Dances with Molecules

Controlling chemical reactions with laser light

By RICHARD LIPKIN

Even in the world of large, clumsy objects, a mere flash of light can alter the course of matter.

Consider this scene. A thousand cars descend on a football stadium on a Sunday afternoon. In one hideously long line, drivers queue up to park. A single light with alternating arrows controls the traffic flow. When a green arrow flashes left, cars roll into lot A. When another arrow points right, they cruise into lot B. After an hour or so, the lots contain about 500 parked vehicles apiece.

But suppose someone wants to change the rate at which the two lots fill or the distribution of autos between them—putting, say, 800 vehicles in one lot and 200 in the other. What simple maneuver would do the trick?

The answer, in this particular case, proves to be rather simple. Just change the timing of the traffic light.

In a crude sense, this analogy gives a feeling for the way chemists want to use lasers to control the rate and direction of chemical reactions.

Given a set of molecules that can combine in two possible ways, scientists wonder how they can most effectively use a laser to prod the chemical reaction one way or the other—that is, to direct the molecules as if they were cars rolling past a forked intersection.

"Historically, most chemistry has been done by mixing elements together and heating them," says Richard N. Zare, a chemist at Stanford University. Just blend the ingredients, add a little heat and pressure, and see how a compound cooks up. "But the trouble with heating something is that the energy shows up in the molecules as random motion," he adds. "The energy breaks old chemical bonds, makes new ones, and overcomes barriers to transitions."

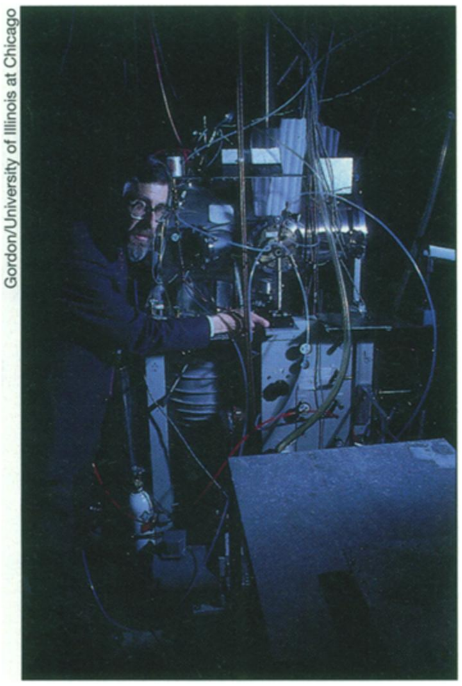
The tantalizing question is how to perform more efficient chemistry. Or, as Zare puts it, "Is there a better way to run a chemical reaction?"

Lasers offer intriguing possibilities. With their ability to deliver small, uniform bundles of energy to tiny targets, lasers have in recent years spurred many chemists to rethink how to trigger reactions.

In theory, photons of just the right energy can drive atoms into excited states, make or break chemical bonds, or become absorbed by some molecules while being deflected by others. In practice, though, such precise control has proved elusive in the laboratory.

Only recently have several teams of chemists begun to show how to put theory into practice by controlling some simple molecular reactions with lasers.

Robert J. Gordon, a chemist at the University of Illinois at Chicago, and his colleagues recently achieved "coherent phase control" of hydrogen disulfide molecules by firing ultraviolet lasers of different wavelengths at them. The two beams agitate the molecules in different ways. By varying the phase difference—the relative locations of the crests and valleys of the waves—of the two lasers, the researchers can control how the molecules break apart.


Gordon/University of Illinois at Chicago

Gordon's apparatus converts a single laser beam into two overlapping beams with different frequencies. By shifting the phase difference of the two beams, Gordon can vary the speed and outcome of a chemical reaction.

Beginning with a molecule that contains two hydrogen atoms and one sulfur atom, they can control its rate of ionization. Their report, which appeared in the April 8 Journal of Chemical Physics, constitutes the first observation of a successfully directed chemical reaction for a molecule with more than two atoms.

Recently, in a similar experiment using molecules of hydrogen iodide, Gordon's group succeeded in varying the amounts of two different reaction products merely by altering the phase difference between the two lasers.

"This work is very exciting," says David J. Tannor, a chemist at the University of Notre Dame in South Bend, Ind. "It's important because Gordon's group is successfully using the phase properties of laser light to manipulate the outcome of a photochemical reaction."

By finely adjusting the relative phases of the two lasers, the researchers can push the molecules into specific high-energy states.

"The laser expands the atoms," says Gordon. "An electron goes into a high orbit so that it's ready to be ejected. The molecule can then either release an electron or break a bond."

This expansion sets the stage for a specific reaction to occur.

"If you have two different ways of producing a molecular product," says Gordon, "then the phase difference between the light of each laser can be used to regulate the speed of the reaction. If more than one outcome is possible, the beams can steer the reaction in a desired direction.

"Ultimately, we want to be able to select specific chemical bonds and break them with a laser pulse," Gordon adds. "That would permit us to increase or decrease one reaction product versus another."

Taking a different approach to stimulating molecules with lasers, Kent R. Wilson, a chemist at the University of California, San Diego, and his colleagues are "shaping" laser pulses rather than creating interference with two beams.

The key idea behind Wilson's method falls into the same general camp as Gordon's in that both groups employ coherent light to direct the outcome of a reaction. The difference, however, shows up in the way the researchers deliver the light energy. Rather than adjust the interplay of two distinct light beams, Wilson's apparatus emits a series of ultrashort bursts of energy, or femtosecond pulses, each lasting a few millionths of a billionth of a second.

Each pulse comes as a carefully sculpted wave of energy, Wilson says, and in some cases bears a distinctive chirp, or frequency signature. By tinkering with the shape of a laser's light waves, the scientists can deliver energy to a molecule with tremendous accuracy and efficiency, striking it in exactly the right way to trigger a specific reaction.

Reporting in an upcoming Physical Review Letters, Wilson's team describes how its laser delivers tailored "vibrational wave packets" of energy to molecules of iodine, pumping the atoms into excited states. Using theory to figure out how best to shape the laser pulse, the team says the experimental results coincide well with prediction.

"We did not just excite matter with light and observe the results as we changed the properties of the pulse," the scientists state. "We chose a goal for our material system, predicted the best possible field to reach that goal, and then attempted to create that field in the laboratory."

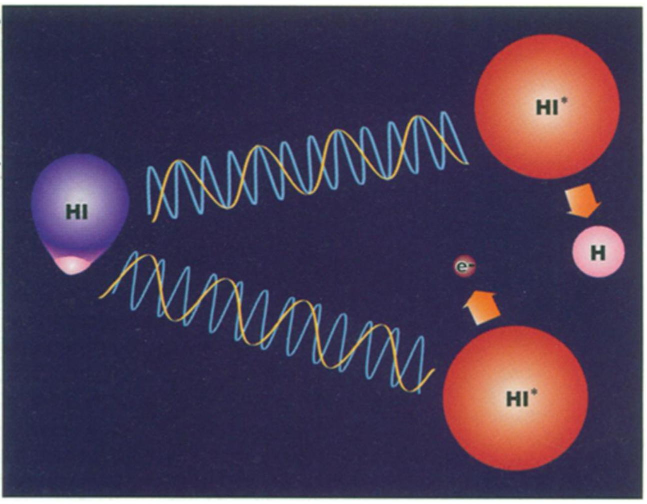
Indeed, excitement has arisen in the chemical community not because these experimental results prompt an entirely new set of ideas, but because they confirm the suspicion that what once appeared possible but improbable can now be done.

"Ever since the development of the laser, the quest to use light to control the future of matter has been one of the Holy Grails of chemistry," Wilson says.

"Can we develop general ways to use lasers to specifically manipulate the quantum behavior of atoms and molecules?" Wilson and his coworkers ask in Accounts of Chemical Research, 1995, issue 3. "Can we develop novel synthetic methods to produce exotic new molecules, states of molecules, or even molecular devices, such as programmable optics or nanomachines?"

Such radical thinking permeates the field of laser chemistry. Nearly a decade has passed since theoreticians first proposed schemes to achieve laser-mediated molecular control. In 1986, chemists Paul Brumer of the University of Toronto and Moshe Shapiro of Israel's Weizmann Institute wrote of "actively" controlling matter with light by way of quantum mechanical interference. Shortly thereafter, David Tannor and chemist Stuart A. Rice of the University of Chicago proposed an alternative method to achieve the same effect with short bursts of laser light.

These two theoretical paradigms for laser chemistry dominated the experimental world, shaping the goals of many laboratories. As it turns out, both theoretical visions have led to important results. Gordon's group, for example, evidences the Brumer-Shapiro scenario, while Wilson's group fleshes out the Tannor-Rice model.



Gordon/University of Illinois at Chicago

T*wo overlapping laser beams with different frequencies excite a molecule of hydrogen iodide (left). The molecule then ejects either a hydrogen atom (top right) or an electron (bottom right). The path that the reaction takes depends on the phase difference between the two laser beams.*

Taking yet another tack toward laser control of molecular behavior, Paul B. Corkum and Emmanuel Dupont, physicists at Canada's National Research Council in Ottawa, have shown how laser light can change the direction of electrical current flows in a semiconductor.

In the May 1 Physical Review Letters, the two scientists describe how to combine two laser beams in such a way that their phase difference causes optically stimulated electrons to move right or left in a semiconducting material. Moreover, the effect is not random, the scientists explain. They can reliably control the amount of current produced, as well as its direction of flow.

In all three approaches, the researchers have had to overcome formidable technical obstacles in order to control electrons with laser light. Though the concept of laser chemistry beckoned for decades, "experimental examples were limited," says Zare. "But the recent results of Gordon, Wilson, and Corkum are encouraging. Hopefully, they will stimulate more experiments."

An alternative approach to laser-controlled chemistry derives from the work of physical chemist Herschel A. Rabitz of Princeton University. Rabitz and his colleagues have used the mathematics of control theory to improve the efficiency of photochemical reactions. Unlike big solid objects, molecules constantly move about, rotating and vibrating according to their level of energy. In Rabitz's approach, sculpted laser pulses alter the internal motions of molecules: To vibrate a molecule in a particular way that will trigger a reaction, you need to know what kind of light pulse would get that molecule twitching.

"You might say that the goal of our research is to use light to get molecules to dance to our tunes," Rabitz says.

So what might come of all this laser chemistry? Are its goals realistic? Brumer suggests that the first applications will appear in the pharmaceutical industry. Many molecules come in both right- and left-handed forms. In some cases, one of these forms constitutes a beneficial drug, while the other causes harm.

Drug companies spend great amounts of time and money separating one group of molecules from the other. If lasers could enhance drug synthesis, however, yielding large quantities of desired compounds free of unwanted side products, some medications could become safer and cheaper.

Likewise, laser-controlled semiconductors could promote new optical switches, potentially improving computers and communications systems.

"In 1986, theory was way ahead of experiment in this field," says Tannor. "People thought laser chemistry was impossible to do." Now, he says, "the situation has reversed. Experiment is ahead of theory."

An explosion in laser technology in the past few years has given former pipe dreams some solidity. "We're still far away from fully understanding the complete internal motions of molecules," Tannor says. "But we're on the verge of being able to interrogate reactions very thoroughly, which will give us very detailed knowledge of how molecules move."

Such knowledge might lead not only to atom-by-atom construction of molecules and materials, but also perhaps to improved ways to gather solar energy, Tannor says. Earth's most effective solar energy systems—green plants—can transform the sun's rays into chemical energy with up to 95 percent efficiency. "It's possible," says Tannor, "that the knowledge we gain from light-controlled chemistry could someday lead to synthetic light-harvesting systems."

Wilson speculates that the quest to control matter with light may lead some chemists to pursue "late-night dreams." And yet, he adds, "like all dreams, they may not come to pass."

"We hope that the process of our dreaming, and the progress of our search, may lead us to outcomes that are of value," Wilson muses, "even if they are not our original goals." ☐