

Exotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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2018 Morino Foundation for Molecular Science
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Keywords Surface & Interface Science, Nonlinear Optical Spectroscopy, Water Molecules

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning probe microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used recently developed heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-

order nonlinear susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected $\text{Im}\chi^{(2)}$ SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

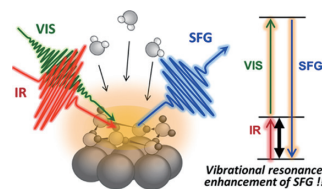


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji *et al.*, “Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice,” *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- K. Shirai *et al.*, “Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO₂ Photocatalyst,” *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Top-most Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).
- F. Kato *et al.*, “Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice,” *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
- T. Sugimoto *et al.*, “Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces,” *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).

1. Interface Engineering of the Thermodynamic Properties of Strongly Correlated Many-Body Protons in Crystalline Ice¹⁾

The static and dynamic behavior of strongly correlated protons play crucial roles in rendering exotic properties and enabling a wide range of applications of nanoscale hydrogen-bonded (HB) materials in physics, chemistry and biology. However, because of the difficulty in probing and manipulating the proton configuration in nanomaterials, controlling the cooperative behavior of many-body protons has not been realized.

In this study, we demonstrate the possibility of designing and controlling the physical properties of strongly correlated many-body protons through systematic sum-frequency generation (SFG) spectroscopy of crystalline-ice nanofilms. Since the second-order nonlinear susceptibility tensor $\chi^{(2)}$ is nonzero for non-centrosymmetric systems, the homodyne-detected SFG intensity $|\chi^{(2)}|^2$ increases with increasing the number of water molecules with net orientational preference, and thus can be used as the signature of the emergence of ferroelectric proton ordering. Because of the strong correlation of many-body protons imposed by the ice rules,^{2,3)} protons in the hydrogen-bond (HB) network of crystalline ice provide an interesting platform for studying fundamental emergent properties of strongly correlated proton systems. Here, we employ SFG spectroscopy of heteroepitaxial crystalline-ice nanofilms grown on Pt(111) surface precovered by a well-defined single layer of either carbon monoxide (CO) molecules or oxygen (O) atoms to study the effects of interface termination on mesoscopic characteristics of many-body protons.

The intensities of the $|\chi^{(2)}|^2$ -SFG spectra were shown as a function of ice thickness for these substrates (Figure 1). We found that the SFG signal derived from ice film on CO precovered Pt(111) continues to increase as that on bare Pt(111).^{2,3)} In contrast, negligibly small $|\chi^{(2)}|^2$ -SFG intensity (Figure 1) suggests that ice film on oxygen precovered Pt substrate is paraelectric. Our observations on the two different types of intercalated layer directly demonstrate that the thermodynamic properties of emergent ferroelectric proton ordering are extensively tuned by the interface engineering at the angstrom scale.

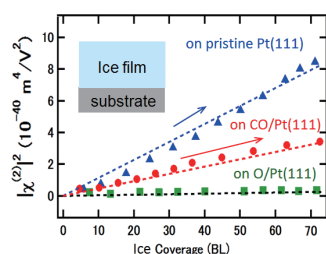


Figure 2. Thickness dependence of the $|\chi^{(2)}|^2$ -SFG intensity of crystalline ice films on pristine Pt(111), CO- and O-precovered Pt(111) at 140 K.¹⁾

2. Operando FT-IR Spectroscopy of Steam-Methane-Reforming Photocatalyst under Irradiation of Intensity Modulated UV Light⁴⁾

Photocatalytic steam-methane reforming is an attractive

chemical technology for hydrogen production from abundant resources of methane and water. In the case of photocatalytic reaction, photo-generated electron plays key roles in hydrogen production. However, the dynamics of photogenerated electrons under reaction condition have been unclear. To uncover the behavior of reactive photo-excited electrons, we conducted *operando* FT-IR spectroscopy of metal loaded Ga_2O_3 photocatalysts under irradiation of intensity modulated UV light. We succeeded in observing a correlation between the reaction activity and a broad mid-infrared absorption band derived from the photo-generated electrons shallowly trapped at the photocatalyst surfaces.

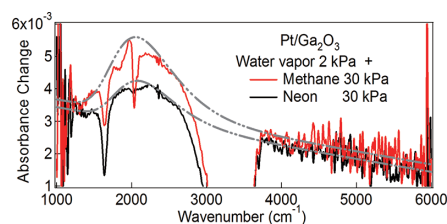


Figure 3. Comparison of the IR absorbance spectra measured in the non-reactive Ne gas and the reactive methane gas environment for Pt loaded Ga_2O_3 photocatalysts.⁴⁾

3. Critical Role of Interfacial Water Molecules on the Photocatalytic Methane Activation⁵⁾

Recent expectations for effective use of natural gas have led to an interest in chemical technology for methane activation. Photocatalytic approach has a potential to convert methane at ambient conditions. However, the microscopic understanding on photocatalytic reaction mechanism, especially robust C–H bond activation mechanism, remains an open question. Here, combining *in-situ* MS-IR spectroscopy and systematic reaction measurements under various partial pressures of methane and water, we demonstrate that photo-activated interfacial water molecules facilitate the first C–H dissociation and shift the rate-determining step. Our reaction observation on typical three photocatalysts (Ga_2O_3 , NaTaO_3 , TiO_2) clarified the existence of critical partial pressure of methane at approximately 0.5 atm, around which the reaction rates markedly increased with methane partial pressure. *Operando* IR measurements showed that H atom extraction from methane by photo-activated water was accelerated at the same critical partial pressure of methane, suggesting that the first C–H activation and adsorption of methane was directly assisted by interfacial water.

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