

tems, the phenomena observed by Reed and colleagues would be seen with arbitrarily low light intensities. In principle, they'd be obtained in realizations in which light was sent into the photonic crystal one photon at a time.

With a bullet

To date, the phenomena predicted by the MIT team have not been tested experimentally. But Reed, working with Neil Holmes and Jerry Forbes of Lawrence Livermore National Laboratory, is contemplating experiments that may realize the effects seen in the simulations. Reed and his California colleagues plan to use a room-sized gun to shoot a projectile at a multilayer photonic-crystal film. Reed admits the experiment is "literally a one-shot deal." The powerful compressive wave generated in the photonic crystal will destroy the target, although there's plenty of time to gather the necessary data before the crystal disintegrates.

Other methods for compressing photonic crystals are not so violent. Laser or acoustic generation of compressive waves is a possibility. And cleverly designed systems can mimic the effects of compressive waves without the need to physically compress a photonic crystal.

In one scenario, light scatters off a photonic crystal that is rolled into a spiral jellyroll shape and rapidly rotated about the spiral's axis. At first blush, that system looks nothing like the shocked photonic crystal simulated at MIT, but the physics of the two systems is quite similar.

As Joannopoulos explains it, one can think of the compressive shock front as forming the boundary between

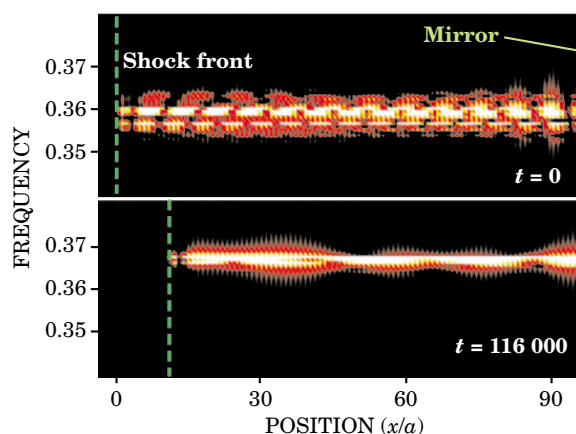


Figure 3. Light bandwidth narrows when light bounces between an advancing shock front and the mirror at the right-hand boundary of this image. Over the course of this simulation, the shock front moves about 10 pre-shock lattice periods a , and the frequency band is narrowed by about a factor of four. The dimensionless frequency is measured in units of c/a where c is the vacuum speed of light. The dimensionless time t is measured in units of a/c . (Adapted from ref. 1.)

two photonic crystals with different periodicities. As the front advances over a lattice period, the number of unit cells on the compressed side behind the front increases by one, at the expense of a unit decrease on the front side. The mathematics of the phenomena discovered by the MIT team can be traced to the transfer of cells from one photonic crystal to another.

How is Joannopoulos's explanation related to a jellyroll? Light impinging from a fixed direction on a rotating spiral sees an oscillating number of unit cells, which, in effect, resembles the

shunting of cells implemented in the MIT simulation.

The phenomena observed at MIT can be tuned by changing parameters such as the lattice period. If they could be realized in a controlled way, the phenomena could see a wealth of applications. The ability to increase light frequency may have applications in FM communications, for example. Or, photonic crystals that trap light could serve as delay-line analogs in computers that rely on photon propagation. In time, solar cells might use band-

narrowing devices to efficiently harness the energy of the broad solar spectrum.

In its most recent simulations, the MIT group considered shock fronts that left in their wake not only a change in dielectric periodicity but also changes in the dielectric function due to material strain. The shocks were designed so that, in contrast to the system illustrated in figure 1, the bands in the shock region were lowered compared to their counterparts in the pre-shock region. As a consequence of that novel band evolution, light bouncing off an advancing shock front was shifted to lower frequencies. Such so-called negative Doppler shifts have been predicted for left-handed materials (see *PHYSICS TODAY*, May 2000, page 17), but the photonic crystals simulated at MIT were not left-handed; the physics leading to the unusual Doppler shifts in the two cases appears to be completely different.

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Watching a Molecule Break Up Reveals How Quickly It Changes Shape

It takes less than 60 femtoseconds for a doubly charged acetylene ion to change into its structural isomer vinylidene.

In papers that dissect the physics of chemical reactions, you'll often find a cartoon. The molecules in the cartoon appear as colored blobs or stick figures. Simple arrows indicate key motions. More succinctly than words or Hamiltonians, the cartoon embodies and conveys what's going on.

Getting to the point where one can draw such a cartoon is an arduous journey. Even for simple molecules whose structures are known, solving the quantum mechanical equations

requires months of computer time. It's just as hard in the lab. Between reactants and products lies a host of short-lived quasistable intermediaries whose existence—let alone properties—is difficult to pin down.

But now a team of researchers has taken a different, more direct route to distilling the essential physics of a reaction. Using an innovative spectroscopic method, Timur Osipov of Kansas State University, his thesis adviser Lew Cocke, and their collabo-

rators in the US and Germany have succeeded in tracking and timing how an acetylene molecule changes into its structural isomer vinylidene.¹

The transformation is simple—the hopping of a hydrogen atom from one carbon atom to another—and the molecule is small. But, says MIT's Bob Field, "It's really an extraordinary accomplishment."

Hydrogen swapping

Acetylene has the chemical formula C_2H_2 . Its four atoms are arranged in a straight line: two triply bonded carbons on the inside, two hydrogens on

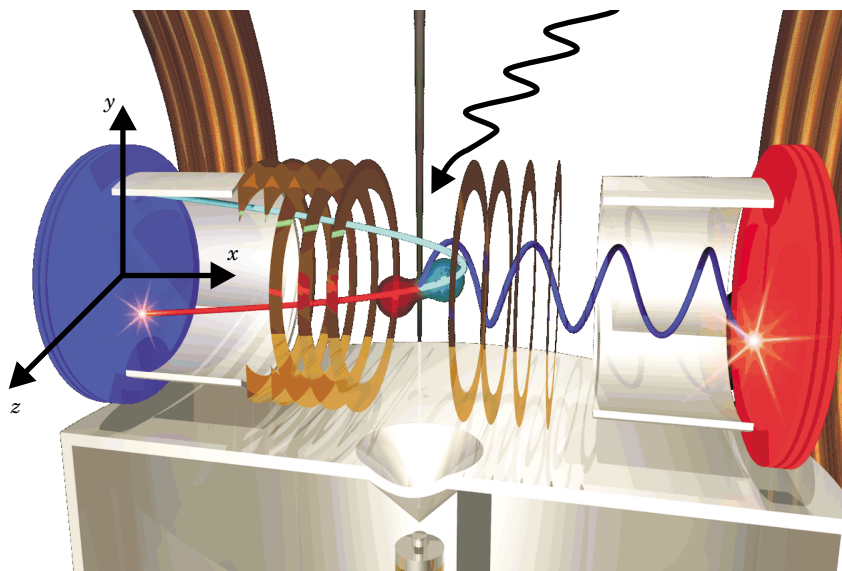


Figure 1. In the COLTRIMS experiment, x rays traveling in the z direction and polarized in the x direction ionize acetylene molecules streaming in the y direction. A series of copper rings produces an electric field in the x direction that accelerates cations toward the blue particle detector and electrons toward the red particle detector. Helmholtz coils generate a magnetic field that prevents the photoelectrons from escaping. (Adapted from a short movie that appears at <http://hsbpc1.ikf.physik.uni-frankfurt.de/photonmolecule/photonmolecule.html>.)

the outside. To make vinylidene, its free-radical isomer, remove a hydrogen atom from one of the carbons and attach it to the other.

Although hot-burning acetylene is industrially important, physicists and chemists are just as interested in its role as a model system. The acetylene-to-vinylidene isomerization involves what organic chemists call a 1,2 hydrogen shift. Many important reactions, especially in biology, include the shift. For measuring or modeling it, acetylene offers one of the simplest subjects.

But simple doesn't mean easy. Vinylidene is so short-lived that its status as molecule has been controversial for 20 years. Just recently, after running their computer models of acetylene's vibrational eigenstates for 10 months, Emory University's Joel Bowman, Alex Brown, and Shengli Zou concluded that vinylidene is indeed a stable isomer.²

Osipov's thesis work on acetylene is one fruit of a decades-long collaboration between Cocks's group at Kansas State and Hörst Schmidt-Böcking's group at Frankfurt University. Other team members include Reinhardt Dörner, Thorsten Weber, Ottmar Jagutzki, and Lothar Schmidt of Frankfurt University, Allan Landers of Western Michigan University, and Mike Prior of Lawrence Berkeley National Laboratory (LBNL).

The team uses cold-target recoil-ion-momentum spectroscopy (COLTRIMS).

Developed mostly in Frankfurt, COLTRIMS combines detector concepts from particle physics with cryogenic techniques from atomic physics. The union provides a complete picture of the momentum acquired by each molecular fragment in each fragmentation.

Different splitting

Studying isomerization requires a way to tell the two isomers apart. Acetylene and vinylidene weigh the same, but if you sever the bond between the two carbons, the two isomers fragment differently: Acetylene splits into two CH fragments, whereas vinylidene splits into CH₂ and C. Ionizing the fragments and applying an electric field, as in COLTRIMS, endows the fragments with different and distinguishing velocities.

But something is also needed to trigger the isomerization, and if you're interested in time scales, you need a stopwatch, too. Nature obligingly furnishes the trigger. Using an x ray to knock out an inner-shell photoelectron from one of the carbons creates a "core-excited" acetylene cation that deexcites by emitting a second, Auger electron. Five years ago, Xavier Gadéa of Paul Sabatier University in Toulouse, France, suggested that a core-excited acetylene cation could form a vinylidene cation.³ Because Osipov and company needed to ionize acetylene anyway to use COLTRIMS, x rays could act as both ionizer and trigger.

The x rays for photoionizing acetylene don't have to be especially energetic; 290 eV suffices to reach the carbon K edge. But, to give fragments enough time to reach the detector before the next round of ionization, the x rays have to arrive in short, widely spaced bunches. To use such bunches, the COLTRIMS team took their experiment to the Advanced Light Source at LBNL, where, for four weeks a year, the delay between pulses is stretched from the normal 2 ns to 150 ns.

Figure 1 shows the COLTRIMS experiment. Cold acetylene molecules spout upward from a nozzle and cross a beam of linearly polarized x rays. Ionized by the x-ray broadside, the cations acquire a second positive charge when they emit an Auger electron. Holding two positive charges, one at each end, is too strenuous for a small molecular ion. Whether acetylene or vinylidene, the dication breaks apart into two singly charged cations. An electric field accelerates the cations, which fly off to strike a particle detector.

Meanwhile, the same field accelerates the photoelectrons in the opposite direction toward another detector. By itself, the electric field lacks the strength to steer the photoelectrons onto the detector, so a magnetic field is added to confine them. The Auger electrons, being more energetic, mostly miss the detector. Any that don't are discounted by the detector's electronics.

In principle, determining the momenta of each pair of cations boils down to applying the simple dynamics of accelerated ions. The ingredients are the two-dimensional positions of the cations on the detector and the cations' time of flight, which is determined by subtracting the ionization time (supplied by the clock that synchronizes the x rays) from the arrival time (measured by the detector).

In practice, however, you need to discern differences in time of flight. Acetylene and vinylidene break up along the carbon-carbon bond, so the biggest differences in time of flight arise when a dication's axis lines up with the electric field and, right after breakup, one fragment shoots forward and the other backward.

To boost the number of such events, the x-ray polarization is aligned with the electric field. This arrangement helps because acetylene's electrons inhabit orbitals that follow the molecule's linear shape. The closer the photon's electric field parallels the molecular axis, the greater the ionization yield. Selecting events of modest

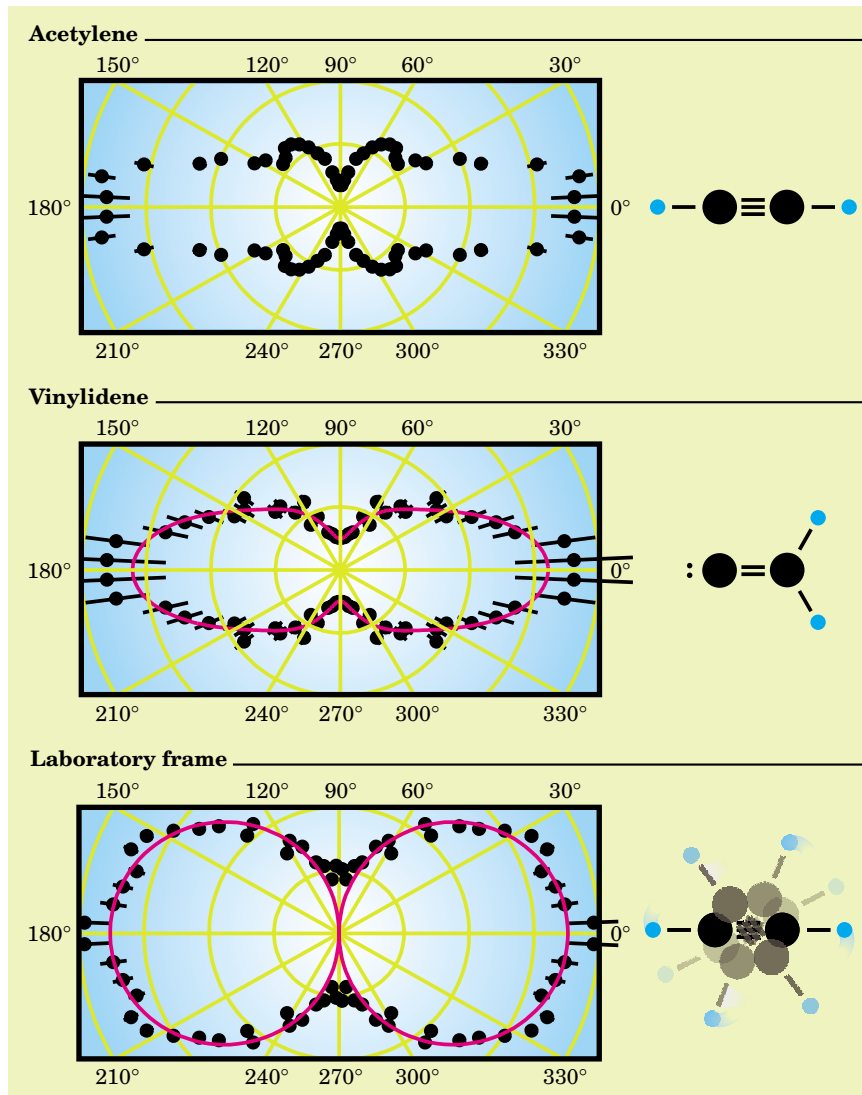


Figure 2. Angular distributions of photoelectrons. The sharpness of the top distribution indicates that acetylene dications fragment promptly. If they took longer to fragment and had time to tumble, the distribution would look like the one in the bottom panel. The vinylidene distribution in the middle panel falls between the other two, indicating that vinylidene dications break apart soon after their isomerization from acetylene. (Adapted from ref. 1.)

transverse momenta also sharpens the distinction between acetylene and vinylidene.

Osipov found that about 30% of the photoionized acetylene dications isomerize to vinylidene before breaking up. But, given that the isomerization occurs before the fragments reach the detector, how could he and his collaborators determine isomerization time? Their answer is ingenious.

Once dislodged, an inner shell electron takes a mere 40 attoseconds to escape the molecule. Although there's a modest probability that a photoelectron will flee in directions diagonal to the molecular axis, most of the time the photoelectron's escape route runs parallel to the axis. In the molecular

reference frame, the distribution of escape directions at photoionization, $\sigma^+(\phi)$, looks like a cigar with a central, butterfly-shaped protuberance.

COLTRIMS can't determine $\sigma^+(\phi)$, but it can determine $\sigma^{++}(\phi)$, the distribution of escape directions measured with respect to the molecular axis at fragmentation. Cocke and Osipov realized that photoionization, being so prompt and directed, could act as a stopwatch. If a dication fragments right after photoionization, they reasoned, $\sigma^{++}(\phi)$ would look pretty much like the unmeasured but predictable $\sigma^+(\phi)$. The top panel of figure 2 shows that for acetylene fragments $\sigma^{++}(\phi)$ does indeed share the same slim, butterfly-crossed shape of

$\sigma^+(\phi)$. Evidently, acetylene dications break up promptly.

But suppose—hypothetically—that an acetylene dication does have time to tumble about before it breaks up. In that case, $\sigma^{++}(\phi)$ would lose its resemblance to $\sigma^+(\phi)$. Of course, acetylene's lifetime can't be artificially extended, but the effect can be mimicked by measuring escape directions in the lab frame rather than in the molecular frame. The bottom panel of figure 2 shows the resulting distribution.

Vinylidene's $\sigma^{++}(\phi)$, which appears in the middle panel of figure 2, falls between the other two—as if the isomer's birth and life last long enough for the dication to rotate a bit, but not enough to wash out the distribution.

To determine vinylidene's rotation angle, Osipov took acetylene's $\sigma^{++}(\phi)$ and then, in a computer program, added varying amounts of rotation-induced blur until it matched vinylidene's $\sigma^{++}(\phi)$. That happened at a rotation angle of 20° .

In the acetylene-to-vinylidene isomerization, a hydrogen atom swings around its carbon until the other carbon captures it. At the same time, to conserve angular momentum, the rest of the molecule rotates in the opposite direction. A back-of-the-envelope calculation says that angle is also 20° . Apparently, vinylidene's birth is so quick that the dication barely survives long enough to rotate much further.

To derive an upper limit to the isomerization time scale, Osipov determined how much additional rotation the data could accommodate. His conservative estimate was 10° . To convert the angle into a time, he assumed that a vinylidene dication is set spinning by the ejection of the Auger electron. Using the other side of his figurative envelope, he derived the momentum kick and, from it, an isomerization timescale of less than 60 femtoseconds.

Chemists would love to know how fast neutral acetylene isomerizes. Unfortunately, the relationship between the neutral's and dication's isomerization time scale is hard to quantify. Osipov's upper limit is, however, suggestively similar to the bending period, inferred from spectra, of hydrogen on the end of acetylene.

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