1D05

Orientational Distribution of Solute Molecules at the Air/Water Interface Determined by Polarization Second Harmonic Generation and Linear Reflection

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Liquid interfaces play important roles in chemistry and biology. The unique properties of the liquid interfaces are primarily ascribed to specific orientation of interfacial molecules brought about by anisotropy across the interface. At the air/water interface, for example, the hydrophobic and hydrophilic functional groups of interfacial solute molecules point upward to the air and downward to bulk water, respectively, which results in the orientational distribution with a finite width. However, the determination of the orientational distribution of solute molecules at liquid interfaces is technically very difficult. Many groups applied polarization second harmonic generation (SHG) to solute molecules at liquid interfaces [1,2], but polarization SHG cannot provide sufficient information to determine the orientational distribution. Very recently, we applied polarization linear reflection (LR) as well as SHG to molecules at solid surfaces, and demonstrated a new method to determine the orientational distribution of the surface molecules [3]. In the present work, we used this method for solute molecules at the air/water interface, and experimentally determined the orientational distribution functions of the solute molecules at the air/water interface.

Polarization SHG and LR measurements were done to study the orientational distribution of surface active molecules at the air/water interface. In polarization SHG measurements, SHG intensity was measured as a function of an input polarization angle, which allowed us to determine the tensor elements of the second-order nonlinear optical susceptibility of the interfacial molecules. Similarly, polarization LR measurements allowed us to determine the tensor elements of the linear optical susceptibility of the interfacial molecules. From the tensor elements of the linear and nonlinear optical susceptibilities, we successfully determined the ensemble average and standard deviation of the tilt angle of the molecules at the air/water interface. The orientational distribution functions of the molecules at the air/water interface were obtained from the ensemble average and standard deviation. Figure 1 shows the orientational distribution functions of coumarin 110 (C110), *p*-nitroaniline (PNA), and *N*,*N*-diethyl-*p*-nitroaniline (DEPNA) at the air/water interface. The experimental data (solid lines) are in good agreement with theoretical data (dashed

lines) computed by classical molecular dynamics simulations. Table 1 shows the peak position and the full width half maximum of the orientational distribution of these solute molecules at the air/water interface.

In this work, polarization SHG and polarization LR were combined to evaluate the orientational distribution of polyatomic surface active molecules at the air/water interface. Although each measurement can give an infinite number of set of orientational angles and its distributions, by combining the two measurements, unique orientational angle and distribution of the solute molecules at the air/water interface could be obtained. These results clearly show that the assumption of δ-function distribution is not relevant, and there is a substantial orientational distribution width.
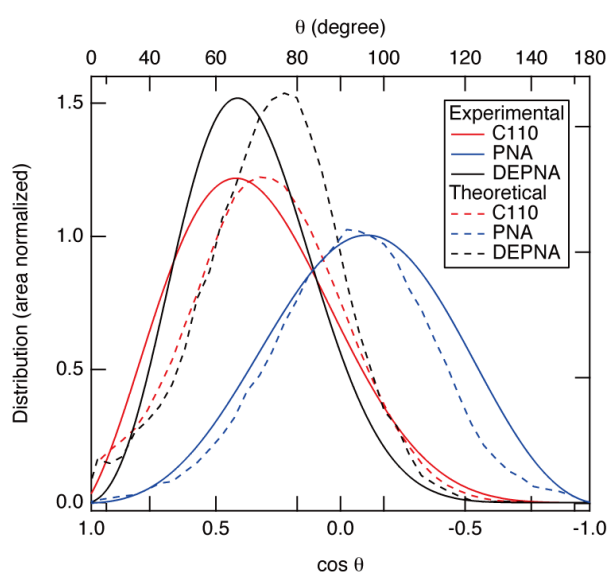

Figure 1. Orientational distributions of C110, PNA, and DEPNA at the air/water interface. Solid lines represent experimental data and dotted lines represent theoretical calculation (MD simulation).

	Experimental		Theoretical (MD)	
	Peak position	Full width Half Maximum	Peak position	Full width Half Maximum
C110	65°	53°	73°	45°
PNA	97°	60°	93°	50°
DEPNA	66°	44°	77°	40°

Table 1. Peak position and the full width half maximum of the orientational distribution of the solute molecules at the air/water interface.

(1) K. T. Nguyen, et al. *J. Am. Chem. Soc.* **132** (2010) 15112. (2) X. Zhang et al. *J. Phys. Chem.* B. **107** (2003) 3183.(3) S. Yamaguchi et al. *J. Phys. Chem. Lett.* **1** (2010) 2662.