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Potential Dependent Structure of the Interfacial Water on the Gold Electrode

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Abstract

Doubly-tunable Sum-Frequency Generation (SFG) spectra demonstrate that the water molecules at gold/electrolyte interface change their orientation with applied potential. At negative potentials, water molecules in the double layer align with their oxygen atom pointing to the solution. As potential became positive to be close to the potential of zero charge (pzc), the SFG signal decreased, suggesting the OH groups of the water molecule are either in random orientation or parallel to the electrode. As potential became more positive than the pzc, the SFG signal increased again with the oxygen-up orientation same as in the negative potential region, indicating that water molecules interact with the adsorbed sulfate anions. The peak position of the SFG spectra indicates a relatively disordered state of water molecules at the gold electrode surface, in contrast to the previously observed ice-like structure of water at electrolyte/oxide interfaces.

Keywords: sum frequency generation, electrochemical methods, surface structure, water, metal-electrolyte interfaces.

Interfacial water molecules play prominent roles in many physical, chemical and biological processes. Although many theoretical studies on the structure of water molecules at various interfaces are available, most of the experimental investigations on the water structure have been carried out in the vapor or bulk aqueous phase [1-3] due to the lack of an effective experimental probe for interfacial study. The structure of the electrode/solution interface under potential control is one of the most important issues in electrochemistry [4] and many spectroscopic techniques such as surface enhanced Raman spectroscopy (SERS)[5, 6], surface infrared spectroscopy[7], surface enhanced infrared spectroscopy (SEIRAS)[8, 9] and X-ray diffraction [10] have been used to investigate the water structure at the electrode/electrolyte interface during the last two decades. X-ray diffraction study, for example, suggested that the water molecules at a silver electrode in NaF solution flipped their dipole when the electrode potential was changed from negative to positive[10].

Vibrational spectroscopy enables not only to determine the orientation of water dipole but also to identify the hydrogen-bonding state of water, i.e., order of water structure. Recently, Sum frequency generation (SFG) spectroscopy [11-13] has emerged as a powerful vibrational spectroscopy to investigate the structures of water molecules at buried interfaces. As SFG is a second order non-linear optical process, which is forbidden in the bulk of a centro-symmetric electrolyte and electrode, the analysis depth of SFG is intrinsically limited to the layer of molecules that are aligned at the interface, in contrast to IR spectroscopy in which signal from bulk water dominates. Furthermore, SFG is free from the ambiguity associated to the choice of reference spectrum and can avoid the necessity of working with a rough electrode as required for SEIRAS and SERS. Actually, SFG has successfully been applied to investigate the structure of the water at liquid/gas and liquid/solid interfaces[14-17]. However, the strong absorption of the IR by both the metal electrode and the bulk water makes the detection of the interfacial water at a smooth electrode difficult[18]. Although SFG in internal reflection configuration with ultrathin metal film [19, 20] can avoid the IR absorption, the existence of the overwhelming nonresonant signal from the gold film still prevents the detection of the weak signal from the interfacial water.

In the present study, we employed a doubly tunable laser system [21-23] for the SFG measurement in internal reflection at the gold electrode/electrolyte interface so that the strong nonresonant contribution from the gold can considerably be suppressed and the resonant signal from the water molecules can be emphasized. At negative potentials, the water molecules in the double layer align with their oxygen atom pointing to the solution. As potential became positive to be close to the potential of zero charge (pzc), the OH groups of the water molecules are either in random orientation or parallel to the electrode. As potential became more positive than the pzc, the SFG signal increased again. Quantitative analysis of the SFG spectra, which takes into account the phase angle between the resonant and nonresonant contributions, suggests that the water molecules at the positive potential takes the oxygen-up orientation as same as in the negative potential region. The oxygen-up orientation at both negative and positive potential regions contrasts with the simple flip-flop behavior of the water molecules reported previously[10, 24], indicating the water molecules interact with the adsorbed sulfate anions at the positive potentials.

The gold films of 25 nm thick were evaporated on IR-grade fused quartz plates with a 5 nm titanium buffer layer in a vacuum chamber of 2×10^{-6} Torr. The deposition rate and substrate temperature were kept at less than 0.01 nm/s and 200 ℃, respectively, in order to obtain a flat film. A Pt foil and Ag/AgCl electrode were used as a counter and reference electrodes, respectively. All the potentials in this paper are quoted against Ag/AgCl. A cyclic voltammogram of the gold film demonstrated that the surface of the gold film was dominated by wide (111) domains.

The doubly tunable laser system [21, 22] consists of two OPO's synchronously pumped by a mode-locked Nd:YAG laser (25 Hz). The two OPOs built around a $LiNbO_3$ and a BBO crystal generate 9 ps pulses tunable from 2.5 to 4 μm (bandwidth: 2 cm^{-1}) and from 460 to 700 nm (bandwidth: 3 cm^{-1}) with output powers of 10 mW and 30 mW, respectively. The incident angles of the quasi co-linear visible and infrared beams onto the cell window are 55° and 65°, respectively. About 5 % of the incident IR and visible beam power is used to generate a reference SFG signal in a

ZnS polycrystalline to compensate for any fluctuation of the infrared beam power. The polarizations of the SFG, visible and IR beams are s, s and p, respectively.

Since the strong nonresonant contribution from the gold due to the gold d-s inter-band transition centered at 550 nm is the reason for a relatively low signal/noise ratio in the SFG spectra measured at 532 nm excitation, the suppression of the nonresonant contribution and the emphasis of the resonant contribution can be expected when the visible wavelength is tuned outside the inter-band transition[25]. The optimum wavelength for the SFG measurements of the gold surface was determined by examining the SFG spectra of the ODT monolayer adsorbed on a 30-nm thick gold film using the internal reflection geometry with various visible wavelengths in the region between 470 and 700 nm. The resonance to non-resonance ratio for the peak at 2880 cm^{-1} attributed to the CH_3 symmetric stretching was lowest when 532 nm light was used. The highest ratio was obtained for the visible wavelength of 470 nm as about 0.5, which was considered to be high enough to resolve the OH bands. Thus, we employed the visible wavelength of 470 nm to observe the OH bands of the water on the gold electrode.

Figure 1(a)-(d) shows SFG spectra in the OH stretching region obtained at the gold electrode in 10 mM sulfuric acid solution at various electrode potentials using the visible wavelength of 470 nm. A broad band centered at around 3500 cm^{-1} was observed with a shoulder around 3250 cm^{-1}. The signal in the 3000-3100 cm^{-1} region was rather constant and seemed to show the level of the non-resonant background. The SFG intensity was the lowest at +0.6 V and the highest at –0.2 V.

To confirm that the broad band around 3500 cm^{-1} is really due to the OH vibration of water molecules, the experiment was repeated by replacing H_2O by D_2O (99.8 %) in the electrolyte solution. The SFG spectra obtained in the D_2O solution (Fig. 1e) showed neither a clear peak nor clear potential dependence. The fact that the SFG spectra in the H_2O solution showed a large potential dependence while that in the D_2O solution showed no peak and did not change with potential clearly indicates that the broad band observed in the spectra is attributed to the OH stretching of the interfacial water molecules. Although an investigation in the OD vibration region should be ideal to confirm the potential dependent water structure, the limited transparency range of the fused quartz plate prevents the detection of the OD bands near 4 μm.

The experimental data were fitted to the following equation [24, 26] assuming two peaks around 3500 cm^{-1} and 3250 cm^{-1}, which are known to be of “liquid-like water”, representing the asymmetric OH stretching (ν_3) of the asymmetrically hydrogen bonded water molecules in a disordered arrangement and of “ice-like water”, representing the symmetric OH stretching (ν_1) of tetrahedrally coordinated water molecules, respectively[24, 27].

$$I_{SFG} = \left| \sum_n \frac{A_n}{\omega_{IR} - \omega_n + i\Gamma} + \left|\chi_{NR}^{(2)}\right| e^{i\varepsilon} \right|^2 \qquad (1)$$

where ω_{IR} is the frequency of the incident IR light and χ_{NR}, ε, A_n and Γ_n are the vibrationally-nonresonant component, the phase angle between the resonant and nonresonant contributions, the strength and damping constant of the surface vibration or rotation mode with frequency ω_n, respectively.

The strengths of the peak at 3500 cm^{-1} (A_{3500}) were plotted against the applied potential in Figure 2. The intensity ratio between the two peaks at 3500 cm^{-1} and 3250 cm^{-1} can be considered as an indicator of the order of the interfacial water[24].

The spectrum obtained at –0.2 V (Fig. 1a) resembled the SEIRA spectra reported by Ataka et al. [8, 9]. The intensity of the peak at 3500 cm^{-1} was higher than that of 3250 cm^{-1} in contrast to the previously reported results observed at electrolyte/oxides interface where the peak at 3250 cm^{-1} corresponding to the ice-like structure of water was higher than that of 3250 cm^{-1}[24, 26]. This result indicates that the interfacial water molecules at the negatively charged gold electrode are rather weakly hydrogen bonded, i.e., disordered. This is also in good agreement with the molecular dynamics simulation for electric double layers, which suggests the lack of hydrogen bonding of the water molecules in the first layer on the metal electrode[3]. The relatively large SFG intensity at the negative potential region suggests that layers of water molecules align rather perpendicular to the surface with their oxygen atom pointing to the solution.

The SFG intensity was the lowest at +0.6 V (Fig. 1c), suggesting either the structure of the interfacial water molecules was more random or the direction of the dipole orientation was closer to parallel to the surface, i.e., water molecules were less SFG active, at this potential than those at other potentials. The SEIRAS study [8, 9] as well as molecular simulation [28] also suggested that the dipole of the interfacial water molecules was parallel to the surface at around the pzc, which is reported to be about 0.3 V in a solution containing 0.05 M $KClO_4$, 0.02 M $HClO_4$ and 5 mM K_2SO_4[29].

As potential became more positive, the SFG intensity increased further, showing water molecules align rather perpendicular to the surface again. It is noteworthy that SFG spectrum gives direct information for the absolute orientation of molecules at an interface, which cannot be obtained by IR or Raman spectroscopy. If the direction of the dipole of interfacial water is changed, the phase angle between the resonant and nonresonant contributions, ε, should be also changed by π. Thus, the upward SFG peak should become a downward dip if the interfacial water molecules flip when the potential was changed from negative to positive across the pzc because the flipping of interfacial water molecules gives the inverse phase relative to the nonresonant contribution from the gold[24, 26, 30, 31]. It is clearly demonstrated in Fig. 3 where experimental result obtained at –0.2 V with a fitting curve (ε = 100 deg.), and the simulated SFG spectrum using the same parameters except for the ε, which is changed by π (ε = –80 deg.) are shown. The fact that the relative phase did not change in all the potential regions as shown in Fig.1 (a)-(d) indicates that the interfacial water molecules did not flip within this potential region and interfacial water molecules still point their oxygen atom to the solution even at potentials more positive than the pzc. This is in contrast to the previous report by Toney et al. They showed that the position of the oxygen atom of the water molecule was different for the negative and positive potentials at the Ag (111) electrode surface in NaF solution, where the specific adsorption of Na^+ and F^- ions are negligible, based on an X-ray scattering and suggested that the interfacial water molecules flipped[10].

The present behavior can be explained by taking the existence of an adlayer of the sulfate anions into account. It is well known that sulfate anions are adsorbed on a gold electrode at potentials more positive than 0.2 V and form an ordered adlayer at 0.9 V[29, 32, 33]. Shi et al. showed the adsorbed species from a solution containing 0.05 M $KClO_4$, 0.02 M $HClO_4$ and 5 mM K_2SO_4 is sulfate, SO_4^{2-}, not bisulfate, HSO_4^-, and net charge of the sulfate adlayer/electrode is negative based on the chronocoulmetric measurement[29]. Thus, the water molecules orient with their hydrogen atoms pointing to the surface, i.e., oxygen-up orientation in the positive potential region due to the interaction between water molecules and adsorbed sulfate anions. Actually, recent electrochemical scanning tunneling microscopy (EC-STM)[34] and SEIRAS[9] investigations suggested that water molecules are incorporated into the ordered adlayer of sulfate anions at the positively charged noble metal electrode in a sulfuric acid solution, although these technique cannot provide the information of the absolute orientation of the water molecules. The present results demonstrate that the orientation of water molecules at the electrode depends not on the charge of the electrode itself but on the net charge and the structure of the adlayer/electrode.

In conclusion, the potential dependent SFG spectra of the interfacial water at the gold electrode/electrolyte solution interface were obtained for the first time by employing 470 nm as the visible input light. The experiment with heavy water confirmed that the bands observed in the OH stretching region came from the interfacial water molecules. The orientation of water molecules at the electrode was found to depend not on the charge of the electrode itself but on the net charge and the structure of the adlayer/electrode. Potential dependent orientation change of water molecules are schematically shown in Fig. 4. At potentials more negative than the pzc, the water molecules in the vicinity of the electrode align on the surface with their hydrogen atoms pointing to the surface (Fig. 4(a)). Interfacial water molecules oriented randomly or more likely with their hydrogen atoms pointing nearly parallel to the surface around the pzc (Fig. 4(b)). At potentials more positive than the pzc, water molecules are incorporated with sulfate anions with their hydrogen atoms pointing to the surface as is the case in the negative potential region (Fig. 4(c)).

Further investigations including the effects of the electrolyte, its concentration, and the surface modifications on the potential dependent behavior of the interfacial water molecules are now in progress.

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Figure captions

Figure 1. SFG spectra in the OH stretching region obtained at the gold electrode in 10 mM sulfuric acid solution using visible wavelength of 470 nm at (a) –0.2 V, (b) +0.2 V, (c) +0.6 V and (d) +1.0 V and fitted curves (solid lines). (e) SFG spectra in the OH stretching region obtained at the gold electrode in 10 mM sulfuric acid D_2O (99.8 %) solution at –0.2 V: open circle and +0.9 V: filled circle. Electrolyte solutions were purged with ultra-pure argon gas prior to each experiment.

Figure 2. The strengths of the peak at 3500 cm^{-1} (A_{3500}) of the spectra shown in Fig. 1(a)-(d) as a function of the applied potential.

Figure 3. SFG spectrum shown in Fig. 1 (a) with the fitted curve (solid line) to Eq. (1) using ε=100 deg and a simulated SFG spectrum with the same parameters of the fitted curve except for ε= –80 deg (dotted line).

Figure 4. Schematic models of the interfacial structure at potentials (a) more negative than, (b) around and (c) more positive than the pzc. Arrows show the direction of the water dipole.

Figures

Figure 1 Nihonyanagi *et al.*

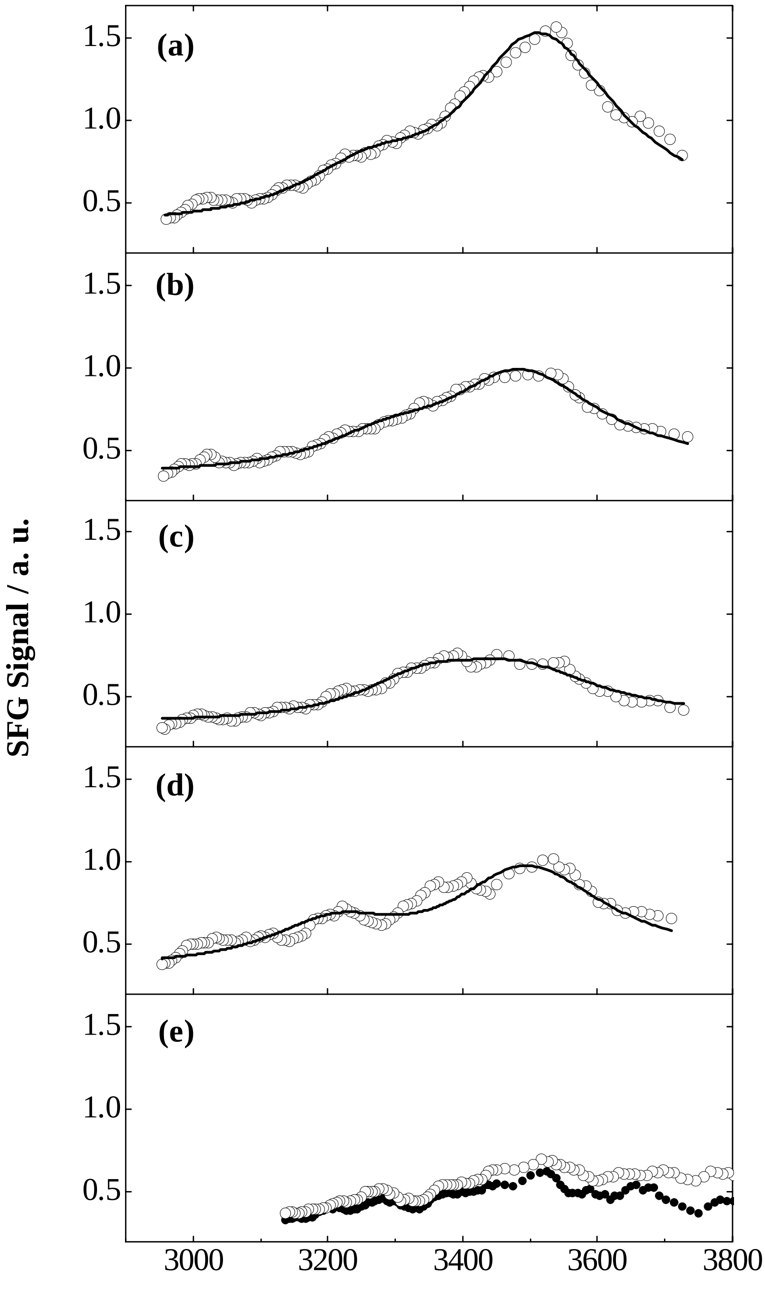

Figure 2 Nihonyanagi *et al*.

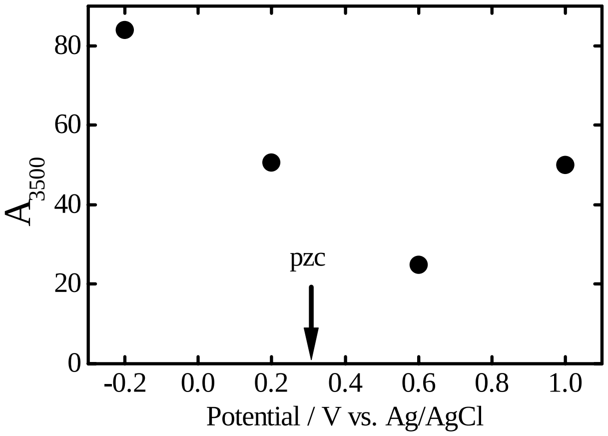

Figure 3 Nihonyanagi et al.

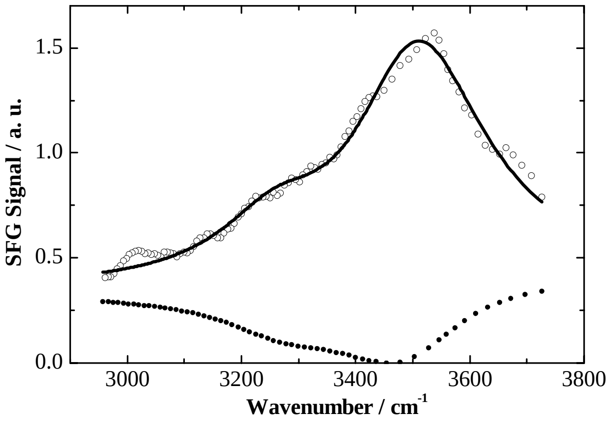

Fig. 4 Nihonyanagi et al.