Training Lasers to Be Chemists

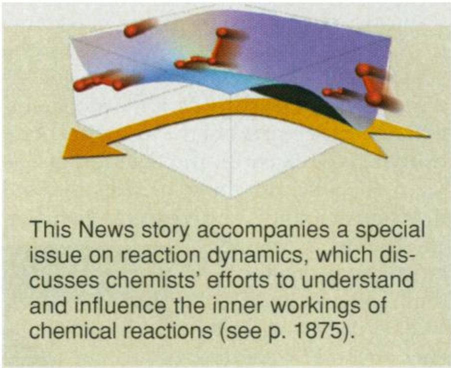
Computer-controlled lasers can learn to coax complex molecules into reacting in specific ways—even when the best means of persuasion can't be calculated in advance

With the abandon of newlyweds on their honeymoon, molecules undergoing a chemical reaction come together in an embrace that can both transform them and create a whole family of offspring in no time. However, chemists, like meddling relatives, are continually searching for ways to coax the partners into producing just the offspring they're looking for. This is not always an easy task, but over the past decade or so researchers have been trying to light the way to particular molecular offspring by delivering precisely tuned, precisely timed laser pulses to the parent molecules as they react.

The potential of this technique—known as coherent control—is enormous. Reactions produce many valuable compounds in only minute quantities, lost among many other products. Coherent control could coax such reactions to produce much more of the desired product. It also has the potential to push reactions down previously unknown pathways, yielding products that might never be produced by traditional methods. But the difficulties have turned out to fully equal the promise, and so far the technique has been successfully applied only to a smattering of simple reactions. The reason: For any molecule containing more than just a handful of atoms, the task of calculating precisely what sort of laser pulse will push it in the desired direction becomes impossibly complicated. "We can't do the experiment because we don't know what the best shaped pulse would be," says Philip Bucksbaum, a laser physicist at the University of Michigan, Ann Arbor.

In recent months, however, several research groups have made remarkable progress by turning to an age-old engineering principle: feedback. They put the control of the input lasers in the hands of a computer program capable of learning, such as a genetic algorithm. After the lasers fire a random array of pulses, the program analyzes the results, calculates how to achieve a better result, and fires another array of improved pulses until it finds the best one possible. For researchers looking to control the reactions of complex molecules, the upshot is that "it's no longer necessary to know everything about your system in advance," says Bucksbaum.

So far, attempts at using computer-controlled feedback to optimize laser control of molecules have been limited to simple demonstrations, such as finding the best light pulse for triggering fluorescence from a dye molecule. But these demonstrations have been so successful that many researchers see feedback as the most promising way to apply coherent control to everything from cancer therapy—where tailored light pulses would prompt optically active molecules to generate cell-killing reactive oxygen—to electronics manufacturing, where pulses would make precise changes in the molecular structure of the polymers used to create circuit patterns. "Learning in quantum systems is a very important development," says Herschel Rabitz, a theoretical chemist at Princeton University. "All of the applications [of coherent control] will have to embrace this."



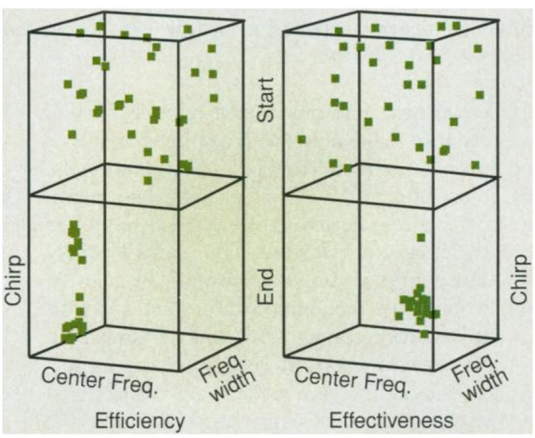
The right light

In conventional chemistry, researchers typically use heat, mechanical mixing, and pressure to influence how compounds react. But this "shake and bake" approach isn't terribly selective, as the changes in external conditions affect all atoms in the molecule indiscriminately. What chemists would like to be able to do is manipulate the electronic structure of the molecule, encouraging individual bonds to break and reattach, and so produce a desired product.

Lasers and other precisely controlled sources of electromagnetic energy offer this possibility. Atoms connected by bonds act something like balls connected by a spring: Knock one of the balls and the spring jiggles or vibrates back and forth. In molecules, heat energy keeps the balls moving and springs jiggling all the time, with each pair of atoms having its own characteristic vibration frequency. Pulses of electromagnetic radiation—most often light—can excite these natural vibrations, causing them to jiggle faster or slower. If tuned just right, the light can cut an electron free or jiggle a bond so much that it breaks, thereby forcing the molecule along one desired reaction path. Researchers began to have enticing success with this approach in the early 1990s (*Science*, 14 October 1994, p. 215).

Among the first reactions to be controlled was the breakdown of the simple molecule H–O–D, in which one of the hydrogens in water is replaced by deuterium, hydrogen's heavy twin. Breaking a single bond in the molecule produces either H–O and D, or H and O–D. Because H and D have different masses, H–O–D's two chemical bonds vibrate at slightly different frequencies. By sending in a laser pulse at one frequency, a chemist can increase the stretching of, say, the H–O bond, making it more likely to break and create H and O–D. Such experiments have become an increasingly popular way to learn about the dynamics of reactions, because they reveal the precise amount of energy needed to drive particular reactions (see Article on p. 1875).

When it comes to more complex molecules, however, things get messy fast. What complicates the picture is that the movement of one spring between two atoms affects the movement of neighboring springs. H–O–D only has two interacting springs, but in complex molecules with 50 or 100 atoms, any change in vibration between one pair instantly feeds into dozens of other bonds. Tracking all these changes quickly becomes an impossible task. "We



Homing in. A random selection of laser pulses (top) converges on the right features (bottom) for optimum efficiency and effectiveness in triggering fluorescence.

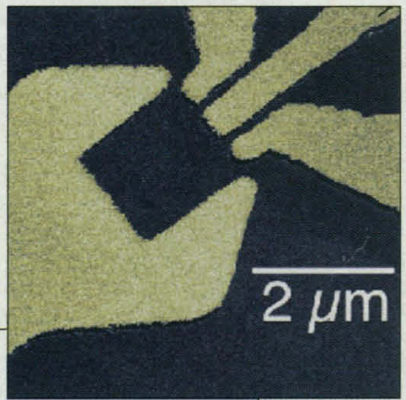
SOURCE: C. J. BARDEEN *ET AL.*, *CHEM. PHYS. LETT.* 280, 151 (1997) have to have the knowledge of these changes to know what kind of light [pulse] will help us meet the goal" of steering the reaction down one particular pathway, says Kent Wilson, a chemist at the University of California, San Diego. With complex molecules that's simply not possible. As a result, he adds, "we realized we're going to have to do something else."

Learning a lesson

That something is feedback. People use feedback all the time to learn skills. And feedback is ubiquitous in the machine world, appearing in everything from airplane guidance-control systems to home thermostats, says Rabitz. Nevertheless, he adds, "it has been a long time coming for the [coherent control] community to think that this is the way to deal with molecules."

Rabitz and Richard Judson of Sandia National Laboratory were the first to explore the approach. Back in 1992, the pair proposed a feedback scheme that would identify the best pulse for exciting a simple molecule. The idea was to deliver a photon blast to a sample and send the results to a computer, which would use this information to predict what shape the next pulse should be. In a computer simulation of an actual laser experiment, Rabitz and Judson reported in *Physical Review Letters* (9 March 1992), the computer quickly learned to create the optimal light pulses needed to excite two-atom molecules to rotate in a unique manner.

Although the simulation suggested that the idea held promise, it wasn't until recently that Wilson's team tested it on real materials in the lab. In the 28 November 1997 issue of *Chemical Physics Letters*, Wilson and San Diego co-workers Christopher Bardeen and Vladislav Yakovlev, along with colleagues at Brown University and Princeton, showed that feedback systems can manipulate real-world molecules.



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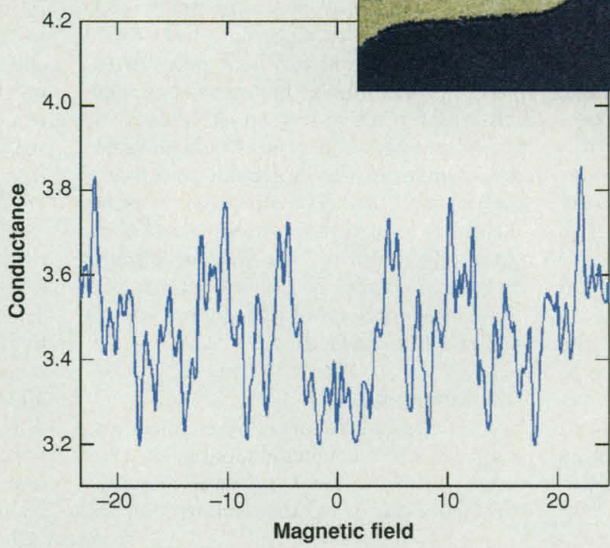

Pacified. Feedback dampens conductivity fluctuations *(above)* through quantum dot *(top)*.

In their experiment, the researchers used large dye molecules—each containing about 100 atoms—that absorb laser light at one frequency and reemit it as fluorescence at a slightly lower frequency. They set two separate goals for their setup. First, find the type of light pulse that would create the brightest fluorescence possible from dye molecules in an organic solvent, no matter how much energy was put in with the laser pulse. Second, find the pulse that would produce fluorescence most efficiently, getting the most light out for the least put in.

Light pulses can vary in many ways, such as duration, colors, and chirp, a measure of how the color composition of a pulse changes from start to finish. For their initial set of pulses, Wilson and his colleagues chose more or less random combinations of features, such as a short duration, red and yellow colors, and a chirp that shifted the light more toward the yellow by the end. After each pulse was fired, a detector recorded how much fluorescence came out of the sample.

Then a computer running a genetic algorithm program treated the pulse characteristics like genes to produce new pulses for the next round. The computer ignored pulses that produced poor results while recombining the characteristics of the successful ones, marrying, for example, the duration of one successful pulse with the color of another and the chirp of a third. The computer then analyzed this second round of pulses and produced a third, and so on.

The team found that after about 17 iterations the computer had come up with solutions to the two different problems. For creating the brightest fluorescence, the best pulse turned out to be one containing photons over a relatively broad range of frequencies, with a chirp that moved from low to high frequencies. For sparking the most efficient fluorescence, the best pulses contained a narrow range of frequencies and the chirp was irrelevant. The results are "very interesting," says Bucksbaum, because it would have been impossible to come up with this solution through sheer calculation alone. "It's just the direction we want to be going in."

It's a direction others are also beginning to take, testing the feedback skills that will ultimately be put to use guiding chemical reactions. At a chemistry meeting last November in Cancún, Mexico, physicists David Reitze and Jeffrey Krause of the University of Florida, Gainesville, presented results from a feedback experiment done with optical crystals that absorb photons at one frequency and reemit them at twice the frequency. They trained a pair of lasers on one such crystal and had their computer determine the combination of color, timing, and beam mixing that turned out the most light at double the frequency. In fact, Krause explains, the answer to the problem was already known in advance, but he and Reitze just wanted to see if their computer-controlled optics system would come up with the right answer. "It got it right away," says Krause.

Charles Marcus and his colleagues at Stanford University have been experimenting with a feedback system that relies on voltages rather than light pulses and controls not a reacting molecule but a tiny semiconductor island known as a quantum dot. But the goal is the same: manipulating the behavior of electrons through feedback. Ordinarily, electrons can flow smoothly through the dot. But add a magnetic field, and the electrons change their interactions with the walls of the quantum dot, causing the amount of current that passes through the dot to fluctuate wildly. With a computer-controlled feedback system that compensated instantly for any change in conductance by applying a voltage to the dot, Marcus and his colleagues found that they could easily squelch the fluctuations and return the electron flow to a steady trickle.

So what's likely to come of the new enthusiasm for feedback in coherent control? Commercial applications will probably be limited, say Rabitz and others. At least for now, using lasers remains an expensive way to process bulk chemicals, although coherent control could gain a foothold in medicine and microelectronics. But the new approach is likely to produce valuable scientific insights into complex molecules. The technique, says Krause, gives researchers the full benefit of hindsight: By knowing what type of light pulse produces the best result, they can determine how their molecule must have wiggled and jiggled to produce it. As a result, says Krause, "this is a way of learning about the dynamics of a system as well as learning how to control it."

–Robert F. Service