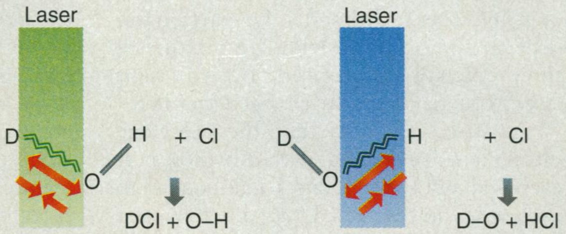
Laser Chemistry: The Light Choice

By administering precise doses of laser light to specific bonds, chemists are beginning to realize a decades-old dream: steering chemical reactions down chosen paths

Almost as soon as the laser was invented, around 1960, chemists began dreaming of where it could take them. They pictured using it to reach into molecules, employing its exquisitely precise energy to jiggle specific bonds and thereby steer chemical reactions in ways nature never intended. "People thought that they were going to be able to go into molecules and cut bonds at will," says chemist Richard Zare of Stanford University. "Laser Alchemy Is Just Around the Corner," promised a 1977 article in *Fortune* magazine. By wielding the laser as a molecular-scale scalpel, it said, chemists would soon be fashioning new fuels and drugs and detergents.

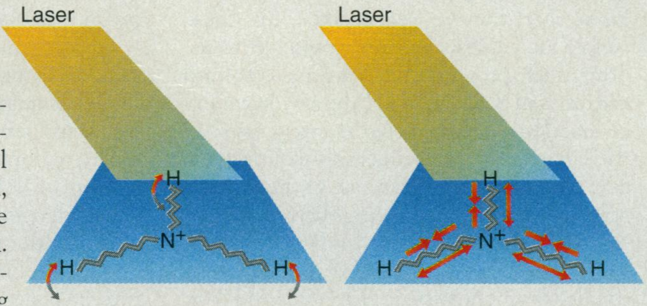


SOURCE: FLEMING CRIM

Alternate routes. Finely tuned laser light can break either of two bonds in a molecule of deuterium-containing water, resulting in different reaction products.

Nature, however, was not so easily manipulated. Chemists found that no matter how carefully they tuned their laser pulses to target specific bonds, the energy quickly leaked throughout their molecules, and in the end had an effect no more specific than the heat of an ordinary Bunsen burner. But a few die-hard chemists have continued to pursue laser-controlled chemistry. By carefully choosing their target molecules, they are finally starting to see results—one of which is reported on page 259 of this issue by Zare and his colleagues. "Now you see experiments under very controlled conditions showing there are effects," he says.

With laser light tuned to specific frequencies, he and other laser chemists have been able to excite certain natural vibrations in the bonds holding together molecules of water, acetylene, and ammonia, making reactions between these compounds and other simple molecules more likely to follow a chosen path. Although that strategy is probably limited to a handful of reactions, say researchers, a few chemists are on the verge of trying out potentially more powerful approaches—for example, using intricately choreographed laser pulses to control each motion of a chosen bond, thereby forcing the molecule along a particular reaction path.



SOURCE: R. ZARE *ET AL.*

Shake it up. Only the "umbrella mode" vibration *(left)* of an ammonia ion affects its reaction course; the "breathing mode" *(right)* has no effect.

One reason this quest for laser control has persisted so long is that it promises a way around the frustrating inefficiency and waste of many chemical processes, says Zare. "We know that most chemistry is done by shake and bake—by putting things together and applying heat." In many cases, heat will push a reaction along several different paths at once—one that produces a trace of some useful product and several others that spew out a pile of useless or dangerous waste. But nudge particular chemical bonds with a laser, and the reactants might be much more likely to follow the less traveled but more useful path.

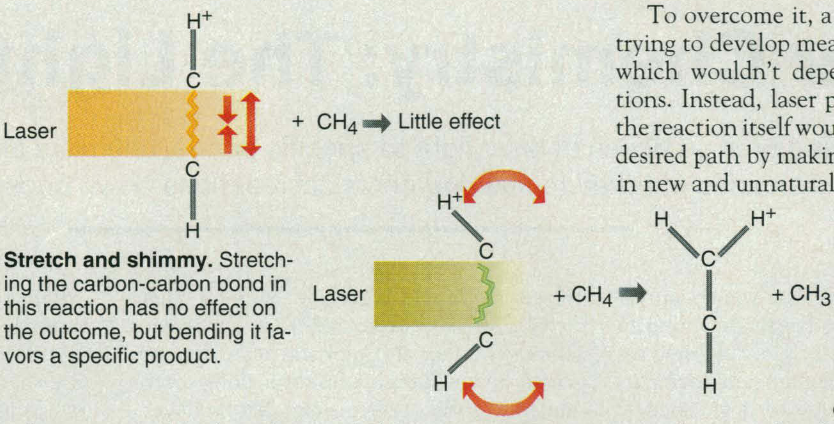
The principle seemed enticingly simple. Each chemical bond in a molecule stretches or bends at certain frequencies depending on its location in the molecule and the kinds of atoms it links. A chemist wanting to encourage a particular bond to break could hit the molecule with laser light tuned to the bond's characteristic frequency. The light would pluck the bond like a guitar string, weakening it and encouraging it to break more readily than another, intrinsically weaker bond. The result would be to steer a reaction—in which chemical bonds are broken and re-formed—along an unnatural course.

The inspiration for trying to put this idea into practice, says Zare, came in the 1960s when chemists found that lasers could exert a simpler kind of control: dislodging an electron from specific atoms or molecules, leaving them positively charged. These chemists applied lasers to a task that had been the bane of the early nuclear weapons program—extracting the small fraction of fissionable isotopes from the mixture that is found in natural uranium. Because different isotopes tend to absorb light at different frequencies, a laser tuned to the right frequency could selectively ionize one isotope in the mixture. The charged isotope could then be extracted with an electric field. Reports that weapons scientists had succeeded in sifting out uranium isotopes in this way got other chemists excited. "People thought if [lasers] could separate isotopes they could do anything," says Zare, including control chemical reactions. "Companies invested millions in this idea."

But it wasn't until 1990 that the idea had its first success, he says. The problem, explains University of Wisconsin chemist Fleming Crim, was that most bonds don't vibrate separately, like guitar strings or springs. In most cases, the bonds "couple" so that energy pumped into one bond almost instantly distributes itself through all the bonds in a molecule. Only a few molecules have bonds sufficiently well-separated, or "uncoupled," for a laser to excite one of them for long enough to influence the course of a chemical reaction. Water is one such molecule, as Crim showed when he made it the star of the first successful laser-controlled reaction.

Lighting the way

Crim actually used a special sort of water, HOD, in which one hydrogen atom is replaced by deuterium, a heavy isotope of hydrogen. When HOD is mixed with chlorine and simply heated, both bonds are equally likely to break, yielding comparable amounts of the fragments OH and OD. But when Crim added laser light to the picture, something very different happened. If he tuned the laser to a frequency calculated to stretch out the bond between the O and H, that bond broke 200 times more often than the other, leaving behind 200 times more OD than OH. When he chose the slightly different frequency that stretched the OD bond, however, the results were reversed, and OH dominated the product.

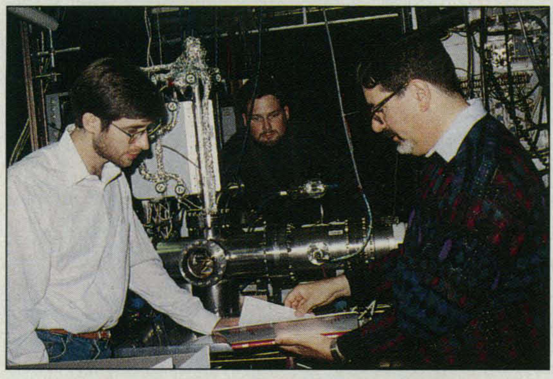


Stretch and shimmy. Stretching the carbon-carbon bond in this reaction has no effect on the outcome, but bending it favors a specific product.

SOURCE: SCOTT ANDERSON

That experiment left chemists wondering whether the same strategy could control the outcome of more complex reactions. In this issue of *Science*, Zare and his Stanford colleagues show that it can. The reaction in question involves a positively charged ammonia ion (NH_3^+), which reacts with another ammonia in which all the hydrogen has been replaced by deuterium (ND_3). The reaction has three possible outcomes, explains Zare, which the presence of deuterium enabled him to distinguish. The ammonia ion can pull either a deuterium or an electron from the ND_3, or the ND_3 can pull a positively charged hydrogen away from the ammonia ion.

Because the three bonds joining the hydrogens to the central nitrogen in the ammonia ion are identical, the Stanford group couldn't control the outcome by targeting a specific bond. Instead, the researchers found that laser pulses could drive the whole ammonia ion into two different vibration modes that sent the reaction along different courses. One laser frequency caused the three bonds to stretch and contract in synchrony (the "breathing mode"); the other bent the hydrogens up and down around the nitrogen like an umbrella turning inside out in the wind (the "umbrella mode"). The breathing mode, he found, had no effect on the outcome of the reaction, which still yielded an equal mixture of products. The umbrella mode, however, enhanced the reaction in which the ion loses a hydrogen to ND_3. Bending the ion's bonds umbrella-style apparently weakened them more than stretching them did.



Taking control. Laser chemists Robert Guettler *(left)*, Glenn Jones *(center)*, and Richard Zare *(right)*.

ALBERT DADIAN

Meanwhile, Scott Anderson and his colleagues of the State University of New York–Stony Brook have exerted a surprising kind of control over a reaction between acetylene and methane, as they reported last month. The reaction has three possible outcomes: The acetylene steals either one or two hydrogens from the methane, or it appropriates the methane's carbon and three of its hydrogens. Ordinarily the reaction follows all three paths, yielding a mixture of three different product sets. But the right laser frequency radically changed that mix.

Anderson explains that the acetylene molecule is bar-shaped, with a hydrogen at each end and two carbons, triple-bonded to each other, in between. Using different laser frequencies, Anderson was able to excite the carbon-carbon bond into two different patterns of vibration, one that bent it back and forth and one that stretched it in and out. The stretching had little effect on the reaction outcome, he says, but the bending mode favored the one in which the acetylene takes just one of the methane's hydrogens. "This was a dramatic effect," says Anderson. "The products of this [reaction] were enhanced by a factor of 30."

What makes this result unexpected, he notes, is that the laser bends a bond—the one linking the carbons—that doesn't break in any of the possible reactions. Anderson speculates that the laser can affect the reaction because the molecule has to change its shape to accommodate the extra hydrogen. It isn't clear just why the laser pulse favors this particular outcome over the others, which also add atoms to the acetylene, but Anderson thinks the bending may push the molecule closer to the shape it assumes with just one added hydrogen.

Micromanaging reactions

Now that they've succeeded with these simple molecules, chemists would like to see how much progress they can make toward the original goal of controlling a wide variety of reactions. The "passive" strategy used in these pioneering experiments—exciting certain natural vibrations in one of the starting reactants and then allowing the reaction to run its course—has its limits, however. Most molecules present the problem that stymied laser chemists in the 1960s and '70s: A laser-excited vibration doesn't stay isolated in a target bond for long enough to influence a reaction.

To overcome it, a few laser chemists are trying to develop means of "active control," which wouldn't depend on natural vibrations. Instead, laser pulses delivered during the reaction itself would chaperone it along a desired path by making the molecules move in new and unnatural ways.

Doing so requires bombarding them with a series of laser pulses delicately timed and modulated so that they match the split-second bends and stretches of individual bonds. Thanks to mathematical tools developed in 1985 by theorists David Tannor of Notre Dame University and Stuart Rice of the University of Chicago, laser chemists can now predict those split-second contortions. And that is enabling chemist Keith Nelson of the Massachusetts Institute of Technology to design precise sequences of laser pulses that could guide a molecule through a reaction. "You are fine-tuning the force applied to each [molecular] motion," he explains.

In a simple molecule like water with one deuterium (HOD), for example, an initial pulse might set the two bonds stretching and contracting at different rates. A second pulse would then be delivered at just the right moment to catch the HO bond as it starts to contract and the DO bond as it starts to stretch. The result: The hydrogen careens back inward while the deuterium is kicked farther out, making that bond more liable to break. That's a hypothetical example, says Nelson, but he has used the technique to manipulate the electronic structure of individual atoms, and his success there has convinced him that he can extend this kind of control to chemical reactions.

While Nelson uses mathematical models and powerful computers to figure out how to influence the motion of molecules, Herschel Rabitz of Princeton University is trying to determine the best possible laser pulse shapes experimentally, using an approach that other chemists have dubbed "obedience training for molecules." The idea, says Rabitz, is to send in one pulse that sets the molecule in motion. Then follow the first pulse with a second, probe pulse; changes in its frequency will reveal the effect of the first pulse on the molecular motion. Like an unruly dog, the molecule quickly teaches its handler the best way of influencing its behavior. "These lasers are incredibly fast," says Rabitz, "so one could conjure up doing thousands if not millions of experiments in an hour."

Paul Brumer of the University of Toronto and Moshe Shapiro of the Weizmann Institute in Israel are taking a more radical approach to active reaction control. Instead of tailoring their laser pulses based on predictions or data about how the molecule vibrates, they are exploiting the implications of quantum mechanics, in which the ball-and-spring picture of a molecule dissolves into a set of overlapping mathematical waves. "If you think of a molecule as jiggling and wiggling, then it's that wiggling which is described by the wave function," explains Brumer. He and Shapiro design their laser pulse to interfere with those waves, changing the wave pattern—and consequently the molecular motion—in some predictable and controlled way. "You want to get the wiggling coalesced in one part of the molecule and minimize it elsewhere," explains Brumer.

Says Wisconsin's Crim, who is trying to extend his passive technique to other reactions, including one between hydrogen cyanide and chlorine, "We are looking in the windows of the house, and these folks are trying to find new passages in." One way or another, he thinks, after 30 years of trying, "someone is going to make this work."

–Faye Flam

Additional Reading

Yu-hui Chiu, Hungshin Fu, Jui-tsen Huang, and Scott L. Anderson, "Large, Mode-selective Vibrational Effect on the Reaction of $C_2H_2^+$ with Methane," *Journal of Chemical Physics* **101**, 5410 (1994).

ENVIRONMENT

Antarctic Ozone Hole Fails to Recover

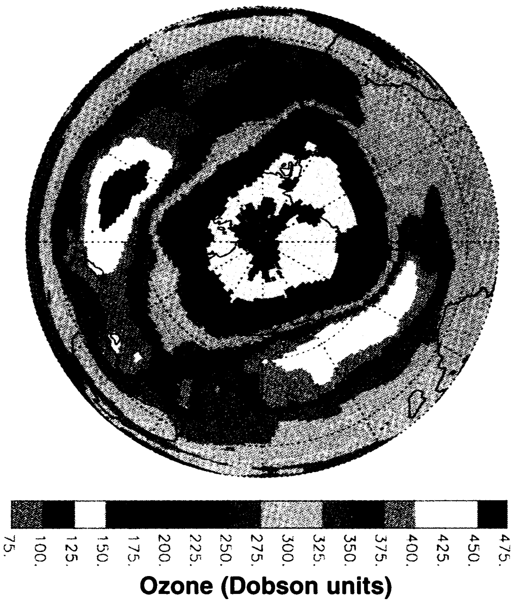
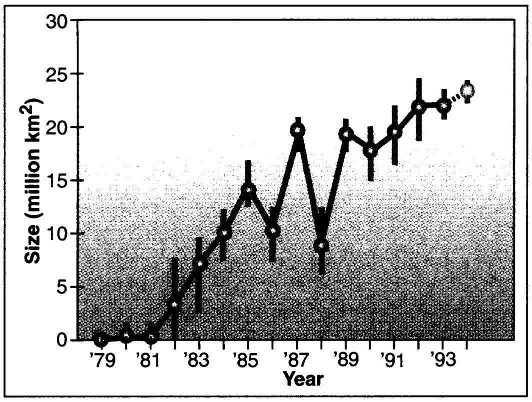


PHOTO: GSFC/NASA

Another bad hole. This year's ozone hole, seen by the TOMS instrument in space, nearly matches last year's in depth and size, continuing a 15-year worsening trend *(right)*.



SOURCE: GSFC/NASA

This was supposed to be a better year for ozone over Antarctica. Not a great one, of course, given that the synthetic chemicals that attack the ozone layer each year at this time as the sun hits the Antarctic stratosphere are still there. But researchers expected that last year's record ozone loss wouldn't be repeated. The reason for their optimism was that the volcanic debris spewed by Mount Pinatubo in 1991, which enhanced the chemical destruction of ozone, is nearly gone. But instead of recovering this year, the ozone hole is nearly as deep and wide as ever. For Antarctic ozone, it's been four bad years in a row.

"It's a little bit of puzzle as to why [ozone] values are as low as they are," says Samuel Oltmans of the National Oceanic and Atmospheric Administration in Boulder, Colorado, who monitors ozone above the South Pole using balloon-borne instruments. The most discouraging possibility is that the ozone hole has recovered as much as it can from Pinatubo, but the hole is being deepened and enlarged by the steady increase of chlorine and bromine from synthetic chemicals. Notes Arlin Krueger of the Goddard Space Flight Center (GSFC) in Greenbelt, Maryland: "Maybe the hole has returned to normal; 'normal' may be a progressively deepening ozone hole."

That's not what many researchers had expected a few months ago. They assumed that last year's record low of 91 Dobson units (DU) of ozone was largely due to the heavy blanket of debris lofted into the stratosphere by Pinatubo. The microscopic debris particles, they knew, provide hospitable sites for the chemical reactions that help destroy ozone. Now that most of the debris has settled out, it seemed, ozone should not drop much lower than 125 DU, the typical annual minimum just before the eruption. Although chlorine and bromine levels have increased since then, most researchers thought that their effect might not have grown much, as the regions of the stratosphere where conditions are most favorable to ozone destruction were already suffering almost total loss.

But as of last week, this year's total ozone losses over Antarctica had nearly kept pace with last year's. So far, Oltmans has measured ozone levels over the South Pole as low as 102 DU—comparable to 1992's 105 DU and 1991's 108 DU—and they could have dipped lower before the recovery begins this week. All these figures are a far cry from the measurements of the late 1970s, before the hole began to form, when ozone values were about 280 DU at this time of year. The Total Ozone Mapping Spectrometer (TOMS) aboard the Russian Meteor-3 spacecraft, meanwhile, showed that this year's hole covers about 24 million square kilometers, just shy of the 1992 record, according to Paul Newman of GSFC.

Researchers see three factors that, alone or in concert, might explain the continuing near-record severity. One is the temperature 15 to 20 kilometers up in the stratosphere, where most of the ozone is lost. The colder it is there, the more effectively chlorine and bromine destroy ozone. This year, the Antarctic stratosphere is a couple of degrees colder than normal, says James Miller of the National Weather Service's Climate Analysis Center in Camp Springs, Maryland. But unusual cold alone probably can't explain the continuing bad news; in 1987, when it was even colder over Antarctica, ozone fell no lower than 121 DU.

In spite of expectations, the Pinatubo debris may also be contributing to the size of the ozone hole. Of the 20 million tons that were originally lofted into the stratosphere, perhaps 3 million still linger, according to Lamont Poole of the Langley Research Center in Hampton, Virginia. And that may be all that's needed for a significant effect on Antarctic ozone, say researchers; the reaction-speeding effect of the aerosol may saturate as its amount increases, and so decreasing the amount wouldn't lead to a proportional improvement in ozone levels.

If unusual cold or lingering volcanic aerosol explains this year's heavy ozone losses, another year could bring some relief. Not so if the increasing amount of chlorine and bromine in the stratosphere is to blame. International controls on chlorofluorocarbons and bromine compounds are expected to halt the increase by 1998 (*Science*, 23 September, p. 1806), but in recent years stratospheric chlorine levels have been rising at the rate of a couple of percent per year. That may have been enough to extend ozone destruction beyond the thin layer where major losses were confined before Pinatubo. If those bounds have been breached, it might take several years before researchers monitoring Antarctic ozone finally see bottom.

–Richard A. Kerr