

Exotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

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Professional Employment

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Awards

2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
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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
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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.

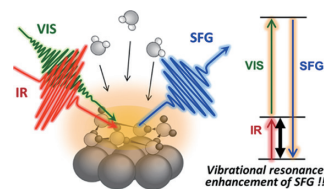


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, “Emergent High- T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film,” *Nat. Phys.* **12**, 1063–1068 (2016).
- 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).
- H. Sato *et al.*, “Operando FT-IR Spectroscopy of Steam-Methane-Reforming Photocatalyst under Irradiation of Intensity Modulated UV Light,” *Vac. Surf. Sci.* **63**, 476–481 (2020).

1. Critical Impacts of Interfacial Water on the Photocatalytic C–H Conversion of Methane¹⁾

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 (Figure 1). 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 (~300 K) and pressures (~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.

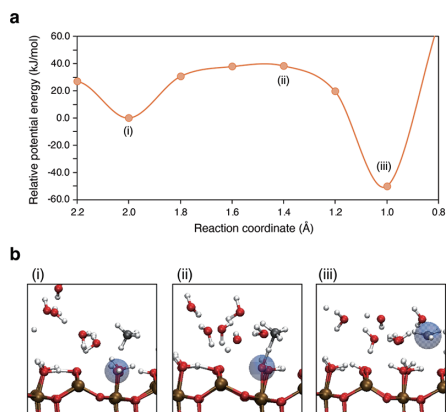


Figure 2. (a) Potential energy curve and (b) snapshots for methane activation under wet conditions on β - Ga_2O_3 surfaces.

2. Beyond Reduction Cocatalysts: Critical Role of Metal Cocatalysts in Photocatalytic Oxidation of Methane with Water^{2,3)}

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

(Figure 2), 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 Ga_2O_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.

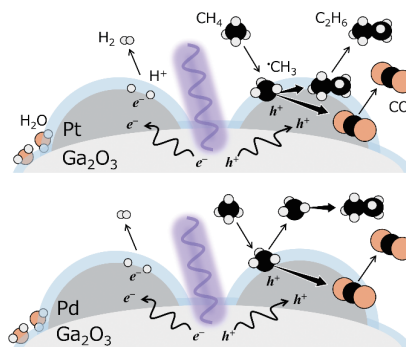


Figure 3. Schematic illustration of the role of metallic cocatalysts on the photocatalytic methane oxidation.

3. Monolayer-Sensitive Coherent Raman Spectroscopy for Molecular Systems on Conductive Surfaces⁴⁾

Highly sensitive and versatile spectroscopy for molecular systems on conductive surfaces, relating with electrochemistry, corrosion processes, and catalytic reactions is crucial in many scientific and technological fields. However, conventional spectroscopy based on spontaneous Raman scattering requires some specific electronic/plasmonic enhancements due to its weak signal, imposing serious restriction on the system to which it is applied. Here, we introduce a monolayer-sensitive and versatile stimulated Raman spectroscopy without using any electronic/plasmonic enhancements. This spectroscopy innovation is achieved by coherent anti-stokes Raman scattering (CARS) with dramatical improvement of signal-to-noise ratio based on an optimally shaped time-delayed pulse; our stimulated and time-resolved Raman observation scheme not only enhance the vibrational signal but also significantly suppress the huge background from conductive surfaces, which is demonstrated by focusing on well-defined self-assembled monolayers on flat gold substrates.

References

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- 2) H. Saito, H. Sato, T. Higashi and T. Sugimoto, submitted.
- 3) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).
- 4) T. Ichii, A. Sakurai and T. Sugimoto, in preparation.