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First-Principles Molecular Dynamics Simulations for Water Interface Science

When water comes in direct contact with another substance, the “water interface” describes the area where their respective molecules meet. It is a place rich with peculiar chemical interactions whose underlying mechanisms are not well understood. Tatsuhiko Ohto at Osaka University is exploring the mysteries of the water interface. He uses first principles molecular dynamics (FPMD) simulations based on "density-functional theory”. These FPMD simulations compute the interactions of individual molecules based on their electronic states. Using a combination of massive simulations on high performance computers (HPC)[*1] and verification testing, his research is expanding the frontiers of FPMD, elucidating photo-catalytic reactions and finding the computational methods most suitable for simulating the water interface.

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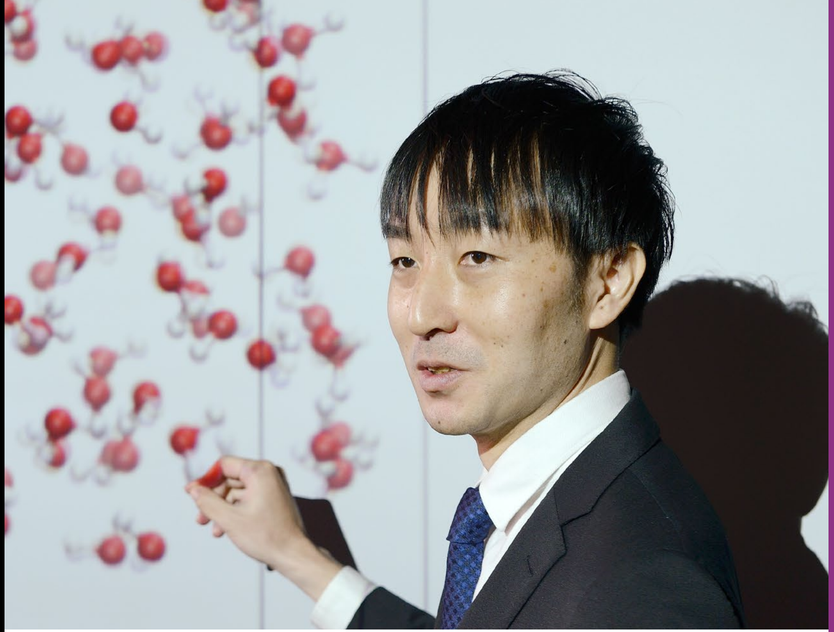


The Water Interface: Where Chemical Interactions Get Interesting

The “water interface” is the molecular boundary between water and the other substances that water comes in contact with. Some of the phenomena that occur here are unique to the water interface, and not seen in either substance by itself. The surface tension between the legs of an insect that walks on water and the water surface, and the ability of lotus flower leaves to repel water, are examples of water interface phenomena.

The interface between water and solids is also where the electrochemical and catalytic reactions needed for industrial technologies

[*1] High Performance Computing uses supercomputers to perform massive-scale calculations, typically to simulate complex real-world interactions for research and development work.

take place. The chemical properties where an electrode meets the electrolyte in a battery, for example, can significantly impact battery performance. And understanding the interface between catalysts and water molecules is important for generating clean hydrogen energy more efficiently.

Tatsuhiko Ohto at Osaka University is using first principles molecular dynamics simulations to elucidate the chemical interactions at the water interface.

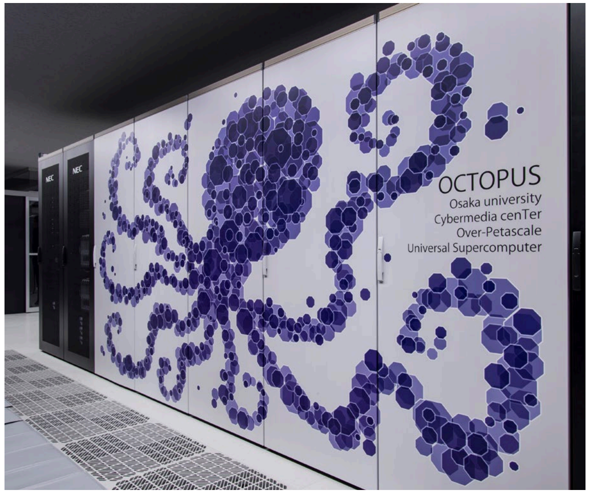
“The interface region is no more than a few water molecules thick. That very narrow region is extremely difficult to observe through experiments. But computer simulations allow us to reproduce those interactions down to the movement of molecules and even individual atoms. These simulations are proving to be an extremely powerful tool for studying what occurs at the interface.” says Ohto.

Simulations Track the Movement of Individual Molecules

Most molecular dynamics simulations to date have approximated these atomic interactions by relying on simple functions, such as that of a spring-like force. These are approximations of *classical force fields*. However, these spring constants and other known parameters might only apply to water molecules away from the interface. There was no guarantee that these values would also hold true for the peculiar place where water interfaces with another material.

Ohto therefore ran “first principles molecular dynamics” (FPMD) simulations based on deeper fundamentals, specifically the force values obtained through “density-functional theory” *quantum mechanical* modelling of the molecules’ electronic structures, rather than parameters obtained through experiments.

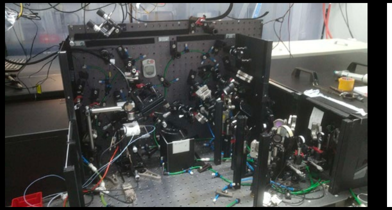
“Even if the simulations tell us what the molecular structure of an interface should be, it’s still just a theory until it’s proven through real world observations. So, we ran experiments using ‘sum frequency generation’ spectroscopy, which measures how the molecules vibrate at the interface. We then confirmed the interface properties predicted by our computations by comparing them to the experimental results.”

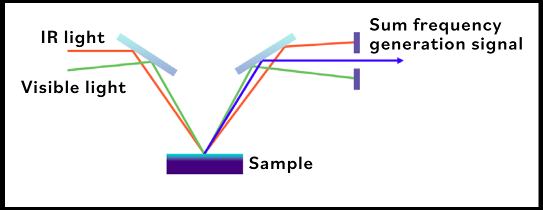


Explanation 1

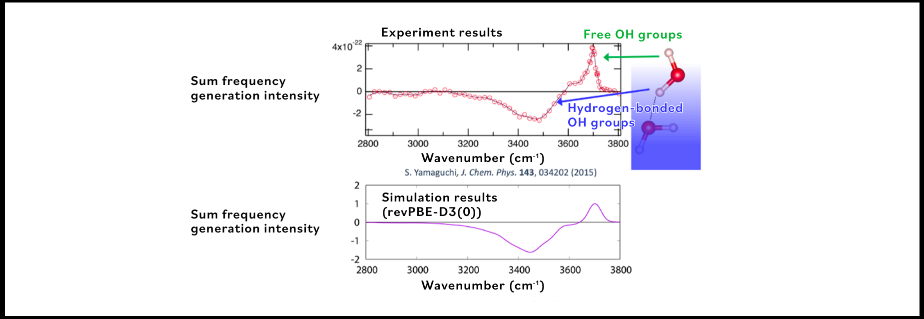
Sum Frequency Generation Spectroscopy Experiments

Ohto used “sum frequency generation” spectroscopy to verify the results of his FPMD simulations. In sum frequency generation, visible light and infrared light are directed onto the same water interface sample at the same time. The light reflected back from that interface is measured. When the frequency of the infrared light matches the vibration frequency of molecules at the interface, the interface *generates* light at a third *frequency*, which is the *sum* of the original two frequencies, hence “sum frequency generation”. The frequency of the infrared light is varied to obtain the shape and intensity of the reflected light spectrum. He then compared those results with the computer simulation findings.





Photograph (left) and diagram (right) of the experimental setup for the sum frequency generation spectroscopy measurements. The measurements were conducted by Ohto’s collaborators at the Max Planck Institute for Polymer Research in Germany.



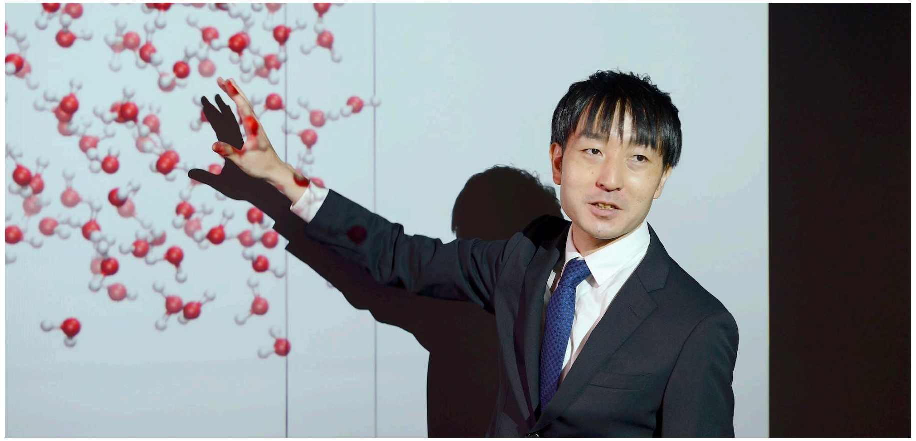
S. Yamaguchi, *J. Chem. Phys.* **143**, 034202 (2015)

Comparison of the sum frequency generation spectra of the water-air interface from the measurements (above) and the FPMD simulations (below). Both show peaks at frequencies around 3500 and 3700 cm^{-1}. These frequencies are thought to correspond to the stretching vibrations of the hydrogen-oxygen bonds in the water molecules at the interface (positive and negative peaks representing the upward and downward orientations of the OH bonds).

Explaining the Mysteries of Photo-catalyst Interfaces

Titanium dioxide is a commonly used photo-catalytic material. Under normal conditions, titanium dioxide is “hydrophobic”, meaning it repels water. But when exposed to ultraviolet light, it becomes “hydrophilic”, attracting water. This change was thought to be caused by “OH groups” (bonded pairs of oxygen and hydrogen atoms) dangling on the surface of the titanium dioxide at the interface. But it had yet to be confirmed.

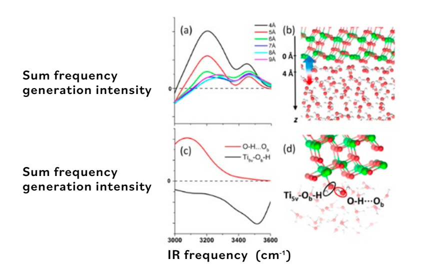
This prompted Ohto to run FPMD computations simulating titanium dioxide with and without OH groups dangling on its surface, and compare those results with the actual sum frequency generation spectra obtained through experiments. The results showed that the hydrophilic or hydrophobic properties correlate strongly to the presence or absence of OH groups. This gives us a better understanding of the photo-catalytic reactions occurring at this interface, and may allow us to produce more effective photo-catalysts in the future.



Explanation 2

First-Principles MD Simulations of the Titanium Dioxide/Water Interface

Ohto performed FPMD simulations with and without OH groups dangling on the surface of the titanium dioxide (see figure below). The measured spectra more closely matched the computer simulations with OH groups present (figure c) than without (figure a). This suggests that OH groups are present on the surface of UV-irradiated titanium dioxide.



Results of FPMD simulations
of the titanium dioxide/water interface.
(a) Depth-dependent sum frequency generation spectra of the OH bonds calculated with FPMD trajectories at the nonhydroxylated titanium dioxide/water interface. (b) A snapshot of the nonhydroxylated titanium dioxide/water interface.
(c) Individual contributions of the O–H hydrogen bonded to O_b atom and the O_b–H group chemisorbed on the five coordinated Ti atom to the sum frequency generation spectrum at the hydroxylated titanium dioxide/water interface.
(d) A snapshot of the hydroxylated titanium dioxide/water interface.

— S. Hosseinpour, T. Ohto et al., *J. Phys. Chem*. Lett. 8, 2195 (2017).

The University of Tokyo’s massively parallel Oakbridge-CX supercomputer and the Osaka University Cybermedia Center’s OCTOPUS supercomputer were used for these FPMD simulations. “HPC is essential for the enormous and complex computations that FPMD requires,” says Ohto.

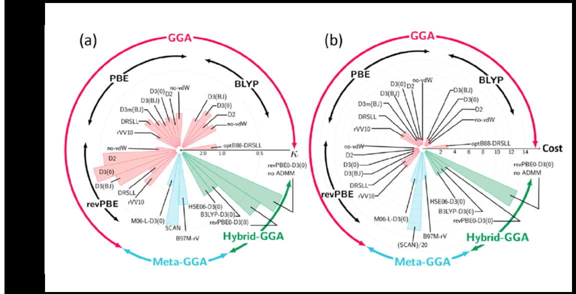
Finding Cost-Effective Calculation Methods

Because it is not possible to get an exact solution for a “many-body problem”, first principles calculations require some amount of approximation. “Density functional theory” is used for this purpose. While the exact expression of the “exchange-correlation functional” that describes the interaction between the electrons of interest is not known, various approximations have been proposed. In general, the more accurate the approximation, the higher its computational cost. So, cost performance is of particular importance for FPMD simulations, which can require tens of thousands of calculation steps. However, it was not well known which approximation formula would provide the most cost-effective calculations for such a distinctive subject of study as material interfaces.

Ohto ran water interface simulations to compare the accuracy and computation time of different approximation formulas. He found that some approximation methods with relatively small computational cost can provide highly accurate results. “Moving forward, we intend to apply these findings to our water interface research,” says Ohto.

Explanation 3

Comparing Approximation Methods for Exchange-Correlation Functionals



(a) Accuracy in approximating the water-air interface

(b) Computational cost

Comparing various approximations of the exchange-correlation functional for FPMD computations of the water interface. Figure (a) on the left shows the accuracy of the calculations (the longer the radius, the more accurate). Figure (b) on the right shows the computational cost (the longer the radius, the longer the calculation time). For example, “revPBE” was found to provide highly accurate approximations with relatively short computation times.

— T. Ohto et al., *J. Phys. Chem*. Lett. 10, 4914 (2019).

Toward More Realistic Water Interface Simulations

The findings of this research provided insights regarding the special properties of the water interface, and also showed the enormous potential of high performance computing for first principles molecular dynamics simulations. Ohto says he hopes to further develop these methods for more complex and more realistic studies of the physical phenomena that occur at the interface.

“We were able to find good calculation methods for the interface between water and air this time,” said Ohto. “In the future, I’d like to apply these methods to more complex water interfaces. In real world chemical reactions, the pH level varies according to the ions, and there are numerous impurities and defects on the surface of a solid. I’ d like to run simulations of water interfaces that are even closer to reality and take those effects into account.”

About the Researcher

Tatsuhiko Ohto says he’s been interested in the natural sciences since childhood. He became curious about astronomy in elementary school, and environmental issues in junior high and high school. An internship at Germany’s world-leading chemical manufacturer BASF during his master’s program led to his interest in research work. Having experienced R&D work in BASF’s computing department, he says he felt that, “there was still a lot left to do in academia”. Upon returning to his university laboratory, and wanting to do research on bigger issues that could be verified experimentally, he decided to pursue his long-standing interest in catalytic reactions. “There aren’t a lot of people working on first principles molecular dynamics, but Fugaku and the rest of Japan’s high-performance computing infrastructure have helped make it available to more people. I think it’s fascinating to be able to trace the movement of molecules and atoms. I hope more people will join in this field.”

Associated Research Projects

- “Development of an Exchange-correlation Functional to Describe Solid-Liquid Interfaces” (hp200081)

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