

Attosecond analysis illuminates a watery mystery

With powerful x-ray free-electron lasers, researchers are making great strides in ultrafast spectroscopy—with lessons about how molecules arrange themselves at rest.

In the 1990 movie *Awakenings*, Robin Williams's character, based on real-life neurologist Oliver Sacks, revived patients from a catatonic state using a drug developed to treat Parkinson's disease. The parkinsonian tremors, he reasoned, if accelerated to the extreme, would appear not as a tremor at all but as immobility. Although the film simplifies the neurological principles, he was right, and the drug worked.

Now, working at SLAC's Linac Coherent Light Source (LCLS), researchers led by Linda Young, Robin Santra, and Xiaosong Li are making a similar connection between fast motion and complete stillness. They set out to develop an experimental capability at the cutting edge of ultrafast science: a pump-probe experiment in which a sample is excited with one x-ray pulse and probed with another, all in less than a femtosecond. And yet, when they applied their technique to liquid water, as illustrated in figure 1, their results had more to say about water's equilibrium structure than about its subfemtosecond dynamics.¹

Laser power

The push to observe matter on faster and faster time scales has been the subject of multiple Nobel Prizes. In 1999 Ahmed Zewail was honored for his work in femtosecond spectroscopy, which for the first time could measure the real-time motions of atomic nuclei, including the making and breaking of chemical bonds (see *PHYSICS TODAY*, December 1999, page 19). Two dozen years later, Pierre Agostini, Anne L'Huillier, and Ferenc Krausz were recognized for bringing the attosecond regime—the next unit of time shorter than femtoseconds and the natural time scale of the motion of electrons—under experimental control (see *PHYSICS TODAY*, December 2023, page 13).

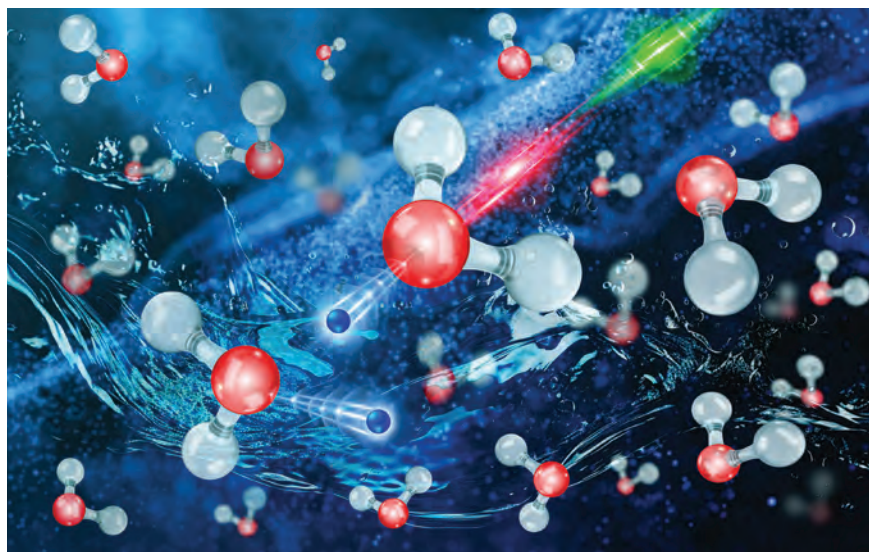


FIGURE 1. LIQUID WATER is pumped and probed by two closely spaced x-ray pulses, represented in this artist's depiction as red and green flashes. The first pulse kicks electrons (blue) out of some of the water molecules, and the second pulse measures the energy levels of the ionized molecules. (Courtesy of Stacy Huang.)

Last year's Nobel focused on one facet of attosecond research: the discovery that attosecond-scale light pulses could be made and characterized with ordinary tabletop lasers. Tabletop attosecond experiments have allowed the measurement of quantities previously thought to be unmeasurable, such as the time scale of the photoelectric effect. But pump-probe experiments with two attosecond-scale pulses have remained largely out of reach to the tabletop approach.

The problem is that the efficiency of tabletop attosecond pulse generation, although higher than one might naively expect, is still extremely low, so the pulses are dim. And pump-probe spectroscopy is a nonlinear technique: To produce a signal, an individual atom or molecule must interact with a photon from the pump pulse and one from the probe pulse. The output, therefore, depends on the product of the pulse intensities, and with weak pulses, it doesn't leave much to see.

But x-ray free-electron lasers (XFELs), such as the LCLS, have also entered the attosecond game. An XFEL wouldn't fit on a tabletop—the LCLS, for example, is more than 3 km long—and only a handful of them are in operation around the

world. But their extraordinarily intense x-ray beams, a billion or more times as bright as synchrotron sources, make them ideal for many applications. (See the article by Phil Bucksbaum and Nora Berrah, *PHYSICS TODAY*, July 2015, page 26.)

An XFEL's x rays don't naturally come out in attosecond-scale bursts. The electron bunches, which pass through magnetic undulators to produce radiation, are typically a few femtoseconds long. But there's a phenomenon called microbunching instability, which speeds up some electrons in a bunch and slows down others, that temporarily transforms a continuous electron bunch into a train of shorter microbunches. It was a major technical challenge to figure out how to control and exploit microbunching to produce attosecond-scale XFEL pulses.² But once the first attosecond pulses were achieved, pulse pairs weren't far behind.³

Twin peaks

Attosecond pump-probe spectroscopy captures how the electrons in an atom, molecule, or material respond in the first instants after being struck by an x ray. Young and her postdoc Shuai Li, who led the experimental team on the new re-

search, had hoped (and still do hope) to use the technique to study the mechanisms of radiation damage in aqueous chemical systems. So for their first experimental target, they chose liquid water. And they happened upon a completely different implication of their measurements.

Water, after all, is a strange substance. Among its many anomalous properties, liquid water can take two structurally distinct forms: a high-density liquid and a low-density liquid. It's only in a deeply supercooled regime with the sinister-sounding name "no-man's-land" that the liquids exist as separate phases. (See "Fast x-ray scattering reveals water's two liquid phases," *PHYSICS TODAY* online, 19 November 2020.) But the distinct structures were thought to leave an imprint on water's room-temperature properties too.

That speculation was fueled by water's x-ray emission spectrum. As shown schematically in figure 2a, x-ray emission spectroscopy kicks an electron out of a low-energy core orbital and measures the energies of the photons emitted

as electrons from other orbitals tumble down to fill the hole. Each valence orbital—marked as $1b_2$, $3a_1$, and $1b_1$ in the figure—should yield photons of a characteristic energy, albeit with some broadening of the spectral peaks to reflect how molecules in a liquid interact randomly with their neighbors.

As figure 2b shows, though, the $1b_1$ peak isn't just broadened; it's split in two. That's not what one would expect from a homogeneous liquid. One explanation, then, is that water isn't really a homogeneous liquid, but rather an amalgamation of globs of molecules with two distinct liquid structures—perhaps the same structures as the low-density and high-density phases of no-man's-land.⁴

But that's not the only possible origin of the split peak. Another is that x-ray emission spectroscopy is measuring something other than water's equilibrium structure. That possibility is easily overlooked, because emission spectroscopy in general isn't designed to study dynamical processes. But the lifetime of inner-shell

holes in oxygen is about 4 fs, which is plenty of time for atoms—especially the lightweight hydrogen atoms—to move around. It's entirely possible that water molecules, once ionized, could quickly distort their structures in ways that affect the x-ray emission spectrum.

Attosecond pump-probe spectroscopy can resolve the ambiguity. As shown in figure 2a, it accesses the same energy transitions as x-ray emission spectroscopy, but in reverse: The first pulse removes an electron from a valence orbital— $1b_2$, $3a_1$, or $1b_1$ —and the second pulse excites a core electron into the vacancy. The researchers measure the energies of the photons absorbed out of the second pulse. Their spectrum, shown in figure 2b, contains a single unsplit $1b_1$ peak.

The delay between the pump and probe pulses was a mere 700 attoseconds, which isn't enough time for atoms to move. Even so, says Santra, "it was not totally obvious that the observed signal would be confined to the attosecond

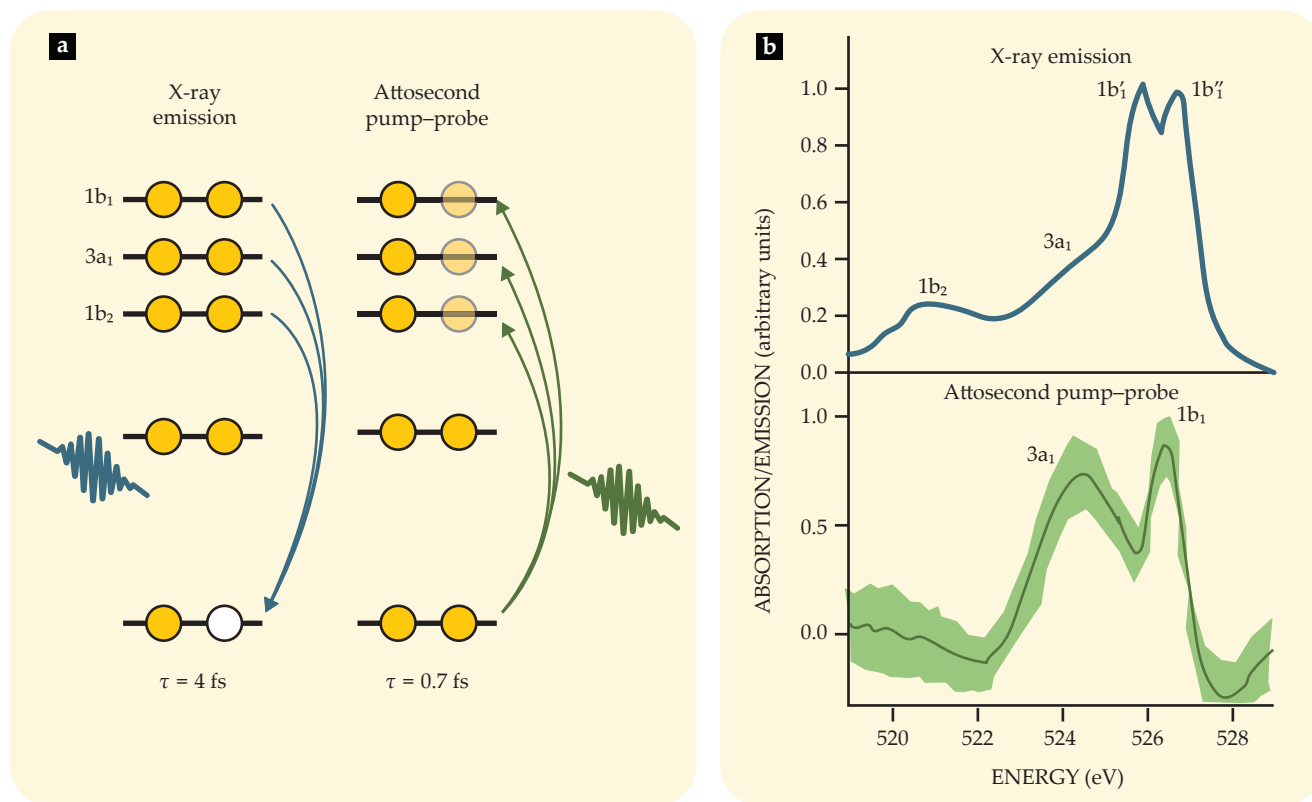


FIGURE 2. TWO SPECTROSCOPIC TECHNIQUES (a) measure the same energy transitions in water, but in reverse order. The big difference between them is the time scale τ of the measurement: X-ray emission spectroscopy gives hydrogen atoms enough time to move around, whereas attosecond pump-probe spectroscopy does not. (b) So when the $1b_1$ peak is split in two in the x-ray emission spectrum but not in the attosecond pump-probe spectrum, the implication is that the splitting is due to hydrogen-atom dynamics, not the result of an inhomogeneous structure of liquid water. (Adapted from ref. 1.)

time scale.” The probe pulse doesn’t merely excite electrons; rather, it creates oscillating superpositions of quantum states that send electromagnetic ripples throughout the liquid. The consequence is that the pump–probe spectrum could be just as affected by hydrogen-atom dynamics as the x-ray emission spectrum is. It took months of theoretical work by Santra, his postdoc Swarnendu Bhattacharyya, Li, and his student Lixin Lu to show that it wasn’t: The ultrafast experiment was a true measurement of what water looks like at rest.

Importantly, the result has nothing to do with the existence of two liquid-water phases in no-man’s-land. And it’s still possible that room-temperature water is a mix of high-density and low-density globs. “The evidence for a liquid–liquid phase

transition is still sound, as far as we can tell,” says Young. “What we’ve demonstrated is that if there are two structural motifs, their impact on the x-ray emission spectrum is much smaller than the impact of hydrogen-atom motion.”

Room to run

Water is far from the only substance whose x-ray emission spectrum might have been misinterpreted. Whereas inner-shell holes in oxygen have lifetimes of 4 fs, those in carbon and nitrogen persist for even longer. Just about all organic molecules, including proteins and DNA, could have x-ray emission spectra slow enough to be muddied by hydrogen dynamics. “But with attosecond methodology, we can outrun the undesirable hydrogen motion,” says Young.

Outrunning all of it could take some time, however. The LCLS, currently the only XFEL equipped for attosecond pump–probe spectroscopy, is already oversubscribed by a factor of five: For every experiment granted beam time, four others get turned away. But as more of the world’s XFELs develop attosecond capabilities, the burden could be eased.

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Highly charged uranium tests the limits of quantum electrodynamics

Technical advances and clever correction schemes separated signals of quantum effects in heavy atoms from the noise.

When it comes to the most tested and precise scientific theories, quantum electrodynamics (QED) ranks at or near the top of the list. The theory of light–matter interactions has predicted, for example, the value of the electron’s magnetic dipole moment to 12 significant figures, and observations published last year are in agreement.¹ That’s equivalent to measuring the distance from New York City to Los Angeles to a precision better than the width of a human hair.² Yet despite QED’s superlative predictions, the theory is more readily validated in light atoms than in heavy atoms.

For low-mass atoms, perturbation theory can precisely predict QED effects, such as a slight change in the transition energy of an electron that’s decaying from an excited atomic orbital to a low-energy orbital. But in a high-mass atom, relativistic and QED effects cannot be well approximated as small disturbances to the system. That’s because such effects scale with $Z\alpha$ —where Z is the

atomic number and $\alpha \approx 1/137$ is the fine structure constant. One can use nonperturbative methods to predict QED effects, and that’s been done for heavy atoms, such as uranium.³ The problem is that the methods have yielded different calculations and aren’t as precise as perturbative approaches.

Previous efforts from 2009 to observe the transition energy of highly ionized uranium with x-ray spectroscopy weren’t precise enough to distinguish one calculation of QED effects in uranium from another.⁴ Since then, advances have been made in predicting QED effects in heavy atomic systems and improving the experimental instrumentation. A team of 34 researchers, led by Martino Trassinelli of the CNRS in Paris and Robert Loetzsch of Germany’s Friedrich Schiller University Jena, now present transition-energy measurements in highly ionized uranium, and they’re precise enough to distinguish small QED effects in high-mass systems.⁵

Uranium that comes around

Willis Lamb and Robert Retherford helped jump-start the field of QED with a 1947 experiment. They observed an unexpected energy difference—what became known as the Lamb shift—between the two lowest excited orbitals of the hydrogen atom,

levels that existing predictions said should have the same energy. In response, researchers developed theoretical techniques to accurately account for the Lamb shift, which is a QED effect caused by the electron interacting with virtual photons.

Shortly after the discovery in the lightest atom, many began to wonder: How would the effects of QED change the behavior of an electron bound to uranium or another heavy element? Validations of QED over the past several decades have mostly been done in light atoms, but an experiment in highly ionized uranium could test for quantum effects in previously untested parameter space.

By the late 2000s, after decades of work, some theorists used nonperturbative methods to precisely calculate QED effects in heavy atoms with strong electric fields.⁴ The advance set a challenging and motivational target for experimentalists: If x-ray spectroscopy measurements of an electron’s transition energy are precise enough, then QED effects in highly ionized uranium are observable.

Measuring a transition energy in a massive system like uranium demands a facility with a storage ring that can produce and hold a lot of ions. For experiments that test QED effects in heavy systems, the only place capable of meeting those requirements is the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany. (The Heavy Ion Research Facility in Lanzhou, China, does offer similar capabilities, but the