

EXQUISITE CONTROL

Roald Hoffmann



Albright-Knox Art Gallery, Buffalo, New York

Figure 1. Giacomo Balla's 1912 oil on canvas entitled *Dynamism of a Dog on a Leash* captures motion in ways that parallel the studies of chemical dynamicists. Note the different ways in which the body parts of the dog, the leash and the dog's mistress move.

The chemical reaction should go, but refuses to do so? Bang on it—with heat, with light, with pressure. Or, so much better, find a catalyst—an ingenious partner in a reaction that cuts down an energy hill that is in the way, or gets involved with the reactant molecules, takes them in hand, so to speak, and guides them in a path around that hill. And then the catalyst is regenerated.

The giant chemical industries of the world offer testimony to our skill at devising ways to make reactions go in ton lots. And yet we would like to exercise still greater control over what happens. For instance, it's no sweat to break the weakest bond in a molecule. But what if the bond we want to break, and no other one, is not the weakest? In this, the last of four *Marginalia* on contemporary chemical dynamics, I look at some fascinating developments in precisely guiding chemical reactions at the microscopic, molecular level.

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The direction may take different forms. Energy in molecules is distributed in their motion (translation), and also in their internal vibrations and rotations. Molecular beams and lasers allow chemists to select very precisely the way a molecule is tweaked—for instance the excitation may be neatly deposited in one vibration. Having prodded the reactants in a very specific way, we can look at what happens to the reaction products. Which bond is energized? Which bond is broken, which formed? Let me begin with one remarkable and simple reaction that has been studied in this way.

One Bond at a Time

For the longest time chemists had been foiled in trying to put energy into a molecule in a selective way. It's clear that just heat, which is the totality of collisions between molecules, is indiscriminate. But one might have thought that using light to excite one particular vibration of a molecule would work. Which vibrations? In Figure 2 are shown the three "normal modes" of vibration of a triatomic molecule, water. It looks like the asymmetric stretch might break an OH bond. But no,

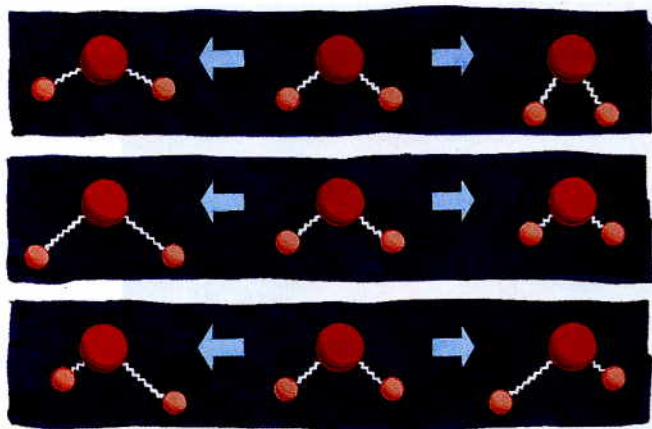
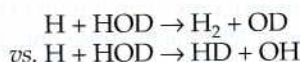


Figure 2. The normal modes of vibration of a water molecule are shown with the "bend" at the top, the "symmetric stretch" in the middle and the "asymmetric stretch" on the bottom. (Oxygen atoms are red; hydrogen, pink.)

inject a dollop of energy (from an infrared laser) into just that vibration, and the energy is just quickly randomized among all the vibrations.

In 1989 Fleming Crim and his coworkers at the University of Wisconsin overcame that. They used the singly deuterated water molecule, HOD; the deuterium served to distinguish two modes of vibration: In one, the O-H bond is mostly vibrating on its own; in the other, the O-D bond is. By tuning a laser to a specific frequency (color), one could excite the third overtone of the O-H stretching motion; by tuning to another color, one could put that energy into the fourth overtone of the O-D bond. An overtone of water is just like an overtone of a vibrating guitar string—a sound emitted at a multiple of the fundamental frequency; one such overtone of a water vibration (the fifth O-H overtone) is responsible for the pale blue-green color of thick water layers.

The two vibrations—O-H stretch and O-D stretch—do not communicate well with each other in water. If you now put in (with still another laser!) a substantial further amount of energy via light, the "O-H excited" HOD breaks the O-H bond preferentially, and the "O-D excited" HOD favors breaking the O-D bond. Similar large selectivities are exhibited in a chemical reaction:



Crim's experiments were the first demonstration of bond-selective laser chemistry—prior to his work people thought that even bonds as distinct as O-H and O-D would quickly randomize any energy put into one bond among the two. Crim and Richard Zare at Stanford have gone on to find several further spectacular selective bond-breaking reactions.

Guidance May Lead in Unexpected Directions

One can also affect a reaction's outcome by choosing the way reactants approach. This is

done by firing beams of gaseous reagents at each other, in which one or both of the reaction partners is at least partially aligned in a specific way. The control one may thus achieve on reaction geometry is impressive; it is also something one cannot do in the liquid state. Let me show you an example that blends molecular beams and selective excitation.

The first reaction encountered in organic chemistry texts is likely to be the chlorination of hydrocarbons. The important, rate-limiting "chain-propagation" step in that reaction (for, say, methane) is $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$. Zare's group recently found a remarkable result in their study of this old chlorination reaction. When the reactants just collide, even if the Cl atoms move in quickly (actually they are fired in), the reaction is difficult. To make the reaction go, a direct hit (in the trade this is called a "small impact parameter") is needed, and this is hard to arrange, for the molecular bullets are very small, metaphorically speaking.

That HCl comes off "backwards" relative to the incoming Cl is understandable. Says Zare, "It's just like three billiard balls of the same mass all colliding in a line, in which the incoming ball nearly stops and the one at the other end takes off in the same direction." In what we call a center-of-mass system, the HCl (made up of the Cl billiard ball coming in and the H hit first) would be going "back," rebounding, viewed from the CH_3 fragment.

To make the collisions more effective, the laser chemists excite selectively and strongly the C-H stretching vibration of methane, CH_4 . Now a lot of HCl is formed (the rate of the reaction increased by more than a factor of a hundred); obviously even glancing collisions are effective. And much of the HCl product moves in the same direction as the incoming Cl. What has changed? Well, the highly excited C-H bond is stretched a lot. It is more likely to be on the "outside" of the rotating CH_4 target that presents itself to the incoming Cl atom (Figure 3). The target for the ar-

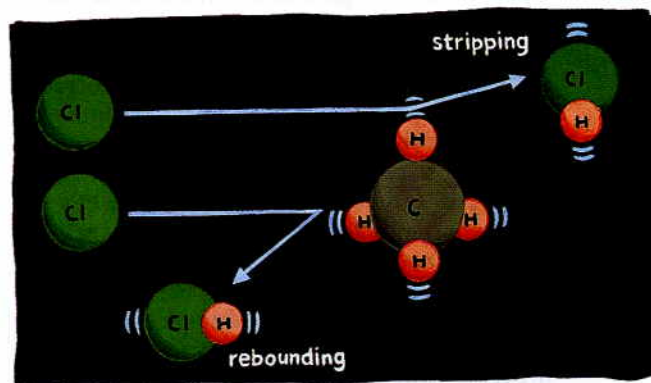


Figure 3. Contrasting reaction dynamics result when a beam of chlorine atoms (Cl) collides with either the ground state or a vibrationally excited methane molecule (CH_4 , center). For the ground state of CH_4 one sees only a few rebounding molecules of hydrochloric acid (HCl). When the methane is set more vigorously vibrating, it presents a bigger target. Then more H atoms are stripped off, even when the Cl atom is not "dead on target."

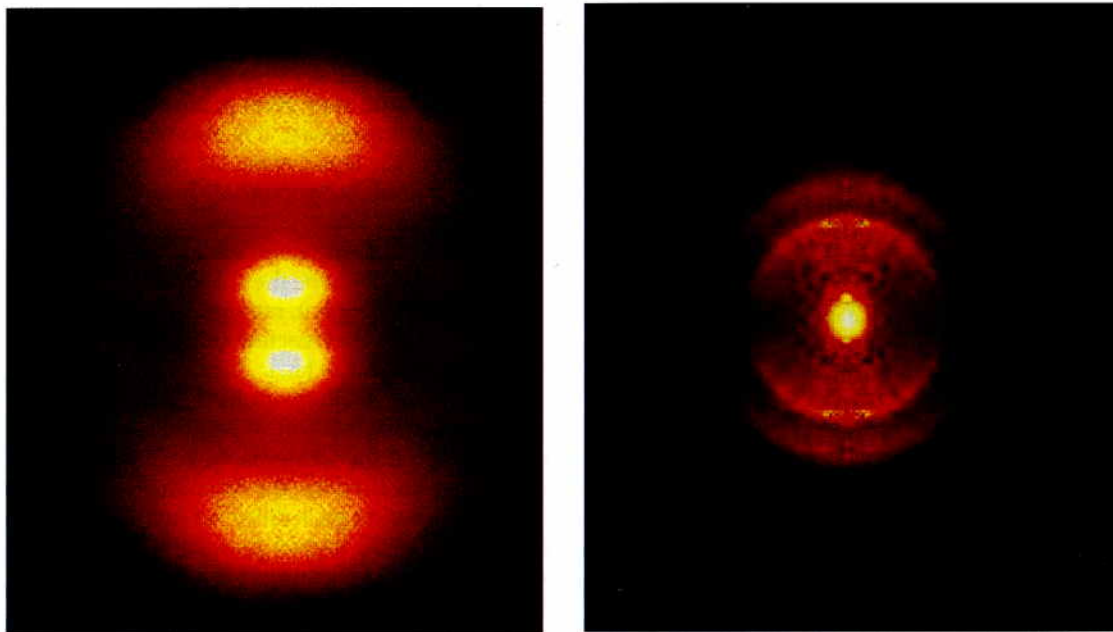


Figure 4. Photographic record (false color) of the velocity and direction of oxygen atoms coming off in the photodissociation of ozone can be made. The highest-velocity oxygen atoms strike farthest from the center. Color signals the number of atoms; yellow means more such atoms than red. The high density close to the vertical axis implies that the oxygen atoms come roughly off along the original O–O bond in ozone. The low-resolution image (*left*) shows that there are both fast and slow oxygen atoms coming off approximately along the bond. The higher-resolution image (*right*) shows rings corresponding to well-defined slow O atom energies, leaving behind highly vibrationally excited O₂ in very specific states.

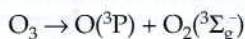
row is effectively bigger, much bigger. And the Cl sweeps along the hydrogen whose bond had been weakened by vibrational excitation, stripping it from the methane.

The preceding examples have shown how energy specifically deposited in the vibrations of a bond or a molecule may dramatically alter the course of a reaction. What follows is a fascinating example of the “microscopic reverse,” molecules vibrating in finely defined ways as a consequence of a chemical reaction.

Ogling the Aftermath

In an earlier Marginalium, I wrote of scanning tunneling microscopy (STM) images showing us molecules in stages of catalysis; in another, I described femtosecond spectroscopy “freezing” molecules in the act of falling apart or coming together. Experiments whose output is a graphic image have immense power; the experiment I am about to describe images quite directly the products of a chemical reaction flying apart.

Paul Houston and his colleagues at Cornell have been looking at what happens when ozone is dissociated in the near ultraviolet, just the region in which ozone optimally shields us from much of the sun’s ultraviolet. The Cornell chemists follow one mode of decomposition, into a certain spin state (triplet) of both O₂ and O:



The fragments travel away from each other, preferentially along a specific direction that is

roughly along the extension of what was an unbroken O–O bond of the parent ozone. In this case the oxygen atoms are detected—the brighter (more yellow) the area in Figure 4, *left*, the more oxygen atoms strike there; the farther from the center of this pattern, the faster moving the oxygen atoms.

The peaks at top and bottom in this roughly resolved image were expected—lots of fast moving O atoms. What was startling was that there were also some slow-moving O atoms (the vertical dumbbell near the center).

Next, conservation of energy comes into play. Knowing the energy in the light, the energy needed to break the O–O bond in ozone and the kinetic energy borne by the fleeing O atom, one can calculate the energy left behind in the unobserved O₂ (actually that energy can be measured in another experiment). Lots of energy in O (outer peaks in Figure 4, *left*) means little energy in O₂. Little energy in O (inner peaks in Figure 4, *left*) implies that there’s a lot of energy in the O₂ molecule left behind.

A lot is a lot—indeed enough to put the O₂ into its 27th and 28th overtone, nearly enough to knock it apart. *That’s* remarkable. The fine-resolution image at right in Figure 4 shows well-defined “halos” that are the result of molecular vibration being quantized—one “halo” corresponds to O atoms that have left behind an O₂ in the 27th vibrational overtone. The other halo, further in, is due to the slower O atoms that leave behind the O₂ in the 28th overtone.

Moving in Two Worlds

The degree of control that chemical dynamicists are beginning to exercise is startling. I love the understanding that emerges. There is also something else that appeals to me personally, both as a quantum chemist and as a builder of conceptual bridges; each of these experiments is not only a *tour de force* of high vacuum technology, optics and electronics—but also a wonderful blend of quantum and classical mechanics. There is no way to understand the chemistry of molecules reacting without moving in both worlds.

Let me elaborate: The molecular beam machines (I've spared you the cost of these) operate on classical billiard-ball logic; the same way of thinking lets us see molecules colliding, fragments bouncing off in certain directions. Simple and foolproof conservation of energy was at work in the Houston experiment. But at the same time, to understand these ingenious experiments one must think in the beautiful and sometimes mysterious logic of quantum physics—think of the uncertainty relationship shaping the wave packets and time resolution in femtosecond spectroscopy, the quantum helicity I described in one Marginalium, the tunneling current that makes STM possible. The laser, that tunable jack-of-all-trades source of strong light, owes its coherence and power to a quantum effect; the energy level spacing that is behind the laser also explains state selection.

Chemical dynamics, the kinetic art, exemplifies in every one of its experiments the intersection of the classical and quantum worlds. It is the realm of the quantum mechanic, just as much as it is of the clever instrument builders. Who are getting to know, finally, what makes chemistry run.

Acknowledgment

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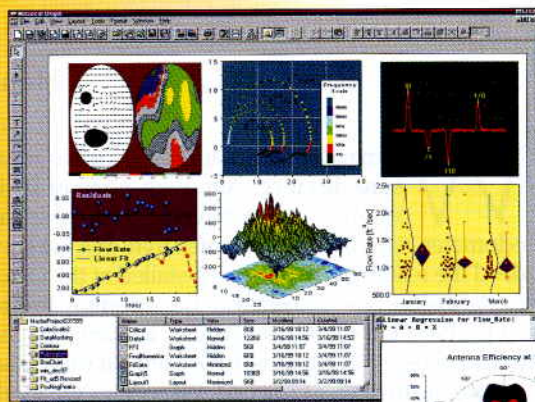
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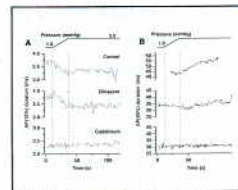
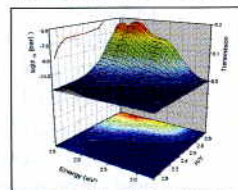
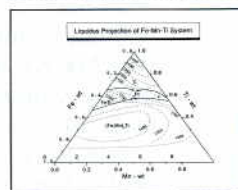
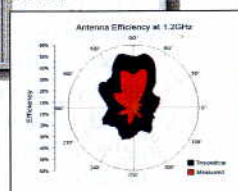
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