Lasers offer surgical control over reactions

With lasers instead of scalpels, eye surgeons perform ever more precise operations. Now, laser-wielding chemists have extended their surgical skills in severing chemical bonds and controlling chemical reactions.

Richard N. Zare and his colleagues at Stanford University have demonstrated that they can excite and then cleave water molecules in specific places. They begin by using an infrared laser to induce vibrations in one bond of a water molecule. Then they knock off one of the molecule's hydrogen atoms by bombarding it with other hydrogen atoms. They describe the new work in the Dec. 1 JOURNAL OF CHEMICAL PHYSICS.

In the same journal, another group describes the theoretical basis for using lasers to make either left- or right-handed versions of mirror-image molecules. This "coherence chemistry" technique could prove important in drug development, says Paul Brumer of the University of Toronto. Many compounds exist in both mirror-image forms, but in most cases, only one of those versions proves therapeutic, he notes.

Brumer and Moshe Shapiro of the Weizmann Institute of Science in Rehovot, Israel, suggest that sequences of laser pulses can split a large molecule in such a way that the reaction is likely to produce the desired mirror-image version. Their calculations show that because of quantum mechanics – in which particles exhibit wavelike properties – "you're canceling out the stuff you don't want," Brumer says.

Scientists only recently gained the ability to control the distribution of energy involved in chemical reactions – a step toward selecting the resulting products (SN: 4/20/91, p.245).

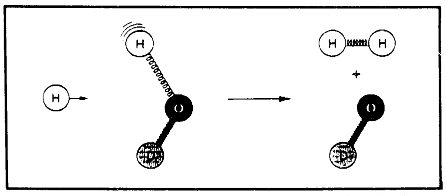
Zare and his co-workers now find that they can choose which hydrogen atom to cleave from a water molecule by taking advantage of slight differences in the quantum-mechanical properties of chemical bonds. The researchers start with "heavy" water containing one atom of hydrogen and another of deuterium (a heavier hydrogen isotope). The bond between the oxygen and the deuterium resonates at a lower energy level than the bond between the oxygen and the normal hydrogen. This enables the scientists to selectively tune their infrared laser to excite one or the other bond, explains study coauthor Michael J. Bronikowski.

After bombarding the excited molecules with hydrogen atoms, the Stanford chemists immediately confirm which product they produced by scanning their reaction chamber with an ultraviolet laser, which causes each product of the water-splitting reaction to emit a characteristic fluorescent "signature."

When they excited the link between oxygen and hydrogen, this bond stretched and weakened so much that in a subsequent collision with a fast-moving hydrogen atom, the water molecule let go of its own hydrogen. This left behind an oxygen-deuterium molecule. Conversely, when the researchers excited the oxygen-deuterium link, they produced a high proportion of hydroxyl (OH) molecules, Bronikowski says. "It's somewhat surprising that it increases the chance of a reaction that much," he adds.

The Stanford work builds on experiments done by F. Fleming Crim of the University of Wisconsin-Madison, who used visible-light laser beams to break heavy water's hydrogen-oxygen bond. But Crim could not shake the link between oxygen and deuterium. "We're really pleased to see the [Stanford] work," he says. "It's a very important result."

He and the Stanford researchers emphasize, however, that the technique applies only to molecules with very specific characteristics. "It's certainly not something that's going to work for [just] any general reaction," says Bronikowski.



Zare/Stanford

Laser energy causes the spring-like link between the oxygen (O) and hydrogen (H) to stretch, while oxygen's bond with deuterium (D) remains unaffected. The result: When a hydrogen atom hits the molecule, only the O-H bond breaks, forming a hydrogen (H_2) molecule.

Indeed, "there are much more sophisticated ways of controlling reactions," says Graham R. Fleming, a physical chemist at the University of Chicago. Like Brumer and others, he believes chemists will eventually figure out how to harness quantum mechanics to inhibit the production of unwanted products, not just to control which bonds break. *– E. Pennisi*

Jerusalem yields 'natural' waterworks

For more than 100 years, archaeologists and historians have puzzled over the haphazard routes, slopes and dimensions of two underground water supply systems discovered beneath the remains of ancient Jerusalem. Although most researchers regard the subterranean waterworks as the products of early, error-prone engineers and construction workers, a new analysis indicates that residents of the holy city skillfully altered a natural network of underground channels and tunnels to ensure a dependable water supply.

Knowledge of the natural passages snaking beneath Jerusalem's defensive walls may have helped the army of David to mount a successful surprise attack – alluded to in the Old Testament – on the city's inhabitants about 3,000 years ago, asserts Israeli geologist Dan Gill in the Dec. 6 SCIENCE.

The dual water networks, built several centuries after David's victory, ferried water into the city from the nearby Gihon Spring, says Gill, of the Geological Survey of Israel in Jerusalem. One system consists of a horizontal tunnel that fed water into a vertical shaft serving as a well, from which water was hauled into an upper tunnel leading farther into Jerusalem. Water also ran through an underground canal to an aboveground reservoir within the city walls.

Geologic clues indicate the underground waterworks resulted from a careful refashioning of natural channels and shafts that had formed in the limestone beneath the city over millions of years, Gill says. For instance, the vertical shaft displays an irregular shape and calcium crust typical of a natural sinkhole, he notes. Ancient residents of Jerusalem probably tracked the limestone fissure leading to the sinkhole and fashioned it into the roughly level lower canal, transforming the shaft into a well. During this process, limestone hewers apparently discovered a branch of the fissure that they eventually hollowed out into the underground canal, Gill contends.

The natural formation of underground channels in limestone also produced the Gihon Spring, he says. "Gihon" translates as "gusher," referring to intermittent pulses of water typically triggered by subterranean passages that act as a periodic siphon, according to Gill.

Because workers followed existing passageways, the waterworks sometimes veer in random directions, contain unnecessarily high ceilings and display other apparent mistakes, he maintains. Interconnected channels and sinkholes branched off from the water supply system and reached the surface, providing ventilation for tunnelers.

Some biblical scholars have interpreted sections of the Old Testament as describing David's use of a hidden passage to capture Jerusalem. The new study supports these claims by establishing that the ancient city contained two underground openings that emerged outside its walls, Gill points out. *– B. Bower*