

Unique Structures, Physicochemical Properties and Quantum Dynamics of Molecular Aggregates at Solid Surfaces

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2018 Associate Professor, Institute for Molecular Science
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Awards

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2014 39th 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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Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, protons in the hydrogen-bond network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature.

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface-induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems. We have used recently

developed phase-resolved sum-frequency generation (SFG) vibrational spectroscopy with heterodyne detection in an ultrahigh vacuum chamber. $\text{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibits positive and negative sign for net-H-up orientation (protons pointing toward vacuum) and net-H-down orientation (toward substrate), respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated through other traditional experimental methods.

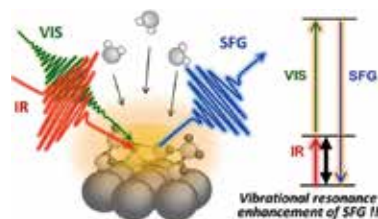


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe and Y. Matsumoto, "Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film," *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji, T. Sugimoto, T. Ishiyama, A. Morita, K. Watanabe and Y. Matsumoto, "Unveiling Subsurface Hydrogen-Bond Structure of

Hexagonal Water Ice," *Phys. Rev. B* **96**, 115405 (14 pages) (2017).

- N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, "Origins of Emergent High- T_c Ferroelectric Ordering in Heteroepitaxial Ice Film: Sum-Frequency Generation Spectroscopy of H_2O and D_2O Ice Films on Pt(111)," *Phys. Rev. B* **97**, 075410 (21 pages) (2018).

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1. Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Proton in Ice^{1,2)}

In the hydrogen-bond network of common water ice, protons are strongly correlated and highly frustrated under the ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton systems. Nevertheless, because of the difficulties in directly observing and quantitatively estimating the local configuration of protons and their ordering dynamics with traditional experimental techniques, little has been understood about thermodynamic properties of the protons especially at low temperature, where quantum effects are of potential importance on the emergence of the ordered state deeply hidden under the highly degenerated configurational disorder. Although materials containing strongly correlated and highly frustrated degree of freedom have a potential to exhibit dramatic and unusual response to external stimuli, it has widely been assumed nowadays that inversion-symmetry breaking at heterointerfaces such as crystalline ice films on solid surfaces has no ability to induce protonic ordering.

In contrast to the current belief, we have demonstrated emergent ferroelectric proton ordering in heteroepitaxial ice film on model platinum substrate.^{1,2)} We found such an exotic proton ordering is thermodynamically stable and has an extremely high critical temperature of ~ 170 K (Figure 2). Anisotropic interaction and protolysis driven by electrostatics at the interface is a key factor in stimulating exotic ferroelectric ordering of protons in the many-body correlated proton system. The concept of significant increase in T_c by heterointerface also suggests the ubiquity of ferroelectric ice in nature such as space and polar stratosphere.

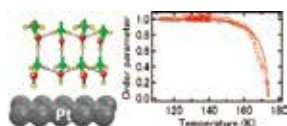


Figure 2. Schematic illustration of net-H-down ferroelectric ordering in ice film on Pt(111) and temperature dependence of the order parameter η normalized by the value at 120 K (red circle).

2. Unveiling Unique Hydrogen-Bond Structure of Ice Surface³⁾

Water ice is one of the most abundant solid substances in nature and its surface plays crucial roles in a variety of processes in physics, chemistry and earth planetary science: Surface premelting for unusual slipperiness in skating and skiing, sublimation and condensation in the atmospheric air and planetary systems, charge generation and separation in thunder cloud, heterogeneous reactions in the Earth's ozone layer and interstellar space, *etc.* Because ice is hydrogen bonded aggregate of water molecules, its surface physico-

chemical properties are dominated not only by the lattice translational structure (position of oxygen atoms) but also by the sublattice structure (orientations of water molecules or configurations of hydrogen atoms) of ice surface.

A surface of solid is not confined to its topmost layer, but consists of transition layers extending to the bulk: Subsurface. As a result of abrupt truncation of materials, the lattice and electronic structures of surface generally differ from those of the bulk, which results in unique physicochemical properties and heterogeneous processes of solid surface. Thus, structural relaxation and reconstruction at solid surface have been intensively studied by low energy electron diffraction, ion and X-ray scattering, and transmission electron microscopy. Although these conventional analytical techniques have been successfully applied to strongly bonded materials: Metals and semiconductors, they cannot be well applied to fragile and insulating solid substances composed of soft molecular systems such as water ice.

To clarify subsurface structure of ice, we have conducted phase-resolved SFG spectroscopy of ice Ih(0001) and analysed the spectra by molecular dynamics simulations combined with *ab initio* quantum calculations.⁴⁾ We found that observed bipolar band shape of the SFG spectra of isotope-diluted OH chromophores is a sensitive indicator of structural rumpling uniquely emerging at the subsurface of ice (Figure 3). In the outermost subsurface between the first (B1) and second (B2) bilayer, the hydrogen bond of $O_{B1}-H\cdots O_{B2}$ is weaker than that of $O_{B1}\cdots H-O_{B2}$. This implies that subsurface O–O distance is laterally altered, depending on the direction of O–H bond along the surface normal: H-up or H-down, which is in stark contrast to bulk hydrogen bonds. This new finding uncovers how water molecules undercoordinated at the topmost surface influence on the subsurface structural rumpling associated with orientational frustration inherent in water ice. The structural rumpling would play key roles in a variety of anomalous physical and chemical properties of ice surface in nature.

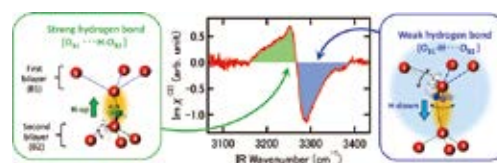


Figure 3. Schematic illustration of subsurface hydrogen-bond network between first and second bilayer of ice-Ih(0001) and the experimentally observed $\text{Im}\chi^{(2)}$ spectrum for the hydrogen-bonded OH-stretching band of isotope diluted ice Ih(0001).

References

- 1) T. Sugimoto, N. Aiga, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Nat. Phys.* **12**, 1063–1068 (2016).
- 2) N. Aiga, T. Sugimoto, Y. Otsuki, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **97**, 075410 (21 pages) (2018).
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Awards

SUGIMOTO, Toshiki; PCCP Prize 2018.

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