Photoemission of core-level electrons is caught in the act

Advances in attosecond x-ray physics enable researchers to glimpse unique electron interactions not seen before in the study of valence electrons.

Electrons move on the time scale of attoseconds, each of which is a vanishingly short billionth of a billionth of a second. For many years, electron motion was unobservable because no laser was capable of producing pulses of light shorter than a few femtoseconds. The ability to measure motion on such time scales is determined by the duration of the laser pulses: If the pulse lengths are too long, the motion can't be calculated with sufficient precision.

At the turn of this century, the attosecond limit was broken by two groups—one led by Pierre Agostini and another by Ferenc Krausz—both of which relied on earlier nonlinear-optics results from Anne L'Huillier and colleagues. For their experimental contributions, the three researchers received the 2023 Nobel Prize in Physics (see Physics Today, December 2023, page 13).

Using ultrafast pulses of light generated from tabletop lasers, the researchers made many observations of processes that were once considered instantaneous. In 2010, for example, Krausz and colleagues found that the photoionization of valence electrons in neon took tens of attoseconds.[1] A follow-up experiment in 2017 led by L'Huillier refined the timing further.[2]

Complex multielectron interactions can be studied with measurements of core electrons—those closest to an atom's nucleus. But their motion and interactions on the attosecond time scale have remained out of reach. The binding energies of such electrons are too high to be studied with attosecond pulses of light from low-energy tabletop lasers.

Now Stanford University's Taran Driver, Agostino Marinelli, and James Cryan and their colleagues have harnessed recent advances in x-ray free-electron lasers (XFELs) to witness the photoelectric effect in core electrons.[3] The new measurement technique, illustrated in figure 1, can shed light on the unique interactions of core electrons with other electrons and how x rays can affect electronic properties of matter.

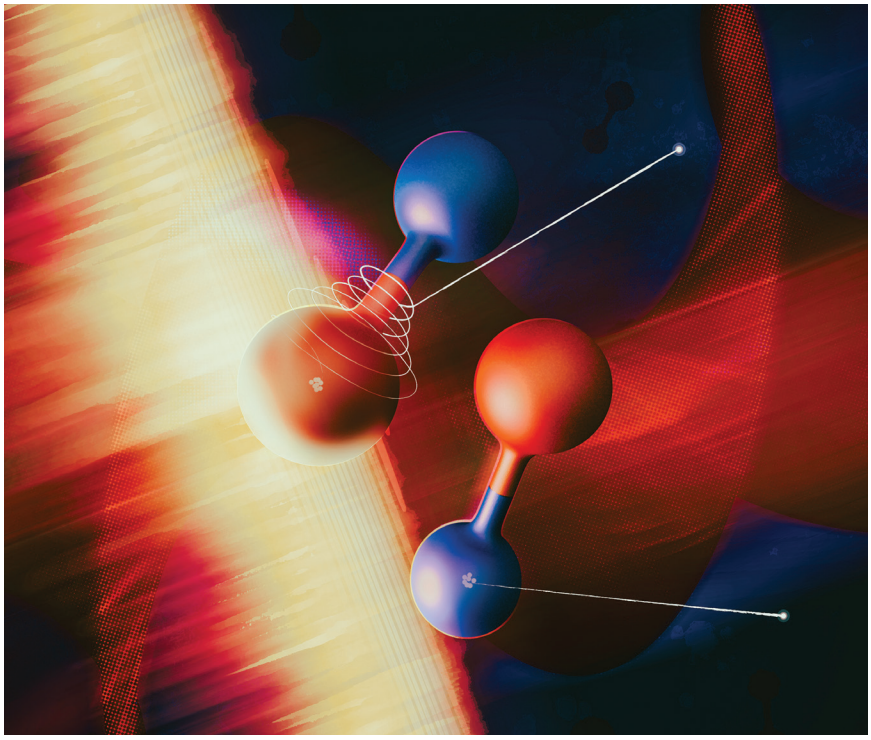

FIGURE 1. AN ULTRAFAST PULSE of bright x-ray light bombards two nitric oxide molecules, initiating photoionization. The time at which the molecules' core electrons (white dots) are emitted can be inferred from the angle at which they are deflected by a circularly polarized IR laser field. (Courtesy of Gregory M. Stewart, SLAC National Accelerator Laboratory.)

Shorter, brighter waves

The workhorses of attosecond experiments are the ultrafast light pulses created by high harmonic generation (HHG). An intense IR laser illuminates a target, usually an atomic or molecular gas, whose electrons are then excited and emit higher-frequency harmonics of the driving laser. With such a source, researchers can produce pulses of extreme UV (XUV) light as short as dozens of attoseconds. (For more on HHG, see the article by Paul Corkum, Physics Today, March 2011, page 36.)

The XUV pulses produced via HHG have high-enough photon energies to excite valence electrons and short-enough durations for researchers to measure the time scale of the electrons' motion. Exciting core electrons, however, requires soft x rays, which have higher energies than XUV photons but not quite as high as that of hard x rays used for medical imaging. Recent efforts have succeeded in producing HHG-based sources at x-ray wavelengths. But the number of photons in an ultrafast pulse decreases as the photon energy increases. That limitation has prevented researchers from using HHG-based sources to study the photoionization of core electrons.

An alternative source of ultrafast pulses is the XFEL. The kilometer-sized

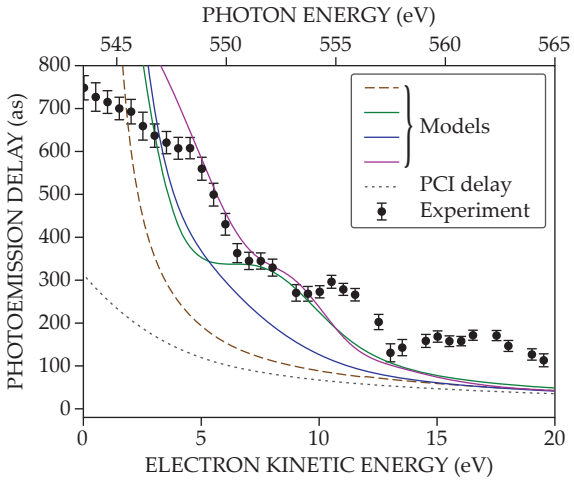

FIGURE 2. HUNDREDS OF ATTOSECONDS is the time it takes for a core electron to be emitted from the shell closest to the oxygen nucleus in a photoionized nitric oxide molecule. To observe such a fleeting event, researchers measured the time delay between the emission of two electrons, which were ejected by an attosecond pulse of light from an x-ray free-electron laser. Especially at the lower and upper ranges of electron kinetic energies, the experimental results differ from model calculations. Some delay (black dotted line) is due to the ejected core electron's postcollision interaction (PCI) with another electron. (Adapted from ref. 3.)

instrument sends a bunch of relativistic electrons through a series of alternating magnets to generate femtosecond x-ray pulses. Compared with tabletop lasers, XFEL sources have several advantages. For example, they generate much more intense pulses of light with a broad range of tunable wavelengths. In addition, the pulse bandwidth is small enough that researchers can home in on particular spectral features of samples.

To create XFEL pulses on the attosecond scale, Alexander Zholents (now at Argonne National Laboratory) proposed a technique in 2005 called enhanced self-amplified spontaneous emission.[4] The resonant interaction of a high-power IR laser with the XFEL electron beam creates an ultrashort current spike in the beam, which could then be used to generate an x-ray pulse that lasts just a few hundred attoseconds.

The type of laser that the method relied on turned out to have many practical and technical challenges. "While these ideas had broad support in the community," says Marinelli, "nobody really knew how to realize them in an experiment, and to this day, nobody has done so. Between 2005 and 2015, not much happened."

Slower than expected

Marinelli studied alternative approaches, and by 2019, he and colleagues had developed a working technique for the Linac Coherent Light Source at SLAC. They realized that rather than using an external IR beam, as Zholents had proposed, they could use the IR radiation emitted in the tail of the XFEL electron beam. The result was a beam with a single high-current spike that generated an isolated attosecond pulse.[5]

Equipped with the necessary attosecond pulses, the researchers measured the photoionization of core electrons in gaseous nitric oxide. Marinelli says, "We did this measurement only a few days after the first-ever demonstration of isolated attosecond soft x-ray pulses at an XFEL."

They made the measurement with the angular-streaking method,[6] in which an ionizing attosecond x-ray pulse is overlapped with a circularly polarized IR laser field. The rotating electric field of the IR laser deflects the photoionized electrons radially, and the time at which the electron is emitted from the molecule can be calculated from the deflection angle.

The new measurement is the first time an attosecond XFEL source was used to measure photoemission delays, and the research team spent a lot of time designing the data analysis, which included a helpful mathematical model by Jun Wang. "To understand what our data were telling us," says Cryan, "we also had to work closely with our theory collaborators, who simulated the physical effects that we had observed."

The timing of the photoionization is defined by the delay of the core electron's ejection relative to a reference event. Compared with the emission of 120 eV valence electrons from the molecule, the oxygen atom's core electrons—with kinetic

energies no higher than 20 eV—were emitted as much as 700 attoseconds later, as seen in figure 2. That's sluggish relative to theoretical predictions, especially in the lower portion of the kinetic energy range that was measured.

When electrons meet

Valence electrons are critical for molecular reactions, but the study of core electrons can reveal other processes. On their way out of a molecule, ionized core electrons can interact with the more weakly bound valence electrons. In fact, the researchers' numerical simulations show that some of the core electrons' delay, plotted in figure 2, may be caused by interactions with valence electrons.

Once it's emitted from its shell, a core electron, unlike a valence electron, is quickly replaced by an electron in a higher-energy orbital farther from the nucleus. Through a process known as Auger–Meitner decay, the energy released when a core vacancy is filled gets transferred to a valence electron, which is then emitted from the molecule after a few femtoseconds.

"Collisions with Auger electrons have not been observed before in photoemission delay experiments," says Kevin Prince, a senior scientist at the Elettra Sincrotrone Trieste research center in Italy. "Multielectron scattering is also new in this context."

Theoretical models have struggled to accurately predict photoemission delay at the lowest electron kinetic energies; figure 2 illustrates the discrepancy between measurements and simulations. The unexpectedly long photoemission delay in the new measurements indicates that core electrons may be more sensitive to multielectron interactions than previously thought. The team has started conducting new XFEL measurements on more complex molecules, which should provide even more information about the unique interactions of core electrons.

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Three glass beads bring into question the timeline of lunar volcanism

Radiometric dating of material returned from the Moon suggests there was active volcanism on the satellite 120 million years ago, nearly 2 billion years more recent than previous estimates.

China's *Chang'e 5* mission brought samples of the Moon back to Earth in December 2020, the first time since the Apollo and Luna missions did so in the 1970s. The next year, the lunar science community was rocked by the finding that volcanic basalts in the new samples were some 2 billion years old,[1,2] about 800 million years younger than any other measured lunar volcanic rocks.[3] Just as theorists were developing models of the Moon's thermal evolution that could explain that finding, Bi-Wen Wang, of the Chinese Academy of Sciences in Beijing, and colleagues are now reporting dramatically younger ages of around 120 million years.[4]

The new age measurements are from 3 glass beads, shown in figure 1, out of a sample of roughly 3000 collected by the *Chang'e 5* probe. Most of the beads have impact origins: When meteorites smash into the lunar surface, small blobs of melted material get thrown upward before cooling and falling to the ground. But glass beads can also be generated by volcanic sprays known as lava fountains. Lunar soils returned by the Apollo missions contained many such beads, all older than 3 billion years.

Although this is the first direct measurement of volcanic material from the Moon to indicate sub-billion-year-old ages, the idea of more recent volcanism isn't totally new. Detailed analyses of lunar surface images have revealed dozens of small volcanic features (see figure 2) known as irregular mare patches (see the article by Brett Denevi, Physics Today, June 2017, page 38). The density of impact craters can be used to appraise the age of a lunar surface. That method has yielded estimates that the largest patches could be less than 100 million years old, but there have been no direct measurements to confirm those assessments.[5]

The latest finding has generated a lot of buzz in the lunar science community. Still, not everyone is convinced that the three beads are conclusively volcanic. The University of Florida's Stephen Elardo, who works on thermal evolution models of the Moon, says explaining the latest finding would require going back to the drawing board. "If there's young volcanism on the Moon, we really need to rethink models about how planets cool off with time," he says. "And that isn't just the Moon, that goes for any planetary bodies."

Winnowing candidates

The Moon is thought to have formed after a collision between Earth and a protoplanet early in our solar system's formation, about 4.5 billion years ago

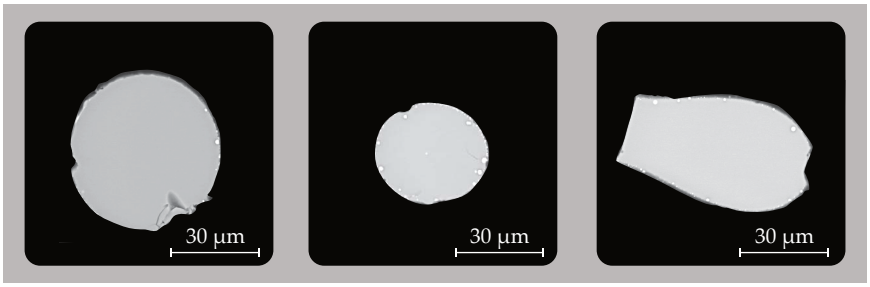

FIGURE 1. BACKSCATTERED ELECTRON IMAGES were used to screen for fractures and compositional variations in glass beads collected by the *Chang'e 5* mission. Three beads from a sample of 3000 were identified as volcanic in origin and found to be 2 billion years younger than any other volcanic material from the Moon. (Adapted from ref. 4.)