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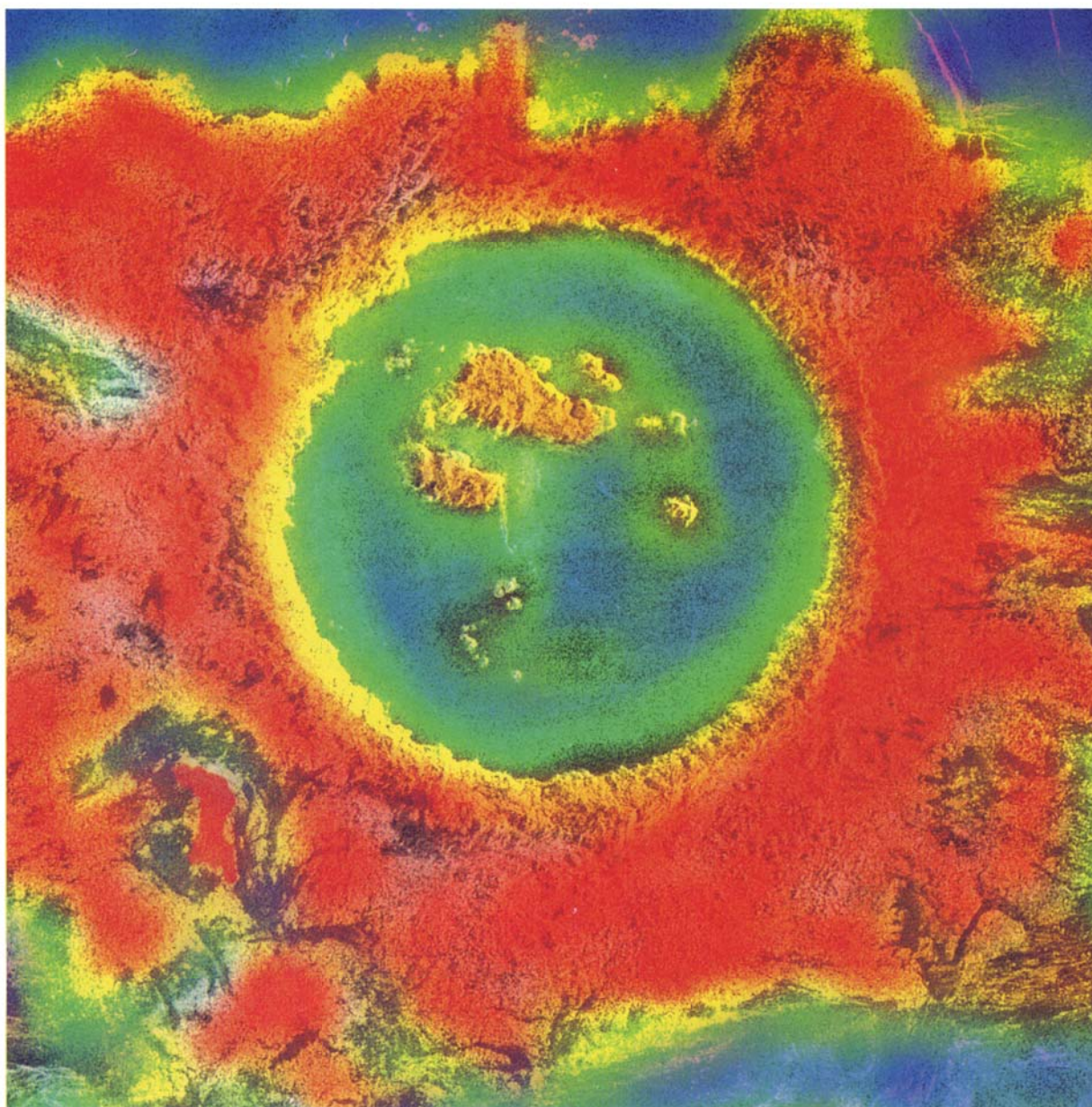
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Photographing the birth of molecules with laser pulses.

Animals that survive winter by freezing solid.

The nuclear holocaust could still happen—by accident.



Venus close-up: radar images from the Magellan spacecraft offer the clearest look yet at the forbidding terrain of the second planet.

The Birth of Molecules

In less than a trillionth of a second, atoms can collide, interact and give birth to molecules. With lasers and molecular beams, it is now possible to witness the motions of molecules as one substance changes to another

by Ahmed H. Zewail

In 1872 railroad magnate Leland Stanford wagered \$25,000 that a galloping horse, at some point in its stride, lifts all four hooves off the ground. To prove it, Stanford employed English photographer Eadweard Muybridge. After many attempts, Muybridge developed a camera shutter that opened and closed for only two thousandths of a second, enabling him to capture on film a horse flying through the air [see illustration at top right]. During the past century, all scientific disciplines from astrophysics to zoology have exploited high-speed photography to revolutionize understanding of animal and mechanical motions that are quicker than the eye can follow.

The time resolution, or shutter speed, needed to photograph the ultrafast motions of molecules is beyond any conventional scale. When a molecule breaks apart into fragments or when it combines with another to form a new molecule, the chemical bonds between atoms break or form in less than a trillionth of a second, or one picosecond. Scientists have hoped to observe molecular motions in real time and to witness the birth of molecules: the instant at which the fate of the molecular reaction is decided and the

final products are determined. Like Muybridge, they needed to develop an ultrafast shutter, but it had to work 10 billion times faster than the 19th-century model.

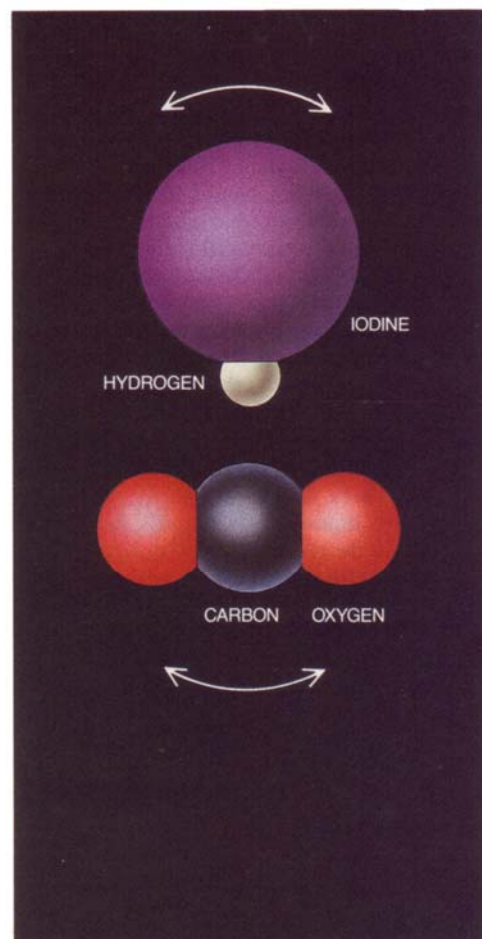
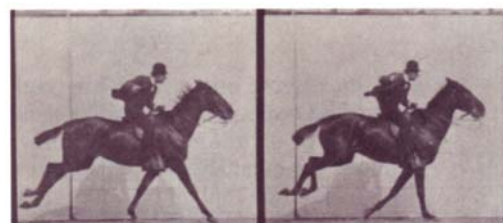
For the past decade our research group at the California Institute of Technology has been developing techniques to observe the dynamics of molecules in real time. From 1985 to 1987 we refined our system of advanced lasers and molecular beams to a point at which we can now record the motions of molecules as they form and break bonds. The reaction can be seen as it proceeds from reactants through transition states and finally to products—chemistry as it happens.

Because transition states exist for less than a trillionth of a second, the time resolution should be shorter—a few quadrillionths of a second, or a few femtoseconds (one is equal to 10^{-15} second). A femtosecond is a smaller unit of time than a tick of even the finest atomic clock. A femtosecond is to a second what a second is to 32 million years. Furthermore, whereas in one second light travels nearly 300,000 kilometers—almost the distance between the earth and the moon—in one femtosecond light travels .3 micron—about the diameter of the smallest bacterium.

Alchemists in ancient Egypt, Greece, Arabia and China did not know about

TIME RESOLUTION of high-speed photography has improved 10 billion times as the technology has evolved from filming movements of animals to capturing the birth of molecules. In one second, a horse gallops 10 meters, as shown in photographs (top) taken by Eadweard Muybridge in 1887. In five trillionths of a second, hydrogen iodide collides with carbon dioxide, creating carbon monoxide, hydroxide and iodine. The illustration (bottom) is based on quantitative observations made at Caltech.

the fundamental importance of this time scale to the change of one substance to another, although they certainly did recognize the art of the transmutation. Only in this century have chemists been able to use a variety of tools to understand the sci-



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ence of molecular reaction dynamics.

At a molecular level a reaction starts when two molecules—call them *A* and *B*—are brought close enough together so that they begin to interact. As the molecules move even closer, other molecular species, which are neither *A* nor *B*, are formed until a new, stable molecule, *C*, is created.

One of these transitory species represents the stage at which the reaction proceeds irreversibly to products. This stage, technically called the transition state, is here denoted as $A \cdots B$. Hence,



The converse process is also possible: when molecule *C* is energized, it can pass through a transition state to form molecules *A* and *B*.

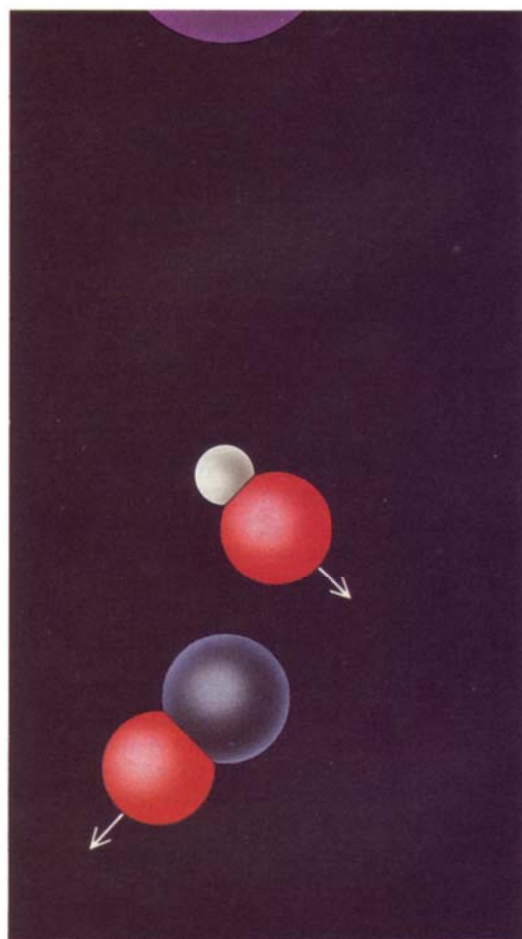
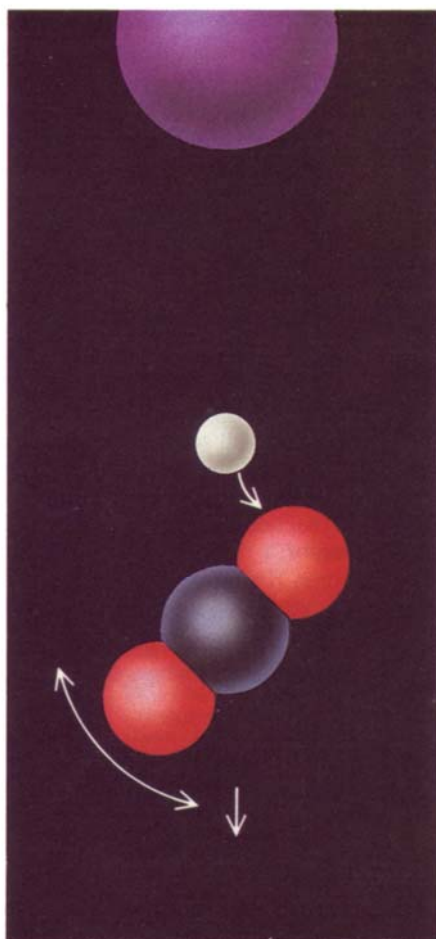
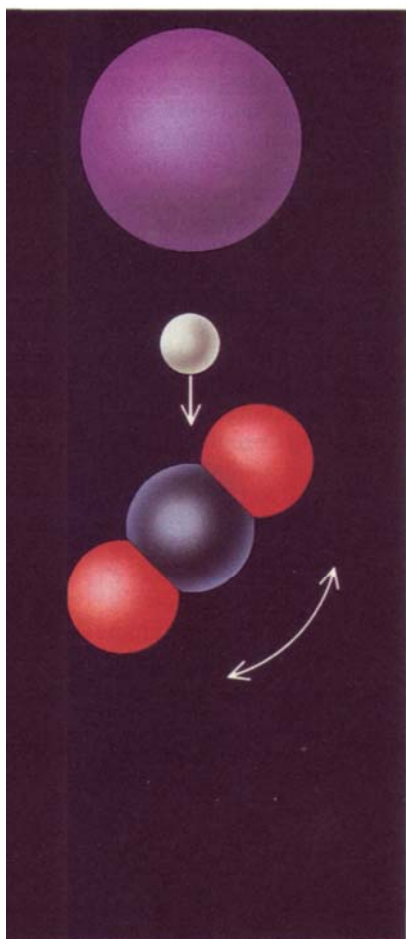
In any chemical reaction the motions

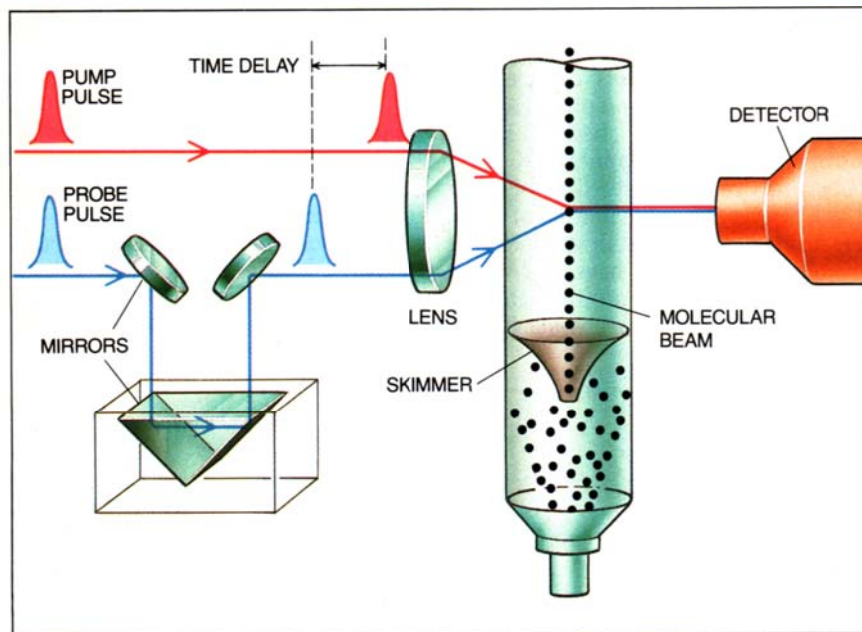
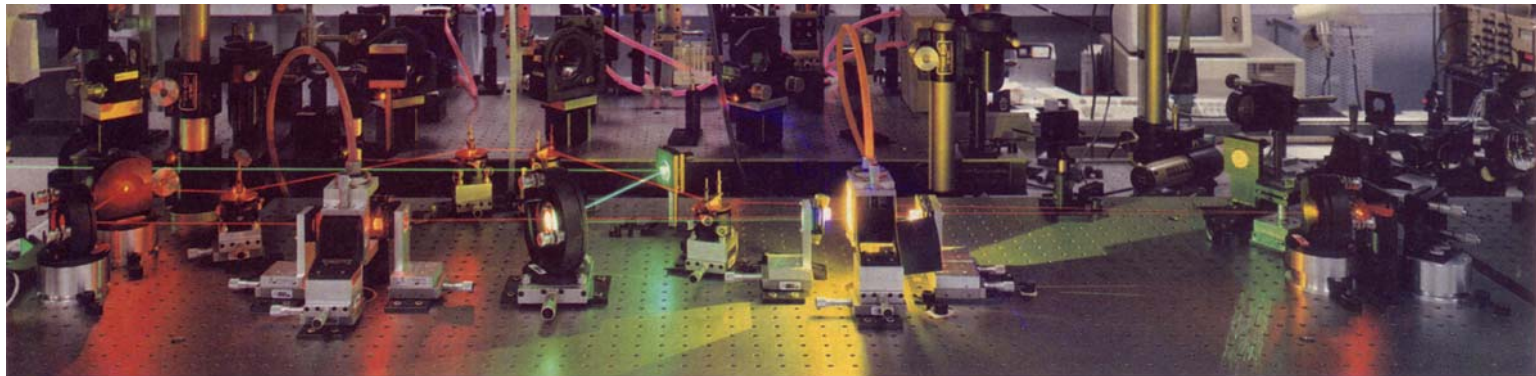
of the electrons and nuclei of atoms determine how the molecules interact, and those interactions in turn create the forces that govern the reaction's dynamics. The molecular motions can be rigorously delineated by the laws of quantum mechanics. In many cases, Newtonian, or classical, mechanics can simply give the transfer of energy and momentum during the course of the reaction, just as effectively as it describes the collision between two objects. If investigators can determine how molecular motions change during the critical transition phase, we can understand how new chemical bonds form and old ones disappear.

In practice, chemists do not keep track of every possible motion of every electron and nucleus in a molecular system. Instead they have discovered clever ways to represent the state of a system. Each state possesses a certain

amount of energy. The potential energy of a molecule when the atoms are a certain distance apart can be represented as a point on a graph. When all the states and their corresponding potential energies are graphed, they form a surface that has mountains and valleys. Molecular systems will spontaneously move from high-energy states (mountains) to low-energy states (valleys), but they require energy to move from valleys to mountains. The bottom of a valley indicates a stable state; the slopes around the valley represent the region of transition states, the different configurations for the atoms in proximity. Chemists technically define a transition state as a saddle point on a potential-energy surface.

If a molecular system is composed of two atoms and if the system's potential energy depends only on the distance that separates the atoms, the





FEMTOSECOND PHOTOGRAPHY captures the dynamics of molecular reactions in real time. The laser system (*above*) generates a pump pulse and a probe pulse. As shown in the illustration (*left*), the pump pulse and the probe pulse leave the laser system at the same time. The probe pulse is diverted so that a time delay of a few femtoseconds is introduced between the two pulses. When the pump pulse hits a molecule in the molecular beam, it initiates a chemical reaction. The probe pulse strikes the molecule a few femtoseconds later. The molecule then emits a spectrum of light, which can be analyzed to determine the dynamics of the atoms in real time.

potential-energy surface reduces to a curve. If the system is governed by the attraction of oppositely charged atoms at “long” distances and by the repulsion of atomic nuclei at “short” distances, the curve will have a single well at “intermediate” distances, indicating that the system is stable there.

For molecular systems composed of many atoms that can move in many ways, the potential-energy surface can be complicated and multidimensional. Nevertheless, the surface is very useful for describing every possible path that molecules may follow—from reactants (valleys) through transition states (mountains) to products (valleys).

One can estimate how long it takes for molecular systems to go through the mountains—that is, the duration of the transition state—by applying ideas from Newtonian mechanics. Heavy molecules or atoms typically emerge from chemical reactions at speeds of 1,000 meters per second. If molecules *A* and *B* are close enough to be in a transition state, then the distance between them is on the order of that of a molecular bond, approximately .1 nanometer (10^{-10} meter). The ratio of this distance to the recoil velocity yields the amount of time during which *A* and *B* form

a transition state—100 femtoseconds. For the “simplest” of all chemical reactions—a light hydrogen atom approaching a hydrogen molecule—the transition state is very short-lived, about 10 femtoseconds. Thus, the time scales for transition states range from about 10 to 100 femtoseconds.

For more than 100 years chemists have studied reaction mechanisms and molecular kinetics in hope of understanding reactivity. In the late 19th century, Swedish scientist Svante Arrhenius took an important step in describing the macroscopic dynamics of chemical reactions. He determined how the rate of a reaction depends on temperature. His famous exponential equation reveals that the rate of a reaction increases as the amount of applied heat increases.

But such equations, which describe the dynamic properties at the macroscopic level, yield information about microscopic molecular dynamics only if a number of assumptions are made. Nevertheless, many aspects of molecular dynamics can be deduced from macroscopic observations, and Arrhenius’s equation remains important to this day.

Some 40 years ago techniques were introduced to study chemical intermediates and fast kinetics for the first time. Ronald G. W. Norrish and George Porter of the University of Cambridge and Manfred Eigen of the Max Planck Institute for Physical Chemistry were able to resolve chemical events that lasted about a thousandth of a second. This time scale was ideal for intermediates but too long for transition states.

To probe the dynamics of molecules as they collide, investigators developed the new methodology of molecular-beam technologies in the 1960s. By releasing molecules into a vacuum and collimating them with a skimmer, chemists created beams of molecules that did not collide with one another. When one beam containing molecules of, say, *A* is crossed with another introducing molecules of *B*, molecules of *A* collide with those of *B* to form a product, *C*. The full collision ($A + B \rightarrow C$) is called a bimolecular reaction. The investigators then detected molecule *C* as it was created in different amounts and in different directions depending on the nature of the forces between *A* and *B*. They used the precollision conditions of the reactants and the postcollision attributes of the products to deduce the dynamics of the collision.

Conversely, a beam of molecules of *C* could be bombarded with light from a laser, energizing the molecules and breaking their chemical bonds to produce fragments *A* and *B*. This dissociation reaction ($C \rightarrow A + B$) could then

be analyzed by measuring the attributes of the fragments. Since the development of molecular beams and other techniques that resolve the quantum states of products, chemists have learned much about the elementary dynamics of reactions. As testimony to the importance of molecular-beam science and reaction dynamics, the 1986 Nobel Prize in chemistry and the 1988 Welch Award were given for contributions in these fields.

In molecular-beam experiments, the sequence of events in a reaction, including the transition states, could not be observed in real time. Chemist Sture Forsén of Lund University came up with an insightful analogy that illustrates the importance of understanding transitory stages in the dynamics. He compared the scientific community to a theater audience watching a drastically shortened version of a classical drama. The audience is shown only the opening scenes of, say, *Hamlet* and its finale. Forsén writes, "The main characters are introduced, then the curtain falls for change of scenery and, as it rises again, we see on the scene floor a considerable number of 'dead' bodies and a few survivors. Not an easy task for the inexperienced to unravel what actually took place in between."

In an attempt to probe transition states more directly than can be done with conventional molecular-beam experiments, chemists turned to new time-averaged techniques and developed methods that record the absorption, emission or scattering of light by transition states. Like molecular beams, these methods do not resolve the events in real time, but they do provide more direct possibilities for examining transition states and dynamics.

In 1979 our research team at Caltech first attempted to enter the field of ultrafast chemistry by using lasers and molecular beams. In those days the time resolution was tens of picoseconds, too gross a time scale for viewing the motion of reactions through transition states. We concentrated on developing techniques to study how energy moves in molecules prior to reactions. By 1984 time resolution in molecular-beam experiments had improved to three picoseconds. That advance allowed us to measure directly the rate of reaction as a molecule changed from one quantum state to another. Still, we needed a technology that could record the spectrum of transition states in real time with femtosecond resolution.

To build such a femtosecond, molecular "camera," we combined the technology of molecular beams with that of ultrashort laser pulses. The molecular

beams allowed us to isolate the reactions in a vacuum; the ultrashort laser pulses gave us the ability to resolve the dynamics with the needed time resolution. During the past five years, advances in laser technology at AT&T Bell Laboratories and other institutions have made it feasible to reach the critical femtosecond time resolution. At the moment, pulses as short as six femtoseconds can be achieved. With such ultrashort pulses, we can obtain a "shutter speed" of approximately 10 femtoseconds.

The principles involved in ultrafast, molecular photography have some similarity to those applied by Muybridge. The key to his work was a special camera shutter that exposed film for only .002 second. To set up the experiment, Muybridge spaced 12 of these cameras half a meter apart alongside a horse track. For each camera he stretched a string across the track to a mechanism that would trigger the shutter when a horse broke through the string.

With this system, Muybridge attained a resolution in each picture of about two centimeters, assuming the horse was galloping at a speed of about 10 meters per second. (The resolution, or definition, is simply the velocity of the motion multiplied by the exposure time.) The speed of the motion divided by the distance between cameras equals the number of frames per second—20 in this case. The motion within a picture becomes sharper as the shutter speed increases. The resolution of the motion improves as the distance between the cameras decreases.

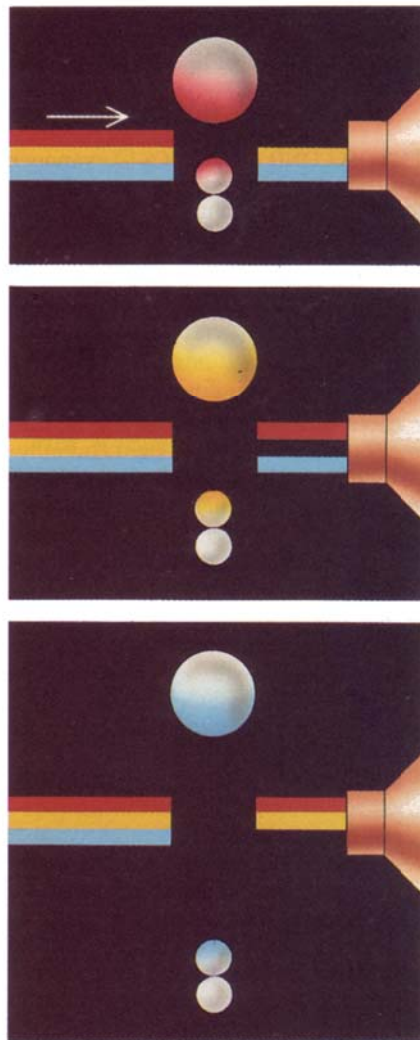
Two aspects of high-speed photography are relevant to femtosecond, molecular photography. First, both types of photography break up a continuous motion into a series of snapshots, or frames. Thus, one can slow down a fast motion as much as one likes so that the eye can see it. Second, both methods must produce enough frames in rapid succession so that the frames can be reassembled to give the illusion of a continuous motion. The change in position of an object from one frame to the next should be gradual, and at least 30 frames should be taken to provide one second of the animation.

In femtosecond, molecular photography, the definition of the frame and the number of frames per second must be adjusted to resolve the elementary nuclear motions of reactions and, most important, ephemeral transition states. The frame definition must be shorter than .1 nanometer. Because the speed of the molecular motion is typically

1,000 meters per second, the shutter resolution must be in a time range of better than 100 femtoseconds.

The conceptual idea behind these femtosecond experiments is rather simple. A first laser flash, called the pump pulse, hits a molecule in isolation, initiating a reaction and setting the experimental clock at zero. A second flash, called the probe pulse, arrives several femtoseconds later and records a snapshot of the reaction at that particular instant. Like the cameras in Muybridge's experiment, a femtosecond, molecular camera records successive images at different times to obtain information about different stages of the reaction.

To produce time delays between the



STATE OF MOLECULAR SYSTEMS can be identified by the light that the molecule absorbs. When atoms in a molecule are relatively close together, they tend to absorb long wavelengths of light (red, for example). When the atoms are farther apart, they tend to absorb short wavelengths of light (blue, for instance). The change in the spectrum is the fingerprint of the atoms in motion.

solve the motion. The detector was made sensitive enough to probe the cyanide molecule when it was free or in the process of separating from the iodine atom. The sensitivity was achieved by using probing laser pulses of different colors in accordance with the spectrum of the molecules. We were thus able to observe the spectral frames changing with time as the reaction progressed from an intact ICN molecule to an iodine atom and molecular fragment, cyanide. We enjoyed discussing the results late into the night.

In 1987 we reported on the probing of the reaction of ICN to iodine and cyanide with enough time resolution to be able to observe the transition state $\{I \cdots CN\}$ directly. We obtained the real-time dynamics of the reaction and then deduced detailed features of the potential-energy surface [see illustration on opposite page].

That experiment made it possible to clock the breaking of an elementary chemical bond on a femtosecond time scale. The findings generated enthusiasm in the scientific community and inspired many more theoretical and experimental studies. The science writer Isaac Asimov provided an interesting description of the experiment. He compared the experiment with sticking a pin in a balloon only four billionths of an inch across—the size of an average molecule.

While we were still building the new femtosecond laser facility in 1986, Bernstein visited us at Caltech, and we

planned to probe the collision and bonding of two molecules, that is, a bimolecular reaction. At first we could not find a way to detect the start of these reactions: the time zero. Although bimolecular reactions last less than a picosecond, the two reactant molecules must first travel to meet each other—a journey that lasts about a million times longer than the reaction itself.

We found a solution to this problem when we studied the investigations of our colleagues at Orsay, France, and at the University of Southern California. By anchoring the two reagents together with a weak van der Waals bond, we could avoid the long time journey and establish the time zero. Fortunately, we had guidance from investigators at U.S.C. who had performed time-integrated studies on the reaction of hydrogen bromide and carbon dioxide.

For our first real-time experiments on these types of bimolecular reactions, we combined hydrogen iodide with carbon dioxide to produce iodine, carbon monoxide and hydroxide:



We wanted to understand this reaction at the elementary level. We broke the bond between hydrogen and iodine with a pump pulse. We then observed with probe pulses that the hydrogen attacks the carbon dioxide and sticks to it for hundreds of femtoseconds. The hydrogen atom then strips one of the oxygen atoms from the carbon. The hy-

droxide molecule finally emerges five picoseconds after the start of the reaction, as we reported in 1987 and earlier this year.

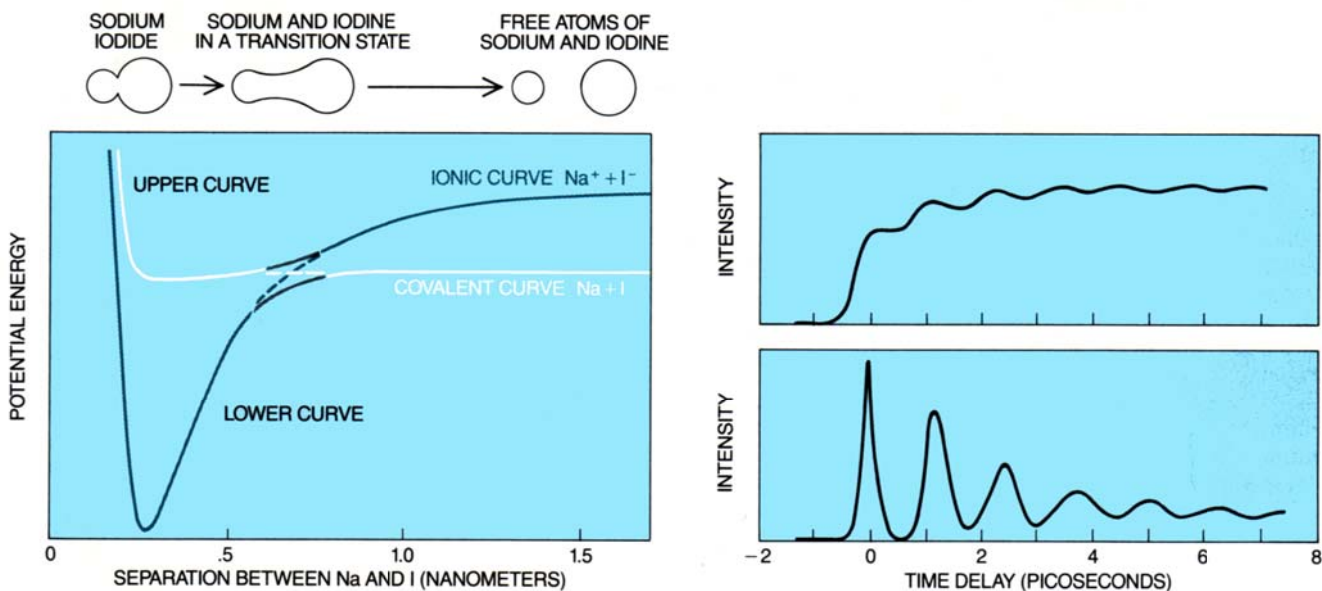
The technique also allowed us to view the dynamics of the transitory collision complex HOCO in real time. We were able to relate this complex to the potential-energy surface representing hydrogen's approach to carbon dioxide. We are still examining the many subtle differences between our results and theory.

Just as physicists like to deal with the hydrogen atom for simplicity, chemical physicists like to understand elementary molecular systems. The simplest of all chemical reactions is that involving two atoms. I thought it would be interesting to direct some efforts at unraveling the dynamics of salt molecules such as sodium iodide:



Alkali halide reactions were the prototype for the "alkali age" of molecular-beam experiments, and it is insightful to study them in the "femtosecond age." Furthermore, researchers at the University of Toronto had investigated the emission spectra of the sodium iodide molecule during its transition to atoms of sodium and iodine.

What intrigued us about sodium iodide is a rather interesting potential-energy surface for the interaction of



FEMTOSECOND MOTIONS of the salt sodium iodide (NaI) reveal the molecular dynamics of the chemical bond linking sodium and iodine. In the potential-energy diagram at the left, the ionic (attractive) curve intersects the covalent (repulsive) curve. As a result, sodium iodide can break up into sodium and iodine, acting in a covalent manner, or sodium iodide can

exist in a high-energy bound state, alternating between covalent and ionic behavior. If sodium iodide dissociates into atoms, then the intensity of part of the spectrum will jump in steps, as shown in the experimental results (*top at right*). If sodium iodide is in its high-energy bound state, then the intensity of part of the spectrum will oscillate (*bottom at right*).

sodium and iodine atoms. If these atoms are brought together, they repel one another, particularly at short distances. On the other hand, if the same elements are brought together as oppositely charged ions of sodium and iodine, they attract each other. In fact, at a short enough distance, a stable salt composed of sodium and iodine ions will be formed. When the sodium and iodine form a covalent bond, they share electrons to create a stable energy state. When the atoms form an ionic bond, the sodium atom donates an electron to the iodine atom to create charged ions that attract.

Nature, however, does not work exactly in this way. Actually, the atoms behave as if they are both ionic and covalent. The true potential-energy curves are therefore composed of an ionic and a covalent curve [see illustration on preceding page]. The ionic curve crosses the covalent curve at a certain distance. In this region of interaction, the molecular system has a mixture of covalent and ionic characteristics; in other words, the molecule has a certain probability of being covalent and a certain probability of being ionic.

Theorists have divided the potential-energy curves into two parts: a lower and an upper. The lower curve, which represents low-energy states, is composed of the ionic curve at short distances and the covalent curve at long distances. The upper curve depicts the opposite situation: it is covalent at short distances and ionic at long distances. The upper curve also represents a state high in energy.

The behavior represented by the lower surface usually dominates when the sodium and iodine atoms are brought together slowly so that they begin to interact. In this case, an electron passes from sodium to iodine to create a stable molecule of sodium iodide. If, however, the atoms come together too rapidly, they can jump, with a certain probability, from the lower to the upper surface. The upper surface no longer represents the covalent repulsive (or slightly bound) curve and instead has a point of least energy (a minimum). Molecules in this potential minimum will thus be somewhat stable. (More specifically, the molecules enter a quasi-bound state.)

We hoped to view the femtosecond dynamics of the bond in sodium iodide as it breaks to form atoms of sodium and iodine. In particular, we focused on the jump from the upper potential surface to the lower one, or vice versa. We observed the motion as the molecules change from being covalent to being ionic and as they go through

the crossing region. The sodium atom gave an electron to the iodine atom at a distance of .7 nanometer. The sodium atom had, in effect, employed its electron as a harpoon to reel in the iodine atom.

To perform the experiment, we first sent a laser pulse to excite the NaI molecules. When the sodium separates about .25 nanometer from the iodine, the bond begins to break. A second pulse is then released to probe the reaction at a point when the sodium iodide bond is completely broken and a sodium atom and an iodine atom are formed. The probe pulse excites the sodium atom and causes it to emit yellow light. By probing the motion from the moment the bond breaks—time zero—until the birth of free sodium atoms, we can count, in real time, the number of sodium atoms that have appeared on the lower curve. But, more important, by detecting the quasi-bound transition species, $\text{Na}\cdots\text{I}$, which has different spectral properties from those of free sodium, we can observe the transition from $\text{Na}\cdots\text{I}$ to free sodium and iodine atoms.

Some of the sodium iodide molecules on the upper curve, when reaching the crossing area, will jump to the lower curve, and their bond will break to form sodium and iodine atoms. The molecules that do not jump but instead remain on the upper curve do not break a bond. They continue to vibrate until they do jump. Hence, pulses of sodium atoms should be evident only after each round-trip in the well of the upper curve. This phenomenon is exactly what we have observed. The results show the motion of the molecule during the breaking of a chemical bond and give the details of the potential energy governing the motion of sodium and iodine atoms.

Laboratories in the U.S. (at IBM) and in Germany (at Freiburg University) are now applying femtosecond techniques to observe the dynamics of many different types of reactions in the gas phase. At Caltech, we are continuing to probe elementary reactions and to examine more complex reactions that involve multiple births (for example, $\text{ABA} \rightarrow \text{AB} + \text{A} \rightarrow \text{A} + \text{B} + \text{A}$). We hope to study the simplest of all reactions, the combination of atomic hydrogen with molecular hydrogen.

We are also exploring large molecular systems with the aim of answering questions about selective reactivity. For example, if a molecule with two identical bonds is energized, do the two bonds break simultaneously or consecutively? To address this general and important question, we studied the dis-

sociation of $\text{C}_2\text{I}_2\text{F}_4$ into iodine and C_2F_4 . (In C_2F_4 , a double bond forms between the carbon atoms.) From real-time studies we found that the reaction proceeds consecutively, despite the molecular equivalence of the two carbon-iodine bonds. Even more remarkable is the discrepancy in the time scale for bond breakage—the first bond breaks in less than half a picosecond, whereas the second bond takes 100 times longer to break!

The ability to view molecular dynamics also suggests new ways of controlling reactions. There are several theoretical schemes for achieving control, and already experimentalists are exploring some new possibilities. The prospect exists for fine-tuning the motion and reactivity of molecules. If successful in the coming decades, laser-customized chemistry may be developed.

Muybridge invented high-speed photography for the fun of it, and today the technique has gone far beyond what he or Stanford could imagine. Although one cannot predict the future, we are certain of the importance and beauty of understanding the science of molecules and their reactions. The door is open for much experimental and theoretical research and for unexpected findings. It is my hope that readers will share in the fun and excitement that we have experienced in learning about the basics of alchemy—the transmutation of one substance to another—by observing the ultrafast motions of molecules.

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