

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

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#### Education

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#### Professional Employment

2012 Assistant Professor, Kyoto University  
2016 JST-PRESTO Researcher [Innovative Catalysts] (–2019)  
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#### Awards

2014 Young Scientist Award, 33<sup>rd</sup> Annual Meeting of the SSSJ  
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  
2018 Morino Foundation for Molecular Science  
2019 12<sup>th</sup> Young Scientist Awards of the Japan Society for Molecular Science  
2019 The 14<sup>th</sup> Young Scientist Award of the Physical Society of Japan

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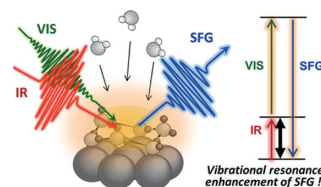
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Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down 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 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 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.*, “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).
- H. Sato *et al.*, “Critical Impacts of Interfacial Water on C–H Activation in Photocatalytic Methane Conversion,” *Commun. Chem.* **6**, 8 (2023).
- H. Sato *et al.*, “Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water,” *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).
- S. Takahashi *et al.*, “Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity,” *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).

## 1. Broadband Tip-Enhanced Nonlinear Optical Response in a Plasmonic Nanocavity<sup>1)</sup>

Squeezing light beyond the diffraction limit and controlling the optical processes caused by the nano-confined light are central issues of nanophotonics. In particular, localized and enhanced light at the plasmonic nanogaps in scanning probe microscopes provides us unique platform for obtaining site-specific optical information at the molecular/atomic scale. Very recently, not only linear but also nonlinear optics have been applied to such tip-enhanced nanoscopy to gain higher sensitivity and spatial resolution. In this context, understanding the intrinsic nonlinear optical properties of plasmonic nanocavities is of growing importance to control the nanosized nonlinear optics more precisely. Recently, we have directly tackled this issue by focusing on second harmonics of wide range of infrared light enhanced in the tip-substrate plasmonic nanogaps. Combining a wavelength-tunable femtosecond pulse laser system with a scanning tunnelling microscope, we for the first time report unexpectedly broad tip-enhanced nonlinear optical response in a plasmonic nanocavity.

We demonstrated that the strong tip-enhancement of second harmonic generation (SHG) is maintained over the visible to infrared wavelength range. The prominent geometrical effects of plasmonic tips dominating this broadband enhancement ability were also verified; while the micrometer-scale tip shafts extend the spectral range of the field enhancement to the near- and mid-infrared region, the nanometer-scale tip apexes mainly contribute to boosting the visible/near-infrared light. This indicates that the nanometer-scale tip apexes and micrometer-scale tip shafts jointly enable the simultaneous enhancement of both infrared excitation and visible/infrared radiation processes, realizing the strongly enhanced SHG over the visible to infrared broadband region. Indeed, we have also succeeded in demonstrating both experimentally and theoretically that the broadband tip-enhanced SHG properties can be significantly altered in response to the micro- and macro-scale tip structures.

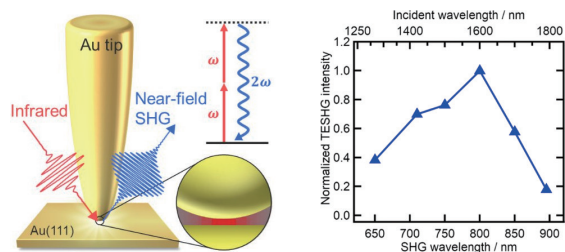


Figure 2. Tip-enhanced second harmonic generation.

## 2. Critical Impacts of Interfacial Water on the Photocatalytic C–H Conversion of Methane<sup>2,3)</sup>

On-site and on-demand photocatalytic methane conversion under ambient conditions is one of the urgent global challenges for the sustainable use of ubiquitous methane resources. However, the lack of microscopic knowledge on its reaction

mechanism prevents the development of engineering strategies for methane photocatalysis. Combining real-time mass spectrometry and *operando* infrared absorption spectroscopy with *ab initio* molecular dynamics simulations, here we report key molecular-level insights into photocatalytic green utilization of methane. Activation of the robust C–H bond of methane is hardly induced by the direct interaction with photogenerated holes trapped at the surface of photocatalyst; instead, the C–H activation is significantly promoted by the photoactivated interfacial water species. The interfacial water hydrates and properly stabilizes hydrocarbon radical intermediates, thereby suppressing their overstabilization. Owing to these water-assisted effects, the photocatalytic conversion rates of methane under wet conditions are dramatically improved by typically more than 30 times at ambient temperatures ( $\sim 300$  K) and pressures ( $\sim 1$  atm) in comparison to those under dry conditions. This study sheds new light on the role of interfacial water and provides a firm basis for design strategies for non-thermal heterogeneous catalysis of methane under ambient conditions.

## 3. Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water<sup>4)</sup>

Environmentally sustainable and selective conversion of methane to valuable chemicals under ambient conditions is pivotal for the development of next-generation photocatalytic technology. However, due to the lack of microscopic knowledge about the non-thermal methane conversion, controlling and modulating photocatalytic oxidation processes driven by photogenerated holes remain a challenge. Here, we report novel function of metal cocatalysts to accept photogenerated holes and dominate the oxidation selectivity of methane, which is clearly beyond the conventional concept in photocatalysis that the metal cocatalysts loaded on the surfaces of semiconductor photocatalysts mostly capture photogenerated electrons and dominate reduction reactions exclusively. The novel photocatalytic role of metal cocatalysts was verified by *operando* molecular spectroscopy combined with real-time mass spectrometry for metal-loaded  $\text{Ga}_2\text{O}_3$  model photocatalysts under methane gas and water vapor at ambient temperature and pressure. Our concept of metal cocatalysts that modulate photocatalytic oxidation as well as reduction opens a new avenue for controlling photocatalytic redox reactions by metal-cocatalyst engineering.

### References

- 1) S. Takahashi, A. Sakurai, T. Mochizuki and T. Sugimoto, *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).
- 2) H. Sato, A. Ishikawa, H. Saito, T. Higashi, K. Takeyasu and T. Sugimoto, *Commun. Chem.* **6**, 8 (2023).
- 3) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).
- 4) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).