Potential-dependent structure of the interfacial water on the gold electrode

S. Nihonyanagi et al., *Surface Science,* **573**, 11-16 (2004)

2014. 07. 19.

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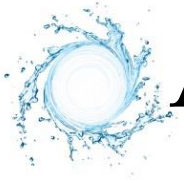


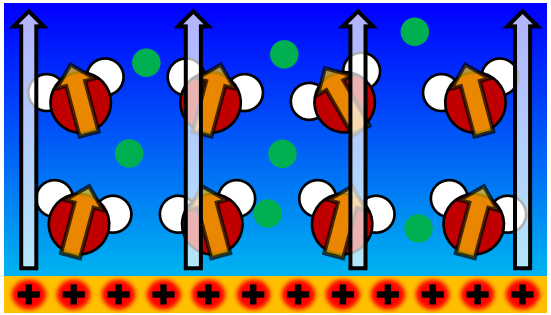
Abstract

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 as 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, morphology, roughness, and topography; Water; Metal–electrolyte interfaces

Motivation



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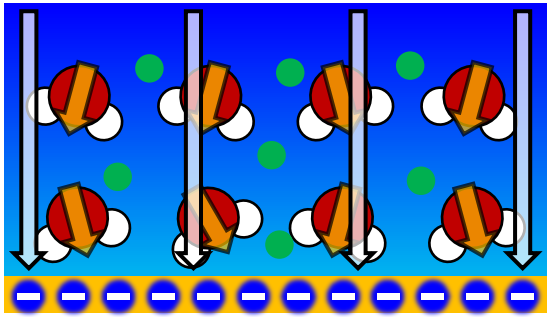
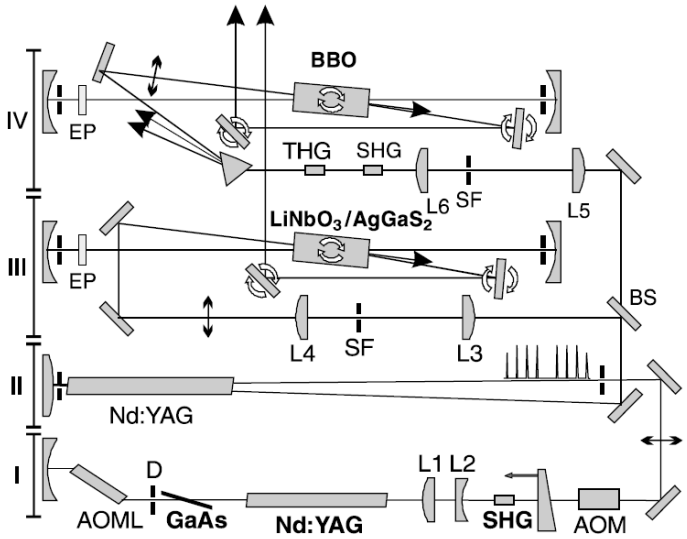


Interfacial water molecules are expected to be ordered near the charged surface, due to the electric field.

Experimental setup

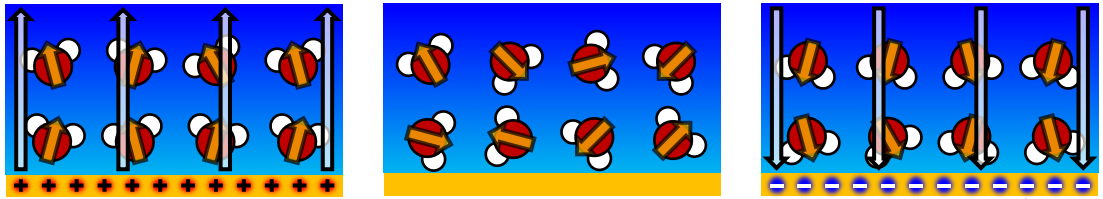


A. A. Mani et al., *Surface Science* **502–503** (2002) 261–267

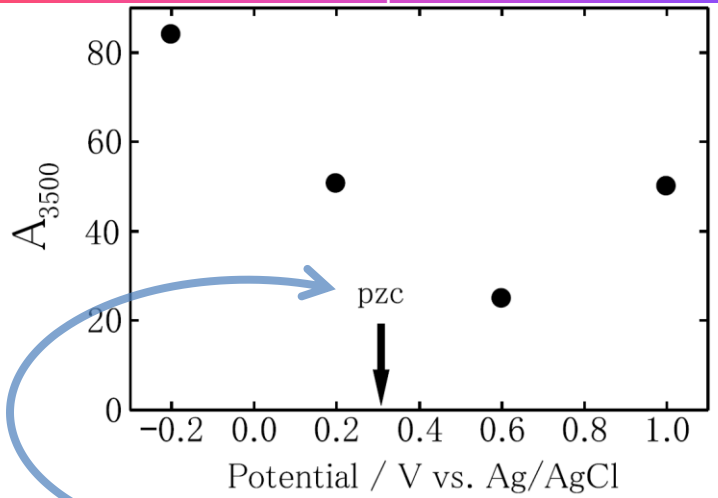
Doubly-tunable Sum-frequency generation setup

Fig. 5. Schematic view of the two-color tunable laser. AOML: Acousto optic mode locker, D: diaphragm, NdYAG laser head, L1and L2 = telescope, SHG: SHG crystal, DM: dichroic mirror, AOM: Acousto-optic modulator, BS: beam splitter, L3 and L4 = telescope, SF: spatial filter, EP: etalon plate, L5 and L6 = telescope, THG: third harmonic crystal.

Results

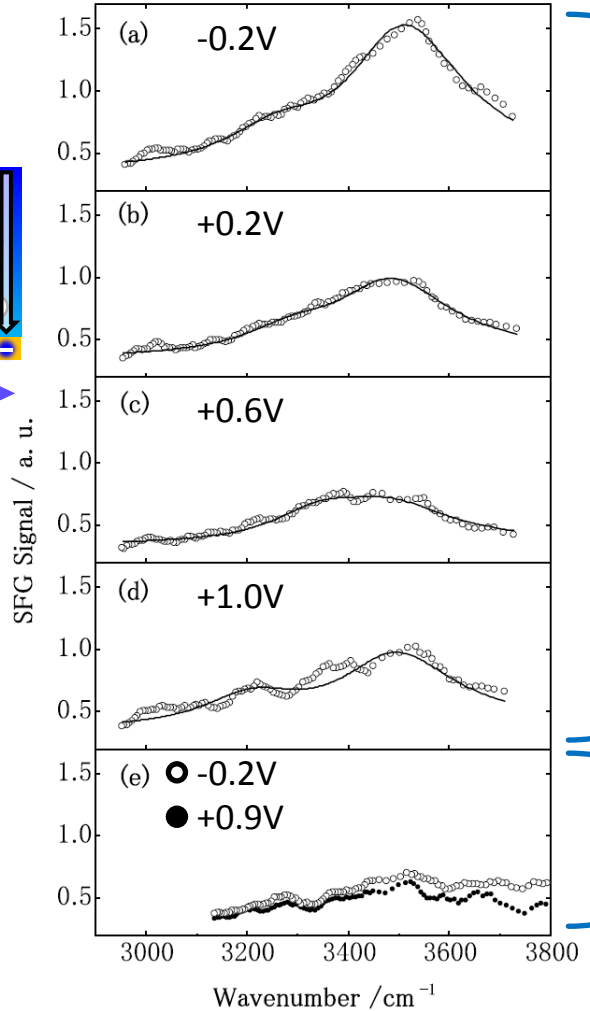


Electric potential



PZC : potential of zero charge

(electric potential corresponding zero surface charge density)



10mM H_2SO_4 in H_2O

10mM H_2SO_4 in D_2O

Results

$$I_{SFG} = \left| \sum_n \frac{A_n}{\omega_{IR} - \omega_n + i\Gamma_n} + \left|\chi^{(2)}_{NR}\right| e^{i\varepsilon} \right|^2$$

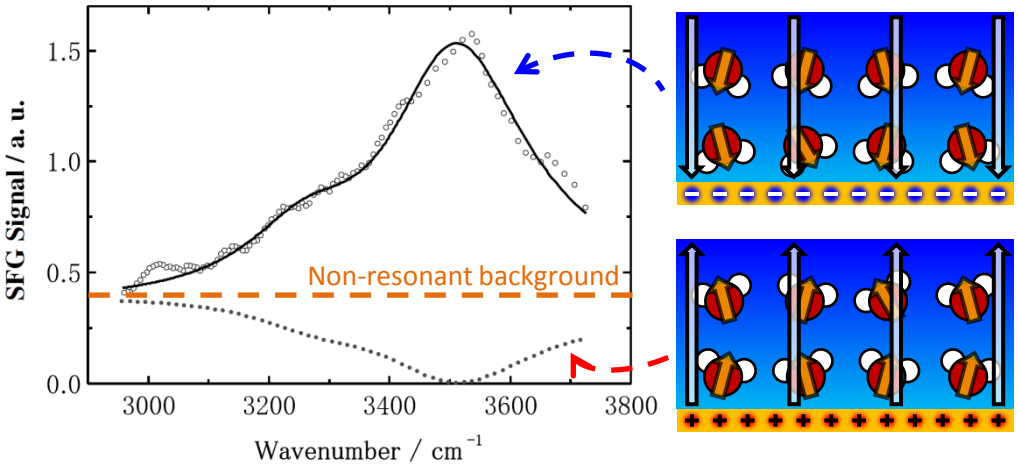
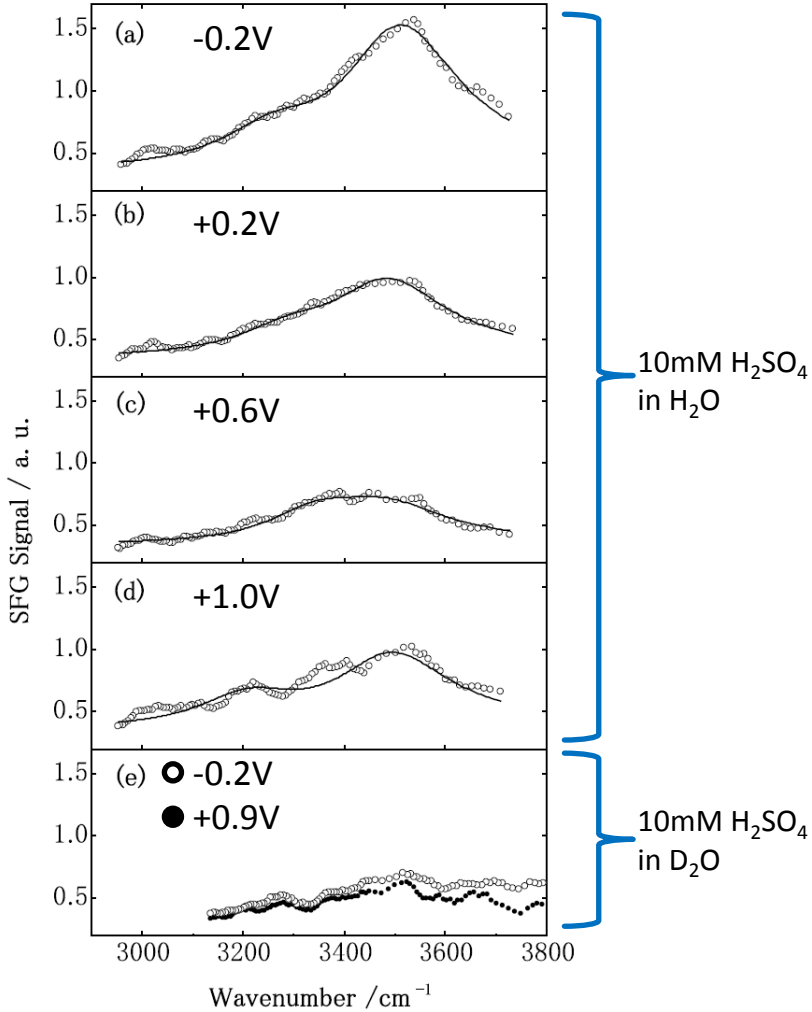


Fig. 3. SFG spectrum shown in Fig. 1(a) with the fitted curve (solid line) to Eq. (1) using $\varepsilon = 100$ deg. and a simulated SFG spectrum with the same parameters of the fitted curve except for $\varepsilon = -80$ deg. (dotted line).



Results

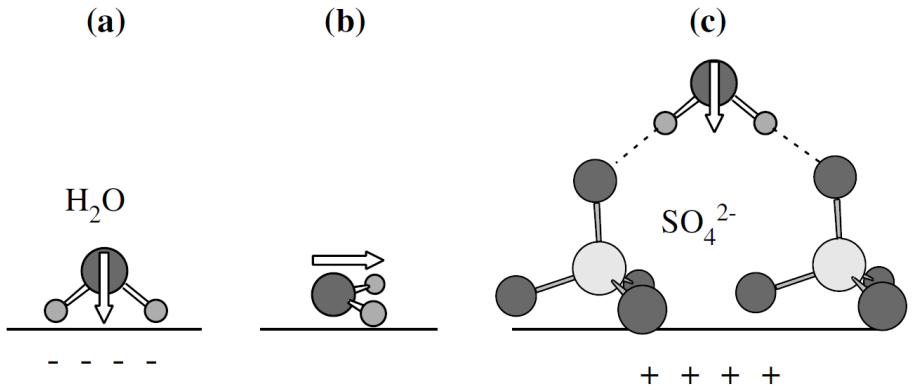


Fig. 4. Schematic models of the interfacial structure at potentials (a) more negative than, (b) around and (c) more positive than the PZC. Arrows show the direction of the water dipole.