

Coulomb-explosion imaging tackles an 11-atom molecule

Until now, the technique was thought to work only on molecules with no more than about five atoms. A powerful x-ray source leaves that limit in the dust.

Sometimes the only way to get a good look at something is to destroy it. When archaeologists excavate a site, they forever disrupt the context of how the artifacts they find were arranged in the ground. For gas-phase chemists, the molecules of interest are so small and move so fast that they can't be directly imaged—unless they're blown to bits.

X-ray diffraction and electron diffraction, cousins of the similar but less destructive crystallography techniques used for studying ordered solid samples, have found success in resolving the structures of isolated biomolecules and viruses. (See *PHYSICS TODAY*, April 2011, page 13.) When it strikes a single molecule, the x-ray or electron pulse breaks bonds and destroys the specimen. Even so, a small fraction of the photons or electrons scatter elastically, just as they do in a crystal. From those particles' diffraction pattern, researchers can extract structural information.

A complementary technique, Coulomb-explosion imaging, is especially well suited to studying smaller molecules in detail. Like diffractive imaging, it involves blasting a molecule with a pulse, usually of photons, that's powerful enough to expel the molecule's electrons, break its chemical bonds, and drive the now positively charged atoms to repel one another. But rather than studying the scattered photons, Coulomb-explosion imagers collect the charged fragments of the molecule itself. By measuring the fragments' momentum and modeling the trajectories the ions followed as they flew apart, researchers can deduce the atoms' starting positions: the molecular structure.



FIGURE 1. REBECCA BOLL works on the Small Quantum Systems instrument at the European X-Ray Free-Electron Laser. Wrapped in aluminum foil is the reaction microscope, which captures the charged fragments of molecules blown up by the powerful x-ray pulses. The foil insulates the equipment while the researchers bake out the residual gases. (Courtesy of European XFEL/Jan Hosan.)

Coulomb-explosion imaging has revealed exotic molecules that are too weakly bound to study spectroscopically (see *PHYSICS TODAY*, July 2015, page 10) and reaction pathways that had only ever been observed indirectly (see the Quick Study by Tomoyuki Endo, Chen Qu, and Heide Ibrahim, *PHYSICS TODAY*, July 2021, page 62). But despite those successes, researchers have limited use of the technique—at least in its purest form—to molecules with approximately five or fewer atoms.

Two assumptions lay behind that presumed restriction. Getting a good Coulomb-explosion image requires placing a positive charge on every atom in a molecule, so that all the pair-wise atomic interactions are dominated by Coulomb repulsion rather than electronic attraction. Researchers assumed that it wouldn't be possible to simultaneously ionize every atom in a large molecule. They also assumed that they could reconstruct a

molecule's structure only if they detected all of its ionic fragments—a daunting task for larger molecules when the detection efficiency for each ion hovers around 60%.

Now, working at the European X-Ray Free-Electron Laser, or EuXFEL, Rebecca Boll (seen in figure 1), Till Jahnke, and colleagues have shown that neither of those assumptions is valid—at least for some molecules.¹ When they pummeled 2-iodopyridine (shown in figure 2a) with the EuXFEL's powerful pulses of soft x rays, the molecule easily expelled enough electrons to ionize all 11 of its atoms.

And even when the researchers detected as few as three of the atoms from any given molecule, the momentum distributions built up from repeated Coulomb explosions were crisp enough to distinguish all five of the molecule's carbon atoms (as seen in figure 2b) and all four of its hydrogen atoms (shown in figure 2c). A theory team led by Robin Santra and his student Julia Schäfer per-

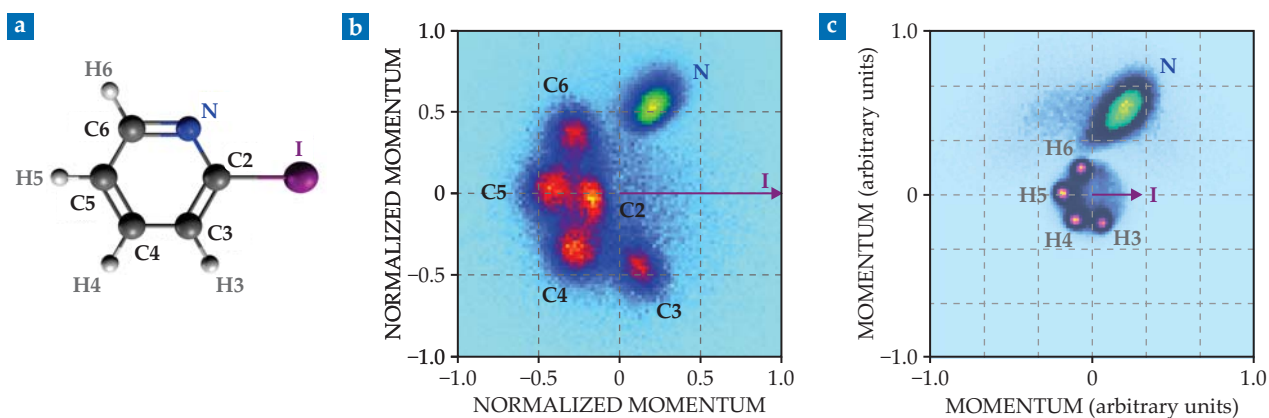


FIGURE 2. THE 11-ATOM MOLECULE 2-iodopyridine is laid bare by Coulomb-explosion imaging. **(a)** The molecular structure, which was already known, centers on a rigid, planar ring of carbon and nitrogen atoms. **(b)** When x-ray ionization breaks the chemical bonds and sends the atoms flying apart, the six ring atoms are readily distinguished by their momentum. **(c)** So are the four hydrogen atoms, the lightest and most challenging atoms to detect. (Adapted from ref. 1.)

formed simulations to relate the momentum measurements back to the molecular structure. The results are a first step toward transforming Coulomb-explosion imaging into a general technique for studying the structures and dynamics of not-so-small molecules.

Unexpected clarity

The researchers didn't set out to overturn the assumptions of Coulomb-explosion imaging. "If we'd said in our proposal that we wanted to image every individual atom in these molecules, we would have been laughed out of the room," says Boll. Rather, the project started with the more modest aim of exploring molecular ionization dynamics under the influence of XFEL pulses.

Before the EuXFEL came on line in 2017, Boll and Santra were part of a team using SLAC's Linac Coherent Light Source (LCLS), also an XFEL, to study ionization of iodomethane (CH_3I) and iodobenzene (similar to 2-iodopyridine, but with an all-carbon hexagonal ring).² They noticed that the XFEL pulses, thanks to multiphoton absorption, removed an astonishing number of electrons from both molecules. Absorption was concentrated on the iodine atom, which had the largest absorption cross section in the molecule, and produced charge states as high as I^{47+} . That's no small feat when the atom has only 53 electrons to begin with.

The charge seemed to spread efficiently from the I atom to other parts of the molecule. In iodobenzene, the researchers saw carbon atoms as highly charged as C^{4+} . But they didn't know which C atoms they were seeing—the

ones adjacent to the I atom or the ones on the opposite side of the ring. And the LCLS experiment wasn't equipped to help figure it out.

Boll and Santra didn't think that Coulomb-explosion imaging could distinguish two atoms of the same element in the same molecule—at least, not without detecting every atom in the molecule, which for a structure as large as iodobenzene would be nearly impossible. But the technique can easily distinguish atoms of different elements because of their different masses.

The original plan for the new EuXFEL experiment, then, was to replace one C atom at a time with a nitrogen atom. If the N atom in 4-iodopyridine (on the opposite side of the ring as the I atom) ended up just as highly charged as the one in 2-iodopyridine, it would follow that the charge is readily redistributed around the ring.

The researchers expected the pattern formed by all the other atoms to be a featureless blob. But to their surprise, when they plotted the C atoms' momentum, the data formed five distinct bunches, one for each position around the ring. The four hydrogen atoms showed an even cleaner bunching. So even if the researchers detect only one of the C or H atoms from a given Coulomb explosion, they can tell which one it is just by measuring its momentum.

What a coincidence

The 2-iodopyridine molecules tumble randomly through space on their way to their destruction by the XFEL beam. The distributions in figure 2 require reorient-

ing the data, molecule by molecule, into a common reference frame with the horizontal axis defined by the I atom's momentum and the vertical axis determined by the N atom's.

The reorientation is possible because the researchers did what's called coincidence mapping: They made their beam of 2-iodopyridine so dilute that each x-ray pulse interacted with at most one molecule. Only under those conditions could they be sure that all the ions detected in a single shot came from the same parent molecule. The data in figure 2 are for threefold coincidences: shots in which they detected the I atom, the N atom, and at least one other. The researchers also collected momentum data for up to eightfold coincidences, which look similar.

Coincidence-mapping experiments can take a long time to build up a meaningful data set. The EuXFEL's high repetition rate, up to 570 pulses per second for these experiments, helps. Without access to such a high-powered facility, other research groups have explored an alternative technique called covariance mapping: simultaneously ionizing many molecules (usually after physically aligning them with polarized light) and using sophisticated data analysis techniques to make up for the fact that they can't definitively trace any two atomic fragments to the same parent molecule.

Covariance mapping has yielded some structural, and even dynamical, information for molecules with more than 20 atoms.³ "But those experiments are always losing some information," says Jahnke. "For example, if you're looking at an ensemble of molecules doing some

dynamical process, those molecules aren't all doing the same thing." Coincidence mapping, although time-consuming and experimentally challenging, yields that molecule-by-molecule information.

Toward molecular movies

In their theoretical analysis, Santra and Schäfer didn't focus on determining bond lengths, bond angles, or other structural details. The equilibrium structure of 2-iodopyridine, like those of most similarly sized molecules, is already known. Instead, starting from that established structure, the theorists simulated the Coulomb-explosion process and showed that it yields momentum distributions much like the ones that were observed. If necessary, they could iteratively adjust the starting configuration to converge on an unknown molecular structure.

Of greater interest than equilibrium structures, though, are the insights that Coulomb-explosion imaging can offer

for molecules in motion: An ultrashort laser pulse initiates a chemical reaction, and the XFEL pulse instigates a Coulomb explosion tens or hundreds of femtoseconds later. Most of what researchers know about what happens during a reaction they learn indirectly, either by studying the reaction products (see, for example, *PHYSICS TODAY*, February 2019, page 14) or by spectroscopically probing the molecules midreaction (see *PHYSICS TODAY*, December 1999, page 19). Coulomb-explosion imaging provides a more direct look.

One barrier to studying the dynamics of 11-atom molecules is figuring out how best to visualize all the data. The two-dimensional momentum plots in figure 2 are deceptively simple, because there's no reason different atoms' momenta need to be plotted on the same pair of axes. Each of the 11 atoms has its own 3D momentum, so one would need 33 axes to plot them all (or 27, after factoring out

the translations and rotations that don't affect the underlying dynamics).

"X-ray diffraction and electron diffraction can resolve molecular structures," says Santra, "but they're purely three-dimensional. They can't map out the whole molecular phase space, which is our goal. With Coulomb-explosion imaging, we're still not detecting everything, but we can get so much more information than traditional techniques provide."

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References

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Glass ages in material time

The long-standing assumption that the same relaxation processes underlie linear and nonlinear aging is now backed up by experiments.

Follow a tour guide around a European city and you're likely to hear the tale that old cathedral windowpanes appear uneven because over hundreds of years, the glass has slowly flowed toward the bottom of the pane. That story is just a myth; such flow in silica would require at least geological time scales.¹ But glassy materials, molecular and otherwise, do slowly evolve toward a metastable equilibrium state—a process known as aging.

Physical aging involves rearrangements in the atoms, molecules, or colloidal particles that make up a glassy material. Such materials are characterized by a glass-transition temperature T_g at which the system falls out of equilibrium because the time scale for rearrangements surpasses that of observations. Below T_g , the materials display nonlinear aging: The evolutions of their densities and other properties are not proportional to the

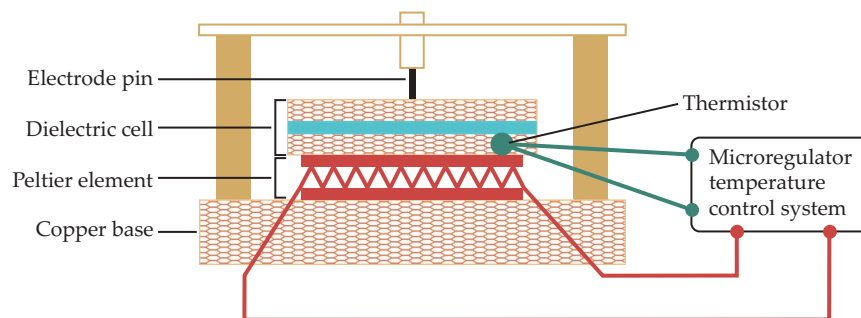


FIGURE 1. A MOLECULAR LIQUID (turquoise) undergoes structural relaxation, known as aging, after being subjected to small temperature changes. The evolution of the 50- μm -thick layer's capacitance reflects changes in its microscopic configuration. An electrode and dielectric cell measure the liquid's capacitance; a thermistor and a Peltier element monitor and regulate its temperature. (Adapted from ref. 4.)

temperature changes. Because the materials are out of equilibrium, the actual form of the relationship is difficult to model or predict.

In 1971 Onbathiveli Narayanaswamy postulated that when exposed to sufficiently small perturbations, a material's response will be in the linear regime.² He also asserted that a glass's nonlinear properties could be extracted from that linear relationship by replacing the regular lab time with a so-called material time: a nonuniformly stretched time that reflects a material's evolving state. The lab

time t and material time ξ are connected by $\gamma(t) = d\xi(t)/dt$, where γ is the time-dependent aging rate.³

Although the material-time formalism has since been widely and successfully used to describe glass aging, it has never been directly tested. Without experiments sufficiently precise to reach the linear regime, extensions to the nonlinear regime have relied on assumptions about, rather than measurements of, linear behavior.

Now Birte Riechers and her coworkers at Roskilde University in Denmark