

# Unique Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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#### Professional Employment

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#### Awards

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2014 39<sup>th</sup> Vacuum Science Paper Award  
2018 PCCP Prize 2018  
2018 CSJ Presentation Award 2018  
2018 Encouragement Award, The Spectroscopic Society of Japan  
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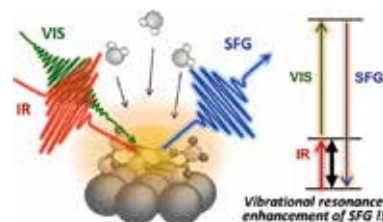
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**Keywords** Water Molecule, Molecular Spectroscopy, Surface Science

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 hetero-

dyne 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 for 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.

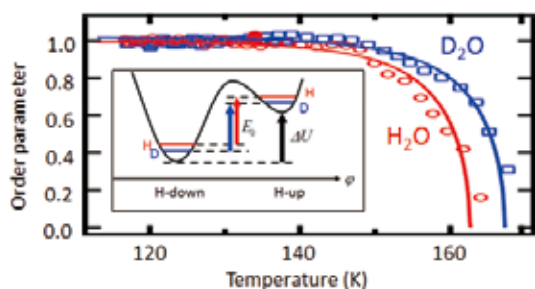
#### Selected Publications

- 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-TiO<sub>2</sub> Photocatalyst,” *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- N. Aiga *et al.*, “Origins of Emergent High- $T_c$  Ferroelectric Ordering in Heteroepitaxial Ice Film: Sum-Frequency Generation Spectroscopy of H<sub>2</sub>O and D<sub>2</sub>O Ice Films on Pt(111),” *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
- T. Sugimoto *et al.*, “Topologically Disordered Mesophase at Topmost Surface of Crystalline Ice Between 120 and 200 K,” *Phys. Rev. B* **99**, 121402(R) (2019).

## 1. Isotope Effects on Emergent High- $T_c$ Ferroelectric Ordering of Strongly Correlated and Frustrated Proton in Ice<sup>1)</sup>

In the hydrogen-bond network of crystalline water ice, orientation of water molecules, *i.e.* configuration of protons, is strongly correlated and highly frustrated under the Pauling's ice rules. Materials with these constraints have a potential to exhibit dramatic and unusual responses to external stimuli. In fact, we have recently demonstrated that inversion-symmetry breaking at a heterointerface in isotope diluted HDO crystalline-ice film grown on Pt(111) induces high- $T_c$  ferroelectric proton ordering.<sup>2)</sup> However, the molecular-level origin of the emergent high- $T_c$  ferroelectric ordering has been unclear.

We have tackled this problem to elucidate fundamental physics behind the heterointerface-induced ferroelectric proton ordering in the crystalline-ice film. Because an isotope shift in the critical temperature of ferro-to-paraelectric transition gives essential information about the mechanism of emergent ferroelectric ordering, we have conducted temperature programmed sum-frequency generation (SFG) spectroscopy of H<sub>2</sub>O and D<sub>2</sub>O ice films on Pt(111). Then, we found that the ferroelectric proton orderings in these films are extremely thermally robust:  $T_c = 164$  K (H<sub>2</sub>O) and 168 K (D<sub>2</sub>O); these are more than twice as large as that of ferroelectric bulk ice XI ( $T_c \sim 72$  K for H<sub>2</sub>O,  $T_c \sim 76$  K for D<sub>2</sub>O). The observed small isotope shift in  $T_c$  of the ferroelectric ice films is beyond the conventional belief: High- $T_c$  hydrogen-bonded ferroelectrics typically have large isotope shifts in  $T_c$ . This result indicates that not only nuclear quantum effects in the hydrogen-bond network of ice film but also the inter-adsorbate and adsorbate-substrate interactions at the ice/Pt interface are responsible for the thermal stability of ferroelectric ordering and its small isotope effect.



**Figure 2.** Temperature dependence of the ferroelectric order parameter of crystalline H<sub>2</sub>O (red) and D<sub>2</sub>O (blue) grown on Pt(111).

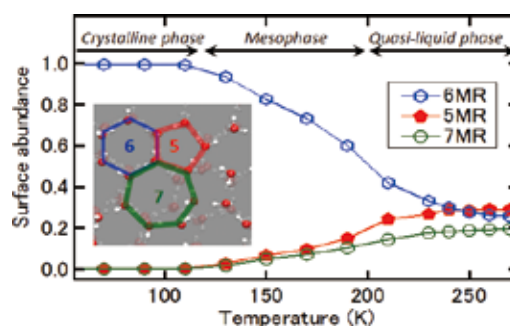
## 2. Unveiling Topologically Disordered Hydrogen-Bond Network at Surface Layer of Hexagonal Crystalline Ice<sup>3,4)</sup>

The surface of crystalline water ice (hexagonal ice Ih) ubiquitous in nature plays a crucial role in a variety of phenomena in physics, chemistry, biology, geology, atmospheric and astronomical sciences. In 1859, Faraday first proposed that a layer of liquid water (quasi liquid) is present on the surface of crystalline ice below the bulk freezing temperature

of 273 K. Ever since, the nature of ice surface and the onset temperature of surface premelting have been intensely explored. Nowadays it is generally believed that the onset temperature of surface disordering of ice Ih is 200 K and the surface structure of ice Ih is perfectly ordered below this temperature. However, we have demonstrated for the first time that surface disordering of ice emerges at 120 K that is much lower than the traditionally believed premelting temperature of 200 K.

By combining surface-specific SFG spectroscopy and the state-of-the-art molecular dynamics simulations, we found that the topmost surface layer of ice Ih(0001) undergoes a cascade of structural transitions from solid to quasi-liquid phase via a liquid-crystal-like mesophase with a topologically disordered hydrogen-bond network between 120 and 200 K; this is in stark contrast to the traditional concept of premelting of ice surface as well as bulk melting of ice where a single first-order phase transition takes place from solid to liquid state at the melting temperature. Our result sheds new light on the effects of undercoordinated water molecules at the surface on melting behavior of ice and thus advances physics of two-dimensional surface phase transition of molecular crystal.

In addition, our finding casts profound impacts on many disciplines. Since the lower limit of temperature of the earth's atmosphere is  $\sim 120$  K, the surface of crystalline ice Ih on earth is unlikely to be the perfectly ordered solid. The existence of glassy mesophase in the temperature range 120–200 K makes the structural and electronic features of ice surface in nature more inhomogeneous than they have ever been expected. The molecular-level structure and dynamics of ice surface clarified in the present study provide a new basis for elucidating the key properties of ice surface that are of great interest in a variety of heterogeneous processes in nature such as cloud seeding and electrification in atmosphere, catalytic destruction of Earth's ozone layer, and even molecular evolution in interstellar space.



**Figure 3.** Temperature dependence of relative abundance of 5-, 6- and 7-membered rings at the topmost surface layer of hexagonal crystalline ice-Ih(0001).

### References

- 1) N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
- 2) T. Sugimoto *et al.*, *Nat. Phys.* **12**, 1063–1068 (2016).
- 3) T. Sugimoto, Y. Otsuki, T. Ishiyama, A. Morita, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **99**, 121402(R) (2019).
- 4) Y. Otsuki, K. Watanabe, T. Sugimoto and Y. Matsumoto, in press.