

ALS

SCIENCE HIGHLIGHT

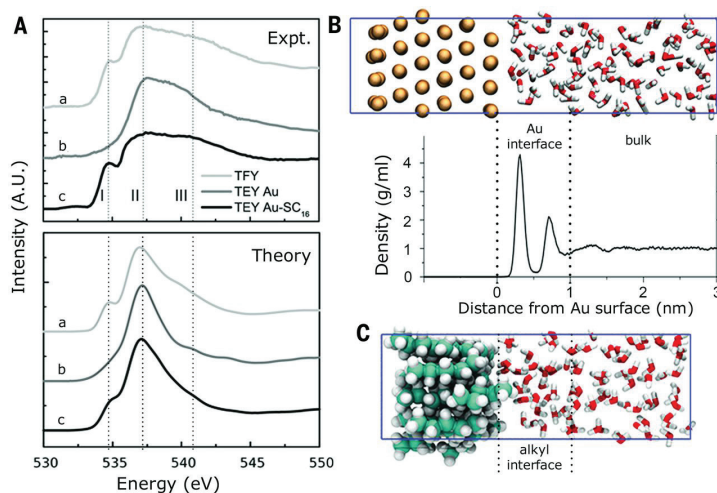
PUBLISHED BY THE ADVANCED LIGHT SOURCE COMMUNICATIONS GROUP

# Molecular Structure of Water at Gold Electrodes Revealed

The structure of liquid water has been intensely studied, but until recently, it has not been clear what happens to it when a surface is introduced. ALS researchers have now made a first-ever observation of the molecular structure of liquid water at a gold surface under different charging conditions. This marks the first time that the scientific community has shown such high sensitivity in an in-situ environment under working electrode conditions.

The structure of water within a nanometer of an electrode surface is known as the electrical double layer. The strong electrical field that builds up across the double layer is what drives electrochemical reactions. ALS researchers explored the structure of the solvent structure in an aqueous electrical double layer at a bare gold electrode. With no applied potential and at positive potentials, the layer is highly structured (resembling ice), with few dangling hydrogen bonds. However, at negative potentials, the layer is more like bulk water, but with half of the water molecules lying roughly flat on the surface.

ALS researchers were able to develop a method not only to look at the molecules next to the electrode surface, but to determine their arrangement



**Experimental and theoretical XAS at the O K-edge of water near the gold electrode, measured under open circuit in the liquid flow cell. Curves marked (a) correspond to the total fluorescence yield spectrum and calculated XAS spectrum for bulk water. Curves marked (b) correspond to the total electron yield (TEY) spectrum and calculated XAS spectrum for the interfacial water molecules next to the gold electrode. Curves marked (c) correspond to the TEY spectrum of water after covering the gold surface with a hexadecanethiol monolayer and calculated XAS spectrum for interfacial water molecules next to an alkyl surface, respectively. Snapshots from AIMD simulations of (B) Au-water, with associated mass density as a function of distance from the surface, and (C) C16SH-water interface, with the gold atoms omitted in the latter case for computational efficiency. The water column separating the Au electrodes is large enough that the water density fluctuations are smoothed beyond the first few layers. Only half of the water column space is shown.**

changes depending on the voltage. With gold as a chemically inert electrode, and slightly saline water as an electrolyte, the researchers used a new twist on x-ray absorption spectroscopy (XAS) to probe

the interface and show how the interfacial molecules are arranged.

Upon absorbing an x-ray photon, the excited water molecule can emit either electrons or photons. The amount of

Publication about this research: J.Velasco-Velez, C. Wu, T.A. Pascal, L.F. Wan, J.-H. Guo, D. Prendergast, and M. Salmeron. "The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy," *Science* **346**, 3624 (2014).

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Research funding: U.S. Department of Energy (DOE), Basic Energy Sciences (BES). Operation of the ALS is supported by the DOE BES.

photon emission, or fluorescence, is one indicator of how many x-ray photons have been absorbed. However, fluorescing x-rays can be detected from molecules ranging from those at the gold surface to those deep (micrometers) inside the



## The Interfacial Layer

When a solid material is immersed in a liquid, the liquid immediately next to its surface differs from that of the bulk liquid at the molecular level. This interfacial layer is critical to our understanding of a diverse set of phenomena from biology to materials science. When the solid surface is charged, just like an electrode in a working battery, it can drive further changes in the interfacial liquid. However, elucidating the molecular structure at the solid-liquid interface under these conditions has proven difficult.

At an electrode surface, the build-up of electrical charge, driven by a potential difference (or voltage), produces a strong electric field that drives molecular rearrangements in the electrolyte next to the electrode.

In the x-ray absorption spectroscopy (XAS) process developed by ALS researchers, a material absorbs x-ray photons at a specific rate as a function of photon energy. A plot of the absorption intensity as a function of energy is referred to as a spectrum, which, like a fingerprint, is characteristic of a given material molecule and its chemical state. Our eyes recognize many materials by their characteristic colors, which are related to their visible light absorption spectra. The x-ray photons used in this study have energies that are about 250 times higher than those of visible light.

Typical XAS measurements are made under vacuum conditions, as x-rays are readily absorbed by matter, even the nitrogen molecules in air. But liquids will quickly evaporate in a vacuum. By using a very thin (100 nm, or a tenth of a micrometer) x-ray transparent window, with a thin coating of gold (20nm), on a sealed liquid sample holder, the researchers were able to expose water molecules in the liquid to x-rays and collect their spectra.

liquid far from the influence of the gold surface, and these dominate the measured spectrum. The challenge was to collect a signal that would be dominated by the interfacial region. Researchers accomplished this by measuring electron emissions because electrons emitted from x-ray excited water molecules travel only nanometer distances through matter.

There's an additional problem that arises when studying liquids in contact with working electrodes because they carry a steady current as in batteries and other electrochemical systems. While the emitted electrons from nearby molecules are detectable, this contribution to the current is dwarfed by the normal "Faradaic" current of the battery at finite voltages. When measuring current off the electrode, it is critical to determine which part is due to the x-rays and which is due to the regular battery current.

To overcome this problem, the researchers pulsed the incoming x-rays from the synchrotron at a known frequency. The current contribution resulting from electron emission by interfacial molecules is thus pulsed as well, and instruments can separate this nanoampere modulated current from the main Faradaic current.

These experiments result in absorption vs. x-ray energy curves (spectra) that reflect

how water molecules within nanometers of the gold surface absorb the x-rays. To translate that information into molecular structure, a theoretical analysis technique was developed by scientists at Berkeley Lab's Molecular Foundry.

It turns out that for a neutral gold surface, a significant number of water molecules next to the gold surface orient with hydrogen (H) atoms pointing toward the gold. Water molecules are bound together by hydrogen bonds, which orient the slightly positively charged H atoms in each molecule towards the slightly negatively charged oxygen (O) atoms of neighboring molecules. This network of hydrogen bonds is what holds water molecules together to make a liquid under conditions of temperature and pressure that we consider comfortable as humans. It is perhaps surprising that the inert gold surface can induce significant numbers of water molecules not to hydrogen-bond to each other but to bond to the gold instead. This number is enhanced when the gold is negatively charged and therefore attracting the more positive H atoms. Furthermore, positively charged gold ions cause water molecules to orient their H atoms away from the gold, which strengthens the hydrogen bond network of the interfacial liquid.

