

LETTERS

Observation of Molecular Association at Liquid/Liquid and Solid/Liquid Interfaces by Second Harmonic Generation Spectroscopy

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Received: September 26, 2000

Structural information on rhodamine dyes adsorbed at heptane/water and hydrophobized silica/water interfaces are obtained by in situ second harmonic generation (SHG) spectroscopy. The SHG spectra provide spectroscopic evidence that the molecular association occurs at both interfaces in a different manner depending on their interfacial coverage. At the heptane/water interface, an “in-plane associate” in which the electronic transition dipoles of each monomer are arranged parallel to one another appears as the sole species present. The number of monomer units making up this associate increases with the interfacial coverage while the tilt angle of the monomer unit is kept constant. By contrast, both a “sandwich dimer” and the in-plane associate are observed at the hydrophobized silica/water interface with increasing interfacial coverage. These results successfully demonstrate differences in adsorption behavior and molecular association between liquid/liquid and solid/liquid interfaces.

Interfacial phenomena arising from organic molecules adsorbed at a variety of liquid interfaces, such as solid/liquid, air/liquid and liquid/liquid interfaces, have been intensively studied by linear¹ and nonlinear optical techniques.^{2,3} However, little is known about the electronic structure of the molecules at interfaces due to experimental inaccessibility. As seen in conventional bulk chemistry, spectroscopic information on the electronic state of molecules is essential for discussing molecular processes at interfaces. In particular, molecular association and assembling at interfaces causes electronic structural changes and induces characteristic properties. The goal of our work is to obtain structural information on molecules adsorbed at the liquid/liquid and solid/liquid interfaces by measuring electronic spectra of those molecules at the actual interfaces. In the preceding paper, we have found that chemical species having different lifetimes formed at the heptane/water interface by time-resolved total internal reflection (TIR) fluorescence spectroscopy.⁴ In this

study, we report the electronic spectra of rhodamine dyes adsorbed at two hydrophobic interfaces, that is, the heptane/water interface (L/L) and the hydrophobized silica/water interface (S/L) using the resonance effect of second harmonic generation (SHG).

The SHG has received much attention in recent years as an experimental method for the investigation of interfacial phenomena,² due to its inherent sensitivity toward molecules at interfaces.⁵ However, only a few attempts have been made so far for the spectroscopic application of SHG to probe the electronic structure of molecules adsorbed at the L/L⁶ and S/L.^{7,8} The SHG signal is remarkably enhanced when the incident laser wavelength, and/or its second harmonic wavelength, is in resonance with an electronic transition between molecular states.^{9–14} By measuring the SHG signal as a function of the incident laser wavelength, electronic spectra of interfacial species can be obtained.¹⁵ This SHG spectroscopy is more powerful than linear spectroscopies using an evanescent wave under TIR with respect to the interfacial sensitivity. The SHG measure-

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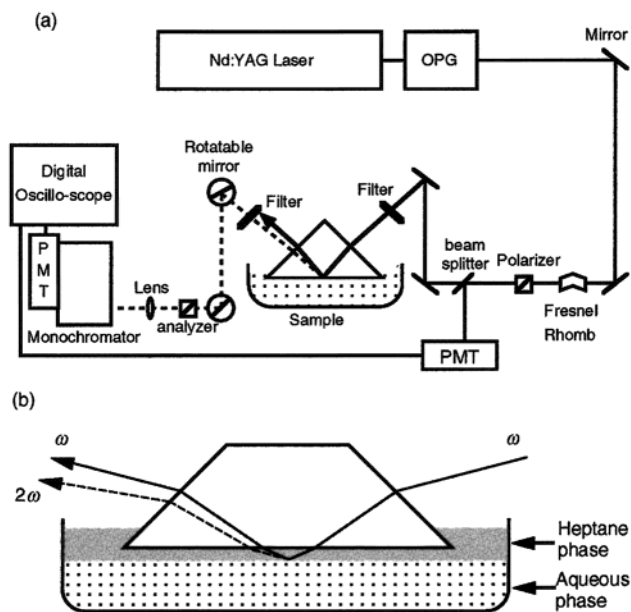


Figure 1. Experimental setup for TIR-SHG spectroscopy at the (a) TMS-modified silica/water and (b) heptane/water interface.

ments under TIR yield much higher sensitivity than normal SHG measurements due to relatively high Frensel factors.^{16–19} Using TIR-SHG spectroscopy we obtained the electronic spectra of rhodamine B (RB) and rhodamine 110 (R110) adsorbed at the L/L as a function of bulk concentrations of these dyes in a water phase containing 0.1 M HCl. The experimental results provide the first spectroscopic evidence for molecular association of rhodamine dyes at the L/L. Moreover, differences in the structures of molecular associates at the L/L and S/L are clearly demonstrated.

The experimental setup for the TIR-SHG spectroscopy is shown in Figure 1. Tunable visible light as a fundamental light was generated using an optical parametric generator (OPG; EKSPLA model 410VIR) pumped by the third harmonic output of a Q-switched Nd:YAG laser (EKSPLA model PL2143B), covering the spectral region of 420–680 nm with 30 ps pulse duration at a repetition rate of 10 Hz. The power of the fundamental light was typically 0.6 mJ/cm². The polarization of the fundamental light was controlled using a Fresnel Rhomb. To achieve the TIR condition, the fundamental light was directed onto the interface through a high-index medium, i.e., heptane or the fused silica hydrophobized with trimethylchlorosilane (TMS) using the standard modification technique.^{20,21} In the case of L/L, the fundamental light was introduced to the entrance face of a quartz dove prism, and refracted into the heptane phase as shown in Figure 1b. The fundamental light was incident on the L/L and S/L at angles of 74.3° and 66.4°, respectively. The SH light generated from the interface, which direction depended on its wavelength, was consistently guided to an analyzer and a detection system using a set of two rotatable mirrors which were synchronously controlled by a computer. The residual fundamental light and unnecessary emissions from the interface were eliminated by a combinations of short pass filters and a monochromator. The SH light and 1% of the fundamental light were simultaneously detected using two photomultiplier tubes and a digital storage oscilloscope. Data points were collected every 3 nm by averaging 30 pulses. To correct wavelength dependence of the OPG output, the SH intensity was divided by the square of the fundamental intensity. The processed data were plotted against the wavelength of fundamental light, and thus, the SHG spectra were obtained. The peak positions in the

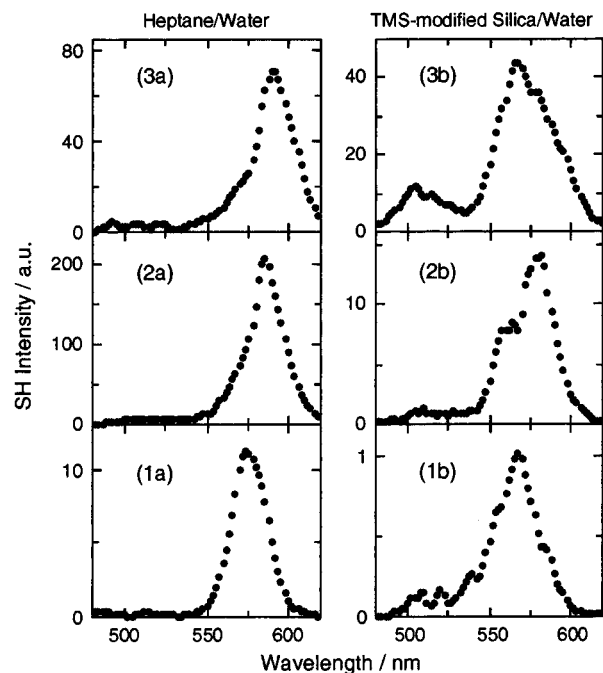


Figure 2. SHG spectra of RB at the (a) heptane/water and (b) TMS-modified silica/water interfaces for various concentrations of RB in the bulk water phase: (1a) 1.0×10^{-7} M, (2a) 1.0×10^{-4} M, (3a) 1.0×10^{-3} M, (1b) 5.0×10^{-6} M, (2b) 1.0×10^{-4} M, (3b) 1.0×10^{-3} M. The spectra were taken using the s-polarized fundamental input and p-polarized SHG output.

spectrum were determined by fitting to the combination of Lorentzian functions based on the two state model.¹³

The SHG spectra acquired from the L/L at various concentrations of RB in the water phase are shown on the left-half of Figure 2. The SHG spectra show a single major peak, which is assigned to a resonance with the S_0 – S_1 electronic transition of RB. The wavelength of the peak maximum is red-shifted from 575 to 592 nm as the concentration of RB in the water phase increases from 1.0×10^{-7} to 1.0×10^{-3} M. The increase of the bulk concentration of RB molecules leads to an increase of the interfacial coverage of RB molecules as discussed later. The observed red-shift reflects the increase in the coverage of RB molecules at the L/L. This observation reveals that there is a dipole–dipole interaction of RB molecules adsorbed at the interface. Considering the dipole–dipole interaction between monomers, we can ascribe the spectral red shift to the formation of “in-plane associates” in which the electronic transition dipoles of each monomer are arranged parallel to one another based on a simple molecular exciton theory.^{22,23} We can consider two possible causes for the coverage-dependent red shifts, that is, changes in molecular orientation of the in-plane associate and the increase in the number of the monomer units making up the associate.^{24,25}

The simple molecular exciton theory suggests that the transition dipoles of the monomer unit are parallel to that of the in-plane associate.²² If the associates are homogeneously formed at the interface, average orientation of a monomer unit with respect to the interface normal can be discussed from the polarization property of the SH light generated from the associates. The input polarization dependence of the p-polarized and s-polarized SH light generated from RB at the L/L is shown in Figure 3 for the concentrations of 1.0×10^{-7} , 2.0×10^{-7} , and 1.0×10^{-5} M. Each polarization curve can be fitted well to the theory¹⁶ and normalized to a maximum SH intensity obtained from theoretical fitting of the p-polarized SH responses.

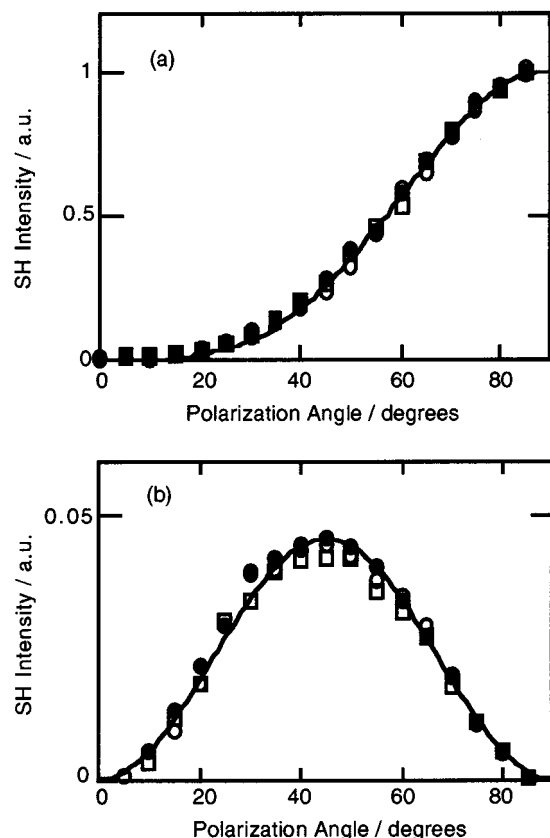


Figure 3. Input polarization dependence of the (a) p-polarized and (b) s-polarized SH light from RB at the heptane/water interface: (open circles) 1.0×10^{-7} M, (open squares) 2.0×10^{-7} M, (filled circles) 1.0×10^{-5} M. Each polarization curve was normalized to a maximum SH intensity obtained from theoretical fitting of the p-polarized SH responses. The input polarization angle is defined as 0° for p-polarized fundamental light and 90° for s-polarized fundamental light. The solid lines at 1.0×10^{-7} M are the theoretical fits used to determine the relative values of three nonzero elements of the surface susceptibility.

The sets of p- and s-polarization curves in Figure 3 do not show any significant difference, suggesting that a molecular orientational angle of RB does not change when the concentration of RB is below 1.0×10^{-5} M. The relative values of three nonzero elements of the surface susceptibility, which determine the molecular orientation,^{26,27} are obtained from the fitting.²⁸ The tilt angle between the transition dipole parallel to the long axis of the xantane ring and the interface normal is calculated as ca. 70° under assumptions of a narrow distribution in the tilt angles and a random orientation of the molecular plane. This result suggests that the molecular orientation of the monomer unit making up the associate is independent of the coverage. We conclude that the coverage-dependent red shifts can be mainly attributed to the increase in the number of monomer units. The resonance peak observed at 575 nm (spectrum 1a), which is red-shifted compared with the peak maximum in the absorption spectrum of RB monomer in a weak polar medium such as poly(methacrylic acid) (563 nm)²⁹ and ethylene glycol (562 nm),³⁰ suggests that the association takes place at the L/L containing even 1.0×10^{-7} M RB in the water phase. The coverage-dependent red shifts of the SHG spectra are also observed for R110 at the L/L. Thus, in-plane association will be a characteristic feature of rhodamine dyes at the L/L.

To obtain further structural insight into the in-plane associates at the L/L, we compare adsorption isotherms for RB and R110. The adsorption isotherms are obtained by plotting the square root of the SH intensities at peak maximum against the bulk

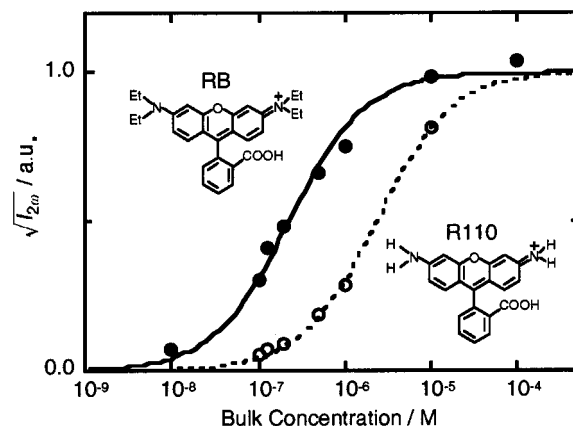


Figure 4. Adsorption isotherms of RB (●) and R110 (○) for the heptane/water interface fitted by a Langmuir model. The SH intensities were normalized to a maximum value obtained by theoretical fitting.

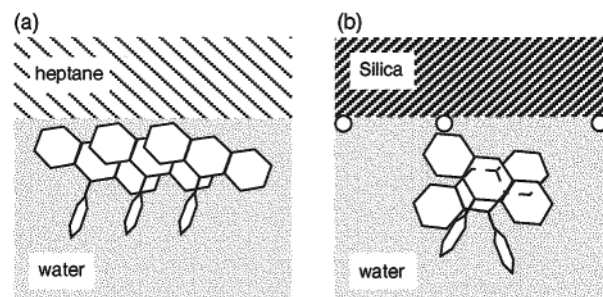


Figure 5. Schematic illustration of the rhodamine dyes at the interfaces: (a) the in-plane associate at the heptane/water interface; (b) the sandwich dimer at the TMS-modified silica/water interface.

concentrations of the dye. The value of the Y-axis equivalent to the interfacial coverage³¹ of the adsorbates increases with the bulk concentration as shown in Figure 4. The results can be fitted well by a Langmuir adsorption isotherm, where the adsorption coefficient, K_{ads} , can be evaluated by a reciprocal of the concentration corresponding to the coverage of 0.5. The K_{ads} values for RB and R110 are estimated as 4.9×10^6 and 4.4×10^5 M⁻¹, respectively. The difference in the K_{ads} values between RB and R110 can be ascribed to the hydrophobicity of these dyes, since R110 has no alkyl chains in the amino groups of the xantane moiety and RB has two diethylamino groups (see structural formulas in Figure 4). The hydrophobicity of xantane moiety of RB should be higher than that of R110. The present results reveal that the hydrophobic interaction of the xantane moiety of rhodamine dye with heptane molecules is responsible for their adsorption at the L/L. From the above discussions, the rhodamine dyes adsorb and form the in-plane associates at the L/L, pointing the xantane moiety toward the heptane phase with a tilt angle as shown schematically in Figure 5a.

The structure of the associates at the L/L shown in Figure 5a differs from that in a bulk solution where existence of a sandwich dimer^{32,33} dominates, and the dimer shows a blue-shifted absorption.³⁴ As seen in Figure 2 (3a), it is noteworthy that the in-plane associates of RB exhibiting the red spectral shifts are predominant at the L/L despite the presence of the sandwich dimers in the water phase. By contrast, molecular association at the S/L is different from that at the L/L. The concentration dependence of SHG spectra of RB at the S/L is shown on the right-half of Figure 2. From Figures 1b, 2b, and 3b, three kinds of peaks can be recognized in the SHG spectra, and their relative intensities vary depending on the concentration of RB in bulk solution. At 5×10^{-6} M, an intense peak appears

at 565 nm as shown in the spectrum (1b). Since this wavelength is close to that of the peak maximum in the absorption spectrum of RB monomer in a weak polar medium, the intense peak can be ascribed to a monomeric species adsorbed at the S/L. When the concentration of RB is 1.0×10^{-4} M (2b), a red-shifted peak appears at 578 nm, similar to the spectrum measured at the L/L, and corresponds to the in-plane associate. At higher concentration, 1.0×10^{-3} M (3b), a blue-shifted peak is observed at 513 nm, and the red-shifted peak remains as a shoulder in the spectrum. The observation of a blue-shifted peak means formation of a dimeric species that has a sandwich type structure, as is usually observed in a concentrated bulk aqueous solution. When neat silica is used instead of the hydrophobized one, the blue-shifted peak cannot be observed at this concentration. The sandwich dimer seems to adsorb onto a TMS group bound to the silica surface as shown schematically in Figure 5b, reflecting the presence of dimers in the water phase. Therefore, the observation of both blue- and red-shifted peaks shows that there are at least two kinds of associates at the S/L.

The difference in the molecular structures of associates at the L/L and S/L was clearly demonstrated by SHG spectroscopy. The chemical species adsorbed at the S/L had different structures, that is, the in-plane associate and the sandwich dimer. In contrast to the S/L, only an in-plane associate could be recognized at the L/L, and formation of a sandwich dimer was suppressed, although the sandwich dimer was dominant in a bulk solution. The hydrophobic property arising from heptane molecules at the L/L would be crucial for inhibition of the sandwich type dimerization. The adsorbate could be considered to be more easily mobilized at the L/L than the S/L, and this high mobility would function favorably for the growth of the in-plane associate while keeping the tilt angle of the monomer unit constant.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (A) No. 11304054 from the Ministry of Education, Science, Sports, and Culture, Japan.

Note Added after ASAP Posting

This Letter was posted ASAP on 12/5/00 with a minor typographical error in the Figure 5 caption. The correct version was posted on 12/11/00.

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