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

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2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2019	JST-PRESTO Researcher [Innovative optics and photonics]
2021	Senior Scientific Research Specialist, Ministry of Education, Culture, Sports, Science and Technology

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	The 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 phase-sensitive sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\mathrm{Im}\chi^{(2)}$ 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 $\mathrm{Im}\chi^{(2)}$ 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.

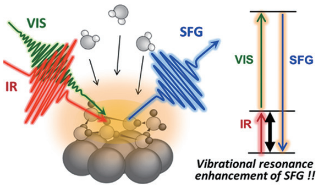

Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020). [review]
- 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).
- Z. Lin *et al.*, "Positive and Negative Impacts of Interfacial Hydrogen Bonds on Photocatalytic Hydrogen Evolution," *J. Am. Chem. Soc.* **146**, 22276–22283 (2024).
- H. Sato *et al.*, "Direct *operando* Identification of Reactive Electron Species Driving Photocatalytic Hydrogen Evolution on Metal-Loaded Oxides," *J. Am. Chem. Soc.* **146**, 24800–24807 (2024).
- A. Sakurai *et al.*, "Tip-Enhanced Sum Frequency Generation for Molecular Vibrational Nanospectroscopy," *Nano Lett.* **25**, 6390–6398 (2025).

1. Tip-Enhanced Sum Frequency Generation for Molecular Vibrational Nanospectroscopy(1)

We achieved the first detection of vibrational sum-frequency generation (VSFG) signals from molecules at the nanometer scale by developing a tip-enhanced VSFG (TE-SFG) system. Conventional VSFG is a powerful tool for probing molecular structures and orientations at surfaces, but its spatial resolution is restricted by the diffraction limit, yielding ensemble-averaged responses from millions of molecules.

To break this barrier, we integrated femtosecond VSFG spectroscopy with scanning tunneling microscopy. By confining IR and near-IR pulses within the nanogap between a metallic substrate and an STM tip, we detected vibrational signals from molecules adsorbed on the surface. The signal emerged only in the tunneling regime and vanished when the tip–substrate distance exceeded 1 nm, demonstrating localization within ~1 nm. Characteristic vibrational modes of terminal methyl groups were clearly resolved, and analysis of the nonlinear susceptibility revealed their absolute orientation.

Electromagnetic simulations clarified that such extreme localization arises from two synergistic enhancement mechanisms: (i) the antenna effect, which enhances mid-IR absorption at the tip apex, and (ii) plasmonic resonance in the nanogap, which boosts the radiation efficiency of the visible VSFG signal.(2) Together, these effects yield an enormous effective signal enhancement on the order of 10^{13}, enabling the near-field response from even a single molecule to dominate over far-field background contributions from ~10^{8} molecules within a laser focal spot.

This achievement represents the first demonstration of molecular vibrational SFG detection at the nanometer scale. By uniting ultrafast vibrational spectroscopy with scanning probe microscopy, TE-SFG establishes a powerful platform for nonlinear optical nanospectroscopy. The method enables ultrahigh spatial resolution and single-molecule sensitivity, paving the way toward single-molecule ultrafast spectroscopy and molecular imaging beyond the diffraction limit. These capabilities hold strong promise for elucidating interfacial molecular processes in catalysis and materials science, offering a novel route for the rational design of advanced functional materials.

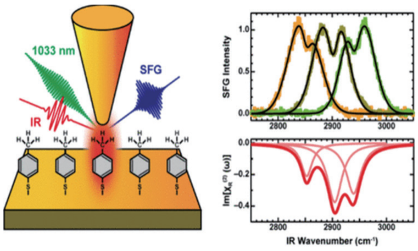

Figure 2. First successful demonstration of near-field tip-enhanced sum-frequency-generation vibrational nanospectroscopy of interfacial molecular systems.

2. Critical Impacts of Metal Cocatalysts on Oxidation Kinetics and Optimal Reaction Conditions of Photocatalytic Methane Reforming(3)

Photocatalytic activation of methane, the main component of natural gas, is a key process for sustainable energy conversion. In this study, we clarified how metal cocatalysts critically regulate oxidation kinetics and determine optimal reaction conditions in photocatalytic methane reforming under ambient temperature.

Traditionally, noble metal cocatalysts supported on semiconductor photocatalysts have been viewed primarily as electron collectors that promote reduction reactions. Our recent paradigm-shifting work demonstrated, however, that metal cocatalysts can also act as efficient acceptors of photogenerated holes.(4) Building on this concept, the present study provides the first direct evidence that cocatalyst loading drastically alters the methane pressure dependence of photocatalytic oxidation, shifting the optimal reaction regime to below ambient pressure.

Through systematic kinetic analysis, we revealed that this effect originates from molecular-level congestion of reactive intermediates during the oxidation process, with metal cocatalysts themselves functioning as active sites for oxidation. These findings overturn the conventional view that cocatalysts serve only reductive roles, highlighting their bidirectional contributions to both oxidation and reduction.

This work demonstrates that precise control of metal cocatalysts enables the microscopic design of surface reaction fields and optimization of reaction processes. By redefining the role of cocatalysts in photocatalysis, the study opens a pathway toward rational catalyst engineering for efficient and sustainable methane utilization.

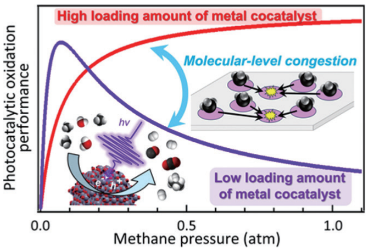

Figure 3. Photocatalytic oxidation kinetics and optimal pressure of methane vary significantly with the loading amount of metal cocatalysts. These variations are well described by kinetic analyses treating molecular-level congestion of oxidation intermediates.

References

1) A. Sakurai, S. Takahashi, T. Mochizuki and T. Sugimoto, *Nano Lett.* **25**, 6390–6398 (2025).
2) S. Takahashi, A. Sakurai, T. Mochizuki and T. Sugimoto, *J. Phys. Chem. Lett.* **14**, 6919–6926 (2023).
3) H. Sato and T. Sugimoto, *Chem. Commun.* **61**, 5942–5945 (2025).
4) H. Saito, H. Sato, T. Higashi and T. Sugimoto, *Angew. Chem., Int. Ed.* **62**, e2023060 (2023).

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