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Quantum Theory of Chemical Reaction Dynamics

David C. Clary

It is now possible to use rigorous quantum scattering theory to perform accurate calculations on the detailed state-to-state dynamics of chemical reactions in the gas phase. Calculations on simple reactions, such as $H + D_2 \rightarrow HD + D$ and $F + H_2 \rightarrow HF + H$, compete with experiment in their accuracy. Recent advances in theory promise to extend such accurate predictions to more complicated reactions, such as $OH + H_2 \rightarrow H_2O + H$, and even to reactions of molecules on solid surfaces. New experimental techniques for probing reaction transition states, such as negative-ion photodetachment spectroscopy and pump-probe femtosecond spectroscopy, are stimulating the development of new theories.

Experiments and theory on chemical reaction dynamics aim to study the details of reactions beyond just simple rate constants at room temperature (*1*). Reactant and product molecules can have different translational energies, varying angles of orientation and different internal quantum states. Developing experiments and theory to study such microscopic aspects of chemical reactions, and to probe directly the structure and lifetimes of reaction transition states (*2*, *3*), has become a major field. The results provide the most detailed insight into the mechanisms of chemical reactions and are useful also in a variety of other contexts. For example, an understanding of both atmospheric (*4*) and combustion processes (*5*) can require data on the chemical reactions of molecules in selected vibrational quantum states, and modeling of the nonequilibrium environments of interstellar clouds (*6*) needs information on the reaction rates of molecules in selected rotational states for low collision energies.

Theory has a special role to play in chemical reaction dynamics as it is often essential for extracting useful information from experimental results. Furthermore, reaction dynamics theory can now provide detailed predictions with an accuracy that can rival experiment on simple reactions in the gas phase (*7*), and the theory has been extended, albeit more approximately, to more complex problems such as reactions of polyatomic molecules (*8*) and reactions on solid surfaces (*9*) and in solution (*10*).

Quantum Reaction Dynamics

The best theory of chemical reactions uses quantum mechanics. The Born-Oppenheimer approximation is usually invoked, allowing electronic and nuclear motion to be separated, so that a calculation reduces to two separate steps: solution of the Schrödinger equation for the electrons with fixed positions of the nuclei to obtain a potential energy surface, followed by solution of the "quantum scattering" Schrödinger equation for the nuclei moving on this potential energy surface.

Significant advances in ab initio quantum chemistry techniques are enabling potential energy surfaces to be calculated to a high accuracy for simple reactions (*11*). However, one problem is that reaction rate constants $k(T)$ often depend exponentially on the height E_a of the barrier in a potential energy surface according to the Arrhenius expression $k(T) = A\exp(-E_a/RT)$, where A is a constant, R is the gas constant, and T is temperature. This exponential dependence shows that E_a needs to be calculated extremely accurately. This constraint presents a major problem for quantum chemistry calculations on reactions involving molecules with several electrons.

In a quantum scattering calculation on a chemical reaction $A + BC(v, j) \rightarrow AB(v', j') + C$ in the gas phase, it is necessary to use coordinates that go smoothly from reactants to products and can describe the initial (v, j) and final (v', j') vibration-rotation molecular states accurately. Devising the most appropriate coordinates has not been straightforward. A useful "hyperspherical coordinate" approach is to take the bonds being broken and formed in the reaction and transform them into polar coordinates (ρ, θ) (*12*). The "hyper-radius" ρ has the advantage that it can be used as a common scattering coordinate for both the entrance and exit channels of the reaction. The time-independent Schrödinger equation $H\Psi = E\Psi$ can then be solved, and scattering boundary conditions can be applied to calculate reaction probabilities selected in all of the vibration-rotation states of reactants and products and with well-defined collision energy. This method has been used quite widely on reactions involving three atoms (*13*) and has also recently been applied to four-atom reactions (*8*).

A different approach is to solve the time-dependent Schrödinger equation for the nuclear motion. This method has the computational advantage that reaction out of individual reactant quantum states can be computed efficiently (*14*). However, it has been difficult until recently to extend this "wave packet" technique to calculate state-to-state reaction probabilities. Therefore, total reaction probabilities summed over all product states are often computed.

The large number of coupled vibrational and rotational states of molecules that can be involved in chemical reactions has made the solution of the nuclear Schrödinger equation computationally expensive. Therefore, the field of theoretical reaction dynamics has had to wait for the modern generation of fast computers with large memory capabilities before reliable calculations have been possible. This is why the field of quantum reaction dynamics is now suddenly blossoming.

Simple Reactions

How well does the best theory do when compared with the best experiments? One of the simplest chemical reactions is $H + D_2(v = 0, j = 0) \rightarrow HD(v', j') + D$. This reaction has been studied in one of the most detailed experiments that can be performed, crossed–molecular beam experi-

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ments, which measure "angular distributions," the direction of state-selected product HD with respect to the initial direction of the center of mass of the reactants (*15*). For low energies, most reactive collisions give product HD moving backward, in the direction opposite that of the reactants, whereas higher energies enable the product HD to move forward. For reactions into particular product states of HD(v', j') at intermediate collision energies, the angular distribution is determined by a subtle balance between these collision energy effects and the energy and angular momentum of the particular (v', j') state of the HD product. Therefore, measurements of these angular distributions provide a severe test of both the potential energy surface and quantum scattering method used in the calculations.

Comparison (Fig. 1) of experimental measurements (*15*) and quantum scattering predictions using the most accurate potential energy surface (*16*) gives essentially perfect agreement for the angular distributions of $H + D_2(v = 0, j = 0) \rightarrow HD(v', j') + D$ for all scattering angles and j' values. Similar excellent agreement between theory and experiment is also found between calculated and measured rate constants for this reaction (*17*). Comparisons such as these on this simplest prototype reaction demonstrate that the first-principles quantum mechanical predictions are as accurate as the results from the best experiments. The major challenge to the field is to extend this reliable predictive ability to more complicated reactions.

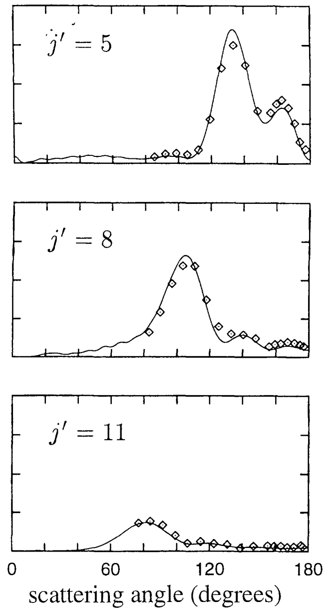

Fig. 1. Predicted (line) (*16*) and experimental (diamonds) (*15*) angular distributions for the reaction $H + D_2(v = 0, j = 0) \rightarrow HD(v' = 1, j') + D$ plotted against the scattering angle. The angular distribution represents the probability of the reaction occurring into a particular scattering angle for the HD products with respect to the direction of the momentum of the reactants. The initial translational energy of the colliding reactants is 1.29 eV. The predicted results are taken from quantum scattering calculations on an accurate potential energy surface (*16*).

Similarly impressive agreement between theoretical predictions and experiment has been obtained for the $F + H_2 \rightarrow HF + H$ reaction (*18*). An informative experimental technique (Fig. 2) has been developed to probe the transition state of reactions such as this (*3*). The experiment involves starting with a beam of negative ions FH_2^-, exciting the ions with a photon having enough energy to remove the electron, and measuring the intensity of detached electrons as a function of their kinetic energy. The products are neutral $F + H_2$ or $HF + H$, and the "photodetachment spectrum" reflects the dynamics on the neutral reactive potential energy surface close to the transition state (Fig. 2). Quantum dynamics calculations (*19*), with highly accurate potential energy surfaces for the parent ion and neutral product, model the complicated structure of this photodetachment spectrum almost within experimental error (Fig. 3) (*20*). The calculations also show that the photodetachment products are mainly $F + H_2$, with the peaks in the photodetachment spectrum correlating with excited rotational states of product $H_2(v, j)$.

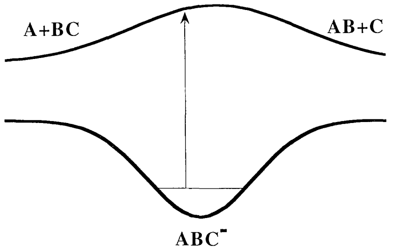

Fig. 2. Schematic diagram of the photodetachment process $ABC^- \rightarrow AB + C + e^-$. If the geometry of the parent ion ABC^- is similar to that for the transition state of the $A + BC \rightarrow AB + C$ reaction, then this process is a direct way to probe experimentally the transition state of a chemical reaction.

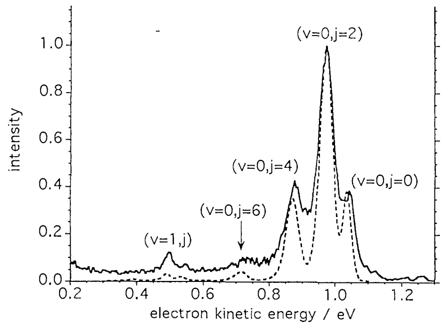

Fig. 3. Experimental (solid line) (*20*) and quantum scattering calculations (dashed line) [from figure 1 of (*19*)] of the photodetachment spectrum for FH_2^-. The calculations show that the peaks in the spectrum correspond to excitation into different (v, j) states in the products $H_2(v, j) + F + e^-$.

It should also be noted that quantum reaction dynamics calculations provide definitive results that can be used to test the accuracy of more approximate theories. For example, such comparisons have shown that classical mechanics works surprisingly well at describing most of the details of chemical reactions such as $F + H_2 \rightarrow HF + H$ (*21*).

Polyatomic Reactions

Given the significant advances in applying quantum theory to reactions involving three atoms, extension of the quantum scattering theory to reactions involving polyatomic molecules has become an active area. The first such calculations were on the reactions $H + HCN \rightarrow H_2 + CN$ and $OH + H_2 \rightarrow H_2O + H$, with the approximation of neglecting some degrees of freedom that describe chemical bonds not broken or formed in the reaction (*22*). Recent theoretical advances are now enabling calculations to be done on such reactions with no dynamics approximations at all.

A remarkable range of experiments has been done on the reaction $OH + H_2 \rightarrow H_2O + H$, and its reverse reaction $H_2O + H \rightarrow OH + H_2$, that probe almost every part of the potential energy surface (Fig. 4). These investigations include studying the effect on the reaction of exciting initial vibrational states of OH and H_2 (*23*), examining the most likely vibrational states of H_2O that are produced in the reaction (*24*),

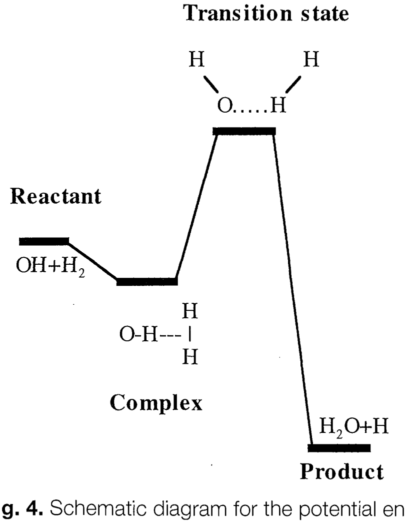

Fig. 4. Schematic diagram for the potential energy surface profile for the reaction $OH + H_2 \rightarrow H_2O + H$.

studying the influence of different vibrational states of H_2O on the reverse reaction (bond-selected chemistry) (*25*), measuring angular distributions for the reaction using both molecular beams and polarized lasers (*26*), scattering hot H atoms off H_2O (*27*), and performing spectroscopic measurements on the OH-H_2 van der Waals prereaction complex (*28*). Experiments have also been performed on the photodetachment of electrons from H_3O^- to probe the dynamics of the $OH + H_2 \rightarrow H_2O + H$ reaction (*29*).

Various types of calculations have been performed to compare with essentially all of these experiments (*8*). For example, the photodetachment experiments on H_3O^- (*29*) are well described (Fig. 5) by a theory that involves bound-state calculations for H_3O^- and quantum scattering computations on the reaction $OH + H_2 \rightarrow H_2O + H$ using potential energy surfaces calculated with the use of quantum chemistry methods (*30*). The theory confirms that the photodetachment experiment on this system starts from two isomeric ions with different geometries, corresponding to H_3O^- and $(OH)^- H_2$, and these geometries each result in different products, $H_2O + H$ or $OH + H_2$, to the right or left of the transition state of Fig. 4, respectively (*29*, *30*). The theory also shows that it is excited vibrational or rotational states of these product molecules that produce the structure in the observed photodetachment spectra (Fig. 5).

The $OH + H_2$ reaction has recently served as a benchmark to stimulate new quantum theories of chemical reaction dynamics capable of treating several degrees of freedom explicitly. For example, a new accurate quantum method that requires treatment of only the reaction geometries close to the transition state was successfully applied to give accurate total reaction probabilities summed over all initial and final states (*31*). Also, time-dependent wave-packet techniques (*32*) and methods involving negative imaginary potentials (*33*) have been cleverly used to calculate total reaction fluxes into particular arrangement channels. Coordinates specially tailored for this type of reaction, such as arrangement channel hyperspherical coordinates (*34*) and recent time-dependent methods (*35*), are now enabling the full state-to-state reaction probability matrix to be computed.

The combination of developments in quantum chemistry for calculating potential energy surfaces and the new reaction dynamics theories will enable useful calculations to be done on even more complicated reactions in the near future. Indeed, the reaction dynamics methods have recently been extended to the state-selected dissociative chemisorption reaction of H_2 molecules on copper surfaces, treating six degrees of freedom explicitly (*36*). This system has become a benchmark for both calculations and experiments on molecule-surface reactions.

Time-Resolved Dynamics

A major recent experimental advance has been the ability to use time-resolved pump-probe laser methods to study chemical processes occurring on a time scale of femtoseconds (10^{-15} s) (*37*). Reactive scattering theory has also been developed to help understand the results of such experiments that can probe directly the transition states of chemical reactions. The reaction $OH + CO \rightarrow CO_2 + H$ is one of the key reactions in both combustion and atmospheric chemistry and has been shown in these experiments to produce a "HOCO" reaction complex that has a lifetime of about 10^{-12} s (*38*). Several reaction dynamics calculations give lifetimes of this order of magnitude (*39*), and calculations also show that the lifetimes vary significantly with different excited vibrational states of the HOCO complex (*40*).

Studies such as these demonstrate that understanding detailed time scales of reactive processes, as opposed to rate constants or cross sections, is leading to new ways of visualizing bonds being broken and formed in chemical reactions. Indeed, the femtosecond spectroscopy experiments have recently been extended to the measurement of the fast time scales of colorful reactions ranging from bond breaking in dimetal carbonyls (*41*) to double proton transfers in DNA base mimics (*42*). Extension of good theory to such systems is an exciting challenge (*43*).

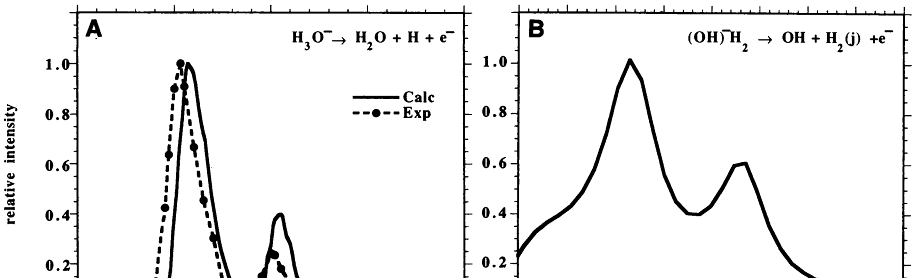

Fig. 5. (**A**) Photodetachment spectrum for $H_3O^- \rightarrow H_2O + H + e^-$ obtained in experiment (circles) (*29*) and quantum scattering calculations (solid line) (*30*). The theory shows that the peaks correspond to excitation of different vibrational states of product H_2O. (**B**) Calculated photodetachment spectrum for $(OH)^- H_2 \rightarrow OH + H_2(v, j) + e^-$ (*30*). Here, the peaks correlate to excitation of different rotational states of product H_2.

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Gas-Phase Ionic Reactions: Dynamics and Mechanism of Nucleophilic Displacements

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Nucleophilic displacement reactions (the S_N2 reaction) of ions in the gas phase are a prototypical reaction system that allows a study of dynamics, mechanisms, and structure-energy relations. This article reviews aspects of the kinetics (especially the applicability of statistical reaction rate theory), the relation of structure and reactivity, and the effects of small numbers of solvent molecules on the reaction and compares the behavior of the ionic reaction in the gas phase with that in solution.

The study of reaction mechanisms plays an important role in chemistry. By understanding the details of the pathways and structural effects in reactions, chemists not only learn how to control them to obtain products of interest, but also discover and invent new chemistry. Ions are used extensively in organic reaction chemistry as reactants, intermediates, and catalysts because they are highly reactive. The solvation energies of ions can be very large, often hundreds of kilocalories per mole, so differences in solvation energy can easily mask differences in intrinsic reactivity between similar species (*1*). Thus, by studying ionic reactions in the gas phase, without solvent, we can learn about the intrinsic behavior in ionic reactions and thereby expose the role of the solvent. Furthermore, by studying the effect on these reactions of adding solvent molecules one at a time (microsolvation), we can learn how reaction dynamics and potential energy surfaces (PESs) change with increasing solvation.

In this overview, we concentrate on the S_N2 reaction, $X^- + RY \rightarrow RX + Y^-$, as a representative reaction involving ionic species. It has been widely studied and is an important reaction for interchanging functional groups and for forming carbon-carbon bonds or activating the molecule for this purpose. We have drawn extensively from our own work, as in a review of this length it is impossible to do justice to all of the important, recent organic mechanistic work from other laboratories (*2–5*) .

The PES for gas-phase S_N2 reactions is now widely believed to be a double-well potential (*1*), in contrast to the situation in solution (*6*) (Fig. 1). The transition state for the S_N2 displacement step (k_2 in Fig. 2) has a tighter configuration and thus entropically less favorable than the transition state for formation or dissociation of the complex (k_{-1} in Fig. 2), so reactions that proceed with measurable rates must typically have transition state energies for the displacement step that lie below the energies of the reactants. Because the energies of intermediates and transition states lie below the energies of the initial reactants, and because gas-phase reactions are often best carried out at low pressure where the intermediates cannot be stabilized, the determination of the transition state energy is more difficult than is the case in solution. Early studies showed that when a complex was formed between methyl chloride and a chloride ion, the chloride that was added could be transferred to another neutral molecule, whereas the chloride in the methyl chloride retained its identity and was not transferred (*7*). Although these halide–methyl halide complexes correspond to intermediates in reactions, the barrier to reaction is sufficiently high that they are effectively unreactive in the displacement process. Recently, it has been possible to characterize S_N2 reactions more completely. Both reactant and product complexes in unsymmetrical reactions have been isolated and shown to be different (*8*, *9*), and it has been possible to activate the reactant complex with infrared multiple photon irradiation (*8*) or by collisions (*9–11*) and complete the reaction. In addition, Dessent and Johnson have cooled the S_N2 ion-dipole complex in a supersonic expan-

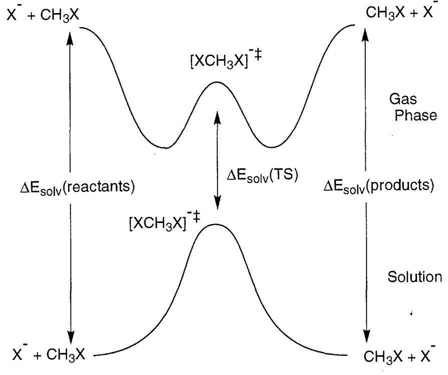

Fig. 1. Gas-phase and solution PES for the S_N2 reaction.

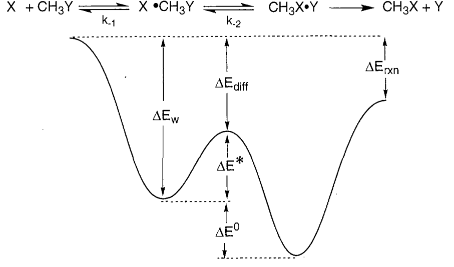

Fig. 2. PES for a generic gas-phase S_N2 reaction.

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