Abstract: The field of gas-phase chemical dynamics has developed superb experimental methods to probe the detailed outcome of gas-phase chemical reactions. These experiments inspired and benchmarked first principles dynamics simulations giving access to an atomic scale picture of the motions that underlie these reactions. This fruitful interplay of experiment and theory is the essence of a dynamical approach perfected on gas-phase reactions, the culmination of which is a standard model of chemical reactivity involving classical trajectories or quantum wave packets moving on a Born–Oppenheimer potential energy surface. Extending the dynamical approach to chemical reactions at surfaces presents challenges of complexity not found in gas-phase study as reactive processes often involve multiple steps, such as inelastic molecule-surface scattering and dissipation, leading to adsorption and subsequent thermal desorption and or bond breaking and making. This paper reviews progress toward understanding the elementary processes involved in surface chemistry using the dynamical approach.

Key points:

- The fruitful interplay between chemistry and physics leads to an atomic scale view of reactions taking places at catalytically active surfaces.
- Improved observations of chemical reactions taking place in complex environments drive the development of new approaches to theoretical chemistry.
- Complex reaction networks from real catalysts are boiled down to their elementary steps and examined from first principles.

KEYWORDS
dynamics, catalysis, graphene, lasers, surface science
problems in surface chemistry, which may often seem impenetrably complex and challenging.

THE ORIGINS OF CHEMICAL DYNAMICS

Seeds leading to the emergence of the field of chemical dynamics were clearly sown during the whirlwind of progress ushered in by the discovery of quantum mechanics, which stirred the pot of physical chemistry with the prospect for a vastly improved understanding of microscopic objects. In 1928, the then dominant journal of physical chemistry, Zeitschrift für physikalische Chemie, split into two. The editors declared their intent to foster the research energy of physics and chemistry necessary to solve the difficult interdisciplinary problems posed by the new journal. In what would become a defining aspect of chemical dynamics, the editors ardently sought contributions from theoretical physicists. And the physicists were eager to contribute.

Dirac set the tone in a seminal paper declaring that "...the underlying physical laws necessary for the mathematical theory of... ...the whole of chemistry are thus completely known." He emphasized that "approximate practical methods of applying quantum mechanics should be developed" as the fundamental equations were too difficult to solve. Born and Oppenheimer successfully reduced the molecular Schrödinger equation to a nuclear wave equation governed by an effective electronic potential, the potential energy surface (PES). This set the stage for Henry Eyring and Michael Polanyi in 1931 to produce the first PES for a chemical reaction—see Figure 1. Theoretical chemistry was well underway as a burgeoning field reaching perhaps its most important milestone, the so-called absolute theory of reaction rates. Chemists now had not only the mathematical theory of chemistry, but in addition, new chemical concepts—for example, PESs and transition states—defined in terms of fundamental physics.

Despite this profound conceptual progress, a cloud hung over this field for decades to come, as only limited means existed to test the approximations introduced by theorists, tests that would be needed to prove that the theories had practical value. By 1933, the Journal of Chemical Physics (JCP) had published its first issue and, reflecting the tentative nature of the young field, its first editor Harold Urey wrote, "...The methods of investigation used are, to a large extent, not those of classical chemistry and the field is not of primary interest to the main body of physicists..." The fact was that methods of experimental verification and numerical simulation lagged dramatically behind the conceptual breakthroughs of the quantum era. This was to change soon and JCP would become the vanguard forum showing the successes of converging the methods of physics with problems of chemistry.

THE EXPERIMENTAL BASIS FOR MODERN CHEMICAL DYNAMICS

The second half of the 20th century witnessed a revolution for the atomic scale viewpoint of chemistry, as molecular spectroscopy, the laser, molecular beams, and high-power computing established themselves as critical tools for probing molecular motions.

Infrared emission spectroscopy

Even before masers and lasers introduced the concept of a population inversion, scientists had evidence of molecules in the atmosphere and in the laboratory with quantum state population distributions far from thermal equilibrium, a glittering signpost for the importance of dynamical processes. Emission spectra from the night sky which could be recorded on photographic plates showed OH(ν =6–9)—the same spectra were seen using flash photolysis to drive the reaction H + O3 → OH(ν) + O2. Similar methods revealed reactions that produced highly vibrationally excited O2 and N2. This field accelerated dramatically with the advent of infrared chemiluminescence, which revealed vibrationally excited HCl produced in the reaction of H+Cl2.

New dynamical concepts also emerged, notably the "Polanyi Rules"—see Figure 2. These state that for exothermic reactions, an energy barrier located early along the reaction path will preferentially produce vibrationally excited products, whereas a late barrier will likely lead to higher product translational energy and require reactant vibration to proceed efficiently. Work in this direction also led to clear ideas about how chemical reactions can produce population inversions and a prediction that a chemical laser could work based on a "partial" population inversion. This prediction was realized only a few years later, exploiting the H + Cl2 → Cl + HCl(ν > 0) reaction to produce a vibrational population inversion.
Laser-induced fluorescence and resonance-enhanced multiphoton ionization

The inventor of the ruby laser\(^{38}\) once described the laser as “a solution seeking a problem.”\(^{50}\) Chemical dynamics had the problems! Due to the ease of constructing gas discharges, c. w. and pulsed “line tunable” lasers using He, Ne,\(^{51,52}\) Ar or Kr,\(^{53}\) and N\(_2/\text{CO}_2,\)\(^{54,55}\) were the first sources of laser light used in this field. Their application quickly led to a new technique that marked a sea change in chemical dynamics, laser-induced fluorescence (LIF).\(^{56}\) This technique enabled quantum-state resolved studies that quickly became a major focus of experimentalists. While LIF was first detected as spontaneous infrared emission produced after infrared laser excitation,\(^{57–59}\) its true potential became evident only after a HeNe laser was used to excite K\(_2\) and this molecule’s emission spectrum was photographically recorded behind the Berkeley 21-foot concave grating.\(^{60}\) Soon after, LIF was detected by a photomultiplier\(^{61}\) and lifetimes of excited electronic states were derived with a phase shift method.\(^{62}\) By observing LIF while tuning a dye laser,\(^{63,64}\) background-free laser excitation spectra were demonstrated—this method was so sensitive that it could be exploited to probe the internal state distribution of reaction products\(^{65}\) and later even to obtain state-resolved angular distributions of reaction products.\(^{66,67}\)

The pulsed ruby laser provided such high peak powers that multiphoton ionization of atoms\(^{68–70}\) could be demonstrated including resonance enhancement.\(^{71}\) Applied first to molecules as a 1+1 resonance enhanced multiphoton neutralization of a 1-keV beam of C\(_2\), a spectrum was obtained by detecting neutral C\(_2\) as a function of the laser wavelength.\(^{72}\) Resonance enhanced multiphoton ionization (REMPI) was first demonstrated using C\(_5\)).\(^{73}\) Soon thereafter, the 3+1 REMPI spectrum of NO \(^{74}\) and the 2+1 REMPI spectrum of I\(_2\))\(^{75}\) were reported followed by REMPI spectra of larger polyatomics.\(^{76,77}\)

Molecular beams

Molecular beams became another vital piece of the experimental tool-box of chemical dynamics—the high-energy physicists’ scattering experiments using charged particles and accelerators were being transitioned to the study of ion–molecule reactions at low, chemically relevant energies.\(^{79,80}\) Reactions could now be studied by crossed molecular beams methods.\(^{81}\) Figure 3 shows an instrument that detects reaction products resulting from the collisions between molecules in two different beams. The densities of the two beams ensured that within the crossing volume of the beams, at most, one collision could occur and the products could escape collision free.

The data observed with this instrument provided the product flux–map in the center-of-mass frame of the reacting molecules. Figure 4 shows an experimentally derived flux map for the F + H\(_2\) → HF(\(v\)) + H reaction.\(^{82}\) Several vibrational states of HF could be resolved and their flux-maps obtained. Experimental observations like these provided attractive targets for the developing field of theoretical chemical dynamics.

Applying external electric fields to polar molecules in low J-states produced molecular beams of oriented molecules and observations of steric effects in chemistry.\(^{83}\) Using pulsed electric fields, deceleration of molecular beams also proved possible,\(^{84,85}\) improving our ability to study quantum effects in collisions between molecules.\(^{86}\) But REMPI detection in combination with the power of molecular beams proved pivotal,\(^{87}\) setting the stage for what was to become one of the most important tools for chemical reaction dynamics, ion imaging.\(^{88}\)

Ion imaging

Ion imaging became possible by applying REMPI to reaction products and detecting them with position sensitive (electron multiplier...
The universal crossed molecular beam machine—nicknamed "Hope." The reaction $\text{H} + \text{Cl}_2 \rightarrow \text{Cl} + \text{HCl}(v)$ as well as many others was observed under "single collision conditions" with this instrument. Laboratory frame scattering data yield the center-of-mass frame product flux-map. See Figure 4. The use of electron bombardment ionization with quadrupole mass spectrometry made product detection "universal," opening the field to the diversity of phenomena that defines chemistry. Reprinted from McDonald JD, Lebreton PR, Lee YT, Herschbach DR. Molecular Beam Kinetics: reactions of deuterium atoms with halogen molecules. J Chem Phys. 1972;56(2):769-788, Copyright 2021, with permission from the AIP Publishing

Like detectors. Ion imaging is a method that provides sensitivity to product angular and speed distributions that had previously only been possible using molecular beam machines with rotating mass spectrometers. It not only represented a dramatic simplification over the universal crossed molecular beam machine, it provided entirely new capability. The method was quickly applied to both products of photodissociation as well as bimolecular reactions and became even more attractive when velocity map imaging demonstrated that speed and angular distributions could be obtained with high resolution. In its initial incarnations, analyzing ion images required that the plane of the ion camera be parallel to a cylindrical symmetry axis of the three-dimensional product distribution, a requirement that is often difficult to fulfill. With the advent of "slice imaging" in 2001, this requirement was relaxed and has over time become the method of choice for problems in chemical dynamics.

**COMPUTATION COMPLETES THE DYNAMICAL APPROACH**

With these new experimental tools, exquisite observations of elementary chemical reactions became available, but it was only with the advent of high power computing that the field could reach its potential, as cooperation between experiment and theory became increasingly valuable.

The extraordinary growth in the capabilities of computers has thoroughly transformed theoretical chemistry; however, the development of efficient and accurate algorithms has been at least as important. The calculation of PESs has evolved from empirical and semi-empirical models, to Hartree–Fock theory, to wavefunction-based methods that include electron–electron correlation, such as valence-bond, Möller–Plesset perturbation, coupled-cluster, and configuration interaction theories. In parallel, density functional theory (DFT) has emerged within a "sweet spot," balancing accuracy with affordability for larger molecular systems. Machine learning algorithms now provide efficient and accurate fitting of high-dimensional PESs to ab initio energies.

Methods for tracing out the atomic motions governed by PESs have also advanced, from classical mechanics, to time-independent quantum scattering theory, to time-dependent wave-packet motion. Classical mechanics remains the workhorse, especially on-the-fly methods that compute the classical forces as the trajectory proceeds, usually by DFT. The design of algorithms has adapted to hardware advances like parallel computing and the use of graphical processing units as computational engines. Widely available
The quantum H+H2→H2+H reaction and the standard model of reactivity

The simplest chemical reaction—H+H2→H2+H—became the test system for detailed and quantitative comparisons between theory and experiment\(^{112,113}\) three decades after Eyring and Polanyi’s PES (Figure 1). The first modern dynamical calculations used a computer with 2800 vacuum tubes and weighing five tons\(^{40,114}\) to solve Newton’s equations on Eyring and Polanyi’s 1931 semi-empirical PES. They found that both reactant translation and vibration promoted reaction. The first successful crossed-beam experiments for D+H2→HD+H reaction\(^{115}\) stimulated further theoretical advances: the reaction cross-section versus energy was calculated with classical mechanics\(^{105}\) using an improved semi-empirical PES.\(^{116}\) Soon, quantum dynamics calculations using time-independent scattering theory on semi-empirical PESs appeared, first with approximations\(^{106,117}\) and then with numerically exact solutions.\(^{107,118}\) Quantum mechanical resonances were predicted\(^{119}\)—peculiar oscillations in the reaction probability’s dependence on collision energy that arise because a piece of the wave packet becomes stalled at the transition state. Theory also predicted quantized bottleneck states (QBS),\(^{120}\) where wave-packet motion through the quantized transition state produces interferences.

Experiments, however, turned out to be tremendously challenging—one group used beams of tritium to investigate H+T2→HT+T capturing the T-atom products on MoO3 “buttons” arranged around the reaction zone. By later scraping off the MoO3 and analyzing the samples with a scintillation counter, angular distributions could be derived.\(^{121}\) Eventually, angular distributions of scattered products could be seen using electron bombardment ionization detection.\(^{122}\) This showed that the transition state was short lived and products formed by a rebound mechanism. Soon, nascent low-resolution product speed distributions were obtained.\(^{123,124}\) Resolution was dramatically improved by photolyzing D2S, providing D atom beams with relatively narrow speed distributions. When reacted with H2, angular and speed distributions exhibited multiple peaks, corresponding to individual vibrational states of the HD product.\(^{125,126}\) Photolyzing DI led the first CM contour plot of scattered product flux for the D+H2→HD+H reaction and a comparison to theoretical predictions could be made.\(^{127}\) This work also suggested how quantum resonances might be detected.\(^{128}\)

The Rydberg-atom tagging method was the next experimental advance. Here, H or D atom products are pumped with two laser pulses to a high Rydberg state only a smidge below the ionization limit, using a two-photon transition, for example, \(1s \rightarrow 2p \rightarrow 4s\). The metastable neutral is immune to space charge and stray fields and can be easily ionized and detected after a long (\(<25\) cm) flight distance, providing extraordinarily high-resolution measurements for obtaining H and D atom translational energies. When combined with photolytic D atom sources, Rydberg tagging provides an excellent experimental test of theory: the HD(v,J) ro-vibrationally state-resolved differential scattering angular distributions for the D+H2→HD+H reaction.\(^{129}\) When compared to the best calculations then available, it could be seen that quasi-classical trajectory (QCT) simulations worked well at \(E_i = 1.29\) eV, but not at \(E_i = 0.53\) eV.\(^{130}\) Also, some PESs worked better than others.\(^{131}\)

The influence of quantum mechanics on the H3 reaction is profound. Applying the Rydberg tagging approach led to direct observation\(^{123,124}\) of the influence of the predicted QBS-states.\(^{120}\) Perhaps most spectacular are observations of Berry’s phase\(^{135}\) influencing the reaction. When three H-atoms are arranged in an equilateral triangular geometry, the two lowest electronic states, \(\varphi_1\) and \(\varphi_2\), are degenerate as they are forbidden by symmetry to interact with one another, \(\langle \varphi_1 \mid \hat{H} \mid \varphi_2 \rangle \equiv 0\). On the other hand, at all nonsymmetric structures, the two states mix and split. This gives rise to a “conical intersection” marked with an \(x\) in Figure 5(a). In fact, conical intersections are very important in chemistry.\(^{136-139}\) For the DHH isotopologue shown in Figure 5, reaction can occur via two pathways: the red pathway is a simple abstraction of green H by brown H, while the green pathway involves...
Quantum interference through a conical intersection: (a) a cut through the HHD PES showing the conical intersection (×) and three transition states (T) that connect three stable arrangements of the atoms. Note the color of the atoms. Direct abstraction visits one transition-state (RED ARROW), while the spiral or roaming reaction visits two (GREEN ARROW). Both paths lead to the same products. (b) The experiment (∙) detects reactive flux arriving in the backward scattering direction producing $\text{H}_2(\nu' = 2, J' = 3)$ as the incidence energy is scanned. The oscillations are due to quantum interference between the two topological pathways. The red line shows quantum scattering calculations that neglect the phase-shift of $\pi$ (geometric phase) introduced by traversal around a conical intersection. The blue curve accounts for the geometric phase. Reprinted from Xie Y, Zhao H, Wang Y, et al. Quantum interference in $\text{H} + \text{HD} \rightarrow \text{H}_2 + \text{D}$ between direct abstraction and roaming insertion pathways. Science. 2020; 368(6492):767, Copyright 2021, with permission from AAAS

a failed reactive attack of brown H on D followed by a complex internal rearrangement (sometimes called a spiral reaction) allowing abstraction of green H by brown H. Since the identical products, $\text{H}_2 + \text{D}$, formed via two pathways, interference arises.

But beyond this, quantum mechanics requires that when a conical intersection is traversed, the phase of the quantum flux passing on opposite sides of the conical intersection must be shifted by $\pi$ with respect to one another—Berry’s phase. Obviously, this affects the interference. These observations relied on Rydberg-atom tagging, but REMPI-based methods like ion imaging and Photoloc have also been crucial to revealing the dynamics of this system. The basis of this success and the others that space does not allow us to present is the concept that chemical reactivity involves quantum mechanical motion of nuclei on a Born–Oppenheimer PES. The remarkable agreement between the predictions of the theory and the observations from experiment earns this concept the name the standard model of chemical reactivity.

Classical roaming reaction

The standard model affords the possibility of computing and illustrating the time-dependent motions of individual atoms through a chemically reactive encounter by following, for each atom, either the classical mechanical position or the quantum mechanical expectation value of position. It is even possible to make movies of reactions using calculated trajectories, effectively providing a microscope with time and space resolution far better than will ever be experimentally possible. One of the most inspiring examples of this is the gas-phase roaming reaction, first reported in the unimolecular decomposition of $\text{H}_2\text{CO}$. Following up on suspicions that the reaction $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ may proceed by more than one mechanism, ion imaging applied to obtain speed and angular distributions of specific rotation-vibration states of $\text{CO}(\nu, J_{\text{CO}})$ showed that when CO is produced with low rotational excitation, $\text{H}_2$ is produced with low speed and high vibrational excitation, and vice versa. Using a six-dimensional Born–Oppenheimer PES to calculate classical trajectories, theory reproduced the experimental observations—compare blue and black curves. There are two classes of trajectories; one reveals a concerted molecular elimination of $\text{H}_2$ achieved by passing over a barrier. This
channel leads to low vibrational states of H₂ and high rotational states of CO.

The second class of reactions is shown in Figure 7. Here, a highly excited formaldehyde molecule breaks one of its C-H bonds, but with insufficient energy for the H atom to escape. It orbits about the HCO excited formaldehyde molecule breaks one of its C-H bonds, but with reaction in CH₂O decomposition with H (green), C (white), and O (red). Note the high vibrational excitation of H₂ products seen also experimentally. Used with permission of Arthur Suits and Joel Bowman.

**Electronically nonadiabatic dynamics**

The reaction of H⁺ + H₂ → H₂⁺ + H appears superficially simpler than the H₃ reaction→H₃⁺ has one less electron. However, looks may deceive—this reaction may occur in three ways. Isotopic labeling helps illustrate this. Reacting H⁺ with D₂ may involve ion exchange, producing HD + D⁺, electron transfer, producing H + D₂⁺, or ion exchange with electron transfer, forming HD⁺ + D. We need to extend the standard model to consider the quantum motion of protons influenced by an avoided intersection between the two lowest energy electronic states of H₃⁺.

In a reactive encounter, the nonadiabatic coupling—Figure 8(d)—is defined as:

\[
\mathbf{D}_{12} = \langle \varphi_2 | \nabla \varphi_1 \rangle
\]

and controls the probability of a transition between the two PESs. Here, \( \varphi_1 \) and \( \varphi_2 \) are the adiabatic wave functions and \( \nabla \) defines the positions of the nuclei. \(|\mathbf{D}_{12}|^2\) is a measure of how rapidly nuclear motion flips the electronic wavefunction from one electronic state to the other. \(|\mathbf{D}_{12}|\) is large at the avoided crossing when the incident proton wavepacket is at a distance ~8Å, ensuring nearly unit probability of a change in adiabatic state (no electron transfer) as the system passes through the crossing. As the wavepacket moves closer, it may branch onto both PESs. Further branching can occur each time wavepackets enter regions of space where \(|\mathbf{D}_{12}|\) is large.

The H₂⁺ reaction inspired a successful approximate method, “trajectory surface hopping,” a procedure for integrating the classical mechanical equations of motion of the nuclei on a single adiabatic PES, until a hop to a different PES occurs at random according to probabilities determined from the magnitude of \(|\mathbf{D}_{12}|\). Application of this theory to the H⁺ + D₂ reaction reproduced quite accurately the experimentally measured absolute cross sections for the three reaction channels as a function of energy—see Figure 9.

In the initial version of surface hopping, transitions between PESs occurred only at positions of maximal nonadiabatic coupling. This is unrealistic. Nonadiabatic coupling can be significant over broad regions of space, meaning that wavepackets may enter into strong coupling regions without reaching an avoided crossing. Multiple transitions may occur leading to different pathways with different quantum mechanical phases, resulting in interference effects. Well-defined avoided crossings may not even exist.

Theoretical advances to address these issues are continually being developed. In Ehrenfest theory, atoms evolve classically on a weighted average of the PESs—here, the weightings are computed by integrating the time-dependent Schrödinger equation for the electrons along the trajectory. In an improved surface hopping theory, at every instant in time, the atoms evolve by classical mechanics on a single adiabatic PES, but with the possibility of a hop to a different PES at each time step. Hops occur probabilistically according to the electronic state amplitudes obtained from integration of the time-dependent electronic Schrödinger equation. Many variations of surface hopping have since evolved, including methods for introducing quantum decoherence. An extension of Gaussian wavepacket propagation—multiple spawning—allows new wavepackets to be spawned to account for bifurcation on different PESs. Semi-classical and quantum mechanical methods, such as multi-configuration time-dependent Hartree, are becoming more widely used as well. A number of approaches for computing the required excited state PESs and nonadiabatic couplings are under development, but details are outside the scope of this review.

There have been many beautiful experimental studies of gas-phase nonadiabatic dynamics. Molecular beam studies have been performed on reactions of O(3P, 1D) and S(3P, 1D) with H₂, employing Rydberg tagging to detect product H atoms. Reactions of O(3P) with ethylene have employed soft electron-ionization mass-spectrometry to unravel the multiple product channels of this reaction. Femtosecond soft X-ray spectroscopy of the electro-cyclic ring-opening reaction of 1,3-cyclohexadiene revealed the ultrafast time scales of the nonadiabatic events. The conical intersection dynamics of the RNA base uracil was studied using a UV pump with stimulated-Raman probe. All of these studies were successfully modeled by surface hopping calculations.
A simple charge transfer reaction, \( H^+ + H_2 \rightarrow H^+_2 + H \), may proceed by three pathways involving electron transfer, proton exchange, or electron transfer with proton exchange. \( R_1 \) and \( R_2 \) are the distances between atoms 1&2 and 2&3, respectively. Panel (a) shows the situation when one atom is far away. Two potentials are present describing the two possible choices of placing two electrons on two centers. Panels (b) and (c) show how these states interact at closer approach. Panel (d) shows the nonadiabatic coupling between the two states as a function of nuclear positions, more specifically, the magnitude of the component of the vector \( \vec{D}_{12} \) for motion in the \( R_1 \) direction. Distances are in units of \( a_0 \).

(a–d) Product flux contour maps for a simple charge transfer reaction. (a) Experimental and (b) trajectory surface hopping result for \( D^+ + HD \rightarrow D^+ + H \). (c) Experimental and (d) trajectory surface hopping result for \( D^+ + HD \rightarrow D + HD^+ \). The collision energy in the center-of-mass frame was \( E_{\text{COM}} = 5.5 \text{ eV} \) and the energy of the reactant ion was \( E_{D^+} = 9.2 \text{ eV} \). (e) Integral cross sections as a function of laboratory collisional energy. Enlarged symbols represent results of trajectory surface hopping calculations. Small symbols are experimental results. Note the theory was performed prior to the experiments.

**Transition state theory**

Chemistry is the science of materials conversion and while thermodynamics tells us which reactions are fundamentally possible, to be of practical importance, we must design chemical pathways to reach the desired products using rapid reactions. This simple argument lies the entire field of catalysis and drives much of synthetic chemistry. One of the major motivations to develop an atomic scale foundation of understanding in chemical dynamics is the desire for a predictive theory of chemical reaction rates. Transition state theory (TST) has filled this need, allowing us to exploit our understanding of chemical dynamics to make quantitative predictions about the speed of a reaction.
In its original formulation, Eyring postulated a special state of the system—the activated complex—that when formed, would with almost complete certainty, go on to products. In a remarkable leap of insight, he assumed that this species would be in thermal equilibrium with the reactants. If one could determine its energy and structure—necessary to obtain its entropy—the activated complex’s concentration as well as the speed of passage on to products could be found with statistical mechanics.\(^{34}\) At the time these ideas were developed, it was difficult to predict theoretically many of these quantities. However, the development of computational chemistry has provided all of the machinery necessary for making these calculations accurately for many gas-phase reactions.

The current formulation of TST prescribes a dividing plane that separates reactants from products such that every trajectory that originates in the reactant region of configuration space and evolves to the product region must pass through the dividing plane at least once. The TST thermal rate constant is equal to the equilibrium one-way flux through the dividing plane in the direction of reactant to product. Thus, TST provides an upper bound to the rate constant, since some trajectories might pass through the dividing plane more than once or pass through without leading to product—so, the equilibrium flux will include nonreactive events. The location of the dividing plane is usually chosen at the reaction barrier, but ways that are more sophisticated can be used, including variational TST,\(^ {180}\) in which the location of the dividing plane is chosen to minimize the TST rate. Improvement to TST can be obtained by running classical trajectories to count the number of recrossing events and reduce the TST rate accordingly.\(^ {181}\) This technique is particularly advantageous in cases where the reaction barrier height is high, perhaps many times \(kT\). An effective way to simulate this is to initiate trajectories at the dividing plane, integrate forward and backward in time, and modify the TST rate constant by the fraction of trajectories that underwent recrossings.

TST has been extremely successful and many comparisons between measured and predicted rates have proven its validity. It has been particularly important in atmospheric\(^ {182}\) and combustion chemistry\(^ {183}\) and finds widespread use to predict reaction rates, especially where they are impossible to measure. It is also worth contemplating that TST has led to a deeper understanding of how enzymes work.\(^ {184}\) Many concepts of enzyme catalytic activity—correlated conformational fluctuations, dynamical and nonequilibrium effects, electrostatic preorganization, entropic guidance, fluctuating barrier height, near-attack configurations, reactant destabilization, and tunneling—can be understood within the language of modern TST. In this language, “the entire and sole source of the catalytic power of enzymes is due to the lowering of the free energy of activation and any increase in the generalized transmission coefficient….\(^ {184}\)” These insights about some of the most complex catalysts in nature are a culmination of nearly a century of effort starting with the \(\text{H}_2\) reaction and should make us optimistic that applying the dynamical approach to surface chemistry can lead to similar successes.

To summarize this section, “the dynamical approach” applied to gas-phase reactions has led to a standard model of chemical reactivity, involving quantum motion of nuclei on an electronically adiabatic Born–Oppenheimer PES. The classical approximation often holds and the standard model can be generalized to involve multiple electronic states. The standard model has allowed us to develop and validate a nearly exact predictive theory of gas-phase reaction rates derived from TST.

### Extending the Dynamical Approach to Surfaces

Extending the dynamical approach to problems in surface chemistry may appear impenetrably complex and challenging. The remainder of this review breaks down the complexity and reveals the commonalties to gas-phase dynamics. Progress derives from adapting the basic concepts and many exquisite theoretical and experimental tools of gas-phase dynamics to problems at surfaces and inventing new ones based on the spirit of the dynamical approach.

The most obvious challenge facing the extension of the dynamical approach to surfaces is that surfaces are big and they are dense. In a crossed molecular beam experiment, most of the molecules in one beam pass through the other without colliding, ensuring single collision conditions where we can observe elementary reaction steps. In contrast, in a beam-surface scattering experiment, every molecule collides. While this contributes to strong signals, molecule-surface encounters may involve many collisions. Hence, the challenge of size is not just one of high-dimensionality; rather, we need to disentangle a sequence of elementary events and learn about each one individually. In this spirit, we have sections below on Dissipation and Inelastic Scattering (Section 5), Adsorption—Desorption (Section 6), and Dynamics of Reactions at Surfaces (Section 7). Inelastic encounters of atoms and molecules with surfaces determine whether adsorption takes place; likewise, adsorption is often the step preceding reactions, which must compete against reactant desorption.

The fact that multiple elementary processes typically occur even in the best-designed experiments makes cooperation with theory all the more important. On the other hand, theoretical tools for surface dynamics often require new approximations meaning they require testing against experiment. Most significantly, wave function-based methods for treating electron correlation are generally too computationally demanding to be applicable to molecule–surface interactions. As a result, DFT, with plane-wave basis functions, generalized gradient approximation (GGA) functionals,\(^ {185}\) and the inclusion of dispersion,\(^ {186}\) dominates the computation of PESs. The quantum mechanical methods for computing atomic motions that revealed such detailed and definitive behavior in gas-phase reactions are not often applicable for describing molecule–surface interactions, except in reduced dimensions, for example, under the extreme assumption that the surface atoms do not move. As a result, classical mechanics, sometimes augmented by dissipative or nonadiabatic features, remains the workhorse for simulating chemical dynamics at surfaces.

On-the-fly dynamics calculations have made many contributions, but new machine learning algorithms\(^ {103}\) are slowly replacing them with full-dimensional analytical PESs constructed by fitting to DFT energies.
We also face new experimental challenges when making the leap from the gas phase to surfaces. Of course, we need ultra high vacuum (UHV) ($\sim 10^{-10}$ mbar) to establish conditions where surfaces remain clean and we need the tools of surface science for cleaning and characterizing the sample. Fortunately, these tools are now commercially available and offer no significant barrier to entering the field.

The truly daunting challenges include the following. We often do not know a priori the reactive site, as adsorption and diffusion as well as the surface heterogeneity are conditions not faced in the gas phase. A theoretician working to understand experiments in the gas phase takes comfort in knowing the stoichiometry of the transition state. In surface reactions, knowing which atoms to include in a model of reactivity may be the first puzzle to solve. Of course, the surface itself behaves like a reactant. Yet, there are few tools available to excite specific motions of the solid to investigate their influence on reactivity—most studies simply vary the temperature. More subtle problems also arise. Gas-phase experimentalists take for granted tools that offer detection sensitivities of as low as one molecule per cm$^2$; common methods in surface science offer adsorbate detection sensitivities of about $10^{13}$ molecules cm$^{-2}$ or 0.01 of a monolayer (ML).

While the challenges and limitations described above present barriers, they also provide opportunities for great progress through a combination of ingenuity, advancing technology, and theory development. It is a common occurrence—in fact, many examples can be found in Section 2 of this review—that today’s sensation or “miracle experiment” becomes tomorrow’s routine calibration measurement. In experimental science, the more we learn, the more we are able to learn. This inevitable improvement of measurement methods should make us optimistic about meeting the challenges.

**DISSIPATION AND INELASTIC SCATTERING**

Breaking or making chemical bonds consumes or releases energy that, in gas-phase reactions, flows among the translation, vibrational, rotational, and electronic degrees of freedom of the species actively involved. In surface chemistry, energy can also flow between the reacting species and the substrate vibrational (phonon) and electronic degrees of freedom. Probing and understanding these energy transfer pathways are central topics in surface dynamics.

Lifetimes of vibrationally excited molecules adsorbed on surfaces (Section 5.1) reveal important mechanisms of dissipation; whereas, energy, angle, and quantum state resolved differential inelastic surface scattering experiments (Sections 5.2–5.6) reveal more directly the flow of energy among the degrees of freedom of the incident and scattered species and the flow of energy to and from the surface. An important aspect of this work is the large role played by nonadiabatic electronic excitation in certain energy transfer processes. The theory of these nonadiabatic effects is taken up in Section 5.7. Finally, we present high-resolution inelastic scattering experiments of H and D atoms (Section 5.8) together with molecular dynamics simulations that have proved to be an excellent testing ground of the dynamical approach in surface chemistry.

**Vibrational relaxation rates of adsorbates**

Lifetimes of vibrationally excited molecules on surfaces have been inferred from infrared lineshapes and measured directly using infrared pump-probe methods. Lifetimes range from milliseconds for CO$^*$($\nu = 1$) physisorbed on NaCl$^{187,188}$ to 2–3 ps for chemisorbed CO on metals. $^{189–193}$ The long lifetime of CO$^*$($\nu = 1$) on NaCl reflects the fact that more than thirteen phonons must be excited to relax the molecule—CO’s vibrational frequency ($\sim 2100$ cm$^{-1}$) is much higher than the highest frequency phonon of NaCl ($\sim 160$ cm$^{-1}$). The anharmonicity of the PES is so small initially that excited CO vibration does not easily decay to other vibrational degrees of freedom. In fact, relaxation occurs via an electromagnetic interaction independent of the PES—the Sommerfeld ground wave limit. $^{186}$ When CO is chemisorbed on metals, the coupling to phonons is no more favorable; therefore, the ps vibrational lifetimes observed suggest that vibrational relaxation via excitation of electron–hole pairs (EHPs) in the metal is highly efficient.

The importance of vibrational relaxation to excite EHPs has been confirmed by a variety of theoretical methods. One of the first used is Fermi’s golden rule (FGR) with the jellium approximation for the metallic conduction electrons to study H$_2$ relaxation near Al, Mg, and Na surfaces. $^{194,195}$ Similarly, CO on a Cu cluster was examined using FGR with DFT. $^{196}$ A Newns–Anderson Hamiltonian approach showed similar results for CO and CN adsorbed on Ag, Cu, Au, and Pt. $^{197}$ Electronic friction methods for CO on Cu(100) employed a local-density friction approximation (LDFA) and also yielded picosecond lifetimes. $^{198}$ Recently, pump-probe measurements of the vibrational relaxation of physisorbed CO on Au(111) showed a lifetime of $\sim 50$ ps, much longer than chemisorbed CO$^{199}$—a recent theoretical treatment was consistent with this measurement. $^{200}$ Such long vibrational lifetimes for physisorbed species suggest that reactions of vibrationally excited adsorbates$^{201}$ may be more important than previously believed.

All of these studies investigated the high-frequency CO stretch. For other modes and lower frequency stretch modes, phonons can play a significant role in coupling to adsorbate vibrations, as shown by FGR calculations of vibrational lifetimes of all four vibrational modes of CO on Cu(100) using finite-sized Cu clusters at the Hartree–Fock level. $^{202–204}$ Here, EHP excitation entirely dominated the lifetime of the internal stretch (3.3 ps) and bend (2.3 ps) modes, while phonon excitation significantly contributed to the lifetimes of the CO–surface stretch (22 ps) and the frustrated translational modes (14 ps). $^{204}$ All four of these lifetimes are in reasonable accord with experiment. $^{189,192}$ The conclusions are that EHP excitations dominate the relaxation of the internal stretch and bending modes, whereas the molecule–surface stretch and frustrated translational modes relax mainly via phonons. It is not known whether these trends hold for other adsorbates or other metal surfaces.

**Early molecular beam surface scattering experiments**

The success of molecular beam scattering experiments in gas-phase dynamics created a lot of enthusiasm that similar success was possible...
by the application of these techniques to surfaces. Early experiments faced limitations stemming from the difficulty of combining beam and surface science methods. High-performance molecular beam machines typically had poor vacuum and it was necessary to work with surfaces at elevated temperatures to prevent contamination or to use continuous epitaxial deposition to maintain a clean surface.\textsuperscript{205,206} UHV surface science machines retrofitted with rotating detectors for beam surface scattering, usually using effusive beams,\textsuperscript{207} did not have the full molecular beam performance as their gas-phase cousins. Angular distributions of scattered rare gas atoms and small diatomic molecules were an important focus of these studies.

Measured angular distributions often showed broad lobes centered near the direction of specular reflection of the incident beam. These lobes resulted from incident species striking the moving surface atoms, exchanging energy and momentum, and then returning to the gas phase. The angular position and width of the lobes provided information on momentum and energy exchange with the surface. Treating surface atoms as hard cubes moving with a thermal velocity distribution\textsuperscript{208} had success in predicting observed trends. The hard cube model forces parallel momentum conservation and, hence, the normal momentum transfer could be determined by conservation of energy and momentum and knowledge of the masses and velocities of the incoming species and surface atom. Improved versions of the hard cube model included adding a spring to the hard cube to represent the lattice vibration (soft cube model),\textsuperscript{209} and treating the substrate atoms as having truncated spherical caps\textsuperscript{210} to allow modeling of parallel momentum transfer. This later refinement was particularly necessary to obtain agreement with measurements at hyperthermal incidence energies.\textsuperscript{211}

Velocity distributions of molecules scattered from clean and well-characterized surfaces became available only after combining UHV surface science techniques with state-of-the-art molecular beam methods. In one of the first instruments,\textsuperscript{212} three differentially pumped supersonic beam sources were directed at the surface, producing molecules with narrow velocity distributions. A differentially pumped mass spectrometer and associated vacuum pumps mounted on a rotating platform sealed with Teflon “tec” seals\textsuperscript{213} provided a rotatable detector, which, with the use of a chopper wheel, allowed for the measurement of scattering-angle resolved times of flight (TOF). Rotation of the solid target allowed variation of the incidence angle. The instrument was bakeable, used UHV compatible pumps, components, and materials of construction and had surface science equipment to clean and characterize the target surfaces. Figure 10 shows an example of measured velocity distribution data for Ar scattering from a Pt(111) surface.\textsuperscript{214} The iso-flux contour plots shown combine results of TOF measurements at many scattering angles. Cuts of the iso-flux plots give the velocity distribution in the directions normal and parallel to the surface. The spread in velocities in the perpendicular direction ($v_y$) is clearly larger than that in the parallel direction ($v_x$) showing the coupling of normal momentum to the surface is larger than that of parallel momentum. The data show the “the law of parallel momentum conservation” that had emerged from interpretations of angular distribution measurements\textsuperscript{215} is not correct, although there is a clear propensity for parallel momentum conservation. Data of this type are also available for a range of incidence energies and angles and for scattering both in and out of the principal scattering plane. Very high-resolution experiments were also done with He atom scattering capable of resolving single phonon excitation of the solid. These experiments primarily probe the structure of the solid rather than reaction dynamics and we refer the interested reader to a recent book on the subject.\textsuperscript{216}

The availability of accurate scattering data stimulated the development of methods to simulate gas-surface scattering. Even for scattering of rare gas atoms from clean, perfect surfaces, it is a challenge to employ an accurate gas–surface interaction potential, energy dissipation to phonons, and quantum mechanical effects. In principle, for metal surfaces, the effects of EHP transitions should also be included, but these appear to be relatively unimportant for rare gas atom scattering.

The first advance in theory beyond the cube models was to integrate the classical equations of motion numerically for the rare gas atom and a slab of surface atoms. These studies modeled the gas–surface interaction using empirical potentials with harmonic interactions among the surface atoms. It was found that, for metal surfaces, Lennard-Jones pairwise additive gas–surface potentials produced too much corrugation; presumably, the metallic electron cloud smooths out the corrugation. This problem was addressed by the addition of a background smoothing potential.\textsuperscript{217} Initial simulations employed only a small number of surface atoms with frictions and fluctuating forces to define surface temperature, $T_S$ and with memory chosen to approximately reproduce the phonon spectrum.\textsuperscript{218} As more powerful computers became available, hundreds of surface atoms could be included, with or without frictions and random forces.\textsuperscript{219,220} To date, however, there do not appear to be any simulations of the scattering of rare gas atoms from surfaces based on accurate \textit{ab initio} PESs.
Simulations based on classical adiabatic molecular dynamics using empirical potentials provide reasonable agreement with measured energy and angular distributions. An example for the direct inelastic scattering of Xe scattering from Pt(111) is shown in Figure 24(a)–(d). For this system, there are two peaks in the TOF spectrum; one resulting from direct “single bounce” inelastic scattering, and the other from molecules that trap on the surface and then desorb. The general agreement of measured rare gas atom scattered velocity distributions with calculations based on a single PES indicates that electronically adiabatic coupling to phonons dominates and that electronically nonadiabatic excitation of EHPs is not important. At higher energies where $E_i \cos(\theta_i) > 3$ eV, the measured energy loss is larger than that calculated from the adiabatic picture, suggesting that nonadiabatic excitation starts to become important, even for rare-gas metal interactions. 221

State-resolved detection of scattered molecules, rotational effects

Probing transitions between a molecule’s rotation-vibration states due to collisions at a surface required state-specific detection techniques. Here, molecular beams deliver rotationally cold molecules in their ground vibrational state moving with controlled and narrow speed distributions, while detecting scattered molecules with LIF or REMPI. Early experiments done with NO showed strong rotational excitation and no vibrational excitation. 222–224 Rotational excitation increased with incidence kinetic energy and a broad nonthermal peak in the rotational state distribution emerged 224; see Figure 11(a). Increased rotational excitation in the scattered molecules arises from a loss of translational energy (T → R coupling), Figure 11(b). This conclusion was supported by independent measurements for NO scattered from Au(111) showing decreased translational energy of the scattered NO when produced in higher energy rotational states. 225–227

The nonthermal rotational states populated at high incidence translational energy were interpreted as a “rotational rainbow,” where a specific orientation angle of the molecule with respect to the surface leads to maximum rotational excitation. The rotational rainbow gets its name from the mathematically analogous optical rainbow, where a specific impact distance of a light ray from the center of a water droplet leads to a maximum scattering angle and an intensity maximum at that angle. 228 Classical trajectory and quantum wavepacket calculations based on empirical potentials provide support for this interpretation 229,230 and rotational rainbows have since been seen many times. 229,231–237 Since then, it was possible to see an N-side and an O-side rainbow for NO scattering using oriented beams of NO 238 and to witness a rainbow in formaldehyde, where the rotation about the CO bond axis exhibits a rainbow. 239

Combining TOF with REMPI provides velocities of scattered, state-selected molecules. Knowing the initial and final translational and rotational energy, we can compute the energy transfer to the lattice. Interestingly, the energy going into the lattice depends on the degree of rotational excitation; molecules that undergo more rotational excitation transfer less energy into the phonons of the substrate, in good agreement with theoretical calculations. 225,240 This anticorrelation of rotational excitation and phonon excitation seems also to be a ubiquitous feature of molecular scattering from surfaces. 9,227,238,241
State-resolved detection of scattered molecules, vibrational effects

Observations of vibrational excitation were reported for REMPI detected NH₃ after its collision with Au(111) surface—umbrella motion in NH₃ gives rise to low-lying vibrational levels that become increasingly populated with increased incidence transitional energy.²⁴² Observed thresholds tellingly close to the detected state’s vibrational excitation energy showed that a minimum of incidence energy was needed to produce each new vibrational states (T→ V coupling). The excitation probability was, furthermore, insensitive to Tₛ. The authors concluded that vibrational excitation was occurring via a direct (single bounce) adiabatic ("mechanical") coupling of the incoming normal motion to the vibrational modes of the molecule.

Efficient vibrational excitation from ν = 0 → 1 was also observed in collisions of NO with a hot Ag(111)²⁴³ surface. In contrast to the results for NH₃, the excitation probability increased exponentially with Tₛ, displaying an Arrhenius-like behavior with an activation energy equal to the NO vibrational spacing. Furthermore, no thresholds were seen in the incidence energy dependence. The authors argued that NO vibrational excitation resulted from an electronically nonadiabatic coupling of NO stretch motion to thermally excited EHPs in the metal and that the coupling increased at higher incidence energies as a closer approach was possible. This interpretation was supported by later measurements of the velocity distributions of scattered NO in the vibrationally elastic and inelastic channels showing the energy for vibrational excitation did not come from translational motion.²⁴⁴

Since this discovery, the literature has filled with reports of similar observations—systems where hot EHPs excite vibrations include: HCl on Au,²⁴⁵ CO on Au,²⁴⁶ and Ag.²⁴⁷ For NO on Au, it was even possible to see Δν = 1, 2, and 3, each displaying an Arrhenius-like behavior with an activation energy equal to \( h \omega_{\text{vib}} \times \Delta \nu \).²⁴⁸ In these experiments, the production of NO(\( \nu = 3 \)) with its vibrational energy of 0.687 eV occurred in collisions of NO (\( \nu = 0 \)) with a hot Au(111) surface at incidence energies of only 0.4 eV²⁴⁸

Figure 12 shows absolute measurements of excitation probabilities of NO(\( \nu = 1 \)) and NO(\( \nu = 2 \)) for NO(\( \nu = 0 \)) colliding with Au(111) over a wide range of incidence energies and surface temperatures.²⁴⁹ These data are particularly valuable for comparison with theories of nonadiabatic energy transfer because the availability of absolute measurements for both single and multiquantum excitation helps distinguish different theoretical treatments of the nonadiabatic coupling. We will return to this topic in Section 5.7.

**Vibrational state-to-state scattering**

Improved observations of vibrationally inelastic scattering are possible using a state-to-state approach, combining optical pumping of molecular beams with REMPI detection of scattered molecules. While experimentally more complex, this set-up also provides improved TOF capability, simplifying the identification of direct scattering channels versus trapping followed by desorption. Simply by varying the delay between the two lasers and separating the laser beams from one another, state-to-state TOF can be performed.²²⁶,²²⁷,²⁵⁰,²⁵¹

IR pumping allows for the production of beams with substantial populations in the \( v = 1-3 \) vibrational states²²⁷ and with stimulated emission pumping (SEP), much higher vibrational states can be reached.²⁵² SEP is the conceptual child of microwave-optical double resonance²⁵³-²⁵⁷ and optical-optical double resonance spectroscopies.²⁵⁸,²⁵⁹ In SEP, molecules are excited or pumped by one laser to an excited electronic state—subsequently, emission is stimulated by a second laser, “pump-dump”-ing the excited state population back to the ground electronic state. By tuning the lasers so that the stimulated emission goes to a vibrationally excited state, this “pump-dump” approach populates the beam with highly vibrationally excited molecules selected by the frequency difference of the two lasers. In surface scattering, SEP is most often performed with pulsed nanosecond lasers.²⁶⁰

The first application of SEP to surface dynamics²⁶¹ prepared NO(\( \nu = 15 \)) and used REMPI to determine the final vibrational state distributions after collision with Au(111)—see Figure 13(a). NO(\( \nu = 15 \)) hardly survives—the most probable state-to-state relaxation process loses eight vibrational quanta (~1.5 eV). Narrow angular distributions indicated single bounce dynamics. Coupling of high-frequency NO vibrations to the phonons of the Au(111) lattice is improbable due to the large energy mismatch between the vibrational energy change and the phonon energy. The remarkable vibrational relaxation was attributed to nonadiabatic electronic effects, specifically the excitation of EHPs of the substrate mediated by vibrational promotion of
electron transfer.\textsuperscript{261} This conclusion was supported by a comparison with data on the scattering of NO\((v = 12)\) from an LiF crystal shown in Figure 13(b), where little vibrational relaxation is observed. Unlike a metal, insulators like LiF have no continuum of low-lying electronic excitations. Nonadiabatic electronic excitations are thus not possible for LiF and vibrational relaxation occurs by the much weaker coupling to phonons.

Since that time, methods have continued to improve. Spontaneous emission from the intermediate “stepping-stone state” used in SEP produces vibrationally excited states indiscriminately, which is usually an unwanted background. The utility of pump-dump optical excitation improves dramatically when using a “sweep” laser that dissociates the stepping-stone state within a few ns after pump-dump has been performed, removing most of the spontaneous emission and concomitant background.\textsuperscript{262} It also proved possible to develop a variant of SEP that was used to produce highly vibrationally excited CO exploiting perturbations.\textsuperscript{263} Overtone pumping of HCl and NO to low lying vibrational states was another path to additional data.

We now have rich and extensive data on the inelastic scattering of vibrationally excited molecules colliding with metal surfaces—it is one of the best-studied examples of the failure of the Born–Oppenheimer approximation to describe molecular interactions at metal surfaces.\textsuperscript{6–9} State-to-state data are now available for vibrational relaxation and excitation of HCl,\textsuperscript{264–266} NO,\textsuperscript{267–269} and CO\textsuperscript{247,270} prepared with both low and high levels of initial vibrational excitation. Most work has been done on Au(111) and Ag(111). Remarkably, Ag(111) induces much larger vibrational relaxation probabilities\textsuperscript{271} than Au(111)—see Figure 14(a).

While Ag and Au have many similarities, it is noteworthy that Ag possesses a substantially lower work function than Au (4.5 vs. 5.3 eV). NO vibrational relaxation is believed to occur by an electron transfer-mediated mechanism involving a transient anion, NO\textsuperscript{−}. If true, it would not be surprising that the work function plays an important role. Systematic control of the work function was achieved using atomically layered films of Ag grown on Au(111).\textsuperscript{272} Silver grows layer by layer on Au, hence, only when the nth layer closes does the n+ 1th layer begin to grow. Evaporating Ag onto Au with a Ag-beam block moving continuously across the Au crystal allows fabrication of an atomically defined edge structure—see inset of Figure 14(b). Using this wedge in a molecular beam surface scattering experiment, one can examine the inelastic scattering seen when the beam of vibrationally excited molecules collides at different positions on the wedge.

Figure 14(b) shows the results of such measurements. The survival probability of NO\((v = 2)\) decreases with increasing Ag coverage—furthermore, as each atomic layer closes, there is a discontinuity in the survival probability. Such discontinuities are also seen in the layer dependence of the surface work function—this is perhaps the strongest evidence that work function is central to the mechanism of nonadiabatic vibrational energy exchange between the molecule and the surface, consistent with a transient NO\textsuperscript{−} anion mechanism.\textsuperscript{272}

A mechanism involving a transient negative ion formed by electron transfer to either NO or CO helps to explain many of the observations. Both the vertical electron binding energy at the outer turning point of vibration, \(E_{v}\textsuperscript{EHP}(r_{\text{outer}})\), and the work function, \(\Phi\), determine if electron transfer is energetically possible. There is actually a very good correlation between vibrational relaxation probability and \(E_{v}\textsuperscript{EHP}(r_{\text{outer}}) - \Phi\) across a large number of systems as shown in Figure 15.

Experiments with oriented NO were also developed, where either N or O faces the surface upon collision.\textsuperscript{238,273,274} Vibrational relaxation is more efficient when N is oriented toward the surface than away,\textsuperscript{274,275} consistent with theoretical predictions that electron transfer is more labile for this orientation.\textsuperscript{276}

Vibrationally promoted electron emission

Taken together, there is compelling evidence that vibrational relaxation of NO and CO molecules colliding with a metal surface occurs via an electron transfer process. If vibrational energy lost resulted in low energy excitations of many electrons, electron emission could not occur. However, if many quanta of vibrational energy can be channeled to a single electron giving it enough energy to overcome the work function, not only will emission be possible, but it also will be a strong sign that “one electron does all the work,” a concept consistent with an electron transfer process. Thus, looking for electron emission and measuring its quantum yield can teach us something very important about the dynamics of the EHP excitation.

When highly vibrationally excited NO with variable incidence vibrational energy was scattered from a surface with 1.6 eV work function,\textsuperscript{279} prepared by dosing a sub-ML amount of Cs on Au(111),
**FIGURE 14** The influence of work function on electronically nonadiabatic vibrational relaxation. (a) NO($v_1 = 11$) colliding Au(111) and Ag(111). The multiquantum vibrational relaxation is much stronger on Ag, whose work function (4.5 eV) is substantially lower than that of Au (5.3 eV). (b) A wedged sample of atomically layered Ag on Au (inset) is translated through a molecular beam of NO($v_2$). The REMPI signal reports vibrational survival probability as a function of Ag layer thickness. Coverage dependence of the first (solid line), second (dashed line), and part of the third (dashed-dot line) ML of silver are shown. A discontinuity in the survival probability appears as the first and second atomic layers close. A similar discontinuity is seen in the coverage dependence of the work function.\(^{272}\)

**FIGURE 15** Vibrational relaxation probability in scattering as a function of the vertical electron binding energy minus the work function.\(^9\) The incidence energy for all data is $\sim 0.6$ eV so the turning point is similar for all systems. AgCl denotes a monolayer of Cl on Ag(111). Au and Ag both refer to the (111) facet. Republished with permission of IOP Publishing, Ltd, from Park GB, Krüger BC, Borodin D, Kitsopoulos TN, Wodtke AM. Fundamental mechanisms for molecular energy conversion and chemical reactions at surfaces. Rep Prog Phys. 2019;82(9):096401; Copyright 2021, permission conveyed through Copyright Clearance Center, Inc.

Electron emission was readily observed as soon as the vibrational energy exceeded the work function.\(^{277}\) See Figure 16. This directly shows that vibrational energy has been used to excite a single electron. Furthermore, this is not a rare or highly forbidden channel—the yield is large, reaching over 10% for $v = 18$.

An inverse velocity dependence gives further evidence of a transient negative ion formation, since, due to increasing image charge stabilization, a newly formed negative ion must emit its electron before getting too close the surface.\(^{278}\) Measurements of the energy distributions of emitted electrons provided information on the number of quanta of vibration that go into exciting the emitted electrons.\(^{280,281}\) The sum of the measured electron energy and the work function is simply the vibrational energy that couples into a single electron. The measurements showed that when NO($v = 16$) collides at the surface, with highest probability, 10 vibrational quanta couple into a single electron.\(^{281}\)

The results presented in this and the preceding five sections provide a rather complete experimental characterization of the electronically nonadiabatic dynamics of molecules interacting with metal surfaces. Key observations include vibrational excitation and de-excitation as well as multiquantum vibrational relaxation, vibrationally promoted electron emission, and strong orientation effects. These observations...
provide strong evidence of an electron transfer-mediated mechanism involving transient anions. They remain, however, a challenge for electronically nonadiabatic theory of surface chemistry,\textsuperscript{267} to which we now turn.

**Theory of nonadiabatic coupling to EHP excitations**

Vibrational lifetimes, vibrationally inelastic collisions, and vibrationally promoted electron emission all give strong evidence of the importance of the coupling of vibrational motion to EHP excitations. The theory of this coupling divides into two classes, weak coupling where the changes in vibrational state in a coupling event are small, and strong coupling where the changes can be large. The next two sections discuss these two approaches in turn.

**Electronic friction**

The introduction of an electronic friction in classical mechanical simulations to account for the dissipation of energy via EHP excitations arose first in calculations of the slowing of ions moving through metals,\textsuperscript{282–286} and was carried over to the interaction of atoms and molecules with metal surfaces.\textsuperscript{287–291} There are two general strategies used to compute electronic friction. The simplest and most often used is referred to as the LDFA and is based on the response of the free electron gas density at the position of the atom.\textsuperscript{286} A number of methods have been employed to partition the local electron density computed by DFT into an atomic part and a free electron part, including carrying out a separate DFT calculation of the substrate without the adsorbate,\textsuperscript{292,293} or adapting approximate models, such as embedded atom,\textsuperscript{289,294} atoms in molecules,\textsuperscript{198} or effective medium theory (EMT).\textsuperscript{295–298} The sticking probability of H atoms on a number of transition metal surfaces is predicted to be dominated by EHP energy exchange.\textsuperscript{289,292,296,298} LDFA calculations of the scattering of H atoms from Au(111) achieve good agreement with molecular beam results.\textsuperscript{298} LDFA has also been employed to predict chemi-currents in the conduction electrons induced by scattering of H atoms from gold and silver surfaces.\textsuperscript{297} In contrast to the dominance of EHP energy transfer in the interaction of H atoms with metal surfaces, calculations for H\textsubscript{2} on Cu(110),\textsuperscript{299} H\textsubscript{2} on Ru(0001),\textsuperscript{294} N\textsubscript{2} on W(110),\textsuperscript{299} and N\textsubscript{2} on Fe(110)\textsuperscript{300} indicate that EHP excitations appear to have little effect on molecular dissociative sticking probabilities. The LDFA has been applied to vibrational lifetimes of adsorbates as well.\textsuperscript{196} There is controversy, however, about whether LDFA can accurately compute the full electronic friction tensor.\textsuperscript{301,302}

The second strategy for incorporating electronic friction in molecular dynamics simulations of chemistry on metal surfaces is based on the Ehrenfest\textsuperscript{162} mean-field theory of nonadiabatic dynamics. While Ehrenfest theory has been employed directly to describe nonadiabatic interactions of O atoms with graphite\textsuperscript{303} and Li\textsuperscript{+} ions with aluminum,\textsuperscript{304} the computational time is substantial. However, in the weak coupling limit, the Ehrenfest equation can be transformed into a generalized Langevin equation: molecular dynamics with electronic friction,\textsuperscript{305} with classical motion evolving on the ground state PES and subject to frictions and fluctuating forces arising from EHP transitions. The friction and random force satisfy the fluctuation-dissipation theorem,\textsuperscript{306} such that the system properly approaches the desired temperature. In principle, the frictional terms include memory of the past evolution of the system. While memory effects may well be important to describe frequency-dependent friction due to, for example, electronic resonances or nonuniform densities of states, to our knowledge, memory effects have not been explored in this context. Rather, in practice, memory effects have been neglected. In this Markov limit, the equations that result for the electronic friction are given by FGR.\textsuperscript{194–196,203} Note that the friction is a tensor of the components of the atomic velocity vectors, for example, for a diatomic molecule, it is a 6 × 6 tensor, and in general is not diagonal in either Cartesian or normal mode coordinates.\textsuperscript{307} The implementation of FGR sometimes presents numerical difficulties, in part due to representing the electronic continuum by discrete levels. A DFT-based procedure, dubbed orbital-dependent friction (ODF), appears to overcome these issues and provides accurate and stable results.\textsuperscript{308,309} ODF in the Markov approximation has been applied to compute lifetimes of the C-O stretch, CO-surface stretch, bend and frustrated translation vibrational modes of CO on Cu, Ag, Ni, and Pt surfaces, obtaining good agreement with experiment, where available.\textsuperscript{308} One exception to this is CO on Au, where great care must be taken with electronic structure theory to ensure an accurate description of the physisorption binding in this system.\textsuperscript{310} Importantly, the off-diagonal elements of the friction tensor are significant in some cases. ODF with electronic frictions computed on-the-fly for scattering and dissociative chemisorption of H\textsubscript{2} indicated that the major pathway for energy transfer was via the H-H stretching mode.\textsuperscript{311,312} Moreover, they observed a dynamical steering due to tensorial friction that influenced the scattering. Overall, however, they observed a minor effect of nonadiabaticity on the probability of chemisorption,\textsuperscript{313} in agreement with prior LDFA studies for H\textsubscript{2} on Cu(110)\textsuperscript{299} and Ru(0001).\textsuperscript{294} Recently, a symmetry-adapted neural network representation of the electronic friction tensor has been developed and promises to render ODF calculations quite practical.\textsuperscript{314}

**Independent electron surface hopping**

The experiments shown in Figure 13 of the scattering of vibrationally excited NO ($\nu = 15$) from a gold surface\textsuperscript{261} revealed huge amounts of energy transfer, with the vibrational distribution of scattered NO molecules peaking at $\nu = 7$ and 8. These results not only demonstrated unequivocally the importance of nonadiabatic EHP excitations, but also strongly implicated a mechanism of transient electron transfer from the surface to the NO molecule. Vibrationally promoted electron emission, discussed in the previous section, also implicates electron transfer. Electron transfer is clearly an example of strong coupling between the substrate electrons and the molecule, and casts doubt on the applicability of electronic friction theories of any sort, since they all rest on a weak coupling approximation. With a sufficiently large friction constant, a friction theory can account for large vibrational
energy transfer, but it is not likely to be able to reproduce the detailed behavior that was observed in subsequent experiments (see Section 5.5 and Figure 15), and certainly cannot properly describe electron transfer. The observation of electron emission induced by impact of a highly vibrationally excited molecule on a low work surface (Section 5.6) is also clearly beyond the scope of friction theories, all of which would describe electronic excitation as a sequence of single vibrational quantum transitions.

Inspired by the NO/Au experiments, surface hopping theory was extended to treat nonadiabatic transitions among the continuum of electronic levels of a metal. This independent electron surface hopping (IESH) theory represents the metallic continuum by a coarse-grained set of single electron levels, initially populated according to a Fermi function at the surface temperature. For the NO/Au system, application of IESH requires a diabatic \((N+1) \times (N+1)\) Hamiltonian matrix with the negative ion state of NO coupled to the \(N\) conduction electron states. The diabatic Hamiltonian was constructed as follows. First, a \(2 \times 2\) diabatic matrix was calculated. For a given nuclear geometry, the ground state energy and the charge on the NO molecule were computed by DFT. This produced two of the three pieces of information required to define a \(2 \times 2\) matrix. The third piece of information was obtained by repeating the DFT calculation with a weak applied electric field in the direction of the normal to the surface plane. The approximation that the main result of the weak field was to lower or raise the energy of the negative ion state provided the third piece of information required to construct the \(2 \times 2\) matrix. The \(2 \times 2\) matrix was then expanded to the needed \((N+1) \times (N+1)\) diabatic matrix under two additional approximations: (1) the density of electronic states of the metal is assumed uniform, and (2) the coupling of the negative ion state to each conduction electron state was held constant. The diabatic Hamiltonian was then calculated for all relevant N, O, and Au positions and fit to analytical expressions. The IESH simulations were carried out by diagonalizing the diabatic Hamiltonian at every time step to obtain the \(N+1\) energies as well as the nonadiabatic couplings, while integrating the time-dependent Schrödinger equation to obtain the instantaneous amplitudes of each excited state as required to determine stochastic hops between states. Simultaneously, the classical equations of motion were integrated for the atoms governed by the forces on the occupied electronic state. With \(N = 60–80\) levels, the IESH simulations proved quite feasible.

The initial comparisons of the IESH simulations with the experimental results were quite encouraging. For example, Figure 12 shows a comparison of measurements (filled symbols) and IESH theory (open symbols) for multiquantum vibrational excitation for NO \((v = 0)\) scattering from Au(111). The agreement is good. In contrast, an electronic-friction calculation using the same Hamiltonian used in IESH severely underestimates the excitation probability. However, later experiments revealed shortcomings of the IESH calculations, notably that predicted sticking probabilities were too high due to an unrealistically attractive adiabatic PES. This artificially enhanced IESH's predicted probabilities for multiquantum vibrational relaxation at low incidence energy and led to a fortuitous agreement with the experimental observations of Figure 13. When comparisons were made at high incidence energies, where trapping was absent in the theory, IESH predicted too little multiquantum vibrational relaxation. This is at least partly due to the fact that the adiabatic PES used here also has no dissociation channel. Since then, a more realistic PES has been developed, one that is less attractive and allows for dissociative adsorption of NO on Au(111). Adiabatic calculations using this PES predict enhanced multiquantum vibrational relaxation, but still substantially less than seen in experiment. A renewed attempt to test IESH using this improved PES is warranted, but this will also require accurate calculations of excited and charge-transfer states. New electronic friction approaches have also been reported and reproduce some of the data seen in the laboratory—but multiquantum vibrational relaxation is still not captured by friction theory as it predicts that only low energy EHPs can be excited.

IESH still appears to be the theory in front-runner status to eventually solve the problem of NO vibrationally inelastic scattering on noble metals and while it is tempting to assign much of the disagreement between simulation and experiment to the input PES used in IESH, other more fundamental issues may prove important. Specifically, the approximations invoked to construct the \((N+1) \times (N+1)\) diabatic Hamiltonian were relatively crude and remain untested. Further work to test IESH against available experimental results is clearly needed.

High-resolution inelastic scattering–Rydberg-atom tagging

Rydberg-atom tagging was a breakthrough for the experiments on the H3 reaction—see Section 3.1—and it has proved similarly useful in surface scattering once the technical hurdles of implementing it for UHV were overcome. Photolysis sources of H and D atoms provide atomic beams with narrow energy distributions and tunable hyperthermal energies, making possible many unique new experiments in surface reaction dynamics. Furthermore, the fact that the method excels for H atoms facilitates cooperation with theory.

H atom scattering from metals

The first experiments investigated inelastic scattering of H and D atoms from transition metal surfaces, aiming to observe the contribution of nonadiabatic electronic excitation to the energy loss. The mere fact that H atoms stick to metals with high probability is suggestive that there must be large contribution of EHP excitation to the energy loss, since otherwise, due to the mass disparity, it would not be possible for an incident H atom to lose enough energy to adsorb. Hence, it was long suspected that EHP excitation is needed for sticking of H at metals. Furthermore, calculations of the energy loss by the best adiabatic methods predicted an energy loss of order 2%. It appeared that Rydberg-atom tagging would easily provide the energy resolution necessary to detect any extra contributions to the energy loss due to nonadiabaticity.

Figure 17(a) shows the energy loss spectrum measured with Rydberg-atom tagging for H atoms incident on Au(111) with 2.76 eV
translational energy. The energy loss peaks at 0.7 eV and extends to 2.3 eV, far higher than the energy loss derived from the best adiabatic models and consistent with the idea that nonadiabatic excitation of EHPs dominates the energy loss. A comparison to scattering from an insulator (a multilayer Xe film adsorbed on Au), also shown in Figure 17(a), demonstrates the dramatically smaller energy loss when EHP excitations are eliminated. Figure 17(b) shows simulations of the scattering using a full-dimensional PES fitting an EMT function to DFT data, and a self-consistent treatment of adiabatic and nonadiabatic contributions at the level of the LDFA. Calculations which include electronic friction (squares) agree well with the measurements (x’s), while calculations done without nonadiabatic energy loss (closed circles) show far too little energy loss.

Both experiment and theory could be extended to H and D scattering from Pt, Ag, Pd, Cu, and Ni in all cases, a PES was generated by fitting an EMT function to DFT data, and a self-consistent treatment of adiabatic and nonadiabatic contributions at the level of the LDFA. Calculations which include electronic friction (squares) agree well with the measurements (x’s), while calculations done without nonadiabatic energy loss (closed circles) show far too little energy loss.

A practical way to estimate the sticking coefficient for H or D to any metal, by knowing only the metal’s mass, M.

\[
S(E_{in}, \vec{c}_{in}, M) = \left( S_0 + a \cdot E_{in} + b \cdot M \right) \times \left( 1 - h \left( \vec{c}_{in} - \vec{c} \right) \left( 1 - \cos(\vec{c}_{in} - \vec{c}) d \cdot h(E_{in} - \vec{c}) \right) \right) \tag{2}
\]

where \( h \) is the Heaviside step function and the parameters for H are given by:

\[
S_0 = 1.081, \ a = -0.125 \ \text{eV}^{-1}, \ b = -8.4 \times 10^{-4} \ \text{u}^{-1}, \ c = 28.88^\circ, \ d = 0.443 \ \text{eV}^{-1}, \ e = 1.166 \ \text{eV}.
\]

and for D by:

\[
S_0 = 1.112, \ a = -0.124 \ \text{eV}^{-1}, \ b = -1.2 \times 10^{-3} \ \text{u}^{-1}, \ c = 28.62^\circ, \ d = 1.196 \ \text{eV}^{-1}, \ e = 0.474 \ \text{eV}.
\]

We give these parameters in this review as an erratum was published clarifying the parameters that might be overlooked in a perusal of the primary literature.

Similar to what was possible for formaldehyde roaming reactions (Section 3.2), animations of H atom trajectories reveal the atomic scale mechanisms of adsorption of H atoms on metals. Figure 18 shows such an animation. Remarkably, adsorption trajectories involve H-atom penetration to the first subsurface layer, where it remains trapped for ~250 fs until sufficient energy can be transferred to nearby surface gold atoms opening an “escape hatch.” It then returns to the surface still with a substantial fraction of its initial translational energy and equilibrates over about 1 ps. This should not be entirely surprising. Electronically adiabatic simulations show H atoms penetrating and even passing through a four-layer thick slab of fcc Au.
FIGURE 18 The dominant mechanism for H atom adsorption involves penetration and resurfacing. This animation shows a single MD trajectory, where an incident H atom moves under the influence of the Born–Oppenheimer PES and a drag force induced by electronic friction. The trajectory has an initial kinetic energy of 2.7 eV.

Imaging covalent bond formation: H atom scattering from graphene

H atom adsorption on graphite or graphene is quite different from its adsorption on metals—it is an activated process driven by covalent C-H bond formation and $sp^2 \rightarrow sp^3$ re-hybridization of the C-framework is required to make this happen. Studying the scattering of H and D from graphene with tunable incidence energies above and below the barrier to adsorption thus presents an opportunity to probe the dynamics of transient bond formation. Experimentally, the H or D energy is tuned by varying the incidence angle, $\theta_i$, while holding the incidence energy, $E_i$, constant, as only the normal component of the incidence kinetic energy, $E_n = E_i \cos^2(\theta_i)$, is effective in overcoming the barrier.

Figure 19(a–c) shows H atom scattering flux maps for $E_i = 1.9$ eV, where $E_n = 0.49, 0.78$, and $1.11$ eV, respectively. For the lowest value of $E_n$, H atoms lose little energy (quasi-elastic), but as $E_n$ increases, a second peak appears exhibiting $\sim 1$ eV energy loss. At the highest $E_n$, almost no quasi-elastic scattering is seen. The narrow angular distributions seen under all conditions rule out trapping and raise the question of how a light H atom can lose so much energy in a sub-picosecond collision. Theoretical simulations of the scattering provide an answer to that question.

Figure 19 panels(d–f) show the simulation results, which are a good example of the power of current computational techniques for surface reaction dynamics. Here, a high-dimensional neural network (HDNN) was used to provide a representation of the H-graphene PES. Importantly, the PES is a function of both H and C atom coordinates and accurately represents the potential for large displacements of the C atoms from their equilibrium positions in graphene. This was achieved by using machine learning algorithms to train the HDNN to energies calculated with DFT, including configurations of the H and C atoms from ab initio molecular dynamics (AIMD) (on the fly DFT) trajectory calculation. The comparison between simulations, based on hundreds of thousands of trajectories, and the experimental results is remarkably good.

The success of the trajectory simulations allows us to learn more about the process of covalent C-H bond formation and other scattering phenomena seen in experiment. Figure 20 shows two animated trajectories representative of the quasi-elastic channel and transient chemical bond formation, respectively. For the quasi-elastic channel, one sees little change to the C-C motion, while the H-atom is scattered in a plane near the specular direction. For transient chemical bond formation, the H-atom scattering on average remains close to the specular angle, but there is a high probability for the trajectory to emerge in a plane
Two Channels in H atom scattering from graphene

- Quasi-elastic Channel

- Transient Chemical Bond Formation

rotated from that of the quasi-elastic trajectory. The directional forces involved in the transient C-H bond formation are responsible for this.

From analysis of trajectories like this, a simple but perhaps unexpected picture emerges. For transient chemical bond formation, the H atom approach triggers an electronic change to the system within about 10 fs, where the attacked C-atom in the graphene experiences a partial electronic rehybridization from sp² to sp³. Of course, this also affects the electronic bonding to its neighbors. The fastest response to this electronic change is to excite in plane C-C stretching. In fact, it is the next nearest neighbor C-atoms (and not the C-atom being attacked by the H atom) that begin moving first. Only later does the H-attacked C-atom begin to pucker out of plane, exerting a drag on the departing H atom. The transfer of energy to these four atoms accounts for most of the large energy loss observed in experiment.

It is worth noting that the energy loss seen here is actually much larger than anything seen for H atoms scattered from metals. The adiabatic (i.e., mechanical energy transfer) is so efficient due to the transient chemical bond formation that it is difficult to rule out (or in) the possibility of EHP excitation. It is also worth considering that the simulations have neglected the presence of the underlying substrate—the experiments were done with graphene grown on Pt(111). It would be very interesting to see how H atom inelastic scattering depends on variation of the substrate. Experimentally, one may grow graphene on a variety of materials. Theoretically, it would appear possible to extend neural networks and DFT to include the substrate in simulations.

The examples shown so far have been restricted to studies of inelastic scattering, but they have already brought some of the features of adsorption into focus. We now turn to a systematic presentation of the dynamics of adsorption and desorption.

**FIGURE 20** The trajectories found in molecular dynamics simulations of H scattering from graphene. Top and side views visible simultaneously

**FIGURE 21** Lennard-Jones view of dissociative adsorption. Blue curves represent the potential energy of an intact AB molecule as it approaches the surface; red curves represent the potential energy of molecular fragments A and B. (a) Nonactivated adsorption: here, the energy of the crossing point (transition state) is lower than that of the gas-phase molecule. (b) Activated adsorption: here, the transition state is higher than the asymptotic energy. (c) A 2D PES makes the situation clearer

the arrows in these two reactions, a molecule can desorb intact—molecular desorption—or undergo "recombinative desorption."

In 1932, Lennard-Jones[^330] presented a 1D picture of dissociative adsorption—see Figure 21(a) and (b). This view involves an undisassociated AB molecule’s potential (blue curves) and a potential for the dissociated fragments A and B (red curves). In fact, the blue and red curves do not intersect—a two-dimensional PES—Figure 21(c)—is needed to see that the transition state (+) is not located on either curve. These reactions are best described as concerted motion along a multidimensional PES, with many of the same issues arising that influence gas-phase dynamics: curvature of the reaction path, early or late transition states, distribution of energy among degrees of freedom, molecular orientation, and so forth. Many additional features not present in gas-phase reactions influence reactions at surfaces, including energy dissipation, surface corrugation, or surface defects, steps, and other special reaction sites. The rate of desorption is one of the most accessible kinetics measurements in surface chemistry. Temperature programmed desorption detects the rate of desorption as the temperature is ramped. The rate is measured from high to low adsorbate coverage, θ,
first-order kinetics are then seen. 331,332 Reprinted from Opila R, monolayers and the islands evaporate into a “2 D gas.” Ordinary temperature, a phase transition occurs at a coverage of 0.3 that desorption takes place from the edges of large islands. At this temperature, a phase transition occurs at a coverage of 0.3 monolayers and the islands evaporate into a “2 D gas.” Ordinary first-order kinetics are then seen.331,332 Reprinted from Opila R, Gomer R. Thermal-desorption of XE from the W(110) plane, Surf Sci. 1981;112(1-2):1-22, Copyright 2021, with permission from Elsevier that is, the number of adsorbed molecules per unit area on the surface, which plays the role of concentration in gas-phase kinetics.

Influence of coverage on adsorption and desorption

The dependence of desorption rates on coverage can be complex and sometimes mystifying. Figure 22 shows a beautiful example, the isothermal desorption of Xe from W(110). The presence of attractive interactions between adsorbates can have striking effects on desorption rates. Here, there is a sharp change of slope in the rate which arises when a first-order two-dimensional phase transition occurs at $\theta = 0.3$.332 The free energies of the two phases are continuous through the transition, but the enthalpies and entropies that control the rate of desorption can be very different.332

Influence of steps on desorption

Desorption can also take place from different surface sites, for example, from terraces and steps. The step desorption's pre-factor can be several orders of magnitude larger than that of terrace desorption.333 This is an entropic effect where a step-bound adsorbate is constrained to live in a lower entropy 1D world compared to a terrace bound species. The reduced entropy of the adsorbate dramatically enhances the desorption rate.

Peculiar coverage dependencies can arise when adsorbates are able to diffuse to defects, which commonly bind molecules more strongly than do terraces.334 Figure 23(a) and (b) shows the energetic landscape and the desorption measurements, respectively. In experiment, the initial rate of desorption is rapid—terrace desorption—until the terrace sites are empty and then desorption decelerates being limited by the rate of step to terrace diffusion.335

Detecting trapping/desorption

In the previous section, we have seen the results of many beautiful experiments that infer the nature of molecule–surface interactions from measurements of the quantum state, speed, and angular distributions of molecules undergoing direct scattering, conditions where the molecule has no time to reach equilibrium with the solid. Langmuir considered this process of molecular “reflection” already in 1917 and pointed out the importance of and difficulty associated with distinguishing “reflection” from condensation followed by evaporation.336

With the experimental tools now available, this is readily accomplished. See Figure 24.

Using a molecular beam with a narrow velocity distribution, Xe atoms scattered from Pt(111) exhibit distinctly bimodal TOF distributions, the slower fraction trapping and then desorbing, while the faster fraction scatters directly.337 The angular distribution of direct scattering is also much narrower than that of trapping/desorption. Naturally, the residence time and the speed distribution of trapping/desorption depends on $T_s$. Figure 24(e–j) shows vibrational state-to-state TOF experiments.310 Here, CO($v = 2$) is prepared in a molecular beam just 0.5-mm before collision with a Au(111) surface. The returning CO molecules are state specifically detected about ~1-cm away from the surface by REMPI and their TOF recorded by scanning the delay between the two laser pulses. Just as for Xe on Pt(111), two contributions to the speed distribution are seen. As the residence time is similar to the vibrational relaxation lifetime of CO($v = 1, 2$) on Au(111),319 the trapping/desorption component detected in vibrationally excited states of CO appears to increase with $T_s$. This system has also been studied by molecular dynamics on an HDNN PES.338 Inspired by ideas developed in this work, it was possible to show that collisions of CO on Au(111) first pass through a metastable chemisorption well before partially equilibrating in a physisorption well, the lowest energy surface binding site.310

Detailed balance, or why the desorption rate depends on the sticking probability

The properties of thermal equilibrium can be used to great advantage when studying trapping and desorption. To see this, consider adsorption in the language of TST, where the flux through a “point of no return” dividing plane in the adsorption direction is:

$$F_{TST}(\theta, T) = \frac{k_B T}{h} Q_{2D} \exp(\mu(\theta, T)/k_B T)$$

(3)

where $k_B$ is Boltzmann's constant, $\mu(\theta, T)$ is the chemical potential of the gas, $Q_{2D}$ is a simplified two-dimensional ideal gas partition function for a noninteracting adsorbate, and $h$ is Planck’s constant—see Ref. [339] and Figure 25.
FIGURE 23 Desorption from steps and terraces. (a) Model of NO binding at steps and terraces of Pt(111) developed to describe: (1) thermal desorption from terraces and (2) thermal diffusion from steps to terraces followed by thermal desorption. The fast component is simple desorption from terraces, while the slow component is a sequential process involving thermal diffusion from steps to terraces followed by desorption from terraces. (b) Experimentally observed bi-exponential desorption predicted by this model of CO desorption from Pt(111). The fast component is simple desorption from terraces, while the slow component is a sequential process involving thermal diffusion from steps to terraces followed by desorption from terraces.

FIGURE 24 Distinguishing direct scattering from trapping/desorption. (a–d) TOF measurements of Xe scattering from Pt(111). (a) Xe beam incident at 75° from the surface normal with $E_i = 0.14$ eV; also shown are scattered Xe detected at: (b) 0°, (c) 45°, and (d) 75°. The fast feature is direct scattering, while the slow feature is trapping desorption. The solid lines in (a–d) are MD simulations—the circles are from experiment. (e–j) State-to-state TOF measurements of CO scattering from Au(111). A pulsed beam of CO($v = 2$) collides with Au(111). REMPI detects specific vibrational states of scattered CO several cm from surface and the TOF is recorded. Both direct scattering and trapping desorption are seen, proving that CO($v = 2$) can survive a trapping desorption encounter with Au(111).

Of course, some molecules that pass through the dividing plane may not trap, but instead bounce back from the surface introducing a recrossing correction that is the sticking probability, $P_s(\theta, T)$. The recrossing corrected TST rate of adsorption then becomes:

$$R_{ads} = P_s(\theta, T) F_{TST}(\theta, T)$$

Note that at equilibrium, the adsorption and desorption rates must balance.

$$R_{des} = R_{ads} = P_s(\theta, T) F_{TST}(\theta, T)$$

Remarkably, the rate of desorption is proportional to the sticking probability—this is, at first glance nonintuitive, but it expresses the
The analysis of the velocity distribution of the trapping-desorption fraction for Ar scattered from hydrogen-covered W(100) showed that at low $T_3$ the mean energy of desorbed atoms was $2k_BT$, in accord with a Maxwellian distribution at the $T_2$. This is consistent with a near-unity trapping probability at low gas and surface temperature. At higher surface temperatures, the mean energy of the desorbed atoms was markedly lower than $2k_BT$, consistent with a decrease of the trapping probability at higher gas and surface temperatures. Furthermore, at low surface temperatures, the trapping-desorption fraction obeyed the $\cos \theta$ angular distribution required if the sticking probability were unity, but at higher surface temperature, the angular distribution was observed to be broader than $\cos \theta$. This indicates that the trapping probability depends more strongly on the component of gas momentum normal to the surface plane than parallel to it, resulting in a larger decrease of normal momentum than parallel. Molecular beam and computational studies of Ar scattered from Pt(111) confirm that momentum in the normal direction is accommodated more rapidly than the parallel component, and that at higher surface temperatures for which the Ar residence time is less than 100 ps, atoms desorb prior to accommodating their parallel component of momentum.

Dissociative adsorption and recombinative desorption of molecules is more complicated and more interesting than that of intact adsorption/desorption. The sticking probability, in principle, can depend on not only the surface temperature and the initial translational energy and angle of approach of the molecule, but also on its initial electronic or spin-orbit state, the initial vibrational state, the initial rotational energy and polarization, and the initial orientation of the molecule. The design and fruition of extraordinary spectroscopic and molecular beam techniques, coupled with advanced computational modeling, has provided detailed and quantitative knowledge of the dynamics of molecular bond-breaking and making at surfaces. Recently, detailed balance together with an elaborate microkinetic analysis has been used to show that adsorption to a physisorption well may be facilitated by transient chemisorption in a metastable well with stronger molecule surface interactions.

**FIGURE 25** Transition state theory of adsorption and desorption. It is convenient to define the point of no return to be a plane parallel to the surface at large distance. When this is done, the thermal sticking coefficient can be used to correct the recrossing error in TST. (a) High-energy molecules are less likely to stick. This appears as a recrossing error in TST. Consequently, desorption rates are higher for low energy molecules and the translational temperature of desorbing molecules can be lower than $T_2$. (b) Low energy molecules are more likely to recross and energy distributions of desorbing molecules can be hyperthermal.

The nonequilibrium dynamics of desorption is encoded in the sticking probability’s dependence on incidence conditions, coverage, and temperature.

In fact, Equation (5) can be written in terms of the speed, $s$, angle, $\delta$, and quantum state ($v, J, M$)-specific sticking probabilities.

$$P_s(\delta, s, v, J, M)_{\text{TST}}(T) = R_{\text{des}}(\delta, s, v, J, M)$$

Measurements of state-specific and velocity-resolved rates of desorption reliably predict their corresponding sticking probabilities.

**Application of detailed balance**

The design and fruition of extraordinary spectroscopic and molecular beam techniques, coupled with advanced computational modeling, has provided detailed and quantitative knowledge of the dynamics of molecular bond-breaking and making at surfaces. Recently, detailed balance together with an elaborate microkinetic analysis has been used to show that adsorption to a physisorption well may be facilitated by transient chemisorption in a metastable well with stronger molecule surface interactions.

**DYNAMICS OF REACTIONS AT SURFACES**

Even prior to the quantum revolution, Langmuir and others were thinking about atoms and molecules on surfaces. Langmuir’s brilliant interpretations of simple yet rigorous experiments led him to intuit key aspects of possible reaction mechanism at surfaces, one where surfaces resemble a checkerboard on which every square can be occupied by only one atom or molecule. Through adsorption and diffusion, molecules and atoms end up on neighboring squares and react with one another. Reactions and desorption remove molecules from the surface creating empty spaces for subsequent adsorption to occur. The elementary steps (highlighted above in bold) of this so-called Langmuir–Hinshelwood (LH) mechanism have all become central topics in the study of reactions at surfaces.

An alternative to this mechanism is that of Eley and Rideal. In this “ER” mechanism, a gas-phase atom or molecule collides at the binding site of a chemisorbed atom or molecule and reacts without coming into thermal equilibrium with the solid. Modern experimental methods readily distinguish LH from ER, since the energy available to the products is typically much higher for ER reactions than for LH—less chemical energy is lost to the solid—and ER reactions exhibit a “memory effect,” where the speed, angle, or quantum state of the incident reactant influence the speed, angle, and quantum state of the product. This is obviously not the case for an LH reaction where the reactants equilibrate with the solid before reaction.

Intrinsic to LH is the idea that adsorbed reactants thermalize with the surface and that products form at a speed controlled by thermal reaction and diffusion. Nevertheless, LH reactions can produce
hyperthermal products—for example, when two adsorbed H atoms thermally desorb from a copper surface, they must overcome a substantial barrier; the H₂ formed at the barrier has no time to equilibrate with the solid and is ejected from the surface with a great deal of translational (and vibrational) energy. These nonthermal effects lend themselves to state, speed, and angle-resolved experiments that are particularly sensitive to the PES of the reaction in the vicinity of the transition state, allowing the extension of the dynamical approach from the gas-phase to reactions at surfaces.

This section contains highlights of work on nonthermal ER reactions and direct dissociative adsorption, together with an exposition of the problems of measuring and predicting the rates of thermal reactions. Arguably, the most important goal of the dynamical approach for surface chemistry is to accurately predict thermal reaction rates—see, for example, Ref. [355]. Thermal surface reactions are by far the most common in nature and must be measured for practical use. Predicting thermal rates represents the true payoff for a highly developed theoretical understanding. For this, we need detailed dynamical experiments capable of probing the key features of the PESs of elementary reaction steps, thereby testing the computational methods used to generate them. We also need means to determine reaction mechanisms—LH versus ER for example—but even more basic than that, we must find out which elementary reactions are important, and determine the active sites of those reactions.

**Vibrational and translational promotion of surface reactions**

**H₂ on copper**

One of the best understood systems is the reaction $\text{H}_2(\text{g}) \rightarrow \text{Cu}(111) \rightarrow 2\text{H}^+$, which has been studied in both directions and for different isotopologues and previously reviewed.9 The reaction has served a similar role for the theoretical development of surface chemistry as the H₂ reaction has for gas-phase reactions. Experiments on dissociative adsorption and associative desorption show that there are two reaction mechanisms, an activated dissociation process that is promoted by field free ion TOF, their velocities are obtained. The hydrocarbon molecule’s motion depends on four quantities, $H_2(v, J, M, \vec{v})$—the quantum numbers for molecular vibration, rotation, alignment, and the velocity vector. Ro-vibrational state resolved reaction thresholds, $E_0(v, J)$, provide the magnitude of translational energy needed for each ro-vibrational state to react. These can be determined both experimentally 257 and theoretically 245 and agreement is good. Analogous work has extended this to include alignment effects, where $E_0(v, J, M, \vec{v})$ is measured 261,362. H₂ with its bond-axis parallel to the surface requires less translational energy to react than molecules with another alignment. This confirms aspects of the transition state structure for the reaction, where the H–H bond lies parallel to the surface over a bridge site of Cu(111). 363 The reaction has also been studied in this way on stepped surfaces 2H⁺ Cu(211) → H₂(g). Unlike many surface reactions, here steps are somewhat less reactive than terraces. 257

Application of the dynamical approach to this reaction involves improving theory to reach agreement with data like that just described, in this case optimizing a Born–Oppenheimer PES, using a semi-empirical specific reaction parameter (SRP) functional. 363 The fact that this has proven possible is apparently due to the fact that the most important complications anticipated in moving from the gas phase to metal surfaces—the influence of phonons and EHPs—do not appear to affect this reaction greatly. 264

**HCl on gold and silver**

The situation appears to be much more challenging for the reaction HCl(\text{g}) Au(111) → H⁺ + Cl⁻. Inelastic scattering probabilities for collisions at Au 266 and Ag 264 were measured as a function of surface temperature and incidence energy of translation. These results suggest that hot EHPs excite H + Cl interatomic motion efficiently near the transition state for dissociative adsorption. The dissociative adsorption probability’s dependence on vibrational and translational incidence energy was also measured with a hot-nozzle technique. 265 The experimentally derived reaction probabilities were much smaller than predicted by theories using a 6D Born–Oppenheimer PES with quantum wave packets. 264 Some improvement was found using a different functional. 267 Classical AIMD calculations that allow the surface atoms to move also failed to bridge the gap to experiment 268; furthermore, the reaction path and barrier height depend strongly on choice of functional. 269 A new PES has been developed with a higher reaction barrier but agreement with experiment is still poor. 265

In related work on the ER reaction: H(g) → Au(111) → HCl(g), AIMD calculations produced HCl vibrational excitation far larger than that seen in experiment. By including LDFA friction, vibrational excitation was reduced 370 and trajectories showed H atoms lose energy before reacting with Cl⁻, a plausible influence of electronic friction on reactivity. But the HCl vibrational distribution was still much hotter than seen experimentally—compare figure 18 of Ref. [352] with figure 2 of Ref. [370], possibly an indication of the limitations of the LDFA.

While the research on this reaction, so far, is no success story, it is without doubt one of the most interesting for future study. It has recently been suggested that for reactions where the difference between the surface work function and the electron affinity of the adsorbate is smaller than 7 eV, DFT-GGA calculations of barrier heights may be unreliable. 571 As seen in Figure 15, it is precisely under these conditions that electronically nonadiabatic coupling between...
adsorbate nuclear motion and the solids EHPs may become important. In fact, there is strong experimental evidence that this reaction\textsuperscript{266} and the analogous reaction on Ag(111)\textsuperscript{264} may be strongly influenced by such nonadiabatic coupling. Hence, this reaction presents a challenge to theory's ability to accurately calculate adiabatic electronic energies as well as nonadiabatic dynamics. Meeting those challenges will no doubt lead to better theoretical methods and deeper understanding.

Dissociation of polyatomic molecules on metal surfaces

Both theoretical and experimental studies of the vibrational and translational promotion of surface reactions have extended to those involving reactants with more than two atoms. Some of the reactions that have attracted attention include: CH\textsubscript{4}(\textsuperscript{1}A\textsubscript{g}) \rightarrow CH\textsubscript{3}(\textsuperscript{2}B\textsubscript{1}) + H\textsuperscript{\ast}\textsubscript{372–375}, H\textsubscript{2}O\textsubscript{\textsuperscript{1}A\textsubscript{g}} + \textsuperscript{1}Cu \rightarrow OH\textsuperscript{\ast} + H\textsuperscript{\ast}\textsubscript{372}, NH\textsubscript{3}(\textsuperscript{1}A\textsubscript{g}) \rightarrow NH\textsubscript{2}(\textsuperscript{1}A\textsubscript{g}) + H\textsuperscript{\ast}\textsubscript{376}, CO\textsubscript{2}(\textsuperscript{1}A\textsubscript{g}) \rightarrow CO\textsuperscript{\ast} + O\textsuperscript{\ast}\textsubscript{377} and CH\textsubscript{2}OH\textsubscript{\textsuperscript{1}A\textsubscript{g}} \rightarrow CH\textsubscript{3}O\textsuperscript{\ast} + H\textsuperscript{\ast}\textsubscript{378}.

The influence of vibrational excitation on dissociative adsorption was first seen by changing the beam source temperature and seed gas to thermally excite CH\textsubscript{4} vibrations.\textsuperscript{380,381} This influence of vibration is more cleanly seen with laser pre-excitation of the molecule, where a molecular beam of methane with controlled translational energy is excited by a c. w. infrared laser with high power and coherence producing selected vibrational states. Auger electron or reflection absorption infrared spectroscopy (RAIRS) is then used to look for the buildup of reaction products on the surface.\textsuperscript{375} Studies like this have demonstrated mode specificity\textsuperscript{279,382,383}—see Figure 26—and bond selectivity\textsuperscript{384} as well as steric effects\textsuperscript{385} in chemisorption reactions, highlighting the nonstatistical and complex nature of gas–surface reaction dynamics.\textsuperscript{273} These studies have also demonstrated that surface atom motion plays an important role in determining the ease with which the gas-phase molecule surmounts the reaction barrier.\textsuperscript{386} It is even possible to reveal the dynamics of reaction at specific surface sites.\textsuperscript{387}

While the many degrees of freedom of methane make full-dimensional quantum calculations challenging,\textsuperscript{388} an approximate 15 DOF quantum method has been demonstrated using a reaction path Hamiltonian,\textsuperscript{389} originally developed for gas-phase problems.\textsuperscript{390} The “quantum reaction path” method provides an accurate description of the translational motion and nine internal molecular DOFs of methane, and while a vibrationally adiabatic basis set is used, all vibrationally nonadiabatic couplings are included. This method was the first to succeed in capturing mode-specific reactivity like that shown in Figure 26. It also avoids an artifact of classical mechanics, where zero point energy can flow within the molecule—such effects are difficult to avoid when using QCT and AIMD trajectories.\textsuperscript{391}

Beyond this, the quantum reaction path method also helped reveal the influence of surface atom motion on the reaction, seen experimentally as a strong surface temperature dependence of the reaction probability.\textsuperscript{392} DFT calculations show that the barrier to dissociation is modulated by the out-of-plane motion of the metal atom most intimately involved with the transition state.\textsuperscript{393} For methane on Ni, the effect of this on the reaction probability was treated in an approximate way, using a lattice sudden model.\textsuperscript{394,395} which effectively averages over the barrier height and momentum distributions along the reaction coordinate produced by thermal motion of the Ni atom.\textsuperscript{396} More recently, this approximate scheme has been validated by 8D quantum dynamics calculations on a 14D PES.\textsuperscript{397} This and the previous studies all conclude Ni-lattice motion is involved in the reaction.

Observing adsorbed reaction intermediates and products with surface-site specificity can be achieved using RAIRS to detect products, and preparing state-selected reactants in a molecular beam. Using CH\textsubscript{3}D with either the C – H or C – D bond pre-excited, RAIRS can distinguish adsorbed products—CH\textsubscript{3}\textsuperscript{\ast} or CDH\textsubscript{2}\textsuperscript{\ast}—at different surface sites.\textsuperscript{387,398} For reactions on Pt (211), at low incidence energies of translation and without vibrational pre-excitation, only dissociation at steps was observed, without isotopic selectivity. However, with vibrational pre-excitation of the C – H bond, only infrared absorption corresponding to CDH\textsubscript{2} bound at steps could be seen at low incidence energies of translation. At higher translational energy, dissociation at terraces appeared and bonds without vibrational excitation became more reactive.\textsuperscript{399} Note that under the conditions of these experiments, CH\textsubscript{3}\textsuperscript{\ast} diffusion is believed to be unimportant. The authors concluded that the barrier to reaction at steps is at least 0.3 eV lower than at terraces—DFT predicted barriers for dissociation at steps and terraces of 0.55 eV and 0.82, respectively, when using an SRP functional.\textsuperscript{400}

The dissociation of water on metals has also attracted attention, inspired by vibrational state selected molecular beam measurements of dissociation probabilities for the reaction D\textsubscript{2}O\textsubscript{\textsuperscript{1}A\textsubscript{g}} \rightarrow OD\textsuperscript{\ast} + D\textsuperscript{\ast}.\textsuperscript{401} Here, vibrational efficacy is larger than the translational, probably related to the late barrier to reaction—see the Polanyi rules (Section 2.1).48 The quantum reaction path method was also applied and after rescaling the barrier height, good agreement with experiment was found.\textsuperscript{402} These calculations exhibited bond
selective dissociation for HOD and again, a strong influence of surface atom motion. A nine DOF PES was also produced and site specific reactivity could be studied; a site averaging model was also tested. Scientists have also begun to explore the properties of water dissociation on other surfaces, like Cu, AgNi, and CuNi alloys. In contrast to these reactions, where the molecule travels over the dissociation barrier on a sub-picosecond time-scale, LH involves newly adsorbed reactants rapidly equilibrating with the solid. Does one then expect vibrational promotion of LH reactions? Recently, the vibrational relaxation lifetime of molecules bound by physisorption interactions has been measured to be ~50 ps, more than an order of magnitude longer than vibrational relaxation for chemisorbed molecules. This helps to explain why it is possible to observe the trapping followed by thermal desorption of a vibrationally excited molecule. These observations suggest that while the LH mechanism involves thermalization of reactant translation and reaction, reactant vibration may relax more slowly and may live long enough to accelerate surface reactions prior to the vibrational energy being lost to the solid.

In an experiment similar to those described in Ref. [375], CH₄ dissociation probabilities on Ir(111) were obtained for selected vibrational states as a function of translational energy. QCT simulations on a PES that had been fitted to 5000 DFT points were performed to obtain the sticking probability dependence on surface temperature as well as incidence translational and vibrational energy of CH₄. Remarkably good agreement with experiment was found. Further analysis of the trajectories showed that at low incidence energy, adsorbed molecules with unrelaxed vibrational excitation could dissociate with higher efficiency than vibrationally cold molecules. TST rate calculations assuming the precursor-mediated mechanism suggested that vibrationally excited states might react at surface defect sites. It is well known that while molecules initially adsorb to majority sites, diffusion to minority defect sites like steps is often much faster than desorption and reaction rates at these defects can be much higher than at majority sites. This intriguing work suggests the same might be true for vibrationally excited molecules physisorbed to catalytic surfaces.

The influence of nonadiabatic electronic effects on reaction probabilities

The question of how strongly Born–Oppenheimer failure influences surface chemical reactions remains unanswered at this time. One problem is that nearly all theoretical studies have so far been limited to modelling electronically nonadiabatic effects with electronic friction at the level of the LDFA. In such calculations, electronic nonadiabaticity is typically small, for example, for H₂O → H₂ + O·, CH₄ → CH³⁺ + H⁺, or H₂O → OH⁺ + H⁺ for H₂O on Cu(111) → 2H⁺. It should not be surprising that friction-based calculations, which all rely on a weak coupling approximation, are limited in their ability to describe strong electronically nonadiabatic effects. Friction fails to describe electronically nonadiabatic multi-quantum vibrational excitation of NO in collisions with Au(111), whereas an IESH model involving strong coupling via an electron transfer reaction gave good agreement—see Figure 12.

Other experimental evidence that tends to contradict the conclusions of LDFA-based friction studies comes from studies where observed chemistries, which were attributed to the reaction of 2H⁺ → H₂(g), and from permeation studies of the same reaction. Further development of electronically nonadiabatic dynamical propagation algorithms is clearly needed, for example, ODF and methods beyond those involving a weak coupling approximation. We also clearly need studies of a wider variety of reactions.

One example of recent progress in this direction deserves mention. Experiments and theory on the dissociative chemisorption, inelastic scattering and associative desorption of N₂ on Ru(0001) have provided compelling evidence that energy dissipation via EHP excitations plays an important role in its reaction dynamics. For example, ab initio electronic dynamics simulations predict vibrational energies of desorbed molecules to be much too high. Friction coefficients obtained by FGR from DFT calculations show that friction can be an order of magnitude larger in the vicinity of the recombination transition state than in the chemisorption state. This was attributed to the charge redistribution that accompanies the formation and breaking of chemical bonds. Since then, using neural networks to fit DFT data, a full-dimensional PES has been produced. This allowed study of the effect of surface atom motion on the reaction. The same PES was used to make a direct comparison between LDFA and ODF methods—this revealed that the latter achieves better agreement with experiment for reaction probabilities and vibrational energy distributions, although it slightly underestimates translational energy loss. While dissipative adsorption of N₂ on Ru has proven a valuable testing ground for these new theories, we caution that the experimental dissociative adsorption probabilities being compared to exhibit large error bars.

Thermal reaction rates

Molecular beams have long been used to measure surface reaction rates. One of the most successful approaches is molecular beam relaxation spectrometry (MBRS) —see Figure 27. For a simple reaction like first-order desorption, the molecular beam delivers and replenishes the adsorbate concentration and the time-dependent product signal is used to extract the desorption rate constant. Note that when the sticking probability is independent of coverage and temperature, the rate constant for desorption and the reaction probability are obtained by simply varying the beam modulation frequency and/or the surface temperature, while recording the phase shift. MBRS has been applied in this way to a large number of reactions, including hydrogen recombination, CO desorption, NO desorption, H₂, and CO oxidation.

CO oxidation

Many consider CO oxidation on Pt and Pd the best-understood reactions in heterogeneous catalysis, yet a review of the results, even
FIGURE 27 Molecular beam relaxation spectrometry (MBRS): By modulating a molecular beam with a chopping wheel, while a mass spectrometer detects the time-dependent reactant and product density. The observed signal depends on the flight-time of the reactant to the surface, $t_1$, the reaction time at the surface, $\tau$, and the flight-time from the surface to the detector, $t_2$. One performs digital acquisition of the product waveforms (time domain) or phase-sensitive lock-in amplification (frequency domain), a technique adapted from fluorescence lifetime and chemical kinetics and first used in a beam surface experiment to distinguish signal from background. The phase-shift of products with respect to reactants reflects the reaction time at the surface. Reprinted from Schwarz JA, Madix RJ. Modulated beam relaxation spectrometry. Surf Sci. 1974;46(1):317-341, Copyright 2021, with permission from Elsevier

including those obtained with MBRS, illustrates the problems encountered in surface kinetics. Due to the ability of MBRS to directly probe the CO residence time and CO₂ formation rate, an LH (and not an ER) mechanism could be proven. O₂ is activated by dissociation forming adsorbed O*, which recombines with diffusionally mobile CO* to form CO₂ with release of energy.

$$O_2(g) \rightarrow 2O^* \quad (R1)$$

$$CO(g) \rightarrow CO^* \quad (R2)$$

$$CO^* \rightarrow CO^* \quad (R3)$$

$$CO^* + O^* \rightarrow CO_2^* \quad (R4)$$

$$CO_2^* \rightarrow CO_2(g) \quad (R5)$$

MBRS showed that reaction (R4) is thermally activated. It is also strongly exoergic as evidenced by the observation of CO₂ with hyperthermal translational and vibrational energy. The large translational energy release is produced by a force directed normal to the surface and produces narrower angular distributions in the desorbing CO₂ products than would be expected for a desorbing molecule that had been at thermal equilibrium with the surface. Clearly, hyperthermal products form by passing over a high barrier to CO₂ formation and are ejected from the surface before they can transfer the energy imparted to them by the reaction back to the surface.

$$CO^* + O^* \rightarrow CO_2(g) \quad (R6)$$

Under other reaction conditions, desorbing CO₂ appears to have first thermalized with the surface—here, translational energies are lower and infrared chemiluminescence is reduced. These observations show that CO₂ formation proceeds over a barrier, releasing part of its exothermicity to product excitation. They also suggest that reactions (R4) and (R6) may involve different elementary reactions at different active sites.

An alternative view postulates that all products form by reaction over a single activation barrier at a single reaction site, but...
due to the strong interactions between the product and the Pt surface, only a fraction desorb promptly with hyperthermal velocities, while the rest become trapped and thermalize with the surface before desorbing.451

A mechanism involving reaction sites at terraces and steps turns out to be important to this reaction. Even on (111) facets of single crystals, where step densities may be as low as $10^{-19}$, reactions at steps can easily be 1000× faster than at terraces. Furthermore, O* binds mainly at step sites452,453 at low coverage and temperatures; furthermore, O2 dissociates more rapidly at steps.454,455

The methods necessary to solve some of these problems became available only after the adaptation of slice ion-imaging to reactive surface scattering456-458—see Figure 28—providing numerous advantages for obtaining rates of elementary surface reactions.

The primary advantages of this method come from its ability to measure simultaneously the product density and speed, leading to the product flux, also called the kinetic trace. Consider a simple first-order reaction, CO desorption from a surface, CO* $\rightarrow$ CO(g), governed by the following kinetic equation:

$$ R_{\text{des}} = \frac{d[\text{CO(g)}]}{dt} = - \frac{d[\text{CO*}]}{dt} = k_{\text{des}}(T)[\text{CO*}] $$

The reaction rate, $R_{\text{des}}$, has units of cm$^{-2}$ s$^{-1}$—a flux. An experiment that automatically provides the flux of desorbing molecules is highly advantageous. Knowledge of the product’s speed is also used to correct each ion signal for the time spent flying from the surface to the laser ionization volume, $t_2$ in Figure 27 for MBRS.436

A third advantage is that different reactions may produce the same product but with different speeds. Figure 29 shows the results of ion imaging applied to the CO oxidation reaction on Pt (111).456 The ion image shown in panel a exhibits a bimodal velocity distribution, shown explicitly in panel b (speed distribution) and panel c (angular distributions). The kinetic trace can be obtained selectively—panel d—for the high-speed (red) and the low-speed (blue) velocity groups. This information immediately suggests a realistic kinetic model.

Motivated to more deeply understand the ion imaging experiments, AIMD trajectories showed that CO2 formation at steps indeed leads to thermalized CO2, while the terrace reaction produces hyperthermal CO2.459 Chemisorbed CO2 may form at step sites, taking on a bent structure with a partial negative charge. CO2 chemisorption is unimportant at Pt terraces.

**Identifying the active site**

Obviously, meaningful comparison of theory and experiment requires knowledge of the reaction site—it makes little sense to compare reaction rates measured at steps to those calculated with a reaction model involving terraces. Since the field’s inception, identifying the active site in surface chemistry has been a bane. A catalytic surface inhabited by adsorbates may exhibit a complex phase diagram of equilibrium structures dependent upon the partial pressure of gases and temperature. For example, when ab initio thermodynamics is used for Ru(0001) in the presence of O2(g) and CO(g), four different surface structures are found.460,461 Each surface structure offers a specific reaction geometry with its own transition state and barrier height.

Oxygen islands are a related example concerning CO and H2 oxidation on Pt and Pd. At low temperature, scanning tunneling microscopy (STM) shows that CO* and O* segregate and reactions occur only at their borders462—just like oil and water, reactants need not mix in
surface chemistry. Most theoretical calculations of CO oxidation barriers consider pairwise interactions between reactants: \( \text{CO}^* \cdots \text{O}^* \). But even with submonolayer \( \text{O}^* \) coverages at relatively high temperatures, two or more phases may form, one packed in a 2x2 lattice in equilibrium with a second phase of uncondensed \( \text{O}^* \). The \( \text{O}^* \)-island phase allows reactions within them or at their edges, obviously with different transition states. This concept was used to explain the observation that CO oxidation does not go to completion during a temperature programmed reaction cycle, suggesting that the island structure of the \( \text{O}^* \) reactants limits reaction. These authors argued that the reaction proceeds by diffusion of adsorbed CO to the perimeters of the immobile adsorbed atomic oxygen islands. Similar effects have been observed previously during temperature programmed reaction and titration studies of the \( \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \xrightarrow{\text{Pt}(111)} \text{H}_2\text{O}(g) \). Data supporting the idea of \( \text{O}^* \) islands are also available for reactions on Pt and Pd. This was rationalized as having to do with the influence of islands at high coverage that became less important at low coverage. The \( \text{O}^* \)-islands discussed so far exist at equilibrium, and phase diagrams of \( \text{O}^* \)-islands on Pt(111) have been calculated from first principles using of \( \text{O}^* \) – \( \text{O}^* \) interactions computed with DFT.

\( \text{O}^* \)-islands can also form under kinetic control. Oxygen dissociation on Pt is precursor mediated: \( \text{O}_2(g) \xrightarrow{\text{Pt}(111)} \text{O}_2^* \xrightarrow{\text{Pt}(111)} 2\text{O}^* \); furthermore, combining STM-experiments with theory, it could be shown that \( \text{O}_2^* \) dissociation proceeds on the upper side of Pt step edges. STM also showed that \( \text{O}_2^* \) dissociation is more likely in the vicinity of \( \text{O}^* \). This set of observations reveals how dissociation kinetics can lead to highly nonequilibrium surface structures, resulting from a dynamic heterogeneity in the adsorption mechanism. In short, a kinetically determined ordering of the adsorbate.

Making measurements on the living catalyst

These studies point out that a catalyst is dynamic, generating active sites due to exposure to reactants, a "living catalyst." This presents another experimental challenge. Since measuring rates of surface reactions requires signal averaging, the catalyst must return to its original state at the end of each measurement to allow for averaging. The dynamic catalyst may make this impossible.

Recently, velocity-resolved kinetics using high-repetition-rate pulsed laser ionization and high-speed ion imaging detection has been achieved. This overcomes the time-consuming scanning of the delay.
between the reaction initiating molecular beam pulse and the laser ionization pulse—Figure 30(a). In the new approach—Figure 30(b)—the reaction is initiated by a single molecular beam pulse and the product formation rate is observed by a sequence of pulses produced by a 1-kHz repetition-rate laser. This increases the data acquisition rate by up to a 1000×. With fiber lasers capable of running at 100 kHz or higher, another 100× improvement is within reach. Thus, what once took hours to measure can now be done in seconds and soon much faster. In addition, this approach overcomes the diffusion problem arising in many molecular beam reactive scattering experiments.473 To demonstrate the problem, consider that if one starts with an O∗-saturated Pt surface and doses it with CO pulses; then, O∗ is removed more rapidly from the part of the surface where the center of the molecular beam is incident. As time passes, most CO2 formed from CO that adsorbed near the center of the beam where O* is depleted, and diffused to the edges of the beam where O* is still present. Using high rep-rate velocity-resolved kinetics, the diffusional influence could be observed and quantitatively modeled.472

Exploiting our dynamical understanding of surface reactions to obtain a predictive theory of reaction rates remains yet an unfulfilled goal, as current limitations of the tools needed to make accurate measurements of reaction rates at well-characterized active sites have prevented meaningful tests of rate-theory. However, with experiments and theory both improving, we are increasingly benefitting from the fruitful interplay and we stand at the threshold of bringing this effort to fruition. Comparing to another subfield of complex chemistry provides some perspective. While surely not more complex, the study of heterogeneous catalysis has suffered from a structural deficit compared to enzymology. Methods to identify enzyme active sites—X-ray and electron diffraction—preceded by decades the theory of enzyme rates and dynamics at the transition state. Analogous methods to routinely identify surface active sites lay still in the future. In comparison to enzymology, we are still groping a bit to realize the structure function relationship. Nevertheless, as we learn more about active sites in heterogeneous catalysis through a fruitful interplay of experiment and theory, there is every reason to be optimistic that a predictive theory of rates will become available. After nearly a century, the dynamical approach is the gift that just keeps on giving, finding application to understand increasingly complex chemistry.

OUTLOOK

In this penultimate section, we wish to express our opinions regarding important directions for future research. This review has cited very little research on electronically inelastic scattering—there is very little. It should be noted that an instrument using a Stark decelerator for surface scattering has been reported and used to investigate electronic quenching of CO a3Π on metals with and without adsorbrates.475 This is certainly an interesting direction for the future.

Perhaps of greatest concern to us is the need to compare theory and experiment on the level of rates of elementary reactions. Here, many more rates must be measured accurately and these must be compared to rates calculated from first principles theory. The experimental methods are now available to obtain accurate rates on simple model surfaces and these must be extended to more complex surfaces that reflect new phenomena present in real catalysts. It will only be with the development of predictive theoretical methods, validated by experiment, that we may one day achieve useful microkinetic models of real catalysts.
An important target is an experimental tool for routine use that can reveal the structure of active sites of surface reactions in real catalysts. Here, the combination of near-field infrared spectroscopy with scanning probe methods\cite{476-478} may be of great importance; however, it will need to work at temperatures relevant to catalysis. Theory can also be crucially important here, for example, providing ab initio equilibrium structures present under realistic catalytic conditions.\cite{479}

We also need new theoretical tools. DFT-GGA is still suspect when it comes to calculating reaction barriers. Accurate wave function-based electronic structure theory\cite{480} perhaps employing self-consistent embedding methods\cite{481-483} or quantum Monte Carlo\cite{484} could at least provide benchmarks for methods. They also have the potential to offer accurate information on excited electronic states. The approximate methods must themselves also improve. Hybrid functionals applied to GGA densities is one promising direction.\cite{371}

A nagging question is to what extent energy dissipation to the solid—for example, due to coupling to EHPs—influences the rates of surface reactions. The influence of friction on reaction rates in liquids and biological systems has been widely demonstrated and quantified, based on the pioneering theory of Kramers.\cite{485} At surfaces, both phonon and EHP dissipation must be considered. For the latter, we require demonstrably correct theoretical methods for electronically nonadiabatic dynamics. Current friction approaches while improving\cite{314} are unlikely to be sufficient as they rely on a weak coupling approximation and are likely not applicable to problems that exhibit strong and localized nonadiabaticity, such as electron transfer. IESH still represents a fruitful avenue of future study and improvement.\cite{316} We also need measurements on a wider variety of systems. Systems for which $E_{\text{vibrational}} - \Phi$ is large and hence electron transfer is more likely (see Figure 15) are promising candidates for observing the influence of nonadiabatic electronic excitation on reaction rates.

The importance of quantum effects in surface chemistry needs much more effort. Recently, H atom beams have been produced at energies as low as 0.2 eV and with such narrow speed distributions, they could not be measured by Rydberg-atom tagging.\cite{486} These could deliver a great deal of excellent quantitative scattering data capable of testing quantum mechanical theories of reaction dynamics. High-dimensional quantum calculations, for example, by unifying the power of multi-configuration time-dependent Hartree dynamics\cite{487,488} with that of neural network PESs\cite{489} appear to be within reach. However, at least until quantum computers become widely accessible, fully quantum mechanical descriptions of catalytic systems are likely to remain intractable. Hence, accurate mixed quantum classical dynamics are extremely important.

Another interesting condensed phase quantum system is CO adsorbed to NaCl. In Section 5.1, we pointed out that CO vibrational relaxation is extremely inefficient. This allows high-resolution infrared emission spectroscopy to be carried out from which two orientation isomers have been identified.\cite{490} Normally, CO adsorbs with the C-atom close to a Na⁺ of the NaCl surface, but an “upside down” isomer has also been observed.\cite{490} Remarkably, experiments reveal well-resolved line spectra. This problem has already drawn interest from theorists developing PESs\cite{491,492} applying quantum dynamical methods.\cite{493} The challenges are formidable, but this system offers a proving ground for testing quantum dynamical methods in the high dimensions of condensed phases, providing a blueprint for exciting experimental and theoretical advances that may lead to fascinating discoveries, and take us systematically toward the dream of predicting and watching the intricate motions of individual atoms during a catalytic reaction.

**CLOSING REMARKS AND APOLOGIES**

In this manuscript, we have not attempted a comprehensive review of the field of chemical dynamics. Rather, our aim has been to highlight the most important concepts and present selected examples from gas-phase dynamics that illustrate how successful the dynamical approach has been and to extend the discussion to encompass the complexity and richness of reactions at surfaces. We have attempted to draw a line from the discovery of quantum mechanics, which inspired chemical dynamics, to the time of this writing in the first days of 2021. This perhaps foolishly ambitious undertaking means we must apologize to all those who do not find their work reviewed here. Beyond limits of time and space, it is hardly possible to be aware of all the significant work occurring over nearly a century. We do hope that those dedicated to the approaches of gas-phase chemical dynamics see here the possibility to extend the reach of their expertise to complex problems in other branches of chemistry.

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**AUTHOR CONTRIBUTIONS**

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**TRANSPARENT PEER REVIEW**

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