

ample failed to flatten properly, Gordon and Webb returned to Buser's original example, which had been at the back of their minds all along. But when the pieces started falling into place, husband and wife were on opposite sides of the Atlantic: Webb at Dartmouth College, Gordon visiting Germany. They compensated with "a lot of transatlantic phone calls and twice-a-day faxes," Webb recalls.

By the time the couple got back together, in France, they had their first example of a pair of sound-alike drums. The two drums are based on bells formed of seven square crosses (like the Red Cross symbol, or the symbol on the Swiss flag), stitched together like the patches in a quilt. By folding each bell along several diagonals, Gordon and Webb ended up with two flat surfaces, each consisting of seven half-crosses (see figure).

To prove these drums were the answer, Gordon and Webb didn't take the obvious route of mathematically "beating" both drums to show they make the same sound—since such calculations can't be exact, a very small frequency difference could have escaped detection. Instead, their proof builds on work by Pierre Bérard of the University of Grenoble, who generalized Sunada's approach and showed how to take a solution of the wave equation on one drum and "transplant" it to the other. In essence, the proof takes a snapshot of each resonance on one drum, cuts it into seven pieces, one for each half-cross, and then reassembles these pieces into a picture of a standing wave on the other drum. If the reassembled picture looks smooth across the cuts and has the right behavior on the boundary, then the exact same solution works for the second drum as well.

With help from Bérard, Buser, and others, the team of Gordon, Webb, and Wolpert have streamlined their proof and found many other examples of sound-alike drums. Triangles turn out to work as well for building the drums as half-crosses (though seven seems to be a magic number). And not all the drums are as intricate as the first pair; some of them have as few as six sides.

The answer to Kac's question closes the book on one problem, but it raises new issues that should keep geometers busy for a while. For example, by showing that you can't hear every property of a drum, the discovery opens the question of just how many properties of a drum—besides its area and perimeter—really are "audible." Then there's the question whether more than two drums can produce the same set of sounds. That would be the ultimate nonconformist's nightmare: Say, everyone marches to the beat of a different drummer, but all the drums sound the same. ■ **BARRY CIPRA**

Controlling Chemical Reactions With Laser Light

Recent advances in laser technology are giving chemists the ability to enhance the breaking of specific chemical bonds

EVER SINCE THE DAYS OF THE ALCHEMISTS, synthetic chemists have had a straightforward goal: increase the yield of the desired product in a chemical reaction, while minimizing the formation of unwanted byproducts. But while this goal may sound straightforward, chemists have generally had to rely on relatively crude means to accomplish it. For example, they tinker with external variables, adjusting the temperature or pressure, or they change the composition of the solvent in which the reaction is run. But they've not been able to go right to the heart of a reaction to bend it to their will—until now.

Within the past few months, thanks to recent progress in laser technology, three independent research teams have shown that they can influence the course of chemical reactions by using laser light as a source of energy to facilitate the breaking of specific chemical bonds. The research so far has been done only with simple model systems, and the researchers are not yet willing to speculate about any eventual practical applications. But says

theoretical chemist David Tannor of Notre Dame University: The work not only "illustrates a very good interplay between theory and experiment, but it opens the potential for vast amounts of control of chemical reactions. Advanced laser technology is allowing this discipline to take off."

One of the advances Tannor is referring to is lasers, first developed about 5 years ago, that can produce extremely brief light pulses, lasting just femtoseconds—or millionths of a billionth of a second. In 1985, when he was a postdoc with Stuart Rice at the University of Chicago, Tannor had in fact proposed that if such ultrafast lasers became available they could be used to guide chemical reactivity. The reason: The duration of the laser pulses would match that of the key events determining chemical reactivity, such as the periodic stretching and relaxation of the bonds holding atoms together in molecules, which also take place

in a matter of femtoseconds. The ability to time laser pulses to deliver energy to reacting molecules at just the right moment would mean that modern-day alchemists could either enhance or inhibit the breaking of particular bonds, thus enabling them to direct the course a reaction takes.

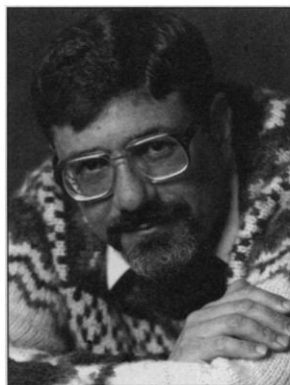
That Tannor was prescient is shown by an experiment, reported in the 2 January issue of *Nature*, in which Caltech chemist Ahmed Zewail and his colleagues used ultrafast laser pulses to control the reaction between molecular iodine (I_2) and xenon that produces xenon iodide. Zewail and his team began with the knowledge that the two iodine atoms in I_2 normally vibrate back and forth, periodically stretching the bond holding them together from 2.5 Å to 5 Å and then contracting it back again.

The idea was to exploit this motion to enhance the reaction between I_2 and xenon by first pumping one pulse of laser light into the reaction mixture to further excite the vibrational motion of the iodine atoms. This first pulse did not provide enough energy to break the bond be-

tween them and promote the formation of xenon iodide, however. That required the input of a second pulse of laser light, the timing of which is critical.

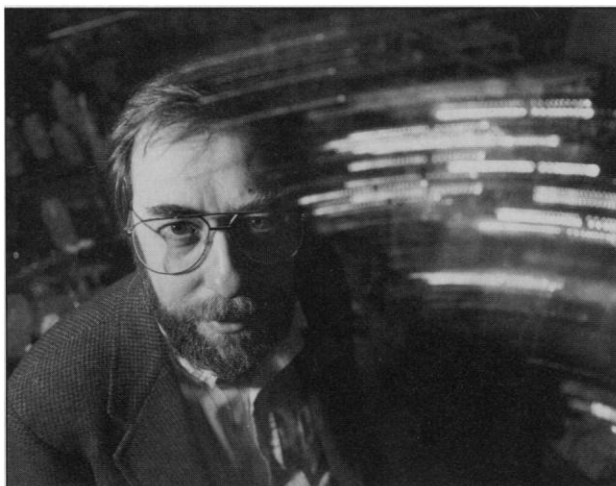
The researchers found that the xenon iodide yield was highest when the two pulses were delivered simultaneously; it dropped sharply when the second pulse was delivered 350 femtoseconds after the first; and went back up again when the interval between the two pulses was 700 femtoseconds. This shows that the best result comes when the follow-up pulse is timed to unload its energy when the bond between the two iodine atoms is stretched to the fullest.

In the Zewail team's work, the second pulse was used to enhance the effect of the first on the I_2 bond. But now another group, led by physical chemist Graham Fleming at the University of Chicago, has taken the method a step further, showing that it's also possible to use a second pulse to cancel the

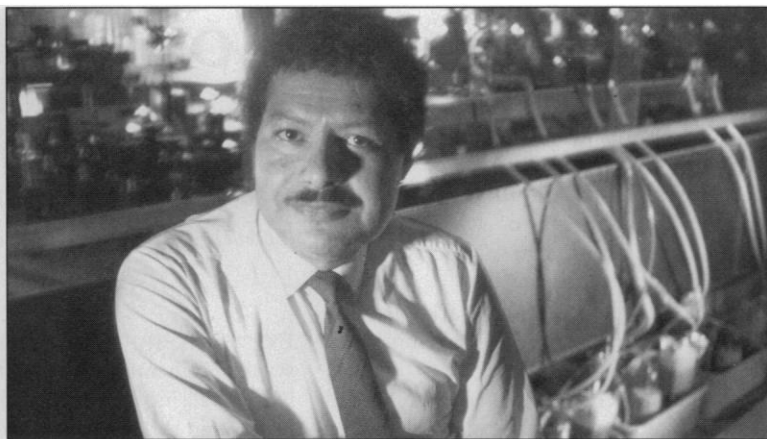


Tuning lasers to specific bonds. Richard Zare.

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MANUELLO PAGINELLI

Ultrafast laser pioneers. Graham Fleming (left) and Ahmed Zewail.

excitatory effects of the first. This experiment is important, says Princeton University chemist Warren Warren, because it goes beyond mere "brute-force excitation," and demonstrates that there's another way to use lasers to control chemical reactivity. Many chemical reactions involve two or more competing pathways, and the Chicago group's work may provide a way of enhancing one at the expense of the other.

The strategy here is to control the light waves in the two laser pulses so that they are either totally in phase or totally out of phase. When Fleming and his Chicago colleagues Norbert Scherer and Jeffrey Cina hit molecular iodine with the two in-phase pulses, they increased the proportion of excited molecules in the population, as indicated by an increase in their fluorescence. But when they used two out-of-phase pulses instead, the second canceled out the effects of the first, resulting in no excitation. Of course, that's no advantage with the iodine molecule, which is very simple, having but one type of bond. However, if a compound has two or more bond types, the first pulse may excite all of them. Then, with appropriate timing of the second pulses, it may be possible to excite further with an in-phase pulse the bond the researcher wants to break, while using an out-of-phase pulse to snuff out the excitability of the others.

Fleming cautions that his work is still in its early stages. Although he's shown that his phase-locked laser system can excite iodine molecules to the transition state, he's not yet used it to control a complete reaction. But he says that should happen within the year. Meanwhile, fellow chemists, including Tannor, are already lauding the work as "neat" and "ingenious."

That's not surprising, given that just 5 years ago one of Fleming's colleagues, writing in the *Journal of Chemical Physics*, said that an experiment of the type performed by the Fleming group was technically impos-

sible because it would be too difficult to keep the phase exactly the same in two successive ultrafast pulses. Even a radio in the lab can cause enough vibration of the equipment to disrupt the phase relations between pulses. The Fleming group succeeded primarily by providing their equipment with several layers of shielding to prevent this from happening. They also used a monochromometer to make sure the pulses were in phase.

While the Zewail and Fleming groups have looked to ultrafast lasers as a way of controlling chemical reactions, other researchers have begun to exploit another advance in laser technology—the development of tunable lasers that can vary the wavelength of the light they generate. The idea here is to tune the laser light to the vibrational frequency of the bond they want to break, thus enhancing its reactivity.

The feasibility of this approach was demonstrated about 2 years ago by F. Fleming Crim of the University of Wisconsin, Madison, and his co-workers. Using water in which one of the two hydrogens was replaced with deuterium, they showed that they could enhance the cleavage of the O-H bond with a laser that they had tuned to the O-H bond frequency. About a year later, Richard Zare of Stanford University and his colleagues further developed this system by showing that they could selectively excite either the O-H or the O-D bond with a tunable laser.

Despite these early successes, however, there are concerns that this strategy, which goes by the rubric of bond-selective chemistry, may not work with more complex molecules. The fear is that in large molecular systems, the energy delivered to a particular bond will be dispersed among other bonds, with a consequent loss of specificity. As Crim puts it: "We may run out of gas because the complexity of the molecules and their mixture of frequencies can't be tackled."

But in mid-April, Zare and his student Robert Guettler will present new results at the American Chemical Society meeting in San Francisco that should hearten supporters of bond-specific chemistry. He has discovered that light from an appropriately tuned laser can stimulate the transfer of a proton from ammonia made with ordinary hydrogen (NH_3) to ammonia made with deuterium (ND_3). Because the eight-atom ammonia system is many times more complicated than the previously studied water system, Zare says, it offers further evidence that lasers can be used to deliver energy preferentially to select bonds, "without it being scrambled among other bond vibrations."

Then again, the ammonia system is much less complex than the reactions that industrial chemists have to deal with, and it remains unclear whether bond-selective chemistry will find widespread application. The same is true for the techniques using timed, ultrafast laser pulses to control chemical reactions. Tannor, for one, is honest about the skepticism he's encountered: "Because of the high cost of lasers, many of my colleagues say I have got to be dreaming to think this strategy will be used in industry." But then again, as Tannor gleefully points out, only a few years ago not many people took buckyball chemistry seriously either. ■ ANNE SIMON MOFFAT

ADDITIONAL READING

M. J. Bronikowski *et al.*, "Bond-specific chemistry: O-D:O-H product ratios for the reactions $\text{H} + \text{HOD}(100)$ and $\text{H} + \text{HOD}(001)$," *Journal of Chemical Physics*, **95**, 11 (1991).

N.F. Scherer *et al.*, "Fluorescence-detected wave packet interferometry: Time-resolved molecular spectroscopy with sequences of femtosecond phase-locked pulses," *Journal of Chemical Physics*, **95**, 1487 (1991).

N.F. Scherer, L. D. Ziegler, and G. R. Fleming, "Heterodyne-detected time-domain measurement of I_2 predissociation and vibrational dynamics in solution," in press, *ibid.*

A. Sinha, M. C. Hsia, and F. F. Crim, "Bond-selected bimolecular chemistry— $\text{H} + \text{HOD}(4\text{-NU-OH}) \rightarrow \text{OD} + \text{H}_2$," *ibid.* **92**, 6333 (1990).