PERSPECTIVES

Transition States of Chemical Reactions

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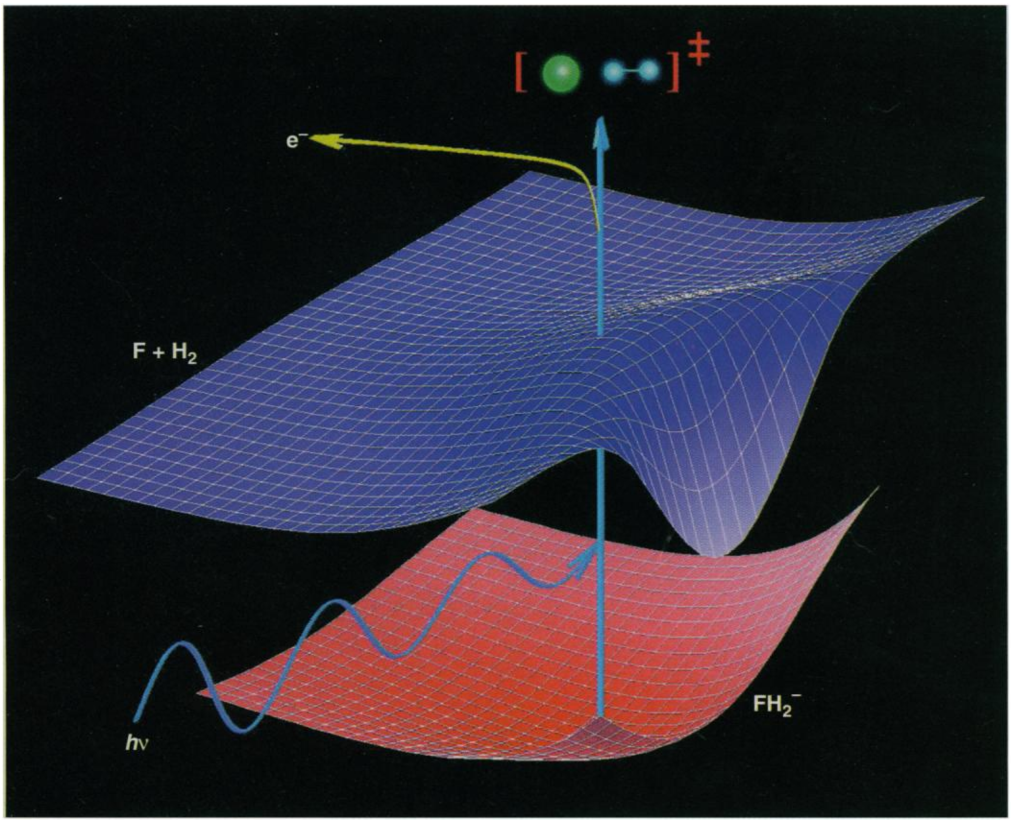
The transition state of a chemical reaction represents the bottleneck between the reagents and products that controls the rate of the reaction. Often transition states are associated with the top of a barrier on a potential energy surface that connects reactants and products, but a more general definition is that it is located at a free-energy minimum along a reaction path between reactants and products. The structural and energetic properties of transition states may be used to estimate reaction rates with Transition State Theory (sometimes known as Absolute Rate Theory), but it is difficult to determine these properties directly from experiment. The report on page 1852 of this issue by Manolopoulos *et al.* (*1*) represents an important breakthrough in our understanding of the transition state of one of the simplest chemical reactions, namely $F + H_2 \rightarrow HF + H$. This work also reveals the current power of theoretical methods for characterization of the structure and dynamics of transition states for reactions involving a small number of atoms.



Transition state spectroscopy. Photon excitation (*hν*) leads to photodetachment of the stable FH_2^- anion (red surface), which makes the transition state region of the $F + H_2$ reaction (purple surface) available for study. The resulting photoelectron spectrum yields vibrational structure characteristic of the $[FH_2]^\ddagger$ transition state. The vertical arrow indicates the electronic transition that takes place during photodetachment, starting from the linear FH_2^- equilibrium geometry. On the purple surface, there are twin saddle points on either side of this linear geometry, corresponding to barriers which separate $F + H_2$ from $HF + H$. [D. W. Arnold and D. M. Neumark, University of California at Berkeley]

Much of our confidence in determining transition state properties, and in the use of Transition State Theory for determining reaction rates, is based on studies of simple gas phase chemical reactions, such as $H + H_2 \rightarrow H_2 + H$ and $F + H_2 \rightarrow HF + H$. Significant interest in the latter reaction began about 25 years ago with the discovery of chemical lasers (lasers in which chemical energy is converted into light) in which the $F + H_2$ reaction plays a key role. As a consequence, $F + H_2$ has been one of the most extensively studied of all the simple gas phase reactions.

In the late 1960s and early 1970s, John Polanyi, who shared the 1986 Nobel Prize, did a famous series of studies of $F + H_2$ (*2*) and similar reactions in which he used infrared chemiluminescence to measure the distribution of product HF vibrational and rotational states. These experiments stimulated the development of potential surfaces with the use of ab initio molecular orbital methods, culminating in a surface by Bender *et al.* (*3*) (the so-called BOPS surface), which indicated that the FH_2 potential surface has a linear F-H-H barrier, with a barrier height of 1.7 kcal mol^{-1}. This was in accord with the intuition of that time, as classical molecular dynamics calculations based on empirical potential surfaces that had linear transition states gave HF product state distributions in good agreement with the Polanyi experiments. It turns out that this intuition was incorrect.

Interest in $F + H_2$ received a second boost from the molecular beam experiments (*4*) of Y. T. Lee (who along with D. Herschbach shared the Nobel Prize with Polanyi) and his group. In these measurements, a beam of F atoms was crossed with a beam of H_2 in a vacuum chamber, and the angular distribution of the HF products was measured with a mass spectrometer. By determining the translational velocity of the HF molecules, these authors were able to also determine the final vibrational state. The results of these experiments were highly unusual, and theorists have struggled to interpret them ever since.

What Lee and co-workers found is that the HF molecules in vibrational state $v = 2$ are produced with an angular distribution typical of a simple direct reaction, in which the HF and H repel each other as soon as they are formed. HF($v = 3$), by contrast, has an angular distribution that suggests the formation of a short-lived complex between HF and H before they separate. Such complexes are called resonances in quantum scattering processes, and the FH_2 resonance was the first, and is still one of the few, scattering resonances to be observed for a reaction having no intermediate bound states. Although resonance effects had been predicted in earlier theoretical studies of $F + H_2$ with surfaces similar to the BOPS surface, the specific features found in the molecular beam measurements were not expected.

The molecular beam studies of $F + H_2$ stimulated significant theoretical work, and substantial effort was expended by quantum chemists to improve on the BOPS surface.

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Surprisingly, these improved calculations produced higher, rather than lower, barriers than BOPS (3 to 4 kcal mol^{-1} rather than 1.7 kcal mol^{-1}). The ensuing frustration among quantum chemists culminated in an article by Schaefer (*5*) in 1985 entitled "The F + H_2 potential energy surface: The ecstasy and the agony." Ecstacy here referred to the BOPS surface, and agony referred to everything subsequent. Eventually, after contributions from a large number of investigators, including Truhlar and co-workers (*6*) and Bauschlicher and co-workers (*7*), it was discovered that improved results could be obtained with more systematic treatments. In addition, it was discovered that the F-H-H barrier had to be nonlinear (*6*).

In 1991, Knowles *et al.* (*8*) reported ab initio calculations that form the basis of the present study (*1*). These calculations represent the most sophisticated ab initio molecular orbital studies to date for FH_2, with a 1.5 kcal mol^{-1} barrier (stated uncertainty of 0.1 kcal mol^{-1}) in which the F-H-H angle is 119°. In the figure, the barrier shows up on the purple surface as a saddle point separating reagents and products. There are actually two symmetrical saddle points in the figure because of symmetry of the potential with respect to the interchange of the two hydrogens.

The high accuracy of the potential shown in the figure represents a major advance in the ability of ab initio molecular orbital methods to describe transition states. Moreover, these calculations were done at a large number of geometries so that a global potential energy function describing FH_2 could be developed. Such global surfaces are essential for accurate quantum scattering calculations of the reaction dynamics, which is the second step in the theoretical modeling.

The development of quantum scattering methods for describing the F + H_2 reaction has advanced significantly in the last few years. A number of groups have developed numerical methods for exactly solving the Schrödinger equation for this and similar reactions, including the work described by Manolopoulos *et al.* (*1*). The application of such methods yields information about the reaction dynamics for which the only significant source of error is in the potential energy surface. Among the results of such calculations are angular distributions that may be compared with molecular beam experiments, vibrational and rotational distributions that may be compared with infrared chemiluminescence data, and cross sections that may be used to determine rate constants. Unfortunately, the results of such applications to F + H_2 before the Manolopoulos work have exhibited significant discrepancy with experiment, particularly with respect to the molecular beam measurements, indicating that the available surfaces were flawed.

At about the same time that the theoretical studies just described were taking place, an important experimental tool for study of transition states was being developed by Neumark and his students at Berkeley (*9*): photodetachment spectroscopy applied to the negative ion precursor of the transition state species. Here, one uses light to knock an electron off of a negative ion in a vacuum chamber and then measures the distribution of kinetic energies of the electron (see figure). Because total energy is conserved, this also measures the energy distribution in the neutral photoproduct. Fortunately, FH_2^- has just the right structural properties to enable observation of the FH_2 transition state by photodetachment spectroscopy in that it is linear with F-H and H-H distances that are very close to those of the FH_2 saddle point.

In 1991, Weaver and Neumark (*10*) presented photodetachment spectra of FH_2^- and its isotopic counterparts FD_2^- and FDH^-, which created significant excitement in the reaction dynamics community. These spectra exhibited vibrational band structure that matched up well with the results of scattering theory calculations (*11*) done with the best surface available at that time (having a linear barrier). Included in the vibrational structure were peaks that were assigned to resonances, presumably the same ones implicated by Lee's molecular beam experiments. Variation of the measured peak locations with different isotope matched up well with the calculated values. Because photodetachment spectroscopy is most sensitive to the behavior of the potential near the maximum in the FH_2^- initial vibrational state shown in the figure, the variation implied that the transition state portion of the potential surface might be correct. However, it was known by that point that there were discrepancies in the theoretical description of the molecular beam experiments, thus setting the stage for the Manolopoulos *et al.* (*1*) work.

Recently, Bradforth, Arnold, Neumark, and Manolopoulos (*12*) provided more detailed photodetachment spectra by using pure *para* hydrogen (hydrogen with only even rotational quantum numbers) in making the FH_2^-. These new spectra allowed a more detailed comparison with theoretical simulations which revealed discrepancies between calculated and measured photodetachment spectra based on potential surfaces with either linear or somewhat bent saddle point geometries. This led to the Manolopoulos *et al.* collaboration (*1*) in which a potential surface from Stark and Werner was combined with accurate quantum scattering calculations done by Manolopoulos and was compared with improved *para* FH_2^- spectra from Arnold, Bradforth, and Neumark. Theory and experiment are now in excellent agreement with respect to details of those spectra, indicating that the transition state region of the potential surface is now accurately determined. There is still evidence for resonances in the calculated and measured spectra, but it is not known at this time if the previous discrepancies with the molecular beam experiments have been resolved with the new potential surface. However, the Manolopoulos *et al.* work appears to be the final chapter in the transition state of FH_2, and it provides confidence in the use of theory to characterize transition states of other reactions.

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