

## Probing the Liquid Water Surface

**W**ATER. It covers 70 percent of Earth's surface, makes up 60 percent of the human body, and forms 90 percent of the composition of blood. Life as we know it wouldn't exist without water. Yet, each molecule of this common, seemingly simple substance—one oxygen atom bound to two hydrogen atoms—holds a world of mystery within its subnanometer-size structure.

Of particular interest to physical and structural chemists is what happens at the interfaces where water meets air or other substances such as proteins. The density of the water molecules, for example, can change by many orders of magnitude between the liquid below the surface and the vapor above the surface. What happens in the transition zone? Much has been theorized and calculated, but corroborating experiments have been difficult to conduct—until now.

A team of researchers from Lawrence Livermore and Lawrence Berkeley national laboratories and the University of California at Berkeley has developed a technique using soft x rays for studying in detail the surfaces of liquid microjets. The groundbreaking work of the collaboration, which included Livermore chemist James Tobin, UC Berkeley chemistry graduate student Kevin Wilson, and UC Berkeley chemistry professor Richard Saykally, was reported in both *Physical Review Letters* and a cover article in the *Journal of Physical Chemistry B*.

The standard technique for examining the chemical structure of a protein at the molecular and atomic levels, for example, uses a frozen sample. Yet, the three-dimensional structure of molecules in a frozen sample differs from that of molecules in a sample at body temperature. “There’s a strong drive to find ways of studying the molecular structures of such substances in their normal biological state,” explains Tobin. “The experimental technique we developed is one possible method.” Ultimately, this technique may allow scientists to better determine the structure of biological systems such as hemoglobin in blood and to understand how proteins move through solution.

### X Rays Measure Atomic Interfaces at Water's Surface

One of the primary tools for probing the electronic structure of interfaces is x-ray absorption spectroscopy. However, this x-ray technique has difficulty measuring the structural interfaces at the atomic and molecular level for liquids, particularly those containing hydrogen atoms. “And hydrogen is a key atomic component in many systems,” says Wilson. “Many of the interesting properties of water are due to the hydrogen bonds between neighboring molecules.” (See the [box on p. 21.](#))

One problem facing scientists who want to examine hydrogen's role in water or other liquids is that the amount of spectroscopic data gathered from hydrogen on the surface or interior of a water sample is extremely small. This weak signal is usually overwhelmed by signals generated from the water vapor that blankets the surface of liquid. Another problem is that with x-ray spectroscopy systems, the sample must be in a vacuum, which means the liquid must be contained or behind a barrier such as a window. “Windows, even thin-walled cells, will interact with the surface of the liquid and absorb a majority of the x-ray signal, leaving us nothing to measure by,” Tobin explains.



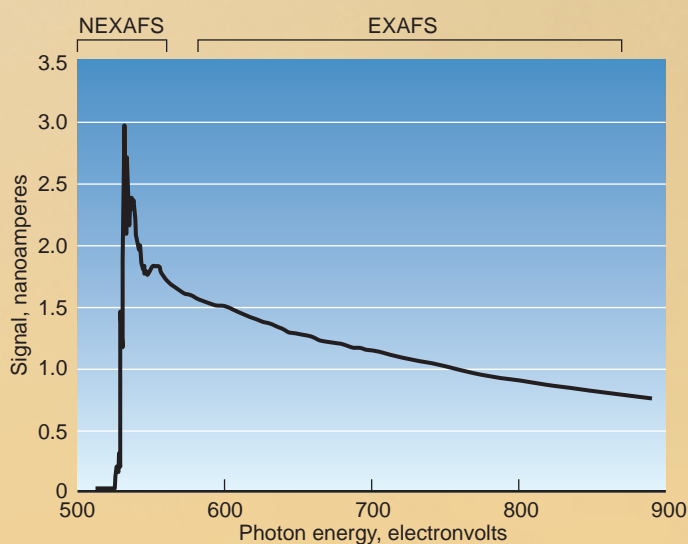
The team overcame these problems, using liquid microjet technology and Lawrence Berkeley's Advanced Light Source (ALS). In the experiments, a 20-micrometer-diameter jet of liquid pressurized to about 3.4 megapascals (500 pounds per square inch) squirts through a very small nozzle. "The smaller the dimensions of a liquid sample, the less vapor there is," explains Wilson. Two other team members, Lawrence Berkeley beamline scientists Bruce Rude and Tony Catalano, devised a pumping system that not only allowed the system to meet the vacuum requirements of the ALS but also reduced the amount of residual vapor. "As far as I know, these experiments were the first time that experiments on a liquid jet were conducted at the ALS," notes Wilson.

To probe the structure of water molecules at the surface of the water jet, researchers use intense x-ray beams of energies at the "soft" end of the spectrum generated by the ALS. The x rays are directed at the jet about 1 to 2 millimeters in front of the nozzle. At this distance, the liquid is still at room temperature and has not yet begun to expand and cool. Because it is impossible to examine anything smaller than the wavelength of light being used, the light waves for studying atoms and molecules must be extremely short. The ALS is ideal for these sorts of measurements, because it can produce light at wavelengths of a few tenths of a nanometer—about the sizes of atoms, molecules, chemical bonds, and the distances between

atomic planes in crystals. Even more importantly, the ALS can supply x rays at 530 electronvolts and above—the amount required to "kick" an electron from the innermost shell of an oxygen atom out of the water molecule. (See the [box on p. 22.](#))

### Electrons at the Edge

Two x-ray spectroscopy techniques were used to examine the structure of the water surface in the microjet: extended x-ray absorption fine structure (EXAFS) and near-edge x-ray absorption fine structure (NEXAFS). Both techniques are based on the fact that atoms will absorb x rays, the amount of absorption depending on the energy level of the x ray and the type of atom doing the absorbing. Generally, the proportion of x rays absorbed (called the absorption coefficient) decreases as x-ray energies increase. However, at energy levels specific to each element, a sudden increase in the absorption coefficient is observed. These energies, called absorption edges, correspond to the energy required to eject an electron



X-ray absorption spectra at the oxygen K edge (530 electronvolts) of water vapor showing the near-edge x-ray absorption-fine-structure (NEXAFS) and extended x-ray absorption-fine-structure (EXAFS) regions of the spectra.

### Water Basics

Water is the most familiar and abundant liquid on Earth. Given its low molecular weight, it should, by all rights, be a gas at such temperatures. The fact that it is not has much to do with its molecular structure. The atoms in a water molecule—two hydrogen and one oxygen—are arranged at the corners of an isosceles triangle. The oxygen atom is located where the two equal sides meet, and the angle between these sides is about 105 degrees. The asymmetrical shape of the molecule arises from a tendency of the four electron pairs in the outermost shell of a tetrahedron around the oxygen nucleus. Two electron pairs from each oxygen form covalent bonds with the two hydrogen atoms. (A covalent bond is created when two atoms share a pair of electrons.) The hydrogen atoms are drawn slightly together, resulting in the V-shaped water molecule. This arrangement results in a polar molecule, with a net negative charge toward the oxygen end and a net positive charge at the hydrogen end. When water molecules are close enough, each oxygen attracts the nearby hydrogen atoms of two other water molecules, forming hydrogen bonds. Although much weaker than the covalent bonds holding the water molecule together, hydrogen bonds are strong enough to keep water liquid at ordinary temperatures, despite its low molecular weight. These hydrogen bonds are also responsible for various other properties of water, such as its high specific heat.



from the atom. For an isolated atom, the sudden peak at the absorption edge occurs as the electron is ejected and then a gradual decrease in x rays absorbed occurs as the x-ray energy levels are increased. However, for atoms in a molecule or in a liquid or solid state, the closeness of other atoms around the absorbing atom causes oscillations in the amount of x-ray absorption just past the absorption edge. These “wiggles” detected in the absorption edge, called EXAFS oscillations, arise from the ejected electron backscattering off neighboring atoms. The structure of the oscillations—that is, their frequency and amplitude—depends on the distance and number of neighboring atoms. The length of bonds between neighboring atoms—such as oxygen atoms or hydrogen atoms in water, for instance—can be determined by analyzing these EXAFS oscillations.

Whereas EXAFS is sensitive to distances between atoms and molecules, NEXAFS is sensitive to bond angles and bond lengths between atoms and molecules. NEXAFS is similar to EXAFS, but instead of providing enough energy to eject an electron, a NEXAFS x ray has just enough energy to cause an electron to jump up to an unoccupied higher energy level. The steplike vertical rise in absorption intensity resides between

the absorption edge and the EXAFS region, hence the “near-edge” designation. The energy at which this rise occurs differs according to the individual element, chemical bond, or molecular orientation. With NEXAFS, researchers tune the x-radiation to different frequencies to help determine the orientation of a molecule on the surface of a liquid and its intramolecular bond lengths.

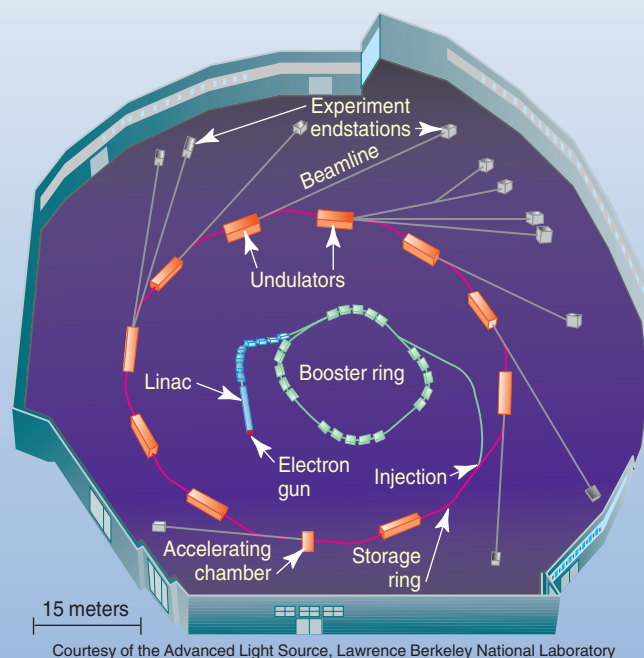
### Measuring the Ties That Bind

In their first experiment, reported in *Physical Review Letters*,<sup>1</sup> the team members made the first definitive observation of EXAFS from hydrogen and quantified the covalent oxygen–hydrogen bond in water vapor as  $0.095 \pm 0.003$  nanometer in length. Their research showed that hydrogen bonds can be directly detected in liquid water, paving the way for future studies of intermolecular hydrogen bonds—structures that are critical to understanding the unique properties of liquid water.

In their second experiment, reported in *The Journal of Physical Chemistry B*,<sup>2</sup> the researchers obtained NEXAFS spectra for the water surface that appear as intermediate between the bulk- and the gas-phase spectra. The appearance

## How the ALS Works

The Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory generates intense light for scientific and technological research. As the world’s brightest source of ultraviolet and soft x-ray beams and the world’s first third-generation synchrotron light source in its energy range, the ALS makes previously impossible studies a reality. Inside the ring structure of the facility, electrons traveling at nearly the speed of light are forced into a circular path by magnets and emit bright ultraviolet and x-ray light that shines down beamlines to experiment stations at the end of the lines. The x-ray light produced is one billion times brighter than the Sun’s. This high brightness means that the x rays are highly concentrated, allowing many x-ray photons per second to be directed onto a tiny area of a material. The increased illumination allows one to “see” in more detail, just as seeing details in a landscape is easier at noon, when there are many photons from the Sun, rather than at dusk, when the photons are fewer. Researchers use the ALS for protein crystallography, ozone photochemistry, x-ray microscopy of biological samples, and optics testing as well as for studying the electronic structure of matter. For more information about the ALS, see [www-als.lbl.gov/](http://www-als.lbl.gov/).

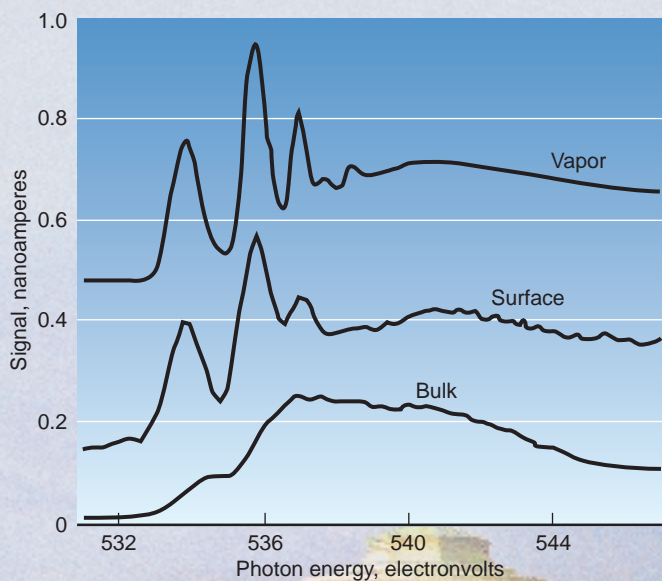




of the surface spectrum is consistent with an interface or surface in which molecules are in transition from the bulk phase to the vapor phase as in evaporation. The researchers measured distances of  $0.3 \pm 0.005$  nanometer between neighboring oxygen atoms on the surface of the microjet, and distances of  $0.285 \pm 0.005$  nanometer between neighboring oxygen atoms about 2.5 nanometers inside the jet. The latter result is in line with previous studies of the bulk liquid. The surface measurement supports results from computer simulations, which predicted that on the surface, weaker hydrogen bonds would exist, leading to water molecules that would be further apart and more mobile compared to molecules below the surface.

“What these experiments showed was that this technique works and works well,” says Tobin. Since the results were published, the team has moved forward, using this technique to examine molecular structures of other solvents such as methanol, ethanol, and isopropyl alcohol. One of the next steps will be to examine sodium chloride solution—in other words, salt water. It’s all just the beginning of obtaining a better understanding of liquid surface chemistry—one of the big unknowns in modern science.

—Ann Parker



Near-edge x-ray absorption-fine-structure (NEXAFS) spectra of water vapor (top), liquid water surface (middle), and bulk, or interior, water (bottom), showing the surface to have an intermediate electronic structure between vapor and the bulk liquid.

**Key Words:** Advanced Light Source (ALS), extended x-ray absorption fine structure (EXAFS), hydrogen bonds, liquid surface chemistry, microjet, molecular structure, near-edge x-ray absorption fine structure (NEXAFS), water, x-ray spectroscopy.

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