σ = 0.5and 0.3 with peak values of 2.5 K per day, and cooling in the top layer (σ = 0.1) at half this rate. This cooling represents anomalous radiative cooling at cloud top as measured by the OLR anomaly. The upper tropospheric heating in a 400-mb layer follows D. L. Hartmann, H. H. Hendon, R. A. Houze [*J. Atmos. Sci.* **41**, 113 (1984)]. At 5°N the sign of the vertical profile of forcing is reversed.

20. R. Mureau, J. D. Opsteegh, J. D. Winston, *Mon. Weather Rev.* **115**, 856 (1987).
21. Other preliminary experiments support the robustness of our results. When the climatological waves are retained, the structure of the response is rather insensitive to the exact longitude of the heating. Point sources at all locations at 15°N between 100° and 150°W, but not elsewhere, produce essentially the same midlatitude pattern, although with varying amplitude. Changes in the vertical heating profile in the model also alter the amplitude but not the pattern of the response.

22. K. Kurihara and T. Tsuyuki, *J. Meteorol. Soc. Jpn.* **65**, 237 (1987); T. Nitta, *ibid.*, p. 373.
23. W. D. Sellers, *Physical Climatology* (Univ. of Chicago Press, Chicago, 1965); J. Shukla and Y. Mintz, *Science* **215**, 1498 (1982); T.-C. Yeh, R. T. Wetherald, S. Manabe, *Mon. Weather Rev.* **112**, 474 (1984).
24. P. D. Sardeshmukh and B. J. Hoskins, *J. Atmos. Sci.* **45**, 1228 (1988).
25. G. Branstator, *J. Atmos. Sci.* **40**, 1689 (1983), P. A. Webster and J. Holton, *ibid.* **39**, 722 (1982).
26. A. Simmons, J. M. Wallace, G. Branstator, *J. Atmos. Sci.* **40**, 1363 (1983).
27. S. E. Zebiak and M. A. Cane, *Mon. Weather Rev.* **115**, 2262 (1987).
28. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

Laser Femtochemistry

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Femtochemistry is concerned with the very act of the molecular motion that brings about chemistry, chemical bond breaking, or bond formation on the femtosecond (10^{-15} second) time scale. With lasers it is now possible to record snapshots of chemical reactions with sub-angstrom resolution. This strobing of the transition-state region between reagents and products provides real time observations that are fundamental to understanding the dynamics of the chemical bond.

THE MOLECULAR EVENTS THAT BRING ABOUT CHEMISTRY, chemical bond breaking or bond formation, occur with awesome rapidity, often in less than 10^{-12} s. One of the fundamental problems in chemistry is to understand how these events, which occur in the region of the transition state between reagents and products, determine the entire course of the reaction, including the fate of the products. In the past the actual dynamics of this region could not be time-resolved, but chemists devised methodologies for describing reactivity. Different approaches (for example, thermodynamics, kinetics, and synthesis) have been used to systematize a large body of experimental data and obtain the energetics (ΔG, ΔH, and so forth), the rates [$k(T)$], and the mechanisms of the reactions, thus establishing the macroscopic picture.

Understanding the detailed dynamics of reactions on the molecular level required new microscopic methods (*1–3*), which were introduced some 30 years ago. Major advances have come from the application of molecular beam, chemiluminescence, and laser techniques (*4*). In the simplest molecular beam experiments, a beam of reagent molecules is directed towards co-reagent molecules (in the form of a target gas or another beam), and the reactive scattering that leads to product molecules is observed. The relative kinetic energy of the reagents can be changed by varying the velocity of one of the reagent molecules with respect to the other reagent involved in the "single collision." For laser–molecular beam experiments, a

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laser can be used to excite one of the reagent molecules and thus influence the reaction probability, or the laser can initiate a unimolecular process by depositing energy in a molecule. In this so-called "half-collision" unimolecular process, the fragmentation of the excited molecule, which can be represented as ABC into A and BC, is the dynamical process of interest.

The ingeniousness of this approach is in using the postcollision (or half-collision) attributes of the products (angular distributions, population and energy distributions, alignment, and so forth) to infer the dynamics of the reactive collision (or half-collision). During the last three decades many reactions have been studied and these methods, with the help of theory, have become the main source of information for deducing the nature of the potential energy surface (PES) of the reaction (*4*).

To directly observe the transition-state region between reagents and products, which is the fundamental feature of reaction dynamics, different methodology is needed. As mentioned above, these states are ultrashort-lived and experiments on a longer time scale provide data that are effectively time-integrated over the course of the collision or half-collision. Smith (*5*), in comparing different experimental approaches, noted that a great deal is known about the "before" and "after" stages of the reaction, but that it is difficult to observe the "during" phase. The problem is perhaps illustrated best by the quotation of Zare and Bernstein (*6*), which describes the choreography of these processes: "The study of chemical reaction kinetics can be likened to the task of making a motion picture of a reaction. The trouble thus far with achieving this goal seems to be the problem of too many would-be actors who strut upon the stage without proper cue and mumble their lines too rapidly to be understood—for chemical reactions occur with the ease of striking a match and at a speed so fast (on a subpicosecond time scale for the making of new bonds and breaking of old ones) as to be a severe challenge to the moviemaker who would like to record individual frames."

In recent years, great progress has been made by several groups (*7–13*) using absorption, emission, scattering, and ion spectroscopy to probe the relevant transition region. Without direct time resolution, they used these clever methods, reviewed recently by Polanyi (*7*), Kinsey (*8*), and Brooks and Curl (*9*), to obtain information on the dynamics in the transition-state region of some elementary reactions. Examples include the dissociation of methyl iodide (*8*)