table I summarizes the obtained values for $\alpha_{\xi\xi\xi}^{(2)}$ and $\chi_{m,yzy}^{(2)}$. It shows that the $\alpha^{(2)}$ values of the biphenyl molecules are quite high [$\alpha^{(2)} - 2.5 \times 10^{-29}$ esu for 2-methyl-4-nitroaniline (MNA) at 1.06 μ [18]]. This high value results from the asymmetry induced in the π-electron system of the biphenyl rings by the presence of the CN group on one side and the hydrocarbon chain on the other side. The length of the latter has no effect on $\alpha^{(2)}$. However, the CN end group, which is a better electron acceptor than COOH, adds considerably to $\alpha^{(2)}$ as evidenced by the much smaller value of $\alpha^{(2)}$ for $C_8H_{17}(C_6H_4)_2COOH$ (8BCA). This is also consistent with the results for the fatty acids, where we find $\alpha^{(2)} \sim 10^{-31}$ esu, practically independent of chain length, indicating that $\alpha^{(2)}$ is dominated by the carboxylic acid group. Replacing a phenyl ring by a pyrimidine ring also causes a significant decrease in $\alpha^{(2)}$ as shown by the result for $C_7H_{15}(C_4N_2H_2)C_6H_4CN$ (7CPP). This presumably arises from an interruption of electron delocalization in the pyrimidine ring.[19] Adding another phenyl ring as in $C_5H_{11}(C_6H_4)_3CN$ (5CT) surprisingly leads to a decrease in $\alpha^{(2)}$ as well, and not to an increase as one might have expected as a result of a larger delocalized π-system.[20] We believe that this decrease may result from a nonplanar arrangement of the three phenyl rings in 5CT.

Table I. Second-order nonlinear polarizability of a number of organic molecules as determined by SHG from a monolayer using 532 nm excitation. The $\chi_{m,yzy}^{(2)}$ for the monolayer is given for a molecular density of $N_s = 3 \times 10^{14}$ cm^{-2}. θ is the angle between the molecular ξ axis and the surface normal.

Molecule		$\chi_{m,yzy}^{(2)}(10^{-16}$ esu) at $N_s = 3 \times 10^{14}$ cm^{-2}	$\theta(°)$	$\alpha_{\xi\xi\xi}^{(2)}(10^{-30}$ esu)
8CB	$C_8H_{17}(C_6H_4)_2CN$	11	71	25
9CB	$C_9H_{19}(C_6H_4)_2CN$	11	71	25
10CB	$C_{10}H_{21}(C_6H_4)_2CN$	11	71	25
12CB	$C_{12}H_{25}(C_6H_4)_2CN$	11	71	25
14FA	$C_{14}H_{29}COOH$	0.05	50	0.08
17FA	$C_{17}H_{35}COOH$	0.04	50	0.07
22FA	$C_{22}H_{45}COOH$	0.04	50	0.07
8BCA	$C_8H_{17}(C_6H_4)_2COOH$	2.8	63	6
7CPP	$C_7H_{15}(C_4N_2H_2)C_6H_4CN$	1.9	79	8
5CT	$C_5H_{11}(C_6H_4)_3CN$	3.5 (532 nm) 6 (586 nm)	60	7.5 (532 nm) 13 (586 nm)

As well as being employed in microlithography[2] and microelectronics,[3] monolayer polymerizations are of fundamental interest since their reactivity and kinetics may be studied under controllable and variable conditions of molecular separation and orientation.[21] We have used SHG to study the polymerization of two long chain monomers: vinyl stearate (VS) and octadecyl methacrylate (ODMA) both spread as a monolayer at a water/air interface. Although these materials do not have large second order nonlinearities the SHG signal can still be used to follow the extent and kinetics of polymerization undergone by the monomer, without disturbance or destruction of the monolayer film.

Table II shows the SHG results for pure water, for a water surface covered with a monomer monolayer, and for a water surface covered with a monolayer of commercially available bulk polymerized sample of the corresponding polymer.[14] The observed SHG intensities are clearly different for the various cases. Furthermore, after irradiating the monomer monolayer for two hours with a weak UV lamp under nitrogen atmosphere the signals became very similar to those of the authentic polymer monolayers, indicating an almost complete UV initiated polymerization (in the absence of UV radiation no change in

4

Table II. Relative intensities and polarization of second harmonic generation from a water surface covered with various monolayers.

System	Relative SHG Intensity[a]	Polarization Ratio[b]
Water only	100	2
Water + VS monolayer (27 $\AA^2$/molecule)	260	1.5
Water + poly VS monolayer[c] (27 $\AA^2$/monomeric unit)	170	0.5
Water + VS monolayer after UV irradiation	180	
Water + ODMA monolayer (26 $\AA^2$/molecule)	370	
Water + poly ODMA monolayer[c] (26 $\AA^2$/monomeric unit)	220	0.5
Water + ODMA monolayer after UV irradiation	250	

[a]The total output SHG signal generated using an input 532 nm laser field polarized at 45° to the plane of incidence.
[b]The ratio of s-polarized to p-polarized SHG output.
[c]Bulk polymerized polymer spread on water.

induced by either the probe laser or the ambient thermal conditions).

The observed decrease in SH intensity upon polymerization can be understood as follows: the second order optical nonlinearity mainly arises from chemical bonds in which the electron distributions are more readily distorted by optical excitations.[22] In VS and ODMA the π electrons in the double bonds are likely to dominate the nonlinearity. Since the polymerization breaks a carbon-carbon double bond, $\alpha^{(2)}$ will decrease.

In order to follow the kinetics of polymerization we also made SHG measurements during UV irradiation.[14] As shown in Fig. 4 the SHG intensity decreases continuously during the reaction. Unfortunately, due to the low values of $\alpha^{(2)}$ and the relatively small changes in SHG intensity during polymerization our measurements were not accurate enough to unequivocally distinguish between first and second order polymerization kinetics. For the case of poly VS and poly ODMA, with only one C=O bond per unit, analysis of the SHG polarization showed that this C=O bond was perpendicular to the water surface. This is in agreement with both theoretical predictions[23] and infrared analysis of monolayers and multilayers which had been transferred onto various substrates.[24-26].

OCTADECYL METHACRYLATE (ODMA)

Irradiation Time (min)

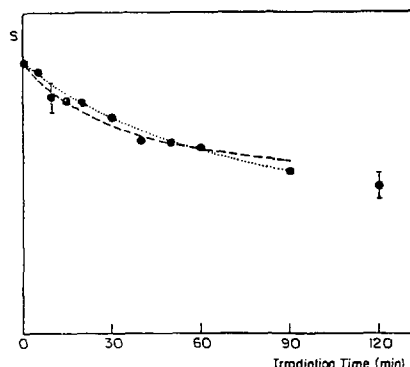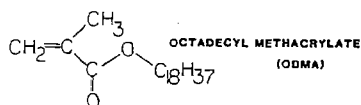Figure 4. The relative SHG intensity (S) is plotted against irradiation time for UV polymerization of ODMA. The data (o) can be fitted satisfactorily by both first order (...) and second order (---) kinetics (see the text). All experimental data points have the same uncertainty, although error bars for most points have been omitted for clarity.

In conclusion, we have shown that SHG is a very sensitive and versatile probe to study molecular monolayers at an air-water interface. As examples we have studied molecular orientation and phase transitions, polymerization reactions and molecular non linear optical coefficients.

5

3. ACKNOWLEDGEMENTS

4. REFERENCES

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