pH-Dependent Water Structure at a Quartz Surface Modified with an Amino-Terminated Monolayer Studied by Sum Frequency Generation (SFG)

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The structures of water at the interfaces between a fused quartz surface modified by a self-assembled monolayer (SAM) of an amino-terminated silane molecule and electrolyte solutions of various pHs were investigated using sum frequency generation (SFG) vibrational spectroscopy. The structure of the interfacial water significantly depended on the solution pH. The effect of the electric double layer generated by the protonation of the amino groups in the SAM and unreacted silanol groups on the quartz substrate is considered to be responsible for the pH-dependence.

Figure 1. The schematic arrangement for the SFG system used in the study.

The interfacial water molecules play prominent roles in many chemical, physical and biological processes. Although many theoretical studies about the structural properties of water molecules on various interfaces have been carried out, the experimental investigations on the structure of water have been mainly done in vapor or bulk aqueous media[1–3] due to a lack of effective experimental probes.[4]

As a second-order nonlinear optical process, the sum frequency generation (SFG) does not occur in media with inversion symmetry.[5] In the IR–visible SFG measurement, a visible laser beam (ω_1) and a tunable infrared laser beam (ω_2) are overlapped at an interface and the SFG signal is measured by scanning ω_2 while keeping ω_1 constant. The intensity of SFG is enhanced when ω_2 is equal to the vibration levels of the molecules at the interface.

Thus, one can obtain surface-specific vibrational spectra of interfaces where the inversion symmetry is broken which is not possible by the traditional vibrational spectroscopy such as IR and Raman scattering. SFG spectroscopy has been recently employed in a number of investigations on the structure of water at solid–liquid,[6,7] liquid–vapor[7–10] and liquid–liquid interfaces.[11] It is very important to clarify the structure of water on the surface of molecular layers with biologically active groups because water plays very important roles in biological process. In the present study, the structure of water at a fused quartz surface modified by a self-assembled monolayer (SAM) with amino groups was investigated using SFG spectroscopy as a function of solution pH to evaluate the water structure at biological interfaces with amino group moieties.

Figure 1 schematically shows the arrangement for the SFG measurement used in the present study. A picosecond Nd: YAG laser (PL2143B, EKSPLA) was employed to pump an OPG/OPA/ DFG system, which generates tunable infrared radiation from 2.3 to 8.5 μm. The second harmonic output (532 nm) from the Nd:YAG laser was used as visible light.

A fused quartz prism with a hemi-cylindrical shape (d=25 mm, l=25 mm, Pier Optics, Japan) was used as the substrate. The quartz prism was thoroughly cleaned by chromic acid solution and then rinsed with Milli-Q water several times. The
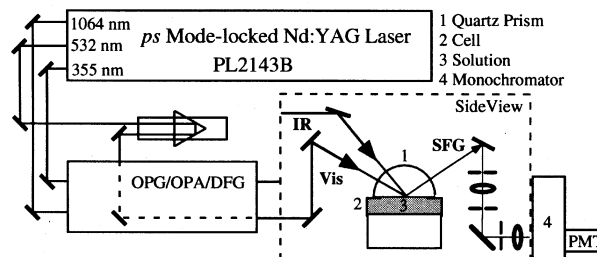
silane molecule of *N*-(2-aminoethyl)-3-aminopropyl-trimethoxysilane ($H_2N(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$: AAS) was used as received from Gelest Inc. The SAM of AAS was constructed by immersing the quartz substrate into a 1% AAS ethanol solution for 2 h. After being rinsed in a sonication bath of ethanol and that of Milli-Q water, the sample was baked at 110°C for 60 min.[12] The other chemicals were Suprapure reagents from Wako Pure Chemicals and were used without further purification.

The flat face of the quartz prism was in contact with the electrolyte solution and the infrared and visible beams were overlapped at the interface with incident angles of 70 and 50 degrees, respectively as shown in Figure 1. Polarization combinations of SFG, visible and IR lights were *s, s* and *p,* respectively.

Figure 2 shows the SFG spectra of an AAS monolayer on the fused quartz in phosphate buffer solutions of various pHs (ionic strength = 10 mM) in the region of 2700–3800 cm^{-1}. The SFG spectra show three resonance bands around 2900 (Peak 1), 3200 (Peak 2), and 3450 cm^{-1} (Peak 3). It is clear that the intensity and shape of the SFG spectra obtained at the AAS-modified quartz surface changed dramatically with pH.

The bands at 3200 and 3450 cm^{-1} were attributed to the O-H stretching of water. The broad band at ~3200 cm^{-1} can be assigned to the symmetric O–H stretching (ν_1) of tetrahedrally coordinated water molecules[13,14] as a peak at the same position is observed in the infrared and Raman spectra of crystalline ice.[1] The broad band around 3450 cm^{-1} can be attributed to the asymmetric O–H stretching (ν_3) of water molecules in a more random arrangement as the peak position agrees with that of an IR band observed in liquid water.[13,14] The intensity ratio between the two peaks can be considered as an index of the order of the interfacial water.[6] These peaks are very broad due to the strong coupling between the vibration of neighboring water molecules and Fermi resonance with the overtone of the HOH bending mode (ν_2).[1]

The small peak that appeared at ~2900 cm^{-1} was assigned to the C–H stretching vibration of the methylene (CH_2) group in the AAS monolayer. As previously reported, only the C–H stretching transitions of the terminal methyl (CH_3) are allowed SFG bands in the highly ordered SAMs such as octadecyltri-
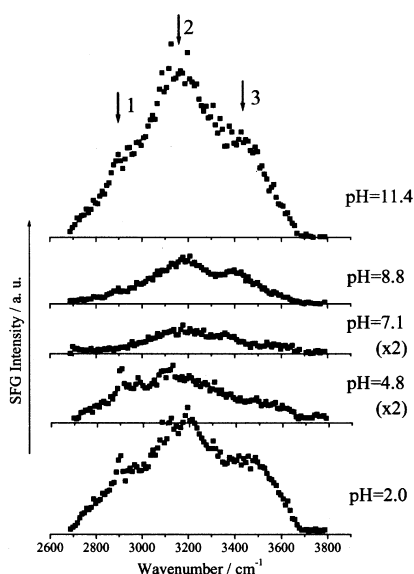
Figure 2. SFG spectra of an AAS-modified fused quartz in phosphate buffer solution of various pHs.

chlorsilane (OTS)[15] because if the CH_2 groups are in the *all-trans* conformation, the C–H transitions are SFG inactive due to the symmetry restriction. A weak C–H stretching band of the CH_2 group observed in the SFG spectra suggests the existence of some *gauche* defects in the AAS monolayer. The intensity of the C–H band was enhanced as a result of the interference with the strong resonance bands in the O–H stretching region. The SFG bands of the N–H stretching in the AAS monolayer were not clearly observed in the spectra. This band was not observed even in air. One possible reason why the N–H band was not observed is that the direction of the N–H bond is parallel to the surface. The N–H band is SFG inactive in this situation. The following discussions concentrated on the O–H bands.

The intensity of the SFG peak at 3200 cm^{-1} was stronger than that at 3450 cm^{-1} in all the solutions investigated. The strong peak at 3200 cm^{-1} demonstrates that water molecules at the interface are arranged in a more ordered structure.

The intensity of the SFG spectrum of the AAS-modified quartz at pH = 2 (Figure 2) was stronger than that of the same surface in the solution of intermediate pH and that of the bare quartz surface in the solution of the same pH. This behavior should be attributed to the chemical properties of the AAS monolayer in the solution. In acidic solution, amino groups of the AAS monolayer are fully protonated and an electric double layer is expected to form on the interface between the quartz and solution. The water molecules in the double layer are immobilized and orientated. The hydration process of the positively charged amino groups in the AAS monolayer on the quartz surface is expected to arrange a larger number of interfacial water molecules in acidic solution than those in neutral solution thus leading to a higher SFG intensity.

The protonated amino groups in the AAS monolayer take on a neutral form when the pH is higher than its pKa. The electric field inside the double layer induced by positively charged amino groups will become weaker with the increase in pH and, therefore, the intensity of the SFG spectra of the interfacial water was expected to become weak as the pH increases. This

was experimentally observed at pH = 4.8 and 7.1 (Figure 2). The pKa of the amino group in solution is much higher but becomes smaller by forming the SAM as recently reported.[16] Surprisingly, however, the intensity of the SFG spectrum of the AAS monolayer became even stronger in a solution of much higher pH (= 11.4). This fact cannot be explained by considering only the chemical nature of the amino group. Du et al. reported that the intensity of the SFG spectra of water on the bare quartz surface in alkaline solution was stronger than that in acidic solution as a result of the deprotonation of the silanol (Si-OH) group, resulting in a negative charge on the quartz surface.[6] Since the intensity and shape of the SFG spectrum of the AAS-modified quartz at pH = 11.4 was comparable to that of the bare quartz but much stronger than that of the quartz covered with the OTS monolayer in the same solution, a similar effect by the deprotonation of unreacted Si-OH species on the AAS-modified quartz surface may be expected. Therefore, this behavior should be attributed to the larger number of defects and lower coverage of the AAS monolayer than those of the OTS monolayer.

Detailed measurements including the dependence of coverage and ionic strength, determinations of orientation of water molecules and exact pKa of the AAS-modified quartz surface are in progress.

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