

# Chemical reaction dynamics

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Edited by Jack Halpern, University of Chicago, Chicago, IL, and approved June 4, 2008 (received for review June 2, 2008)

Understanding the motions of the constituent atoms in reacting molecules lies at the heart of chemistry and is the central focus of chemical reaction dynamics. The most detailed questions one can ask are about the evolution of molecules prepared in a single quantum state to products in individual states, and both calculations and experiments are providing such detailed understanding of increasingly complex systems. A central goal of these studies is uncovering the essential details of chemical change by removing the averaging over the initial conditions that occurs in many cases. Such information provides an exquisite test of theory and helps paint pictures of complicated chemical transformations. The goal of this Special Feature is to provide a snapshot of a portion of the field of chemical reaction dynamics. Much of the work presented here emphasizes a close interplay of experiment and theory in ways that sharpen the conclusions of both and animate future studies. The articles do not completely cover the rich field of chemical reaction dynamics but rather provide a glimpse of some of the emerging insights.

The Special Feature begins with two perspectives. One describes the use of quantum mechanical computations to discover the detailed mechanisms of bimolecular gas-phase chemical reactions (1), and the other discusses using vibrational energy to control chemical reactions in collisions of pairs of reactants and in collisions of a reactant with a surface (2). The research papers in the Special Feature fall into three broad categories: bimolecular reactions, energy flow in isolated molecules, and photodissociation of molecules and complexes. At the heart of all of these experiments and calculations is the specification of the conditions of the reaction, the understanding of the evolution of the molecules, and the determination of the nature of the final products.

A description of elegant molecular beam scattering experiments on a touchstone reaction,  $F + HD$ , shows the power of high resolution scattering experiments to observe quantum mechanical resonances in reactions (3). Both observation and calculation of resonances are great challenges, and this study shows the power of combining theory and experiment to understand them and to obtain a new potential energy surface for the reaction. Another molecular beam scattering study illustrates the insights that come from scattering molecules prepared in selected vibrational states and detecting products with full recoil energy and angular resolution (4). The detailed quantum state information in the experiment allows the inference of the evolution of the initially deposited energy during the course of the reaction and leads to a proposed generalization of simple rules about energy consumption and disposal. A third molecular beam scattering experiment probes the role of vibrational excitation in another class of reaction, metal atom insertion into a bond, and shows that vibrational excitation en-

hances the cross section of the reaction preferentially (5). A theme from both of the studies with vibrationally excited molecules is the ability to probe the consequences of depositing energy into different degrees of freedom.

One often learns about the motions during a reaction by observing products, but it is also possible to probe potential intermediates in a reaction. An example in this Special Feature is a spectroscopic study of the proposed intermediate in the reaction of hydroxyl radicals with nitric acid molecules,  $OH + HONO_2$  (6). Forming the complex and initiating its decomposition with infrared light permits the determination of both the vibrational frequencies and the binding energy of the complex and enables a careful comparison with calculations. Because this complex potentially influences the residence time of nitric acid in the lower atmosphere, the study is an example of the fundamental insights of chemical reaction dynamics connecting to practically important problems. Another example of observing individual quantum states to understand processes in a complex system is a study of the scattering of  $CO_2$  molecules from a liquid surface, an experiment using exceptionally sensitive, high resolution absorption spectroscopy of the scattered products (7). Again, computations in the form of molecular dynamics simulations play an important role in understanding these measurements.

Considering the role of initial excitation in reactions raises the question of the nature of excited molecules, and two papers in this Special Feature use spectroscopic techniques to probe energy flow in vibrationally excited molecules. A time-resolved study using infrared excitation and UV probing follows the flow of vibrational energy out of the  $NH_2$  moiety in 2-aminopyridine and its dimer (8). The vibrational energy flows from the  $NH_2$  symmetric stretch rapidly

through doorway states and, subsequently, more slowly into a dense set of bath states. Hydrogen bonding in the dimer shortens the vibrational lifetime of both the free and bound  $N-H$  stretches. A frequency domain study uses a new combination of infrared and Fourier transform microwave spectroscopy to observe the eigenstates of pent-1-en-4-yne in exquisite detail (9). Perturbations in the spectrum signal the presence of intramolecular energy flow, and careful analysis of the rotational structure in the ground and vibrationally excited molecules shows that the excited molecules isomerize and that the isomerization times are much longer than the predictions of statistical theories.

The third broad category of chemical dynamics discussed in this Special Feature is photodissociation, in which isolated molecules or clusters decompose after promotion to an electronically excited state. As several of the contributions show, photodissociation is another area where theory and experiment meet productively, both in illuminating the interactions among excited state potentials and in revealing the means by which the dissociation populates preferred quantum states. A study of the photodissociation dynamics of phenol and thiophenol demonstrates the power of determining the recoil energy of the fragments with high kinetic energy resolution (10). These experiments identify preferentially populated states of the fragments and, thus, obtain new insights into the behavior of molecules passing through a conical intersection between two excited state surfaces. The competition among dissociation pathways in sev-

Author contributions: F.F.C. wrote the paper.

The author declares no conflict of interest.

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eral electronic states is at the heart of the observed differences between the two molecules studied. Exploring the behavior of excited molecules evolving on multiple potential energy surfaces is the topic of a theoretical study that touches on many of the same issues but in hydrogen bonded complexes of pyrrole with pyridine (11). These complexes are potential models for excited state dynamics in DNA base pairs and are amenable to quantum chemical calculations that explore the dynamics on their multiple potential energy surfaces. Again, the interaction of multiple potential energy surfaces, including the formation of conical intersections, is an essential feature of the system.

A study of the photodissociation of diacetylene uses several excitation wavelengths, including one deep in the UV region, and observes the recoiling hydrogen atoms with ion imaging (12).

Information about the angular and recoil speed distribution of the fragments provides a view back into the decomposition and shows that it occurs by statistical decay after diacetylene converts to high levels of the ground electronic state. A measurement of the lifetime of the energized species potentially changes the picture of the role of diacetylene in the atmosphere of Titan, another example of fundamental chemical dynamics touching on topics that are, literally, far afield. Yet another example of both the practical impact of chemical reaction dynamics and the interplay of theory and experiment is a study of the decomposition of acetaldehyde after initial excitation to an excited state (13). The highly energized molecule that results decomposes by a pathway in which a methyl fragment almost departs but returns to pluck off a hydrogen atom to form vibrationally excited  $\text{CH}_4$  and  $\text{CO}$ .

Spectroscopic measurements observe the high level of excitation in methane, and trajectory calculations reveal the mechanism. This mechanism may be relatively common and, if so, could have important consequences for models of combustion reactions.

These studies point to the breadth and impact of chemical reaction dynamics, even though they encompass only a part of the field. Theoretical and experimental advances promise more new insights and more new connections to other fields, ranging from down-to-earth topics, such as combustion, atmospheric reactions, and biological systems, to heavenly ones, such as planetary atmospheres. The research described in this Special Feature illustrates the ability of chemical reaction dynamics to explore and explain molecular transformations in exquisite and informative detail.

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