

REACTION DYNAMICS

The view from a transition state

Ejecting electrons from negative ions using light can create structures that very closely resemble the transition states of bimolecular reactions. Now, using this technique, trapped quantum states, or ‘resonances’, have been observed in a seven-atom reaction, and theory has been shown to be up to the task of capturing such complex phenomena.

Robert E. Continetti

The concept of the transition state playing a defining role in chemical reactions goes back to the advent of quantum chemistry, and is associated with names such as London, Eyring, Polanyi and others. Characterizing the transition state has been a longstanding goal for both experimental and theoretical physical chemists since the 1930s, and several different approaches have been taken. The most intuitive method by which to study reactions — and their transition states — experimentally is to induce a collision between the reactants under controlled conditions and closely monitor the products in some way, as has been done in crossed molecular-beam experiments. However, one of the most fruitful approaches for the preparation and study of the transition state does not follow this trope; rather, it relies on the measurement of the photoelectron spectra of negative ion complexes with geometries similar to, and characteristic of, the neutral transition state.

This technique was pioneered by Daniel Neumark and co-workers for bihalide hydrogen-exchange reactions 30 years ago¹. In the intervening years, the Neumark group has developed ‘anion photoelectron transition-state spectroscopy’ further and applied it to a range of increasingly complex systems. They have made use of cold anion precursors and a significant increase in spectral resolution through buffer-gas cooling of the parent anions and the development of the slow-electron velocity-map-imaging technique (SEVI). Now, writing in *Nature Chemistry*, Neumark and co-workers report their study of the seven-atom $F + CH_3OH \rightarrow HF + CH_3O$ reaction using these techniques, observing with unprecedented resolution the presence of quantum states near the transition state and excellent agreement between experimental data and quantum-mechanical calculations².

One recent highlight that emerged as a result of advances in the aforementioned techniques was the 2015 joint experimental and theoretical identification of ‘Feshbach resonances’ near the transition state for the

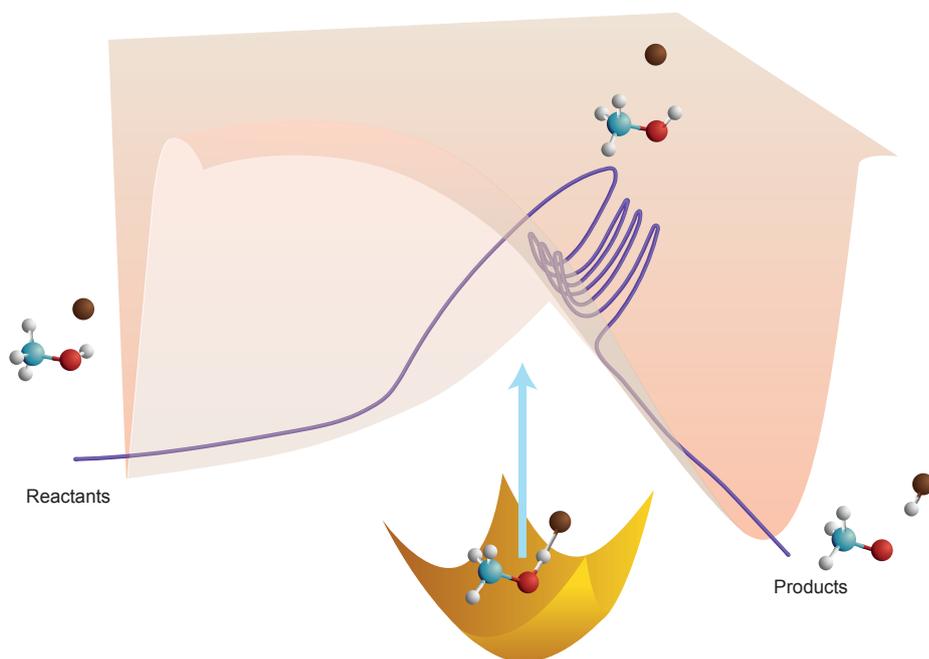


Figure 1 | Feshbach resonances in the $F + CH_3OH \rightarrow HF + CH_3O$ reaction. Rather than studying the direct reaction after inducing the collision of the reactants (as represented in the entrance channel of the potential-energy surface) the transition state is probed using anion photoelectron transition-state spectroscopy. A bound anion that structurally resembles the desired transition state is photodetached, launching the system onto the neutral potential-energy surface and inducing photoelectron emission. The photoelectron spectrum generated is used to identify ‘resonances’, which are transient, metastable quantum states that serve to trap the system near the transition state. The reaction dynamics are represented by the purple classical trajectory, and the inherently quantum mechanical resonances near the transition state are represented by the tangled trajectories near the top of the barrier.

prototypical $F + H_2$ reaction³. Feshbach resonances are transient, metastable quantum states that occur during the course of some reactions. Students during their first lectures in reaction dynamics are taught the simplified notion that reactions traverse an idealized linear trajectory along a simple (pictorially two-dimensional) reaction co-ordinate that features a reaction barrier at the transition state. It’s a helpful teaching aid; however, the situation is not so simple, and in the case of Feshbach resonances, such trajectories can get temporarily ‘trapped’ near the transition state, with the system

temporarily unable to make progress along the idealized reaction coordinate (Fig. 1).

These phenomena are extremely sensitive to the underlying potential-energy surface and probing them provides data that are fundamentally challenging for theoreticians to interpret. A single photodetachment experiment, by virtue of the spectrum of electron kinetic energies recorded, samples the neutral potential-energy surface over a range of configurations determined by the structure of the anion precursor. In photoelectron spectroscopy experiments, any long-lived resonances can be identified

by a structured photoelectron spectrum; however, interpretation of these transition-state ‘fingerprints’ depends on first-principles theory. State-of-the-art quantum chemical calculations are needed to determine the Born–Oppenheimer potential-energy surfaces that govern the interactions on both the anion precursor and the neutral surface, as well as high-dimensionality quantum dynamics calculations. It is for that reason that comparisons between these types of experiments and theoretical predictions play such an important role as benchmarks for theory. Hua Guo, co-workers and others have in recent years pushed these comparisons to the limit with an increasing diversity of global or nearly global anion and neutral potential-energy surfaces as well as the ability to carry out converged quantum wavepacket dynamics calculations on increasingly complex systems⁴.

The advances in theory, coupled with experimental developments, have paved the way for increasingly rigorous tests of more complex systems. Experimentally, the implementation of photoelectron–photofragment coincidence measurements on the $F^-(H_2O)$ anion have provided unique insights into the dynamics near the transition state for the four-atom $F + H_2O \rightarrow HF + OH$ reaction, including the correlation between the region of the transition state accessed in photodetachment, the partitioning of energy among the $HF + OH$ products and the experimental identification of stable and long-lived neutral complexes. Guo and co-workers provided the quantum dynamical insights (explicitly accounting for the full six dimensions) in that system to differentiate between direct and complex Feshbach resonance-mediated processes⁵.

The abstraction of hydrogen atoms by fluorine from more complex molecules

are examples of systems where a reaction coordinate can be conveniently defined even though the system has many more internal degrees of freedom. This brings us to the work reported by Neumark, Guo and co-workers described in *Nature Chemistry*, in which they have shown that in a much more complex system (namely the $F + CH_3OH \rightarrow HF + CH_3O$ reaction and specifically the CH_3OHF^- anion), exquisitely resolved transition-state photoelectron spectra can be measured and understood using first-principles theory. In the Neumark laboratory, the precursor anions can now be cooled down to 5 K; they take advantage of this to measure ultrahigh-resolution photoelectron imaging spectra. Their data reveal vibrationally resolved progressions that reflect the structure of the stable $F-H-OCH_3$ complex in the exit channel of the potential-energy surface as well as a manifold of Feshbach resonance states that correlate with the vibrational states of HF that are accessible in this exothermic reaction. An exact treatment of this 15-dimensional system remains beyond the state of the art, but using a reduced-dimensionality model explicitly considering six dimensions, they have shown that over a wide range of energies, essentially all of the vibrational fine structure related to the Feshbach resonances can be predicted. This represents an important benchmark for both quantum chemistry and quantum dynamics in the effort to study increasingly complex systems.

Is this the end of the road? Not by any means. Indeed the comparison between theory and experiment reported in this work degrades as the energy in the neutral complex by the departing photoelectron increases. This is perhaps as a result of a breakdown in the reduced-dimensionality model as the neutral complex is probed in regions of the

potential-energy surface at higher energies that are not characterized as well. In addition, it must be kept in mind that the theoretical treatment for the photodetachment process itself used in these studies is not complete (it is restricted to ‘s-wave photodetachment’ and does not explicitly solve the electron–molecule half-collision scattering problem of photodetachment or account for electron–molecule resonances). More complete experimental measurements, such as photoelectron–photofragment coincidence measurements with SEVI resolution would be valuable for further resolving the contributions of direct and complex-mediated dynamics.

Finally, we might ask what the practical significance of the role played by Feshbach resonances in more complex systems may be. Could their presence be used to control chemistry through photoexcitation of these transient collision complexes? Could they play a role in modulating chemistry at temperature and pressure extremes? These are all questions that a deep first-principles understanding of the dynamics of complex systems prepared near the transition state can ultimately answer, and the work of Neumark, Guo and co-workers represents an important milestone along that road. □

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NUCLEIC ACID NANOMATERIALS

Silver-wired DNA

DNA double helical structures are supramolecular assemblies that are typically held together by classical Watson–Crick pairing. Now, nucleotide chelation of silver ions supports an extended silver–DNA hybrid duplex featuring an uninterrupted silver array.

Pascal Auffinger and Eric Ennifar

To biochemists, who are accustomed to seeing monovalent (Na^+ , K^+) and divalent (Mg^{2+} , Ca^{2+}) ions associate with nucleic acids, some metals are just not meant to interact with DNA

double helices — silver is one of those. But chemistry is versatile, with rules that spread far beyond our current abilities to understand and manipulate them. As they describe in *Nature Chemistry*,

Jiro Kondo and co-workers¹ have played with those rules to synthesize an elegant and surprising structure of a silver-wired DNA double helix (Fig. 1). The structure was characterized by high-resolution