Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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Education

2007	B.S. Kyoto University
2011	Ph.D. The University of Tokyo

Professional Employment

2012	Assistant Professor, Kyoto University
2016	JST-PRESTO Researcher
2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2020	JST-PRESTO Researcher

Awards

2014	Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014	39th Vacuum Science Paper Award
2018	PCCP Prize 2018
2018	CSJ Presentation Award 2018
2018	Encouragement Award, The Spectroscopic Society of Japan
2018	Morino Foundation for Molecular Science
2019	12th Young Scientist Awards of the Japan Society for Molecular Science
2019	14th Young Scientist Award of the Physical Society of Japan

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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 prove 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.

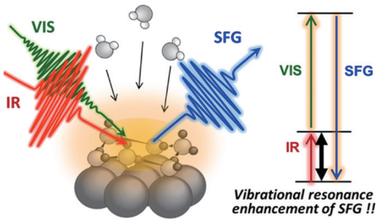

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

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-TiO_2 Photocatalyst," *J. Am. Chem. Soc.* **140**, 1415–1422 (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).
- 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. Direct Evidence for Markedly Enhanced Surface Proton Activity of Crystalline Ice[1)]

Hydrated protons on the ice surfaces critically influence physical and chemical properties of ices. They are generated solely by the thermal ionization of water molecules ($H_2O \leftrightarrows H^+ + OH^-$) in pure water molecular systems. Therefore, the proton activity inherent to water ice is determined by the amount and mobility of hydrated protons derived from the autoionization. Considerable discussions have been made, yet not been settled, on whether the activity of hydrated protons is substantially enhanced at the surface of water ice.

Very recently, we succeeded in directly and quantitatively demonstrating for the first time that the proton activity is significantly enhanced at the surfaces of low-temperature ice. On the basis of simultaneous experimental observation of the H/D isotopic exchange of water molecules at the surface and in the interior of double-layer crystalline-ice films composed of H_2O and D_2O (Figure 2), we reported three major discoveries of the unique enhancement of surface proton activity: (1) proton activity proved by the H/D exchange at the topmost surface is at least three orders of magnitude higher than in the interior even below 160 K; (2) the enhanced proton activity is dominated by autoionization process of water molecules rather than proton transfer process at ice surface; (3) as a consequence of surface promoted autoionization, the concentration of surface hydrated protons is more than six orders of magnitude higher than that in the bulk.

We also found that the cooperative structural fluctuations[2–4)] allowed in the undercoordinated surface molecules but inhibited in the fully coordinated interior molecules facilitate the autoionization and dominate the proton activity at the ice surface. Because the lower limit of temperature of the earth's atmosphere is ~120 K around the mesopause, the surface of crystalline ice on earth is unlikely to be solidly ordered but would inevitably be highly fluctuated. In nature, such dynamic features facilitate the autoionization of water molecules and thus enhance the proton activity at the surface of crystalline ice.

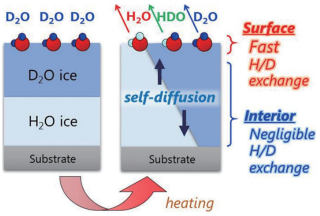

Figure 2. Simultaneous observation of the H/D isotopic exchange of water molecules at the surface and in the interior of double-layer ice films composed of H_2O and D_2O.

2. Thickness Dependent Homogeneous Crystallization of Ultrathin Amorphous Ice[5)]

The crystallization mechanism and kinetics are fundamentally important for thermal stability of amorphous materials. The crystallization of amorphous materials is generally triggered by spontaneous creation of crystalline nuclei. Two processes are distinguishable in terms of the place where crystallized nuclei are formed: *Heterogeneous nucleation* at the surface of material or the interface with the other material, and *homogeneous nucleation* in the bulk. In general, the surface and interface of amorphous thin films serve as nucleation sites. Therefore, it has been traditionally believed that crystallization of amorphous ice thin films also proceeds via the heterogeneous nucleation.

We have focused on the ultrathin films of amorphous ice grow on Pt(111) substrate and systematically investigated the crystallization process by varying the thickness of the films from a few nm to several tens of nm. Simultaneously monitoring the crystallization processes at the surface and in the interior of ice films, we found that the crystallization proceeds via homogeneous nucleation irrespective of the film thickness. This discovery overturned the conventional idea that the crystallization of amorphous ice thin films is initiated by heterogeneous nucleation. Furthermore, we found that the crystallization kinetics and temperature of amorphous ice thin films are highly modulated depending on the thickness of the film (Figure 3), although crystallization itself proceeds via the homogeneous nucleation mechanism. The structural analysis of hydrogen bonds based on vibrational spectroscopy revealed that the strength of hydrogen bonds in the thermodynamically most relaxed amorphous ice films (the state just before crystallization) changes significantly with the film thickness, which shows an evidence of a peculiar size effect.

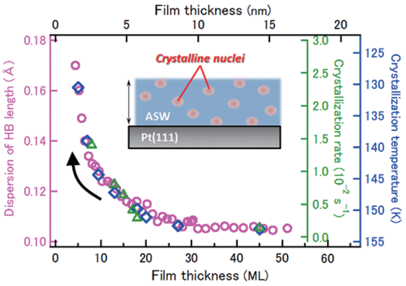

Figure 3. Thickness dependence of the distribution of O–H···O hydrogen bond length (○), crystallization rate (△) and temperature (◇) of the amorphous ice thin films on Pt(111).

References

1) F. Kato, T. Sugimoto and Y. Matsumoto, *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).

2) T. Sugimoto, Y. Otsuki, T. Ishisyama, A. Morita, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **99**, 121402(R) (2019).

3) Y. Otsuki, K. Watanabe, T. Sugimoto and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **21**, 20442–20453 (2019).

4) T. Sugimoto and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).

5) K. Harada, T. Sugimoto, F. Kato, K. Watanabe and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **22**, 1963–1973 (2020).

Awards

SUGIMOTO, Toshiki; 12th Young Scientist Awards of the Japan Society for Molecular Science (2019).
SUGIMOTO, Toshiki; 14th Young Scientist Award of the Physical Society of Japan (2019).