

1P059

## Molecular Structure at the Hydrophilic TiO<sub>2</sub>/Water Interface Studied by Heterodyne-Detected Sum Frequency Generation Spectroscopy

(Molecular Spectroscopy Laboratory, RIKEN<sup>1</sup>; Ultrafast Spectroscopy Research Team, RIKEN Center for Advanced Photonics<sup>2</sup>)

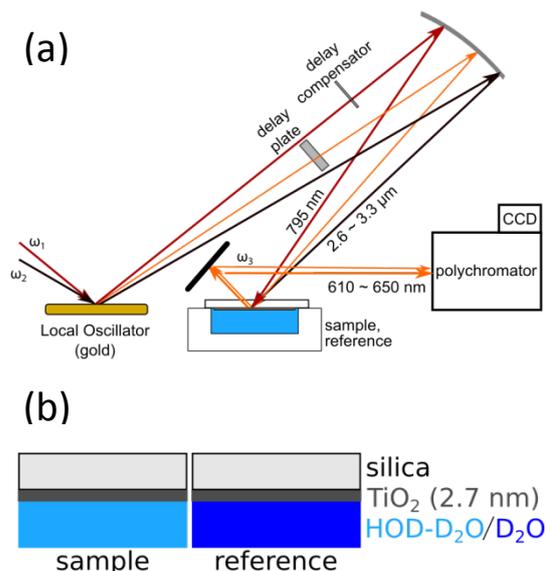
○MYALITSIN, Anton<sup>1</sup>; NIHONYANAGI, Satoshi<sup>1,2</sup>; TAHARA, Tahei<sup>1,2</sup>

**[Introduction]** Titanium dioxide (TiO<sub>2</sub>) is one of the most important materials in heterogeneous photocatalysis.

In particular, TiO<sub>2</sub> 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 TiO<sub>2</sub> surface and identify the reaction intermediates with conventional spectroscopic methods [2]. However, those methods cannot distinguish whether a species is located near the TiO<sub>2</sub> 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 TiO<sub>2</sub>/water interface for the first time under various conditions.

**[Experiment]** The TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>/water interface, we used HD-VSFG spectroscopy (Figure 1a). In this experiment, we used isotopically diluted water (HOD-D<sub>2</sub>O) to suppress inter- and intramolecular vibrational coupling (Figure 2b). The non-resonant signal from the TiO<sub>2</sub>/D<sub>2</sub>O interface was used as a reference.

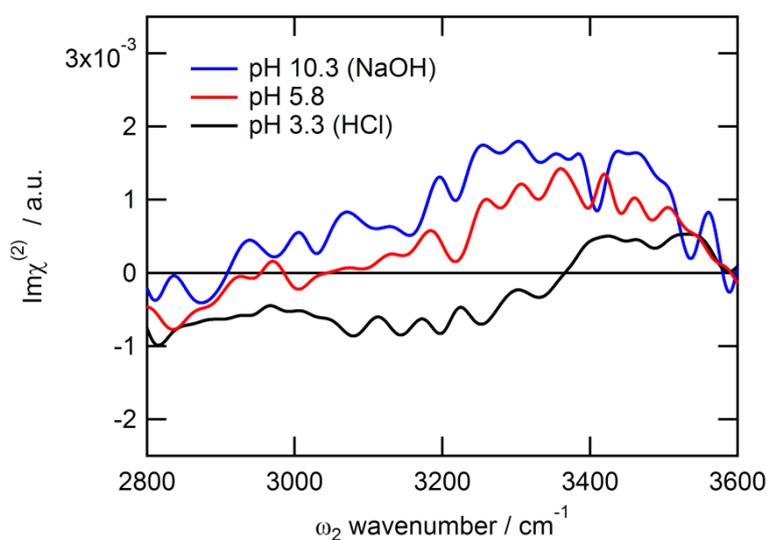
**[Results and Discussion]** Figure 2 shows  $\text{Im}\chi^{(2)}$  of the TiO<sub>2</sub>/HOD-D<sub>2</sub>O interface for pH 10.3, 5.8 and 3.3. At high pH, where TiO<sub>2</sub> is partially negatively charged, water molecules orient with the hydrogen atoms pointing towards the TiO<sub>2</sub> surface (“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 TiO<sub>2</sub>. By changing the pH from basic to acidic, we observed a gradual decrease of the positive OH stretch band. Below the isoelectric point of TiO<sub>2</sub>, a negative band appears in the low frequency region, as the TiO<sub>2</sub> 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 TiO<sub>2</sub>, 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 TiO<sub>2</sub> film with UV light.



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

### **[References]:**

- [1] Fujishima, A.; Honda, K., Nature, **1972**, 238, 37-38.
- [2] Henderson, M. A., Surf. Sci. Rep., **2011**, 66 (6-7), 185.
- [2] Nihonyanagi, S.; Mondal, J.; Yamaguchi, S.; Tahara, T., Ann. Rev. Phys. Chem., **2013**, 64, 579.
- [3] Myalitsin, A.; Urashima, S.; Nihonyanagi, S.; Yamaguchi, S.; Tahara, T.; J. Phys. Chem. C, 2016, 5, 9357.