

Transition State Spectroscopy

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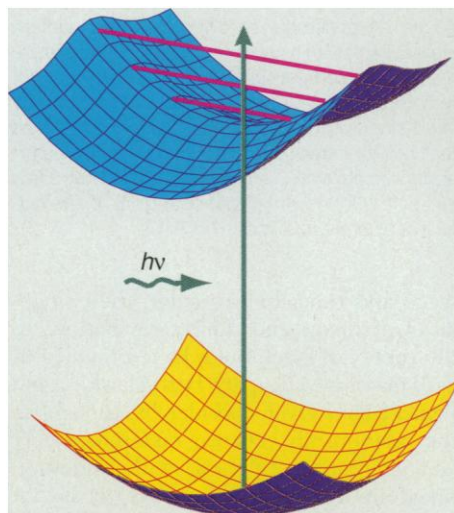
One of the most useful concepts in understanding chemical reactivity is the idea of the transition state. When two reactants undergo a chemical reaction to form products, new chemical bonds are formed while others are broken; one can therefore imagine a molecular configuration intermediate between reactants and products, and this is what chemists refer to as the transition state. The transition state often occurs at the top of a potential energy barrier and acts as a bottleneck in a chemical reaction. The properties of the transition state therefore determine the reaction rate, as well as many of the more detailed attributes that one measures in scattering experiments. Thus, the experimental characterization of the transition state through "transition state spectroscopy" is one of the grand challenges in the field of physical chemistry (1). There has been considerable progress in this area during the last 10 years, but the paper by Wenthold *et al.* in this issue (2) on the transition state for inversion in cyclooctatetraene (C_8H_8) represents a qualitative jump in the complexity of reactions accessible to transition state spectroscopy.

In terms of the potential energy surface for a chemical reaction, the transition state is typically located at a saddle point (see figure) between reactants and products. At the transition state for a reaction involving N atoms, the reaction complex is unstable along one coordinate (the reaction coordinate) and bound along the other $3N-5$ coordinates. Elementary transition state theory tells us that the rate constant for a chemical reaction depends on the transition state geometry, the barrier height at the transition state, and the frequencies of the vibrational modes along its bound coordinates. These are the characteristics of the transition state that one would like to extract from a transition state spectroscopy experiment.

The evanescent nature of the transition state makes it particularly challenging to study experimentally; during the course of a bi- or unimolecular reaction, passage through the transition state occurs on a time scale of 10^{-13} to 10^{-14} s. Whereas the first attempts at transition state spectroscopy focused on probing the transition state formed during a full bimolecular collision, considerably more success has been achieved by use of the basic idea pic-

tured in the figure. In these experiments, the transition state is accessed by photoexcitation of a suitably chosen stable precursor, which can be the ground state of a molecule, a van der Waals complex, or a negative ion. Once on the upper surface, the reactants pass through the transition state en route to products, and a suitable probe of the dynamics on the upper state can yield both spectroscopic and dynamical information on the transition state.

Two general types of experiments of this



In transition. Absorption of light $h\nu$ excites a bound species to the transition state of a potential energy surface for a chemical reaction. The transition state lies at the saddle point between reactants and products.

type have been carried out. In time-resolved experiments (3), the transition state precursor is photoexcited with an ultrafast (~ 100 fs) laser pulse, and a second ultrafast pulse probes the dynamics on the upper potential energy surface. Typically, one monitors the appearance of products on the upper surface as a function of delay time between the laser pulses; this is sensitive to the slope and curvature of the reaction coordinate in the vicinity of the transition state. In frequency-resolved experiments, the transition state precursor is excited with a relatively long pulse (several nanoseconds), and one searches for spectral features associated with the transition state, particularly vibrational motion along the bound coordinates perpendicular to the reaction coordinate. For example, in a study of ketene (H_2C_2O) photolysis to make triplet $CH_2 + CO$, the dissociation rate $k(E)$ as a function of excitation

energy showed clear step-structure associated with vibrational levels of the transition state for unimolecular dissociation (4).

Another frequency-resolved method for probing the transition state is to use a stable negative ion as the transition state precursor and to photodetach order to access the transition state on the ground-state potential energy surface for a neutral reaction (5). The overall process is $AB^- \xrightarrow{h\nu} AB^\ddagger + e^-$, where the energy $h\nu$ is typically from a visible or ultraviolet photon. If the negative ion and neutral transition state have similar geometries, then the photoelectron spectrum of the anion can reveal vibrational structure associated with the neutral transition state.

The photodetachment method has been used with considerable success to study transition states for bimolecular reactions. For example, the geometries of the FH_2^- anion and $FH_2^\ddagger$ transition state for the $F + H_2$ reaction are quite close. The photoelectron spectrum of FH_2^- shows an extended progression in a vibrational mode of FH_2 transition state, and from the peak spacings, it is clear that this is a progression in the $FH_2^\ddagger$ bending mode (6). This observation provides direct evidence that the $FH_2^\ddagger$ transition state is bent, thereby settling a long-running controversy concerning the $F + H_2$ reaction. Moreover, simulations of the FH_2^- photoelectron spectrum using the most recently developed potential energy surface for the $F + H_2$ reaction are in excellent agreement with the experiment, showing that this new surface is accurate in the vicinity of the transition state.

In the work by Wenthold *et al.*, photodetachment of the cyclooctatetraene anion, $C_8H_8^-$, probes the transition state for the ring inversion in neutral C_8H_8 . The anion is planar, whereas the neutral molecule has four equivalent nonplanar minimum-energy structures separated by relatively low (~ 1 eV) energy pathways [see figure 1 of (2)]. The minimum-energy path to get from one structure to another involves passage through a planar transition state; this transition state has good geometric overlap with the negative ion and is therefore accessed by photodetachment of the anion.

In spite of the large number of atoms, the photoelectron spectrum shows resolved vibrational structure. This structure is assigned to the "bond-alternation" vibration in which the four single and double C-C bonds in the planar geometry of C_8H_8 synchronously switch position with one another; the net result is a "pseudorotation" in which the molecule appears to have rotated by 45° [see figure 1 of (2)]. This vibrational mode is clearly associated with the planar transition state; its character is completely different in the nonplanar equilibrium geometry of C_8H_8 . Hence, as in the bimolecular photodetachment experiments, one is observing vibrational motion

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along a bound coordinate at or near the transition state geometry. It is remarkable that only a single such progression is seen in Wenthold's spectrum; this is the result of the high symmetry of the anion and neutral species. Overall, the paper represents an important expansion of transition state spectroscopy from the type of model chemical reactions usually studied by chemical physicists to much more complex species of interest to the wider chemistry community.

References

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To See a World in 80 Kilograms of Rock

Allan Treiman

Of the more than 7500 known meteorites, only 12 are certain to have come from Mars. As the only available samples of Mars, they have become the basis for much of what is known (or hypothesized) about Mars (1). In one sense, the martian meteorites are returned planetary samples no less scientifically important than the Apollo and Luna samples. The martian meteorites are all basalts and related rocks, with a total mass of only 80 kg, and have been subjected to every conceivable analysis; paraphrasing Churchill, "never has so much been learned by so many from so little." The most exciting studies in the last year (including reports at the 27th Lunar and Planetary Science Conference held in Houston in March) emphasize three areas: water, the earliest history of Mars, and how the meteorites got to Earth. In addition, preliminary data on the newest martian meteorite (the twelfth) have just arrived.

Water once flowed on and near the surface of Mars. Valley networks suggest rivers or abundant ground water more than 4 billion years ago, and huge outflow channels bespeak catastrophic floods in the more recent past of this planet. Martian water is recorded in the meteorites by alteration minerals, deposited from the water or formed by chemical reactions with the water. The martian origin of the alteration minerals is certain; they predate the meteorites' scorching passages through Earth's atmosphere.

Nearly all of the martian meteorites contain alteration minerals, meaning that liquid water was widespread (although not abundant) in Mars (2). The youngest martian meteorites crystallized from magma ~170 mil-

lion years ago, so their water-deposited grains must be younger still. The most abundant of the alterations are veinlets of clays, hydrous iron oxides, and salt minerals in the Lafayette meteorite. These veinlets formed from reaction between the rock and warm water (<70°C), as suggested by their mineralogy and by oxygen isotope ratios in the clays and host rock ($\delta^{18}\text{O} \sim +14$ and $+4.5$, respectively); their age is ~300 million



A small slice of Mars. Thin section of the Lafayette martian meteorite, real colors; field of view is 2.3 mm across. The clear (white) cracked grains are pyroxene and olivine. The orange-brown patches are clays and iron oxides formed when the rock was altered on Mars. [Photo from the author]

years (3). The oldest martian meteorite, ALH84001, is devoid of water-bearing alteration minerals but does contain late-stage Mg and Fe carbonate minerals. The temperature at which these carbonates formed is quite uncertain (estimates range from 0° to 700°C) (4). Still, the absence of water-bearing alteration minerals in ALH84001 seems inconsistent with the abundant evidence

for liquid water on ancient Mars.

The earliest history of Mars, before 4.0 billion years ago, is important in itself and as a proxy for Earth's earliest history; little is known of this epoch on Earth because no rocks from that time are preserved. So, it was exciting when Rb-Sr and Sm-Nd radio-isotope studies showed that the ALH84001 martian meteorite formed 4.5 billion years ago, and therefore must be from Mars's most ancient terrane, the southern highlands. The K-Ar radio-isotope system yields a younger age of 4.0 billion years, which probably represents impact metamorphism (5). These ages are comparable to the oldest crystallization ages and the most common impact ages found in lunar highlands rocks, further suggesting a common history of planet formation and impact cratering. It seems likely that early Earth shared these experiences, but it is not clear that ALH84001, a pyroxenite, sheds any light on the nature of Earth's early crust.

Four of the martian meteorites, the Chassigny and the nakhlites, provide a strong constraint on Mars's very early history. These meteorites contain excesses of the isotope ^{142}Nd , which arose from a decay of ^{146}Sm (half-life, 103 million years). The solar system contained a little ^{146}Sm at its inception 4.566 billion years ago, but it had effectively decayed away within a few half-lives. Therefore, the excess ^{142}Nd must derive from

material that had excess ^{146}Sm very early in the solar system, 4.54 billion years ago in this case, only 30 million years after the solar system formed. Mars must have been a full-fledged planet by this time. Further, the material with excess ^{142}Nd must have been preserved intact, inside Mars, from 4.54 billion years until 1.33 billion years ago, when the Chassigny and the nakhlites formed (6). How could this isotopically anomalous material have been preserved in an actively convecting planet for more than 3 billion years?

The passage of rocks from Mars to Earth always seemed improbable: the martian meteorites were accepted as such only after gas identical to Mars's atmosphere was found in them. Even so, their transport to Earth seemed to require singular events: ejection from Mars by a large asteroid impact followed by a unique fragmentation history in space. Recent work, however, shows that ~3% of rocks ejected from Mars will come to Earth, without fragmentation, on relatively short time scales (<20 million years) (7). In addition, the me-

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