

Einsteinium chemistry captured

The creation of a rare molecule offers a peek at how heavy atoms interact with other elements.

Where is the end of the periodic table? Although uranium, with an atomic number Z of 92, is the heaviest element found naturally on Earth, physicists have created dozens of synthetic transuranic elements. No one yet knows whether there's a limit to the elements that can possibly exist. But the ones that have been made so far extend up to $Z = 118$.

Not all of those elements are equally easy to synthesize or study. Kilograms of neptunium, plutonium, americium, and curium ($Z = 93\text{--}96$) are produced in U-burning nuclear reactors through neutron capture followed by beta decay, a process that increases an atom's Z by one. Berkelium, californium, einsteinium, and fermium ($Z = 97\text{--}100$) can also be made by neutron capture, but in drastically smaller quantities and only in specialized facilities such as the one at Oak Ridge National Laboratory (ORNL; see "The overlooked element makers," *PHYSICS TODAY* online, 30 September 2019). Mendelevium ($Z = 101$) and beyond can be made only one atom at a time.

There are ways to study the atomic properties of elements produced atom by atom (see, for example, *PHYSICS TODAY*, June 2015, page 14). But the traditional way of investigating how atoms behave—mixing them with other substances in solution to form chemical compounds—requires a bulk quantity of material. ORNL's two-year production cycle yields just a picogram of Fm, which has yet to be purified. So from the chemist's point of view, the periodic table effectively ends with Es, produced in microgram quantities.

Now Lawrence Berkeley National Laboratory's Rebecca Abergel and her colleagues (two of them shown in figure 1) have performed the most complicated and informative Es chemistry experiment to date.¹ With just a few hundred nanograms of the heavy element—a mere quadrillion atoms or so—the re-



searchers probed both its chemical bonding geometry and its electron energetics. The results could point the way to a better understanding of heavy elements in general and perhaps the discovery of the next new one.

Actinide complex

Abergel and her group are experts in the coordination chemistry of the actinides, the series of radioactive elements with atomic numbers 89–103, usually shown floating below the body of the periodic table, and they're especially interested in how those heavy elements behave inside the human body. They've been working to find new organic molecules that bind to actinide atoms—either to purge the radioactive material from the body in case of contamination or to deliver it to tumor cells for targeted radiotherapy.

Although Es is too scarce to serve as either poison or medicine, the researchers wanted to see if they could push their methods to the limit. They applied for a share of ORNL's most recent biennial Es supply. They got half of it.

When it comes to characterizing new molecules—and any organo-einsteinium molecule would be a new one—the gold

FIGURE 1. KOREY CARTER (left) and Katherine Shield study the chemistry of einsteinium (atomic number 99) in Rebecca Abergel's lab. (Photo by Marilyn Sargent, the Regents of the University of California, Lawrence Berkeley National Laboratory.)

standard is the x-ray crystal structure, a diffraction pattern that reveals each atom's position in exquisite detail. Because that technique requires milligrams of material, Abergel and colleagues' first idea was to encapsulate each Es atom in a large protein molecule to make a big enough sample without much of the heavy metal.

That didn't work. It would have been feasible except that what ORNL had delivered as Es was, in fact, almost half Cf. Unable to separate the elements any more cleanly than the ORNL scientists had done, Abergel and colleagues could only make a mixture of Es-bearing proteins and Cf-bearing proteins. The resulting diffraction pattern would have been a hopeless mess.

So instead of crystallography, the researchers turned to x-ray absorption spectroscopy, a technique that measures the energy needed to remove one of the

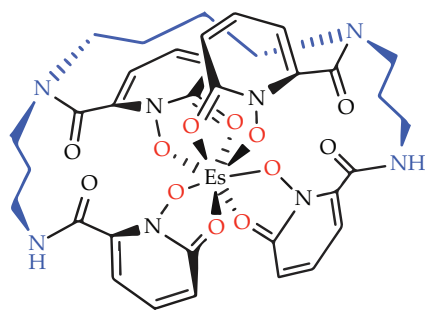


FIGURE 2. MOLECULAR STRUCTURE of an einsteinium complex. A single organic molecule, held together by the backbone shown in blue, wraps around the Es atom and binds to it from all sides. X-ray absorption spectroscopy measures the distance from the central Es atom to the oxygen atoms shown in red, and luminescence spectroscopy yields information about the Es's electronic states. (Adapted from ref. 1.)

tightly bound inner electrons from a high- Z atom. “Those energies are element specific,” explains Abergel, “so it’s straightforward to screen out the contaminants”: Just zoom in on the part of the spectrum that corresponds to the Es excitation.

X-ray absorption spectroscopy doesn’t yield a complete molecular structure the way x-ray crystallography does. But ripples in the spectrum form an interference pattern that gives some information about the distances to the atoms neighboring the heavy atom, and thus how the heavy atom forms chemical bonds.

Furthermore, it’s possible to adapt x-ray absorption spectroscopy to analyze extremely small amounts of material. Freed from the requirement of using a large protein, Abergel and colleagues opted instead to react their Es with a so-called octadentate ligand—a single organic molecule that wraps around a central metal atom and binds to it from all sides—to create the complex shown in figure 2.

Among its other useful properties, the ligand acts as an antenna: It absorbs light in the UV and efficiently channels it to the central metal atom, which emits light at a range of longer wavelengths. That luminescence spectrum, which can be measured with an extremely small sample, carries information about the central atom’s electronic energy levels that complements what x-ray absorption spectroscopy reveals about the spatial arrangement of atoms.

Abergel and colleagues had already studied complexes of the same ligand with several other metals, including lighter actinides. So they could directly compare Es’s chemical behavior with that of other elements.

Pulling the thread

Across most of the periodic table, chemical behavior varies by column. Fluorine,

for example, is much more like its downstairs neighbor chlorine than its left- and right-hand neighbors oxygen and neon. However, because the actinides’ valence electrons lie in f orbitals that don’t strongly influence chemical properties, they’re all expected to behave much like one another.

That’s not what Abergel and colleagues found. In complexes of the same organic ligand with the lighter actinides Am, Cm, and Cf, the metal–oxygen bond length is between 2.42 Å and 2.45 Å. The Es–O bonds, in contrast, are a considerably shorter 2.38 Å. Furthermore, the luminescence spectrum of the Es complex showed an electronic transition that’s higher in energy than for the bare Es ion, whereas for the lighter actinides, the opposite is true.

Says Jenifer Shafer of the Colorado School of Mines, “The prevailing dogma has been that the actinides are just heavy versions of the lanthanides,” the upper row of f -block elements, which all exhibit similar behavior to one another. “It’s been hard to justify work on actinide chemistry without knowing that it will find anything interesting. But now the thread is starting to get pulled on the differences between them.”

Chemical differences among the actinides aren’t wholly unexpected, though, and the culprit is easily identified: relativity. The more highly charged an atomic nucleus, the faster the electrons whiz around it. When an electron’s speed is a significant fraction of the speed of light, its effective mass increases, and all the atom’s electronic orbitals shift in energy in a way that’s extraordinarily difficult to model.

All actinides are affected by relativity, but the heavier ones especially so. The chemistry of Es, in other words, amplifies effects that are already present in lighter atoms, so it’s a valuable benchmark for theorists seeking to model the

lighter, more technologically relevant actinides. If a model works well for Am and Cm but not for Es, it may be on the wrong track.

It’s also possible that Es is showing something not seen in other actinides: a transition to a new regime of spin–orbit coupling. Each electron in an atom has both spin and orbital angular momentum, and there are two distinct ways of representing the atom’s total angular momentum: either as the sum of the total orbital angular momentum L and the total spin S or as the sum of each electron’s combined angular momentum j . The two schemes give different answers and predict different behaviors. “We can compute the angular momentum in each of those schemes individually,” says Valérie Vallet, a CNRS theorist at the University of Lille in France. “It’s harder to predict which one we should use.”

The former approach, called LS coupling, tends to apply when electrons aren’t packed too closely together. It accurately describes most light atoms, and it even works well for molecules containing Am or Cm. The latter coupling scheme, jj coupling, is less commonly seen in atoms and molecules, but it could be behind some of Es’s unusual behavior. “We don’t know that that’s what these photophysical measurements are showing,” says Vallet, “but it calls for further investigation.”

Not the end

With a half-life of less than a year, most of Abergel and colleagues’ Es has decayed away by now. But they still have a little left, and they’re continuing to experiment on it to glean whatever information they can about the chemical differences between Es and other actinides, particularly Cf. “We have a whole library of ligands we’re working through,” says Abergel.

Their ultimate goal is to identify an Es-containing molecule that’s different enough from the analogous Cf molecule that the two can be efficiently separated. Such a find would enable the ORNL scientists to streamline the purification of their next batch of Es, which would make possible the x-ray crystallography experiments Abergel and colleagues had in mind from the start.

It could also lead to the discovery of a new element. The six most recent additions to the periodic table, from nihonium ($Z = 113$) to oganesson ($Z = 118$),

were all made in the same way: by shooting a beam of calcium-48 into an actinide target. With so-called magic numbers of both protons (20) and neutrons (28), ^{48}Ca is unusually stable, and it combines readily enough with actinide nuclei of atomic number Z to yield a few super-heavy atoms of atomic number $Z + 20$.

No new elements have been made in

that way, or any other, since the 2010 discovery of element 117, now called tennessine after ORNL's home state. (See PHYSICS TODAY, June 2010, page 11.) It took longer to discover Ts than Og because the Bk target was harder to work with than the Cf one. Until a big enough Es target can be assembled to make element 119, the ^{48}Ca -fusion technique has

seemingly reached the end of its road. Better Es purification through chemistry may help breathe new life into super-heavy element research.

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Reference

1. K. P. Carter et al., *Nature* **590**, 85 (2021).

Pauli crystals make their experimental debut

When a few ultracold atoms are repeatedly trapped and imaged tens of thousands of times, self-organized patterns emerge out of the quantum blue.

Whereas bosons can condense into a single quantum state, fermions, such as electrons in ordinary solids, are forbidden from doing so. Pauli exclusion is the best-known manifestation of Fermi–Dirac statistics, and it accounts for, among other things, the structure of the periodic table and electrical conductivity in metals.

Identical fermions do not even need to interact to behave as if they repel each other. Indeed, the mere presence of fermionic atoms near one another but unable to occupy the same locations produces an emergent Fermi pressure that prompts the atoms to rearrange themselves. The resulting correlations between atoms can be visualized in geometric structures known as Pauli crystals. Mariusz Gajda coined the name five years ago when he and his colleagues at the Polish Academy of Sciences in Warsaw predicted the phenomenon.¹

Now doctoral student Marvin Holten, postdoc Luca Bayha, and their colleagues, under the direction of Selim Jochim at Heidelberg University, have directly observed Pauli crystals in the momentum correlations of a few lithium-6 atoms trapped in a two-dimensional plane.²

Simulating a solid

Theorists have long tried to account for the electronic behavior of strongly interacting many-body systems by using model Hamiltonians. But when researchers attempt to fabricate materials that embody such Hamiltonians, they often struggle to cope with imperfections, defects, and

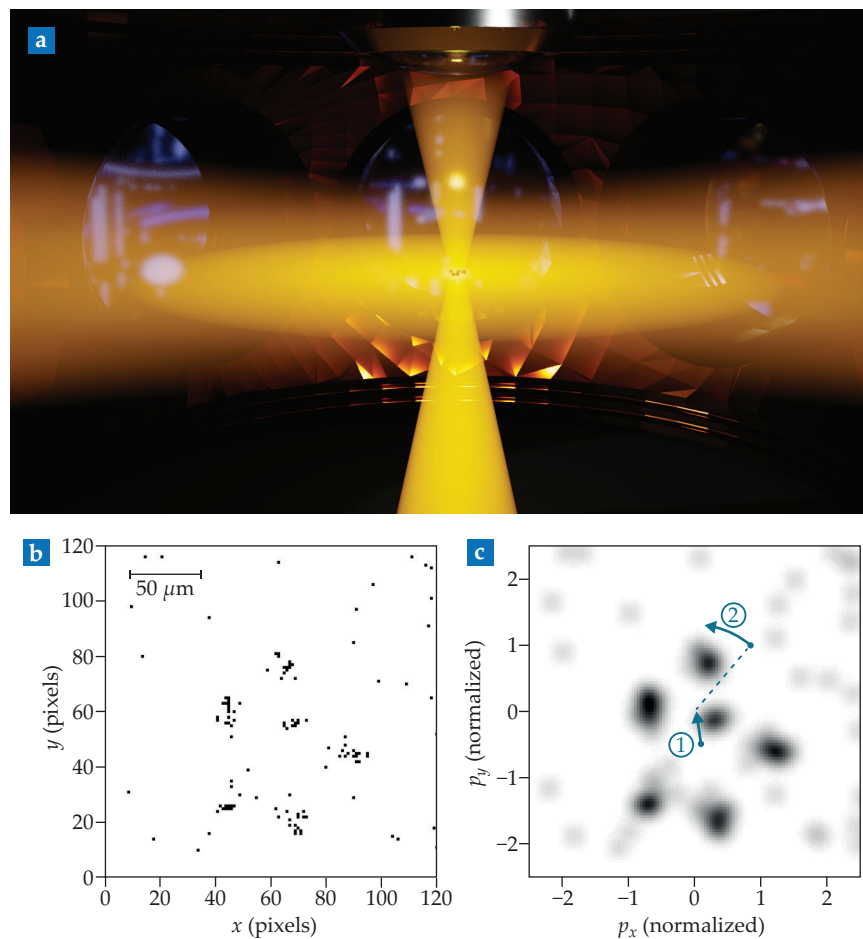


FIGURE 1. SIX ULTRACOLD lithium-6 atoms are trapped in the superposition **(a)** of a focused optical tweezer and a single layer of a one-dimensional optical lattice (yellow disk). The atoms can move in the two-dimensional plane but are frozen vertically. **(b)** When the tweezer is switched off, the atoms expand in the 2D plane until a laser pulse prompts them to fluoresce; photons from each atom are registered as momenta (dots) in a CCD detector. **(c)** To reveal correlations between the atoms, researchers subtract their center-of-mass motion (arrow 1) from each atom's momentum $\mathbf{p}$ (normalized to harmonic oscillator states) and then rotate each image to a common symmetry axis (arrow 2). (Adapted from ref. 2.)

other features of the real material world. A tantalizing alternative, developed about a decade ago, is to study the systems' com-

plicated behavior by using small clouds of ultracold atoms.

To simulate the behavior of itinerant