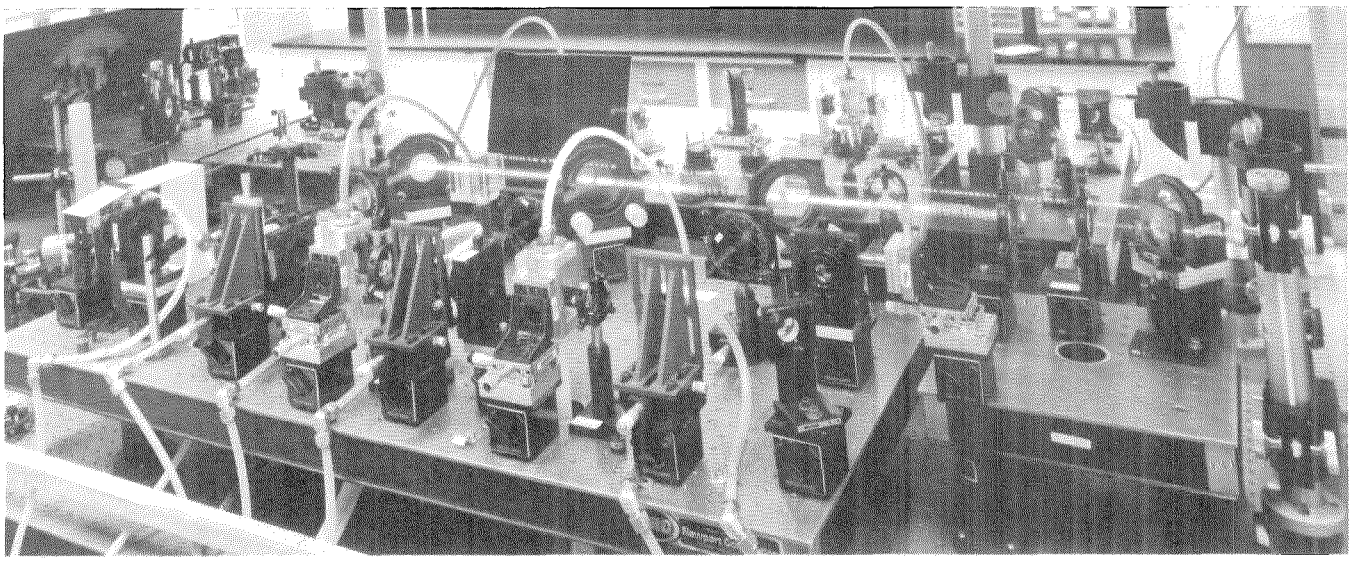
Research in Progress

Perfect Timing



A portion of the optical bench in the femtosecond lab.

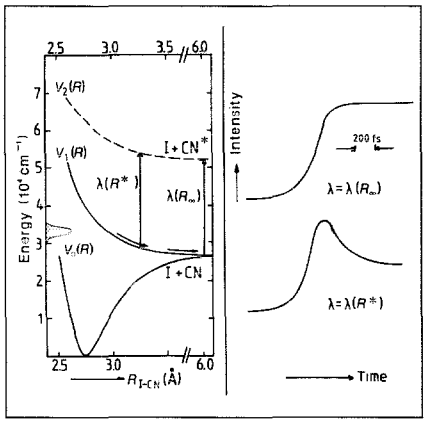
FOR THE FIRST TIME EVER, scientists are watching the birth of molecules. Professor of Chemical Physics Ahmed H. Zewail's group uses ultrashort laser pulses to watch reacting molecules pass through so-called "transition states" before splitting apart into new combinations of atoms. Transition-state molecules are no longer reactants and not yet products—they are ephemeral moments of partially formed bonds. While transition states have been used to describe chemical reactions for decades, the states themselves are so fleeting (lasting for 10^{-12} seconds or less) that they had never been observed directly.

Zewail's group records molecular encounters in a series of "snapshots" a few femtoseconds (fs) apart. A femtosecond (10^{-15} sec) is less than a hairsbreadth of time. Light zips from the earth to the moon in about 1¼ seconds, but travels only one percent of the width of a human hair in a femtosecond. Previous work with the fastest techniques then available produced blurry, time-averaged results for the transition region—like old photographs of a busy street.

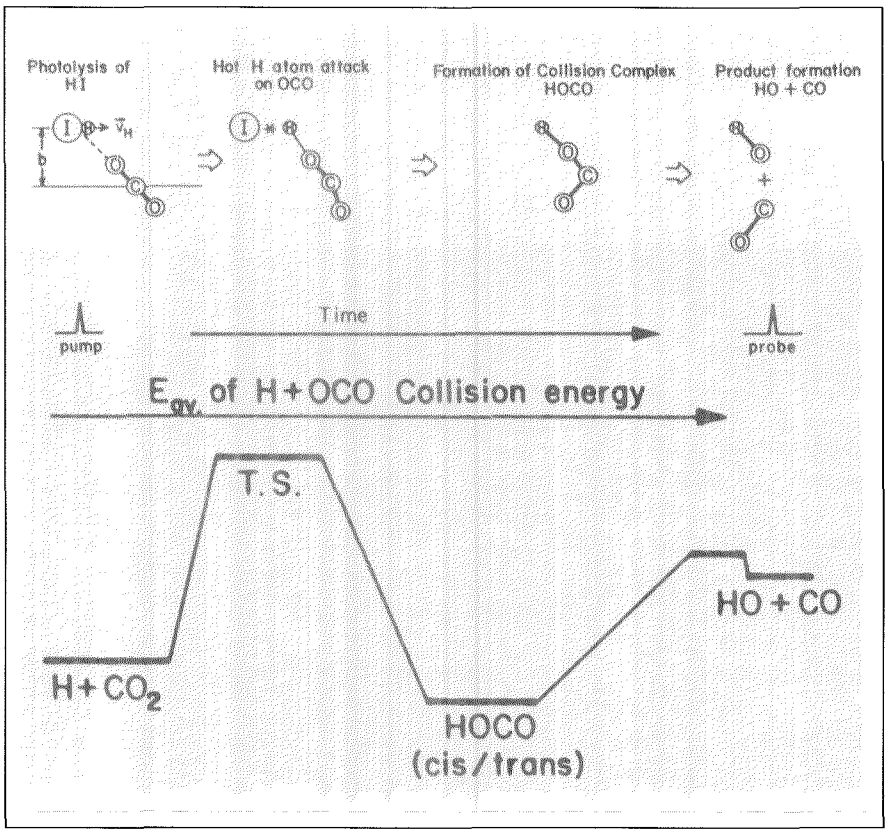
The group works in Caltech's laser facility, where their optical bench—a forest of lenses, prisms, mirrors, filters, and other components on stalklike mountings—is enclosed in sliding plastic panels in a dust-free lab. (A couple of good-sized dust particles could scatter the 0.5- to 0.1-mm-diameter beams.) The enclosure prevents air currents from disturbing the beams, and gives them the exacting degree of stability needed to record femtosecond chemistry (dubbed femtochemistry).

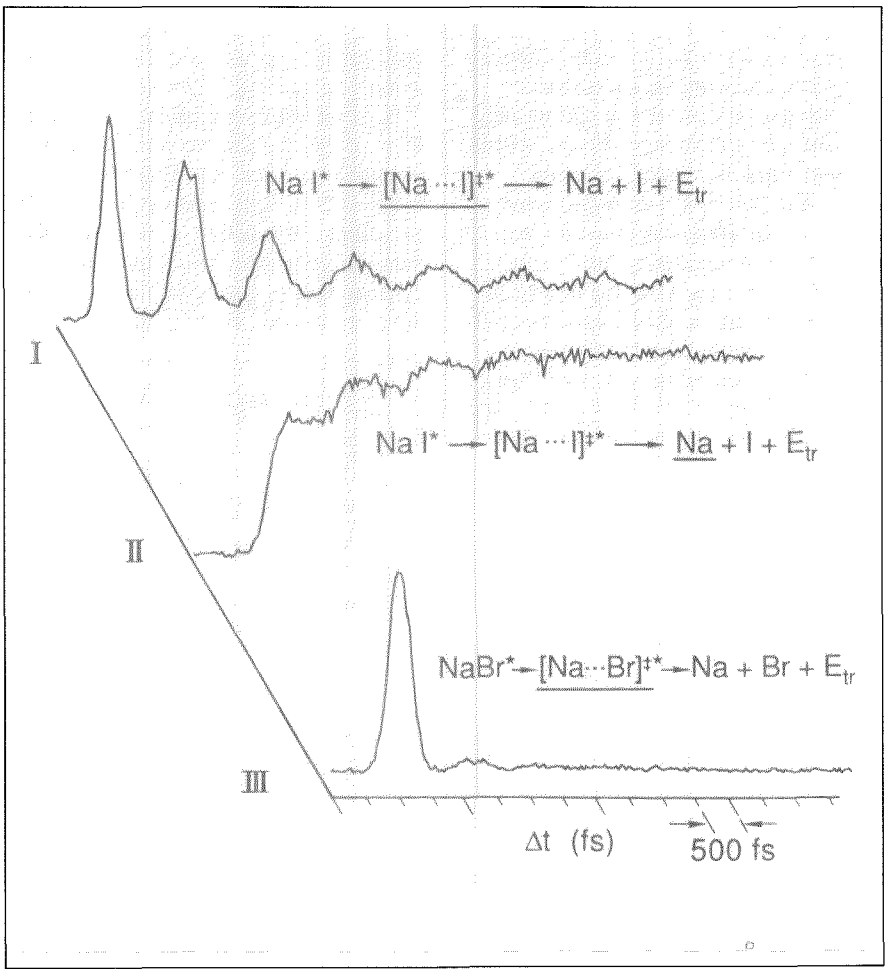
Zewail's technique uses two laser pulses, each about 40-100 fs long. The first pulse—the pump—initiates the reaction and starts the clock. The second one—the probe—"photographs" the molecule after a preset interval.

"We cannot use electronics to get femtosecond time resolution," Zewail says. Time may be money in most places, but in Zewail's lab, time is distance. A partially transparent mirror splits the laser light, sending the pump, or time-zero (t_0), portion directly to the reaction chamber and detouring the rest through a variable-length path. A mirrored prism on a stepping motor controller sets the second path's length to within 100 nanometers (10^{-9} m). The mirror is adjusted until the pulses overlap. "The overlap defines t_0 very accurately, and we take a snapshot of what's happening," Zewail says. "Then we start separating the pulses. If we delay the second pulse by three microns distance, say, that's ten femtoseconds in time, and we take another snapshot. We delay six microns and take another snapshot, and so on." The snapshots assembled in sequence form a "movie" showing the rapid



Dissociating ICN. *(left) Three electronic states [$V_0(R)$, $V_1(R)$, $V_2(R)$] of I–CN. Energy varies with I–CN separation (R). A probe at wavelength $\lambda(R^*)$ corresponding to an intermediate separation gives a transient signal (bottom right); the full separation signal $\lambda(R_\infty)$ appears later (top right).*





motions of atoms within the molecule, a feat never done before.

As a reacting molecule comes apart, its fragments absorb light at specific wavelengths depending on the atoms involved and the distances between them. The probe's snapshot monitors this absorption, so by adjusting the probe to a wavelength corresponding to a particular separation and then varying the delay time, the femtochemist can see exactly when the fragments pass through that configuration on their way to forming products. In a typical experiment, 20 pulses shoot through the reaction chamber every second. Five readings are taken at each delay, 150 delay times in all, yet the run takes less than a minute to complete.

The group has published work on two reactions. Zewail, postdoc Mark Rosker, and graduate student Marcos Dantus are studying the decay of cyanogen iodide (ICN) into iodine (I) and cyanide (CN). Zewail—in collaboration with Richard Bernstein, a Sherman Fairchild Distinguished Scholar from UCLA—and graduate students Norbert Scherer and Lutfur Khundkar are looking at the reaction of hydrogen (H) and carbon dioxide (CO_2) to form carbon monoxide (CO) and hydroxyl (OH). These reactions were chosen because they represent two fundamental chemical processes.

Decomposing cyanogen iodide is what chemists call a unimolecular reaction—only one molecule is involved. Therefore, studying it with the new technique is conceptually quite straightforward. Zap an ICN molecule at the right energy, and it just falls apart—in a mere 200 fs, as it turns out.

Coordinating t_0 on the second reaction is a bit trickier, as the reaction is bimolecular—H and CO_2 start as separate entities. Not only do they have to be properly oriented and close enough to react on cue, but mon-

Top panel: hydrogen reacting with carbon dioxide. The reaction sequence is shown schematically, with the corresponding energy level shown below each step. (T. S. stands for transition state.) The timing of the pump and probe pulses is also shown.

Bottom panel: salt dissociating. I. The Na–I bond resonating. II. Full separation. III. The Na–Br bond resonates once.

atomic hydrogen is too reactive to wait quietly until needed. Both dilemmas are solved by starting with a carbon dioxide-hydrogen iodide complex, loosely held together by intermolecular attractions between hydrogen and oxygen (hydrogen bonds). To make the complex, the group uses a supersonic molecular beam expansion method developed at the other end of the Pasadena Freeway, by Curt Wittig's group at the University of Southern California. The beam cools as it expands, causing its molecules to lose energy and stick together.

The t_0 pulse breaks the H–I bond and simultaneously smacks hydrogen against oxygen as the hydrogen bond compresses; orientation and availability are guaranteed. The researchers could watch the collision complex pause for up to five picoseconds (10^{-12} sec), gathering its forces to go over the energy hump—through the transition state—and form the O–H bond. Once the bond forms, the complex clings together a bit longer to redistribute its energy before the HO–CO bond breaks and the newborn HO and CO molecules fly apart.

In a more recent experiment by postdocs Todd Rose and Mark Rosker, the Zewail group has observed "resonances" as salt molecules react in real time. As molecules of sodium iodide (NaI) start to come apart, the Na–I bond doesn't simply stretch until it snaps. Instead, the bond stretches and compresses (resonates) a half-dozen times or more before coming unglued. On the other hand, sodium bromide (NaBr) stretches only once before final separation. Neither phenomenon had ever been observed in real time before. The work is described in the May 1988 issue of the *Journal of Chemical Physics*, now in press.

"When Linus Pauling was at Caltech 34 years ago, he taught us about the structure of the chemical bond," Zewail says. "Now we are seeing its dynamics in real time." The 1986 Nobel Prize in chemistry went for time-integrated studies of reaction dynamics— using the "before" and "after" molecular states to deduce what must have happened in between. This new work, which looks at the hitherto inaccessible "in-between," opens up "a new era in chemistry," according to Bernstein. "It's a milestone."□—*DS*

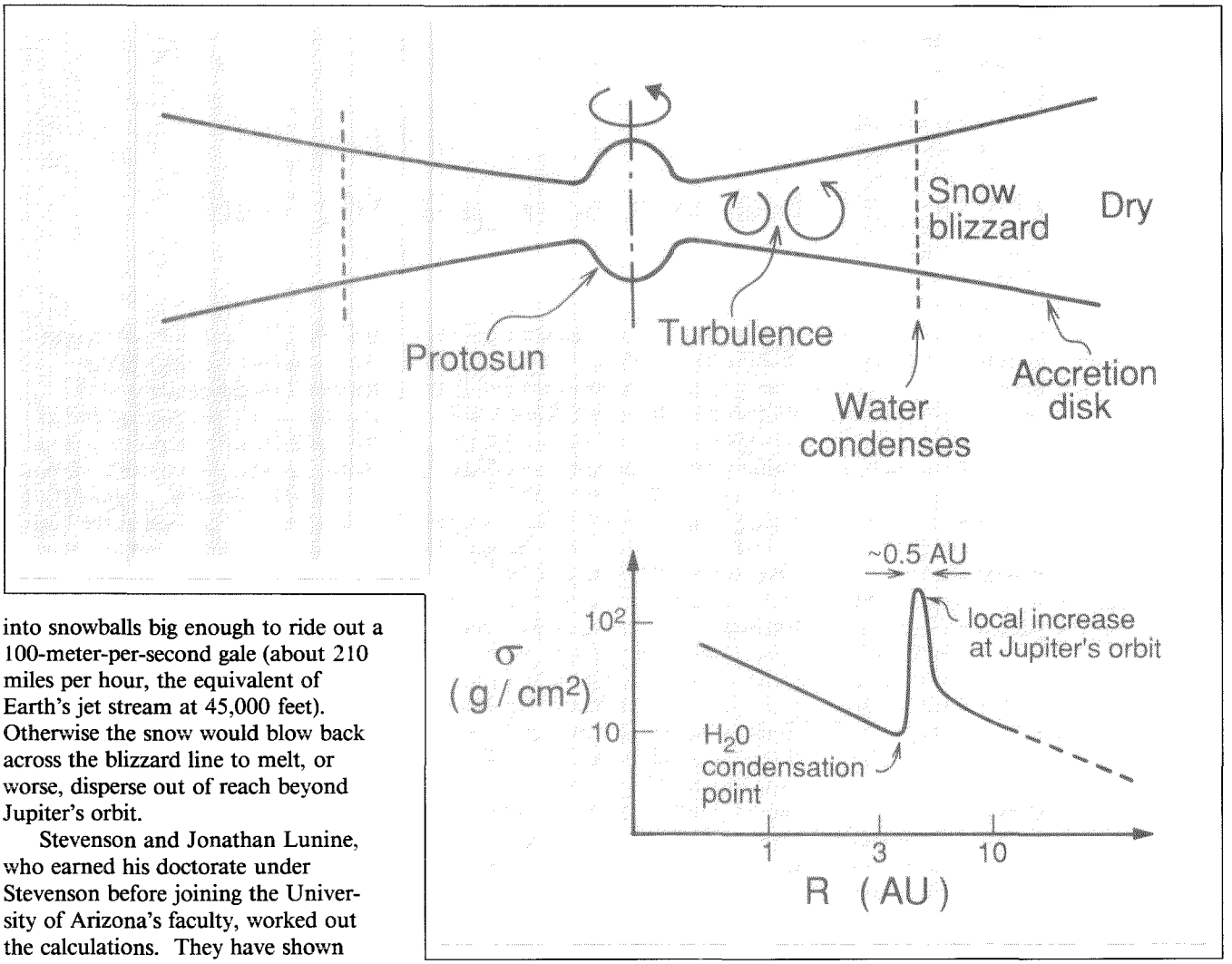
Instant Jupiter: Just Add Water

HOW JUPITER CONDENSED from the roiling gas and dust of the primordial solar system is a mystery, according to Professor of Planetary Science David Stevenson. Not that a giant gasball forming from a gas cloud is baffling—but that swaddled deep within the hydrogen and helium lies an inner core of rock or ice. This core is believed to have formed first, then cloaked itself with the lighter elements. "The cloud heats up as it collapses, and its interior soon reaches a temperature where water and rock are soluble in hydrogen," Stevenson explained. "If you try to make the whole planet all at once, there is a tendency for it all to get mixed up together." The core, 10 percent of Jupiter's radius or approximately Earth's size, has roughly ten times Earth's mass. It would take somewhere around 10 million years to form the way Earth did. (The solar system is about 4.6 billion years old.) But observations of T Tauri objects—gestating sun-sized protostars— imply that the sun lit up at around 1 million years of age, sweeping away the interplanetary cloud. If Jupiter's core finished aggregating 9 million years later, the gas would be long gone. So how could Jupiter form fast enough to capture it?

According to standard theory, a planetary system forms from an interstellar cloud of gas and dust called a presolar nebula. Mutual gravitation collapses the cloud; conservation of angular momentum sets it spinning. The nebula flattens into a disk, perhaps 100 to 200 astronomical units across and one tenth as thick at the periphery. (An astronomical unit, or AU, is the mean distance from Earth to the sun: 93 million miles or 150 million km.) The central accumulation of mass becomes the protosun. Small, solid bodies called planetesimals form elsewhere in the disk. A gravitational shoving match ensues, gradually pushing losers into collision courses—orbits crossing the disk's plane. Shipwrecked planetesimals stick together, or accrete, because part of their kinetic energy turns to heat on impact, and what's left can't overcome the aggregate's gravity. A gravitational truce eventually emerges as the largest survivors settle into stable, coplanar orbits.

The planetesimal casualty rate depends on the accretion disk's local surface density. "If you take all the matter at a given radius, smear it evenly in two dimensions, take a one-centimeter-square cookie cutter, and ask yourself how much material you cut out," Stevenson explained, "that's the surface density." The surface density where Jupiter formed is usually estimated at 5 gm/cm^2. A 20-fold increase would spark runaway accretion. "One object gets just a little bit larger than the others, and its gravitational field focuses the orbits of objects going by it," Stevenson said. "There are no antitrust laws in gravitational physics—one company gobbles up all the others." Instead of nudging its prey into a crossing path over thousands of orbits, a planetary robber baron could engulf the competition in a few passes. Other scientists saw the possibility, but had no plausible story to explain a local increase in density.

Stevenson's tale hangs on the (roughly) inverse relationship between temperature and orbital radius. Jupiter's birthplace was bitterly cold, about 160 K (-170° F), which happens to be water's freezing point at the then-ambient pressure of 10^{-6} atmospheres. Outbound water vapor would turn to snow as it crossed Jupiter's orbit, forming a permanent blizzard in the void. But could enough water cross the orbit in time? And if it could, would a sufficiently dense snowdrift accumulate? The storm's turbulence would have to pack flakes



Top: a cross-section through the accretion disk. Turbulence carries water across the condensation point, where it turns to snow. Bottom: a plot of surface density (σ) vs. distance from the protosun (R), showing the local increase due to the blizzard.

into snowballs big enough to ride out a 100-meter-per-second gale (about 210 miles per hour, the equivalent of Earth's jet stream at 45,000 feet). Otherwise the snow would blow back across the blizzard line to melt, or worse, disperse out of reach beyond Jupiter's orbit.

Stevenson and Jonathan Lunine, who earned his doctorate under Stevenson before joining the University of Arizona's faculty, worked out the calculations. They have shown that a water molecule starting near the protosun—but outside its accretion zone—could wander out to the blizzard line in 10,000 to 100,000 years via random diffusion. (Water heading directly for Jupiter would take only 100 years for the 5-AU voyage.) Ten Earth masses are needed for Jupiter's core. Stevenson and Lunine estimate the disk held as much as 50 Earth masses of water within Jupiter's orbit. The molecules wouldn't be drifting singly, either, but in gas parcels 100 times Earth's size. Parcels collide and intermix, creating that 100 m/sec gale. This windstorm is the key to the whole problem: the theory needs it to move so much gas so fast; conservation of angular momentum provides it automatically to counterbalance material accreting onto the protosun.

When a gas parcel becomes a blizzard, snowballs form instantaneously. (Relatively speaking, of course— astrophysicists have calculated that a meter-sized snowball could form in as little as 1,000 years.) Snowballs perhaps 30 m across would be big enough to stay put, Stevenson believes, and would only take a few thousand more years to form. The runaway accretion zone's area of influence would be about 0.5 AU wide, so snowballs would be unlikely to drift beyond it before dropping anchor. Ten Earth masses of snow could accumulate in 100,000 years, leaving ample time for the core to acquire the gas which, compressed by its own weight, would eventually form the dense layers of metallic hydrogen, liquid hydrogen, and gaseous hydrogen and helium that make up most of Jupiter.

Although there is some indirect evidence for it, the theory will be difficult to verify in the near future, Stevenson said. "We do know there's a core. It could be mostly rock or mostly ice. Unfortunately, we don't have any way of deciding by observation. In my story it's ice, which is the most abundant substance in the universe capable of condensing in the right temperature and pressure range. We can see water ice on Jupiter's satellites— Ganymede, Callisto, and others—and there's lots of it in the outer reaches of the solar system. We could do an indirect test by looking for chemical gradients in the disks around nearby objects like HL Tau, a T Tauri star. Caltech's Millimeter Interferometer in Owens Valley or the Submillimeter Observatory in Hawaii have sufficient spectroscopic and spatial resolution. We might do that in five to ten years, and that's very exciting."□—*DS*