

Phase-locked femtosecond laser directs the outcome of a simple chemical reaction

The up-down pattern of the electric field within intense optical pulses breaks the left-right symmetry of diatomic dissociation.

When chemically reactive atoms or molecules combine, their valence electrons snap into new, energy-minimizing configurations. But suppose you want to steer the reaction toward a particular configuration—an unfavored oxidation state, say, or a specific isomer. Somehow, you'd have to reach into the nascent molecule and, at just the right moment, divert the valence electrons from their habitual target.

Conceivably, the intervention could be effected by means of precisely timed and targeted pulses of electric field. But to pluck and place the electrons at will, the strength, direction, and duration of the pulses should all be adjustable. On the attosecond time scale of atomic electrons, wielding such arbitrary control of electric fields is currently out of reach.

However, as a recent experiment demonstrates, one can now start approaching that ideal. The key lies in exploiting the electric field oscillations within ultrashort pulses of laser light.¹

Marc Vrakking of the FOM Institute for Atomic and Molecular Physics in Amsterdam and Ferenc Krausz of the Max Planck Institute for Quantum Optics in Garching, Germany, led the team

that did the experiment. As befits a first step, the reaction is modest and the system simple: the photodissociation of the singly charged deuterium molecule D_2^+ .

Ordinarily, when the D_2^+ ion breaks up, the single electron has an equal chance of ending up on either deuterium nucleus. But by adjusting the phase of the electric field within femtosecond laser pulses, Vrakking and Krausz can specify which nucleus—left or right—carries off the electron.

A more interesting question

The use of lasers to direct the movement of electrons in reacting molecules was foreshadowed by an earlier experiment. In 2002, Krausz and his collaborators used femtosecond laser pulses like a catapult to drive atomic electrons away from, then back to, the electrons' nuclear partners. That feat yielded attosecond pulses in the extreme UV (see PHYSICS TODAY, April 2003, page 27).

The laser that made the 2002 experiment and the current one possible emits a series of widely spaced few-femtosecond pulses, each of which contains about four oscillations. Thanks to several technological innovations, includ-

ing Theodor Hänsch's Nobel-winning frequency comb, the phase of the oscillations with respect to the amplitude envelope can be fixed.

The phase, known as the carrier envelope phase (CEP), characterizes the pattern of up-and-down oscillations. At one extreme, known as a cosine pulse, the maximum electric field and the peak of the amplitude envelope coincide. At the other extreme, known as a sine pulse, the electric field is zero at the peak of the amplitude envelope.

Although the laser's control equipment can lock the CEP, it can't determine the CEP's value. To make his attosecond pulses, Krausz needed cosine pulses and used a spectroscopic method to determine the CEP. Krausz and his group then began to explore how atomic photoionization depends on CEP.

For those experiments, Krausz positioned detectors to catch photoelectrons flying off parallel and antiparallel to the laser's polarization axis. To detect all the photoelectrons in all directions, Krausz teamed up with Vrakking, whose ion velocity imager can do just that. As they started work, they realized their original goal—measuring the CEP

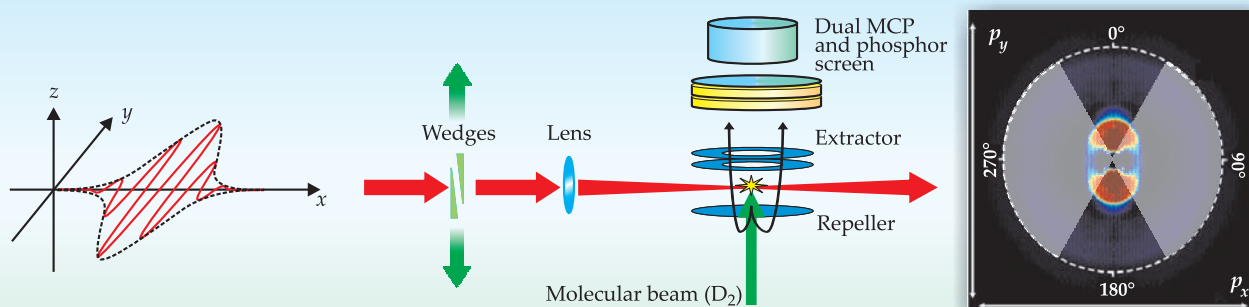


Figure 1. To demonstrate the role of carrier envelope phase (CEP) in molecular dissociation, the Amsterdam–Garching research team focused CEP-locked pulses onto a beam of deuterium molecules. The pulses have enough energy to ionize and split any molecule whose axis happens to align with the pulses' polarization axis (the y-axis here). When the D_2^+ ions dissociate, the D^+ ions are accelerated by the electrostatic field between the repeller (positively charged) and extractor (grounded) toward the microchannel plates (MCP) and phosphor screen. From the position of the ions on the screen, one can derive the ions' initial momenta in the x and y directions. Because of the system's symmetry, the momentum distributions in the x- and z-directions are the same and the ions' total kinetic energy can be calculated. The map on the right shows the distribution with random CEP. To see how CEP influences dissociation, the experimenters moved the glass wedges and compared the counts in the segments centered on 0° and 180°. (Adapted from ref. 1.)

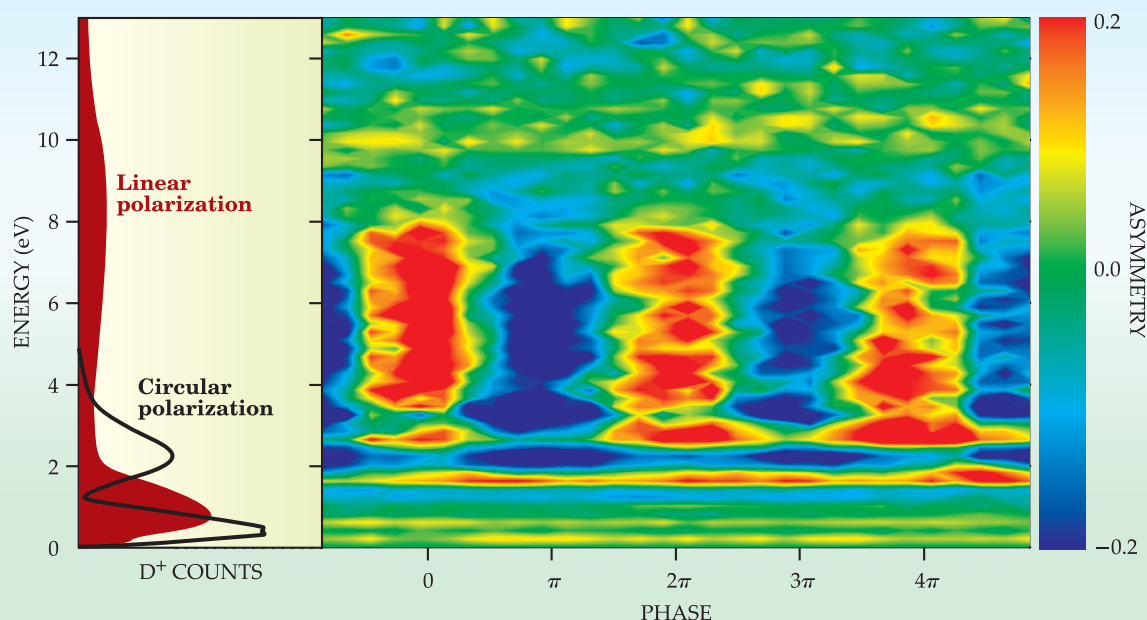


Figure 2. Whether D^+ ions prefer to go in the $-y$ direction (blue), the $+y$ direction (red), or neither direction (green), depends on the carrier envelope phase and the ions' energy. The main panel shows that CEP-dependent asymmetry is reproducible (that is, it has a period of 2π) and that it occurs only between about 3 and 8 eV. The left panel shows that the asymmetry arises only when an electron, removed during ionization, slams back into the D_2^+ ion. Circularly polarized pulses, unlike linearly polarized pulses, can't supply the D_2^+ with enough energy. (Adapted from ref. 1.)

dependence of ionization—suggested a more interesting question: Could the CEP *control* the ionization?

The experiment their team performed boils down to three steps: creating D_2^+ ions, breaking them apart in a controlled way, then recording the pattern of paths taken by D^+ fragments. Deuterium was picked over hydrogen to avoid noise-producing contamination from ambient water molecules.

Krausz's femtosecond phase-locked laser carries out the first two steps. Vrakking's ion velocity imager, which his team installed in Krausz's Garching lab, carries out the third step. Matthias Kling, a postdoc in Vrakking's group, and Aart Verhoef, a graduate student in Krausz's group, set up and ran the experiment. Figure 1 outlines how it works.

Laser pulses pass first through a pair of glass wedges whose separation changes the CEP and then through a lens whose focus intercepts the beam of D_2 molecules. What happens when a pulse hits a molecule depends on the molecule's orientation with respect to the laser's polarization. If the two axes are aligned, the laser ionizes the molecule and excites it into a state from which it splits into a D atom and a D^+ ion. The ion is accelerated toward a microchannel plate detector, whose plane is parallel to the polarization. The ion's position, along with elementary electrostatics, yields the

ion's momentum.

The right side of figure 1 shows what happens if the CEP is not locked and varies randomly from pulse to pulse. The D^+ ions fly off mostly along the axis of polarization. Equal numbers go in the $-y$ and $+y$ directions, which means that after the D_2^+ ions dissociate, their single electrons go one way or the other with equal likelihood.

To determine whether CEP influences dissociation, Kling and Verhoef first locked the CEP, then repeated the experiment at different wedge settings, increasing the phase in steps of $\pi/4$ through 3 full cycles of 2π . To quantify the expected asymmetry of the dissociation, they integrated the counts in the 60-degree-wide segments shown in the figure. The normalized asymmetry A is defined as the difference in the segment counts divided by their sum.

Dissociation

The main panel in figure 2 maps A as a function of the kinetic energy of the D^+ ions and the phase added to the CEP. Below 3 eV and above 8 eV, locking and adjusting the CEP has no influence on whether D^+ ions go in the $-y$ or $+y$ direction. But between 3 eV and 8 eV, A oscillates between -0.2 and $+0.2$ with a telltale period of 2π . In that energy range, changing the CEP is like aiming the reaction left or right.

What's so special about that energy range? The laser pulse has to ionize D_2 as well as split the resulting D_2^+ . At certain (and as yet unknown) values of the CEP, one of the first strong upswings of the electric field strips off an electron from the molecule. The downswing hurls the electron back at the cation, giving it extra energy that ends up, in part, boosting the D^+ ion's kinetic energy above 3 eV. Somehow the collision also makes the breakup of the cation dependent on the direction of the next peak of electric field upswing (that is, on the CEP).

The key role played by the first electron is demonstrated by the left panel in figure 2. When the laser pulse is linearly polarized, the D^+ energy spectrum has a broad peak between 3 and 12 eV within which A is nonzero. But when the laser pulse is circularly polarized, the peak vanishes, presumably because a twisting field can't hurl the first electron back at the molecule.

Vrakking's postdoc Christian Schiedslag analyzed the breakup in terms of energy levels. Right after ionization, the D_2^+ sits in its $1\sigma_g^+$ ground state. The returning electron excites the ion into the $2\sigma_u^+$ state, which, being antibonding, leads to dissociation. If the surviving electron remains in the state through dissociation, the state's parity guarantees that the remaining electron

will end up on either D nucleus with equal probability.

But, according to his calculations, Schiedslag believes the electric field pushed the electron partially into the $1s\sigma_g^+$ state, thereby breaking the wavefunction's symmetry and introducing bias toward one D nucleus over the other. The bias depends on which way the field is pointing and hence on the CEP.

Although the recolliding electron is essential to their experiment, Vrakking and Krausz emphasize that symmetry-breaking CEP dependence can occur without the electron's help. The field itself is what breaks the symmetry, not the first electron, whose presence is a consequence of experimental expedience: It's easier to start with deuterium molecules than with deuterium cations.

Indeed, in a 2004 theory paper, Vladimir Roudnev, Brett Esry, and Itzik Ben-Itzhak of Kansas State University analyzed the dissociation of HD^+ and H_2^+ and found a CEP dependence of comparable magnitude.² Esry would like to see Vrakking and Krausz start directly with HD^+ , H_2^+ or D_2^+ . Those three-body systems (two nuclei, one electron) approach the current limit for solving the time-dependent Schrödinger equation in an intense laser field.

The experimental frontier, as Krausz

sees it, involves improving the ability to shape the pattern of electric field within a pulse. Broadening the frequency range down to the IR and up to the UV (at present it remains all-optical), would bring two benefits. First, at higher energies, the field itself could excite the target molecule. Second, a spectral band spanning several octaves would extend the range over which one can adjust the field's instantaneous amplitude and frequency. The result is stronger CEP dependence and greater freedom to shape the pulse from one subfemtosecond quarter cycle to the next.

Conceivably, as Paul Haljan, Misha Ivanov, and Paul Corkum of Canada's National Research Council proposed ten years ago, a shaped, broadband pulse could excite a molecule from its ground state to one or more excited states.³ A later oscillation in the same pulse could then steer the excited electron inside the chemical bond, changing the atoms it would otherwise connect.

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References

1. M. F. Kling et al., *Science* **312**, 246 (2006).
2. V. Roudnev, B. D. Esry, I. Ben-Itzhak, *Phys. Rev. Lett.* **93**, 163601 (2004).
3. P. Haljan, M. Yu. Ivanov, P. B. Corkum, *Laser Phys.* **7**, 1 (1997).

Colloidal particles crystallize in an increasingly wide range of structures

Two groups working in different size regimes have found similar recipes for making new and potentially useful materials.

A material's properties depend not only on its constituents but also on how the constituents are arranged in space. Diamond, for example, shares the same atomic constituents as graphite and the same tetrahedral structure as silicon, yet it resembles neither black flaky graphite nor gray brittle silicon.

So if you want to make a new material with preternatural properties—a transparent magnet, say, or a chemical-sensing resistor—you may need to choose your construction plan as well as your building blocks. And to avoid having to put each block in its individual place, you'd rather the material assembled itself, like a virus's protein coat or a cell's lipid membrane.

Colloids may provide a path toward that ideal. Their nanometer-to-micrometer particles can be tailored by size and chemistry. And even the simplest colloids—identical hard spheres that neither attract nor repel each other—

will spontaneously crystallize (see Alice Gast and William Russel's PHYSICS TODAY article, December 1998, page 24).

But identical hard spheres arrange themselves into the familiar close-packed face-centered cubic structure (fcc). If they come in two sizes, the number of spontaneously forming structures increases to about five. Still, material designers would prefer to select structures à la carte from a long menu of densities and symmetries.

Now, two groups have more than doubled the number of self-assembled colloidal structures—in two different size regimes. Alfons van Blaaderen of the University of Utrecht in the Netherlands and his collaborators are working with micron-sized plastic and glass particles.¹ As of May, they have found 12 new structures.

Dmitri Talapin and Christopher Murray of IBM's T. J. Watson Research Center in Yorktown Heights, New York,



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