

1P059

Molecular Structure at the Hydrophilic TiO₂/Water Interface Studied by Heterodyne-Detected Sum Frequency Generation Spectroscopy

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[Introduction] Titanium dioxide (TiO₂) is one of the most important materials in heterogeneous photocatalysis.

In particular, TiO₂ is widely used in water splitting and hydrogen production. Since the discovery of the Honda-Fujishima effect in 1972 [1], a lot of effort was invested to understand the reaction pathways of water splitting at the TiO₂ surface and identify the reaction intermediates with conventional spectroscopic methods [2]. However, those methods cannot distinguish whether a species is located near the TiO₂ surface or in the bulk water. In contrast, heterodyne-detected vibrational sum-frequency generation (HD-VSFG) is an interface-selective technique, which allows us to determine the complex second order non-linear polarizability $\chi^{(2)}$. The imaginary part of the $\chi^{(2)}$ spectrum ($\text{Im}\chi^{(2)}$) provides rich information about the hydrogen bond structure and orientation of the interfacial water molecules. Even though HD-VSFG has been used in a large variety of air/water studies [2], its application to the solid/liquid interface has been achieved only very recently [3]. In this study, we present a method to obtain complex $\chi^{(2)}$ spectra from the TiO₂/water interface for the first time under various conditions.

[Experiment] The TiO₂ film was grown on a fused silica substrate by atomic layer deposition (ALD), which allows precise control of the film growth. The thickness of the TiO₂ film was 2.7 nm, as determined by ellipsometry. The surface roughness was estimated to be 0.3 nm by AFM. To study the water structure at the TiO₂/water interface, we used HD-VSFG spectroscopy (Figure 1a). In this experiment, we used isotopically diluted water (HOD-D₂O) to suppress inter- and intramolecular vibrational coupling (Figure 2b). The non-resonant signal from the TiO₂/D₂O interface was used as a reference.

[Results and Discussion] Figure 2 shows $\text{Im}\chi^{(2)}$ of the TiO₂/HOD-D₂O interface for pH 10.3, 5.8 and 3.3. At high pH, where TiO₂ is partially negatively charged, water molecules orient with the hydrogen atoms pointing towards the TiO₂ surface (“H-up” orientation). This can be explained by the alignment of water molecules with the negative electric field, as well as the

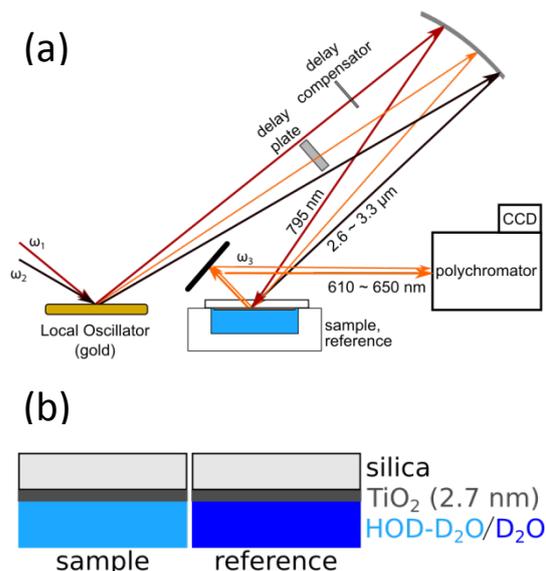


Figure 1: (a) Schematic of the VSFG setup for the buried interface. (b) Schematic of the sample and the reference used.

formation of hydrogen bonds to the oxygen atoms of the TiO₂. By changing the pH from basic to acidic, we observed a gradual decrease of the positive OH stretch band. Below the isoelectric point of TiO₂, a negative band appears in the low frequency region, as the TiO₂ surface becomes positively charged. However, a small positive band seems to remain in the high frequency region, which suggests that some water molecules remain H-up oriented, by forming hydrogen bonds to the oxygen atoms of the TiO₂, similar to our previous observation at the silica/water interface [3].

In this presentation we will also discuss HD-VSFG spectra, which were recorded *in situ* during illumination of the TiO₂ film with UV light.

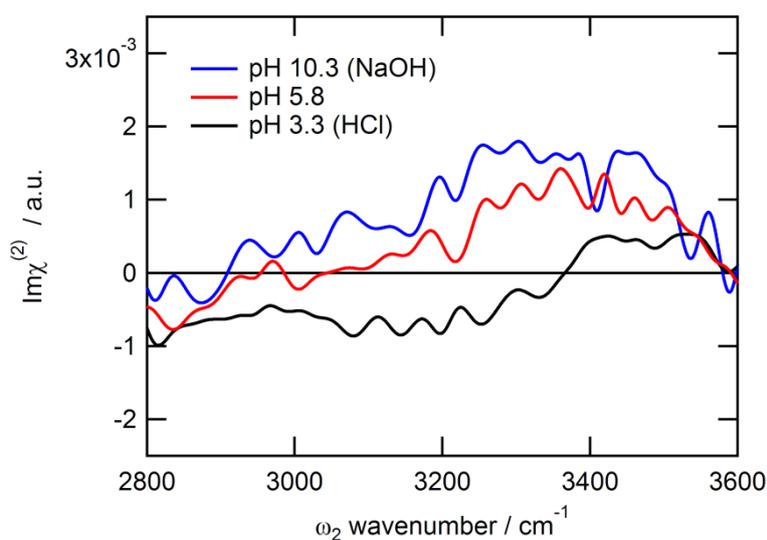


Figure 2: Imaginary part of the $\chi_{\text{eff}}^{(2)}$ spectrum of the TiO₂/HOD-D₂O interface at different pH. The spectra were normalized by $\chi_{\text{eff}}^{(2)}$ of the TiO₂/D₂O interface. The sum-frequency $\omega_1 + \omega_2$, visible ω_1 , and IR ω_2 lights were S-, S-, and P-polarized, respectively.

[References]:

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