'Snapshots' of Bond Breaking and Making

It's hardly satisfying to see merely the beginning and the end of a movie. One misses most of the human drama and can only guess at the intricacies of the plot as it has unfolded.

The same is true for molecules and chemical reactions. Scientists have been able to study the reagents and products of a chemical reaction — its beginning and end. But because they have not had tools fast enough to catch the action in between, they've missed out on directly observing the movements and play of atoms during the making and breaking of bonds. Most studies using lasers to investigate reaction dynamics have used nanosecond-long (10^{-9} sec) pulses, which are too long to allow a glimpse of the atomic drama taking place within picoseconds (10^{-12} sec) during a reaction.

In the last few years, however, lasers with shorter pulses, in the femtosecond (10^{-15} sec) range, have come of age. And using such lasers, Ahmed H. Zewail and his colleagues at the California Institute of Technology in Pasadena have for the first time directly probed the events involved in the birth and destruction of molecules. "It's like having an ultrafast camera now to view these processes," says Zewail, who discussed his work this week in Lake Tahoe, Nev., at the International Conference on Lasers 87.

"We're very excited about it," says Larry Davis of the Air Force Office of Scientific Research in Washington, D.C. "It's the first time a chemical reaction itself is being followed with such a narrow time slice that you can actually get a handle on what's happening as the [molecules] separate from one another."

"It's brilliant work," concurs Kenneth Eisenthal at Columbia University in New York City. "It will stimulate a lot of theoretical work and further experiments."

So far, Zewail's group has examined two elementary reactions: the dissociation of cyanogen iodide (ICN) into iodine (I) and cyanide (CN); and the interaction between hydrogen (H) and carbon dioxide (CO_2) to form carbon monoxide (CO) and hydroxyl (OH). In future studies, Zewail plans to examine more complex reactions.

In their technique, the researchers initiate a reaction by using one laser pulse to pump more than enough energy into a gas of reactants to begin breaking bonds. (In the carbon dioxide reaction, the "pump" pulse breaks hydrogen away from another molecule to which it had been bound and sends it reeling into carbon dioxide molecules.) Zewail's group then sends in a series of "probe" pulses at different delay times and of different energies. When the energy and timing are just right, these pulses are absorbed by molecules undergoing the various transition stages from reactants to products. The researchers detect this absorption by monitoring the light that is reemitted by the molecules, a process called laser-induced fluorescence.

The resulting real-time data, though not "photographs," yield information that paints a graphic portrait of the reaction. From the energy of the pump pulse — which reveals the velocity of the reactant molecules — and from the times of the absorbed probe pulses, Zewail's group can determine the distances between molecules as they separate or come together. And from the energies of the absorbed probes, they can also identify transition species and eventually glean information about their structure, rotations, vibrations, bond lengths and other aspects of their energy states as they evolve in time.

In the hydrogen-carbon dioxide reaction, Zewail says his group confirmed suggestions from earlier, indirect studies that "hydrogen dances around carbon dioxide for a while," forming what is known as a collision complex, rather than stripping off an oxygen immediately. Moreover, the technique enabled the researchers to clock the lifetime of this transition state — 5 picoseconds.

Knowing how molecules transform from one species into another is the essence of chemistry, says Eisenthal. Indeed, last year's Nobel Prize in chemistry was shared by three researchers working on such reaction dynamics. But these studies could offer only indirect hints about transition states. With his technique, Zewail has added an important new wrinkle, enabling chemists to start asking questions such as how transition states are altered by the presence of other molecules, temperature changes or isotopic substitutions. "It's an important first," he says.

— S. Weisburd

Mammoth find fuels extinction debate

Mammoth bones recovered at a gravel pit in England last year are about 12,800 years old and extend the known occurrence of the huge mammals in Britain to near the end of the last Ice Age. The new find, say paleontologists G. Russell Coope of the University of Birmingham, England, and Adrian M. Lister of the University of Cambridge, England, contradicts the widespread scientific view that mammoths disappeared from Britain during the maximum expansion of ice sheets between 18,000 and 15,000 years ago.

The discovery, consisting of an almost complete adult skeleton and partial skeletons of at least three juveniles, is unique in Europe, and the adult skeleton is the best-preserved mammoth of any age yet found in England, report the investigators in the Dec. 3 NATURE.

Tusk fragments from the adult specimen underwent independent radiocarbon dating at two university laboratories. Their age is close to that of two other recent mammoth finds in Europe dated at around 12,000 years old.

A juvenile skull and two juvenile lower jaws contained fossil remains of the blowfly and dung beetle. Since both of these species are now found only in temperate regions, Coope and Lister say the late-Ice Age climate in England may also have been relatively mild.

The age of the British mammoths is only 2,300 years older than the latest known mammoth remains in North America, writes Jeffrey J. Saunders of the Illinois State Museum in Springfield in an accompanying editorial. Additional British mammoth finds may further reduce this age difference, he says, and lend support to the notion that a global climatic change led to mammoth extinctions.

"The new discovery makes it more likely that mammoth extinctions were synchronous in Europe and North America," Lister told SCIENCE NEWS. There may have been a return of cold temperatures around 11,000 years ago that fostered the mammoth demise in North America, he says, although no solid data suggesting such a shift have been uncovered. In Europe, however, there are signs of such a scenario: Analysis of fossil pollen indicates that at about that time, ice sheets briefly returned and reduced the landscape to a sparsely vegetated tundra.

Nevertheless, says Paul S. Martin of the University of Arizona in Tucson, there were far more large-mammal extinctions in North America, where there is little evidence for late-Ice Age climate shifts, than in Europe. Martin stands by his theory that human hunters wiped out many North American species between 12,000 and 10,000 years ago (SN: 10/31/87, p.284).

"Considering how thoroughly most late-Ice Age British deposits have been examined, the news is that mammoths are found so rarely and were probably scarce in Europe at that time," adds Martin. "I'm not bullish on too many more mammoth specimens turning up at late-Ice Age sites in Europe."

— B. Bower