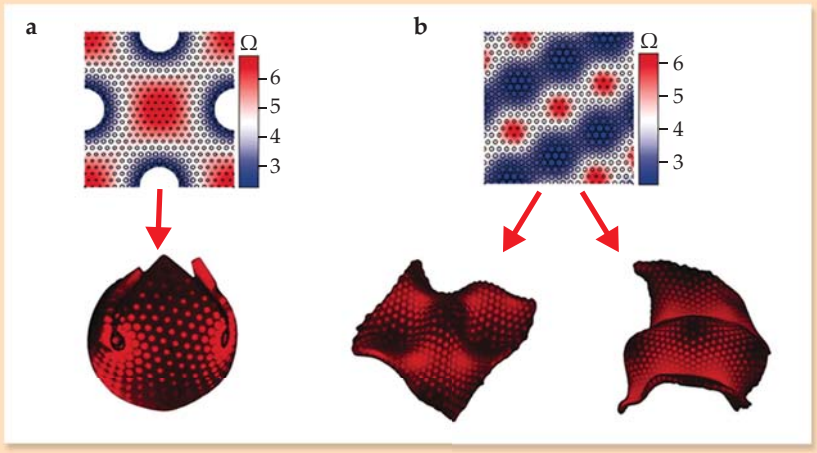

Figure 2. (a) This swelling pattern (top) illustrates the sizes of the mask holes required for a roughly 600-μm square sheet to warp into a spherical shell (bottom). The colors illustrate the range of the gel's local swelling factor Ω. **(b)** A pattern designed to produce an egg carton (left) may inadvertently produce an entirely different shape (right) instead. The three local maxima in growth, lying along the diagonal, each represent a region of positive Gaussian curvature—either a peak or trough. But the buckling configurations, up or down, are nearly degenerate in energy. So even slight variations in parameters such as local thickness can lead to very different shapes. (Adapted from ref. 2.)

extent of the swelling depends on the strength of the cross-linking, which, in turn, depends on the gel's prior exposure to UV light. One can thus tune the shape shifting: The gel's lightly exposed areas have weaker linking and can swell nearly four times as much as its heavily exposed ones—and do so in a few minutes' time.

To pattern a polymer film with the exposures required for it to spontaneously adopt a shape consistent with a target metric, the Amherst team used a photomask made of an evenly spaced array of holes with varying diameters—a process akin to half-tone printing in a newspaper. Provided the polymer sheet wasn't too thin, its elasticity turned out to be sufficient to locally smooth out the sharp contrast between highly cross-linked dots and the lightly cross-linked matrix.

The researchers tested the method by creating shapes, as shown in figure 1, that correspond to several axisymmetric metrics: a saddle, a cap, a dome, and a so-called Enneper minimal surface. Conveniently, they were able to adapt well-established formulas for the metrics from differential geometry; in each case they calculated the pattern of dots needed to produce the appropriate swelling factor Ω at each point on the lattice.

Producing the sphere shown in figure 2a turned out to be trickier. A number of conformal mappings of a sphere onto flat surfaces are known from the field of map projections. But to go beyond a hemisphere, the Amherst researchers had to use a nonaxisymmetric metric that would accommodate the gel's limited ability to swell: Charles Sanders Peirce's 1879 quincuncial projection. Even with it, they had to excise parts of the square where Ω falls below the experimentally accessible range.

Nonetheless, the new method opens the door to shapes of arbitrary complexity. Initial efforts suggest that it's sometimes not enough to find the swelling function that defines a particular metric. For instance, when the group patterned the gel into a corrugated surface, the sheets often failed to adopt the intended egg-carton shape, as suggested in figure 2b. Because of slight variations in film thickness, for example, or the existence of multiple shapes that are locally metastable, sheets can misfold. Indeed, very different shapes may emerge from nearly identical metrics.

The opposite is also true. Two shapes that look nearly identical may come from very different metrics, a fact that may bear on the best way to design certain kinds of objects. Applications in soft robotics, tunable optics, biomedicine, and elsewhere may come eventually. But for now, says Santangelo, "This is a toolkit for doing math with experiments."

Mark Wilson

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Toward an attosecond view of molecules

Theory and experiment combine to examine an important ultrafast process in polyatomic molecules.

Femtosecond spectroscopy was a landmark development in chemical and molecular physics: It allows the motion of atoms, including the breaking and forming of chemical bonds, to be monitored in real time. (See PHYSICS TODAY, December 1999, page 19.) But the much faster motion of the electrons in those atoms still holds many secrets. It falls within the domain of the emerging field of attosecond science.

A key ingredient in every attosecond experimental technique so far has been ionization or probing by a strong laser field. In the prevailing model of strong-field ionization (SFI), used to interpret experimental results, it's assumed for simplicity that only one electron—the one with the highest energy—feels the pull of the ionizing laser field. Perhaps surprisingly, that model works well when applied to noble-gas atoms and some small molecules. But for larger molecules, which host many of the electronic processes researchers want to study, it can fail badly.

Now, Albert Stolow (National Research Council Canada) and colleagues report that they have developed an experimental technique for studying subcycle SFI in polyatomic molecules.[1] In the same paper, Council theorists Michael Spanner and Serguei Patchkovskii present an ab initio method for solving the time-dependent Schrödinger equation for a polyatomic molecule in a strong laser field. Applied

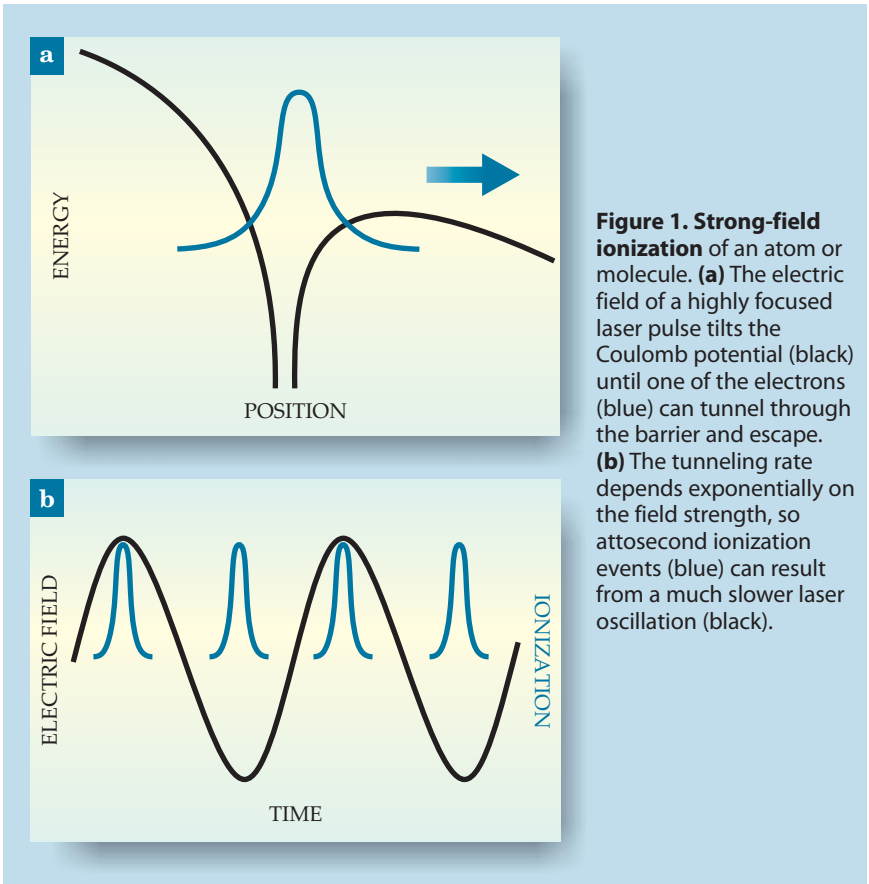

Figure 1. Strong-field ionization of an atom or molecule. **(a)** The electric field of a highly focused laser pulse tilts the Coulomb potential (black) until one of the electrons (blue) can tunnel through the barrier and escape. **(b)** The tunneling rate depends exponentially on the field strength, so attosecond ionization events (blue) can result from a much slower laser oscillation (black).

to two different four-carbon hydrocarbon molecules, the experiment and theory agree well, and both show that several electrons participate in the attosecond-scale ionization.

Ultrafast ionization

An extreme nonlinear process, SFI involves a highly focused laser beam. When the laser's electric field varies slowly relative to the time scale of electron motion, the Coulomb potential of the atom or molecule tilts, as shown in figure 1a, to the point where an electron can tunnel through the potential barrier and escape. Because tunneling probability is exponentially related to the barrier height, ionization only happens at the very peak of the laser field oscillation, as shown in figure 1b. So a visible or near-IR laser beam, with a period of several thousand attoseconds, can create subcycle bursts of ionization lasting only about 100 as.

One can do several things with SFI, depending on whether the laser pulse consists of one oscillation or several and whether it drives the electron and parent ion to recollide or pulls them apart forever. (See the articles in PHYSICS TODAY by Paul Corkum, March 2011, page 36, and by Henry Kapteyn, Margaret Murnane, and Ivan Christov, March 2005, page 39.) An atom or molecule of interest can be ionized directly, or it can interact with a light pulse generated by ionizing a different species. But every attosecond experiment so far has involved direct ionization of the species of interest (and possibly also interaction with a separately generated pulse). To do attosecond science on polyatomic molecules, it's necessary to understand their SFI dynamics.

The model usually invoked to understand those dynamics was developed by Paul Corkum in 1993. It's based on three assumptions: Electrons respond instantaneously to changes in the laser field; tunneling proceeds instantaneously; and only the most weakly bound electron is involved, or "active," in the ionization.[2] Those assumptions made computational modeling feasible. But Stolow had long suspected that their validity was limited to atoms and small molecules.

Beginning in 2001, Stolow and his group published a series of papers[3] showing that the rate of SFI of polyatomic molecules and of transition-metal atoms and clusters can be orders of magnitude different from what's predicted by Corkum's model. But working backward from the measured ionization rates to a real understanding of SFI dynamics would have required intense modeling—and knowing which assumptions were valid for doing that modeling would have required already having an understanding of what was going on. Multiple active electrons were a possible explanation. Curiously, in metal atoms and clusters, they make the ionization slower, not faster: As several electrons move toward the barrier, they raise the effective barrier height for the one that ends up escaping. But not all theorists were convinced. Many thought that the single-active-electron model was still right, but it just needed some refining.

Multiple active electrons

Stolow and colleagues' experimental method probes SFI in molecules without the need for modeling. For their demonstration, the researchers looked at two hydrocarbon molecules, one of which was butane, shown in figure 2a. Removing the highest-energy, most weakly bound electron puts the molecular ion, $C_4H_{10}^+$, in its ground state. Removing a lower-energy electron yields a higher-energy ionic state. All of ionized butane's excited states are inherently unstable, with the parent ion spontaneously breaking apart into smaller fragments, as shown in figure 2b. Observing one of those smaller ions is a sign that subcycle SFI is removing one of the lower-energy electrons.

But it's not definitive proof. It's also possible that the ion is created in its ground state but a later cycle of the same laser pulse promotes it to an excited state. To rule out that possibility, the experimenters measured not just the mass of the remaining ionic fragment but also the kinetic energy of the departing electron in coincidence with the ion. When the molecule absorbs more photons than are needed for ionization, the excess energy is taken up by the electron. The electron kinetic-energy spectrum therefore displays a series of peaks. The spacing between peaks is equal to the laser photon energy, and their absolute position depends on how much energy went into ionization.

In their butane experiment, Stolow and colleagues assigned electrons to one of four spectra, shown in figure 2c, depending on which ion they observed. If SFI always removed the most weakly bound electron but later laser cycles promoted some of the $C_4H_{10}^+$ ions into unstable excited states, all four of the electron–ion coincidence kinetic-energy spectra would be in phase.

That they're not in phase, as shown

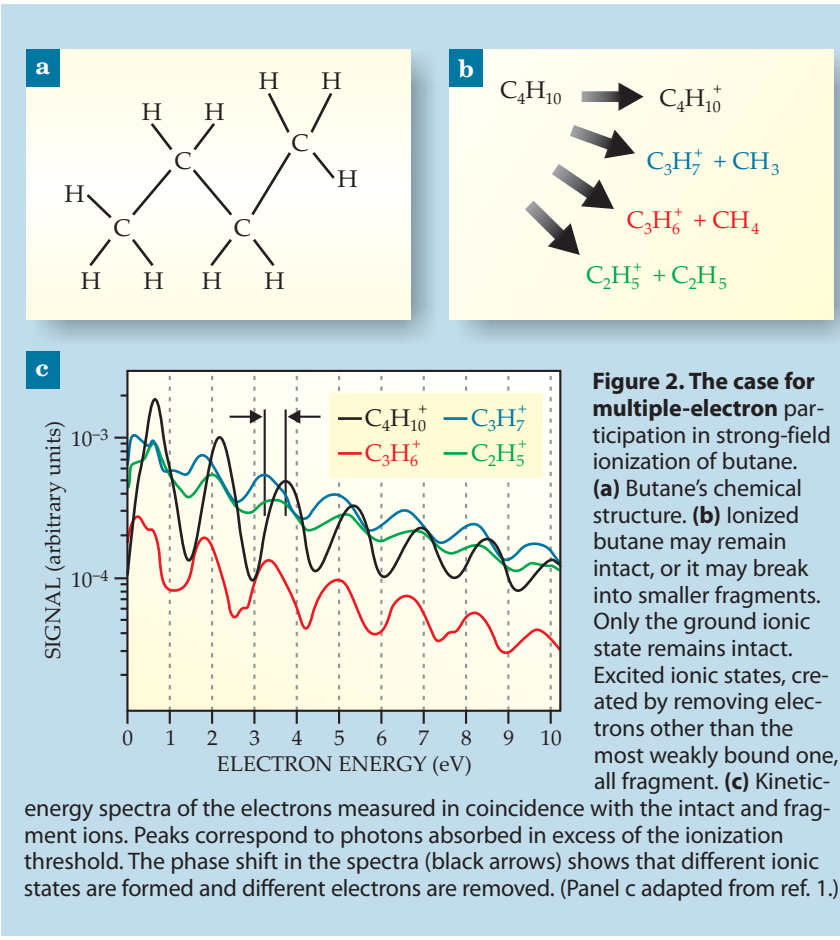

Figure 2. The case for multiple-electron participation in strong-field ionization of butane. **(a)** Butane's chemical structure. **(b)** Ionized butane may remain intact, or it may break into smaller fragments. Only the ground ionic state remains intact. Excited ionic states, created by removing electrons other than the most weakly bound one, all fragment. **(c)** Kinetic-energy spectra of the electrons measured in coincidence with the intact and fragment ions. Peaks correspond to photons absorbed in excess of the ionization threshold. The phase shift in the spectra (black arrows) shows that different ionic states are formed and different electrons are removed. (Panel c adapted from ref. 1.)

by the black arrows in figure 2c, is proof that it's not always the highest-energy electron being removed, and thus several electrons must be active in the subcycle ionization event. The $C_4H_{10}^+$ spectrum position is consistent with formation of the ground ionic state—as it must be, because that's the only state of $C_4H_{10}^+$ that doesn't fragment. The $C_3H_7^+$ and $C_3H_6^+$ spectra are in phase with each other, but they are shifted by 0.4 eV from the $C_4H_{10}^+$ spectrum, consistent with the energy of the first excited ionic state. The $C_2H_5^+$ spectrum is not in phase with any of the others, and its peaks are less pronounced, but it may result from formation of the third excited state.

Computational corroboration

To complement Stolow's experiment, Spanner and Patchkovskii studied the same ionizations computationally, without using any adjustable parameters. The method they developed bridges the gap in complexity between the single-active-electron methods traditionally used in attosecond research and the powerful tools for computing electronic stationary states in quantum chemistry. (See the article by Martin Head-Gordon and Emilio Artacho in PHYSICS TODAY, April 2008, page 58.) Because of their method's computational intensity, they were able to propagate the electron wavefunctions over just half a laser period. Still, their results—the relative yields of the ground and various excited ionized states—agree well with the experiment and confirm the involvement of multiple electrons in the subcycle SFI of polyatomic molecules.

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physics update

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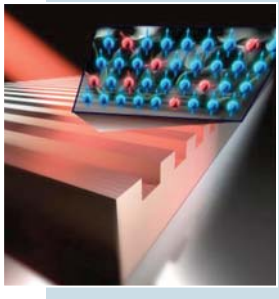

Fast times in ferromagnetic alloys. As magnetic materials for storage and other applications get pushed ever smaller and faster, a solid understanding of their behavior—including the correlated interactions among electrons, photons, and phonons—at those scales will be critical. X rays from synchrotron light sources are one way to obtain element-specific information at ultrafast time scales. Now, scientists from JILA and their colleagues from NIST and Germany have used tabletop techniques to probe magnetic dynamics on the fastest time scales; in particular, they studied the role of the exchange coupling between components in a ferromagnetic alloy. Working with magnetic diffraction gratings of permalloy ($Ni_{0.8}Fe_{0.2}$), as sketched here, the researchers first use a short, strong IR laser pulse to excite the electrons, which causes the alloy to demagnetize. Then, to trace the evolution of the magnetization, they illuminate the gratings with 10-femtosecond bursts of extreme UV light, obtained through high-harmonic generation (see PHYSICS TODAY, March 2005, page 39). At the wavelengths corresponding to the M-shell absorption edge of each element, the reflected light intensity depends on the degree of that element's magnetization, so the researchers can independently and simultaneously monitor the dynamic magnetic response of Fe and Ni, even when alloyed together. In a surprising finding, the Ni demagnetization lags that of Fe by a time on the order of 10–100 fs, depending on the spins' exchange-coupling strength (which can be varied by adding copper); after that delay, Fe and Ni demagnetize at the same rate. Such results, claim the researchers, will provide crucial information for addressing open questions in ultrafast magnetization dynamics. (S. Mathias et al., *Proc. Natl. Acad. Sci. USA* **109**, 4792, 2012.) —RJF