The Dynamics of Molecular Interactions and Chemical Reactions at Metal Surfaces: Testing the Foundations of Theory

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Keywords

Abstract

We review studies of molecular interactions and chemical reactions at metal surfaces, emphasizing progress toward a predictive theory of surface chemistry and catalysis. For chemistry at metal surfaces, a small number of central approximations are typically made: (*a*) the Born-Oppenheimer approximation of electronic adiabaticity, (*b*) the use of density functional theory at the generalized gradient approximation level, (*c*) the classical approximation for nuclear motion, and (*d*) various reduced-dimensionality approximations. Together, these approximations constitute a provisional model for surface chemical reactivity. We review work on some carefully studied examples of molecules interacting at metal surfaces that probe the validity of various aspects of the provisional model.

1. THE STANDARD MODEL OF CHEMICAL REACTIVITY

People have struggled to understand and control chemical transformations since at least the third millennium BCE when smelting copper and alloying with tin ushered in the Bronze Age. For chemists today, this struggle continues. Our most fundamental challenge is to develop predictive theories of chemistry rigorously grounded in the laws of physics. Referring to the implications of the discovery of quantum mechanics for chemistry, Dirac (1, p. 714) identified the problem famously in 1929: "The underlying physical laws necessary for the mathematical theory of . . . chemistry are . . . completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." Notwithstanding advances in computational capability that Dirac could hardly have imagined, he is still right. The theory of chemistry requires approximate methods for practical computations.

Even for the simplest gas-phase chemical reactions, such as $H + HD \rightarrow H_2 + D$, approximations are needed, most notably that of Born & Oppenheimer (2). With the recognition that electrons move much faster than nuclei do, the Born-Oppenheimer approximation (BOA) solves the quantum equations of the electrons for stationary nuclei. Repeating this for many nuclear arrangements resembling reactants, products, the transition state, and structures in between, we obtain the electronically adiabatic potential energy surface (PES) (3) and, from the PES, the atomic-scale forces that control and drive the reaction. For simple gas-phase reactions, highly accurate PESs can now be computed, and converged calculations of the quantum motion of the nuclei on the PES can be performed (4). From the experimental side, crossed–molecular beam methods and Rydberg atom tagging (5) yield product-state-resolved differential cross sections, the most highly detailed observables for a simple gas-phase reaction that one can possibly imagine. Experiments and theory agree quantitatively (6–8).

The construction of a reaction's PES within the BOA using accurate wave-function-based electronic structure theory and the PES to carry out calculations of the nuclear motion with quantum mechanics, as was done for the $H + HD$ reaction or, when appropriate, using the classical approximation, can rightly be called the standard model of chemical reactivity. Although it is not often practical to apply it at the highest level of rigor, we should not underestimate the generality of its impact. Many essential chemical concepts, such as the transition state, activation energy, steric effects, collision complex, and even our understanding of reaction mechanisms (e.g., abstraction versus insertion), make implicit reference to the nature of the PES and thus to the standard model.

1.1. The Central Assumptions of Computational Surface Chemistry

Theoretical surface chemistry deals with a class of complex problems in which additional approximations beyond those made in the standard model are needed. In this review, we focus on four approximations that are widely used in the description of surface chemistry: (*a*) the BOA or electronic adiabaticity, (*b*) the use of density functional theory (DFT) at the generalized gradient approximation (GGA) level, (*c*) the classical approximation for nuclear motion, and (*d*) various reduced-dimensionality approximations.

Surface chemistry involves such a large number of nuclear degrees of freedom that a reduced-dimensionality approach is unavoidable. This might involve neglecting the role of surface atom

motion (9), treating the dynamics of a reacting adsorbate in a restricted region of phase space (e.g., along its reaction path or restricting motion to specific surface sites) (10), or treating only a subset of the reactant molecules' degrees of freedom (11).

The large system size also makes it impossible to use the high-level quantum chemistry techniques employed for simple gas-phase problems. Instead, we use methods based on DFT (12–15) with exchange correlation functionals at the GGA level to treat the electronic states. Unlike quantum chemistry, DFT does not give us a hierarchy of approximate methods to test the accuracy of our results; thus, comparison with experiment is essential to test the validity of DFT results.

For many systems, a complete quantum mechanical description of the nuclear motion is not computationally feasible, and the nuclear motion must be treated in a classical approximation. Zero-point motion can be included by using the quasi-classical trajectory (QCT) method in which the zero-point energy is added to each vibrational mode.

Together with the BOA, these three approximations compose what one might call a provisional model of surface chemical reactivity. Along with improving computing power, the provisional model has made computations of remarkably complex problems in surface chemistry a technical reality. The potential for deep insights makes this line of research extremely attractive, and it is growing in importance and popularity.

1.2. The Growing Importance of Computational Surface Chemistry: Two Examples

When combined with carefully thought-out logical strategies, DFT can be used to develop simple insights for remarkably complex chemical systems. For example, computations of binding energies and activation barrier heights were combined with kinetic Monte Carlo methods to produce first-principles simulations of catalytic CO oxidation at realistic pressures and temperatures (16). Surface structures and compositions occurring during catalytic steady state could be simulated from first principles (17), and their dependence on gas-phase partial pressures and surface temperature were investigated with ab initio atomistic thermodynamics (18) (see **Figure 1**).
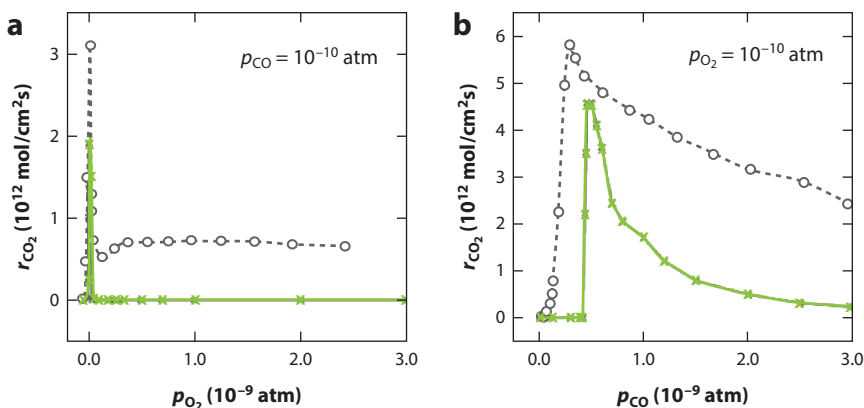
Figure 1

Theoretical simulation and comparison to experiment of CO oxidation on a ruthenium catalyst, showing the rate of CO_2 formation at $T = 350$ K. The experimental steady-state results are presented as dotted lines, and the theoretical results are shown as solid lines. Rates are given (*a*) as a function of p_{O_2} at $p_{CO} = 10^{-10}$ atm and (*b*) as a function of p_{CO} at $p_{O_2} = 10^{-10}$ atm. Figure reprinted from Reference 17.

In other work, binding-energy scaling laws and Brønsted-Evans-Polanyi activation energy scaling were calculated using DFT. With these DFT-derived scaling laws in hand (19), a small number of additional DFT calculations (sometimes just one) allowed the mapping of the energy landscape of complex, multistep catalytic reactions on a new metal or alloy (20–22). Remarkably, catalytic activity and selectivity are correlated with simple descriptors (e.g., specific DFT-derived binding energies). Using activity and selectivity volcano plots based on these descriptors, one can computationally screen new materials (23), providing an approach to the computational optimization of new catalysts (24, 25).

Such progress is breathtaking and naturally attracts increasing attention and new practitioners to the field. It also poses fascinating fundamental questions, which compose the topic of this review. Putting it most generally, does the provisional standard model of surface chemical reactivity work for all cases in surface chemistry? If not, why not? And how can it be modified to develop a better model of surface reactivity?

1.3. The Challenge of Testing Fundamental Assumptions

As an experimentalist considering the rapid advances in computational surface chemistry more closely, one finds it challenging to design experiments that test basic assumptions and approximations. This results partly from the complexity of the systems studied and partly from a lack of necessary experimental tools. This reminds us of an important lesson from the study of simple gas-phase reactions: Theoretical comparisons to well-defined experiments that do not average over many initial and final conditions—often called state-to-state dynamics experiments—can be highly useful to test theory. In short, we strive to perform experiments on surface reactions at the level of detail possible for simple gas-phase reactions, such as $H + HD \rightarrow H_2 + D$, and use those results to test sophisticated theories employing different approaches, assumptions, and approximations.

Computational chemistry is an intrinsically approximate undertaking, in which assumptions are made to reduce computational time. Understanding which assumptions are valid under what conditions is a prerequisite to developing predictive theory. Furthermore, if clever new approaches significantly shorten computations and nevertheless reproduce detailed state-to-state dynamics experiments, there is every reason to believe that these approaches are valid and have predictive value.
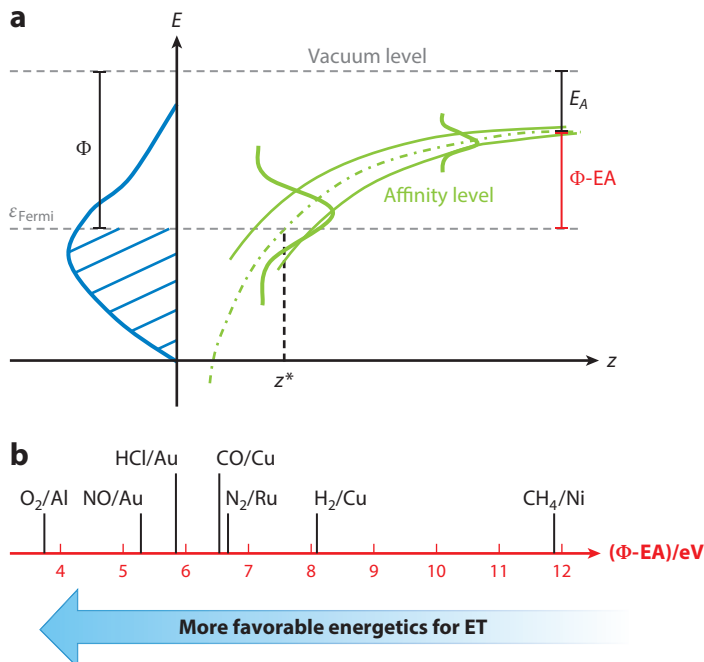
Beyond this, by understanding the validity of central assumptions and approximations, we can develop a conceptual understanding of surface chemistry and how it differs from the gas-phase chemistry of small molecules. It is not simply an attempt to develop the best computational simulation of surface reactions that we are after. Rather, through understanding which assumptions are valid and which are not, we hope to better understand how surface chemistry works.

1.4. Structure of the Review

The study of surface chemistry is an extremely vibrant field, and topics related to this article have been reviewed on several occasions. We direct the interested reader, in particular, to References 26–34.

This review focuses on the comparison of theory and dynamics experiments that test the provisional standard model of surface chemical reactivity. We emphasize a small number of very simple systems that have been studied in great detail.

Understanding situations in which the BOA fails is an important theme, and as shown below, this failure is associated with electron transfer (ET) reactions. Hence, energetic considerations

a

E

Vacuum level

E_A

Φ

Φ-EA

Affinity level

ε_{Fermi}

z

z*

b

HCl/Au   CO/Cu

O$_2$/Al NO/Au   N$_2$/Ru   H$_2$/Cu   CH$_4$/Ni

4   5   6   7   8   9   10   11   12   **(Φ-EA)/eV**

More favorable energetics for ET

Figure 2

Correlation of electron transfer with Born-Oppenheimer failure. (*a*) For a molecule far from a metal surface, the energy required to transfer an electron from the metal to the molecule (the formation of an anion) is given by the difference of the surface work function, Φ, and the electron affinity (EA) or negative ion resonance energy of the molecule. This energy difference has to be overcome to make electron transfer (ET) feasible. As a molecule approaches the metal surface, the negative ion affinity level is stabilized by image charge interaction (150), and the lifetime shortens. The image charge stabilization is eventually limited by repulsive interactions to a maximum value of ∼4 eV. The remaining energy required to overcome the barrier to anion formation can come from the translational and/or vibrational energy of the molecule. (*b*) The energetics of ET are a good indicator of where failure of the Born-Oppenheimer approximation is likely. Systems toward the left are more likely to undergo ET than those on the right, and there is a fuzzy boundary at ∼7 eV, beyond which ET will probably not play a significant role in scattering experiments. [In principle, similar considerations should also apply to ET and the formation of cations, but to our knowledge, there are no known examples of ET at surfaces involving cation formation, although the energetics would seem not to rule it out. An understanding of the reasons cations do not play a role currently escapes us.] For chemisorbed molecules, the flow of charge between the metal and the chemisorption bond orbitals can play a similar role and, owing to longer interaction times, may slightly push the boundary to higher energies. Values for Φ in panel *b* are experimental values for face centered cubic (111) surfaces from Reference 160. The EAs are computational values (composite Gaussian-4 theory) (161), except for the EA of methane, which is taken from Reference 162.

of ET provide guidance about which systems might exhibit BOA failure and which will not (see **Figure 2**).

In the first part of the review, we consider examples in which ET is energetically inaccessible—here we find that the BOA appears to be reliable. We begin with the dissociative adsorption of hydrogen on metal surfaces: The number of molecular degrees of freedom is only six, which is small enough to make full-dimensional quantum scattering theory tractable. A comparison of experiment to full-dimensional quantum theory, full-dimensional QCT theory, and theory in reduced dimensions thus allows us to study the success or failure of several aspects of the provisional model.

We progress logically from diatomic molecule dissociation to a discussion of the dissociative adsorption of CH_4 on metal surfaces, in which effects associated with polyatomic molecules become important, and new approaches to reduced dimensionality are essential. Here we see that clever approximations allow fully quantum mechanical calculations to be made, describing all 15 degrees of freedom of the methane molecule and surface atom motion, providing a remarkable opportunity to evaluate the classical approximation for the case of polyatomic molecules.

We then turn to examples in which ET is energetically accessible and thought to be important, emphasizing CO, NO, and O_2 interactions at metals. As shown below, these systems represent special challenges, straining the provisional model. We find that ET is associated with failure of the BOA, and it can cause problems in standard applications of DFT, even when the BOA holds.

At the end of each of these two sections, we summarize the key points learned as they relate to the four key assumptions of the provisional model. We conclude the review by describing future directions.

2. MOLECULAR INTERACTIONS AT METAL SURFACES NOT MEDIATED BY ELECTRON TRANSFER

Dissociative adsorption is one of the simplest surface chemical reactions and, as such, a natural place to begin our discussion of testing the foundations of the theory of surface chemistry. The molecular system, surface temperature, incidence translational energy, angles, vibrational and rotational states, and molecular orientation all have dramatic effects on the reaction probability, which often varies over orders of magnitude as incidence conditions are changed. This rich behavior can provide stringent tests of theory. Furthermore, activated dissociative adsorption is often the rate-limiting step in industrial catalytic processes, such as the synthesis of ammonia by the reaction of H_2 and N_2 over iron-based catalysts (35). For activated dissociative adsorption, reaction probabilities are determined by a limited region of the PES, namely the barrier between reactants and products. This fact is advantageous in two ways: (*a*) It means that an accurate description of difficult-to-compute van der Waals and other long-range interactions may not be required to obtain accurate results for reaction probabilities, and (*b*) it allows sensitive tests of the ability of theory to predict activation barriers, the features of the PES that are most critical for understanding and predicting heterogeneous catalysis.

2.1. Hydrogen Dissociation on Metal Surfaces

There is only one class of surface reactions in which the basic assumptions underlying chemical theory have been tested at a level close to that achieved for simple gas-phase reactions—hydrogen dissociation on metals (30, 36, 37). Experimental and theoretical studies of hydrogen dissociative adsorption are available for many metals (36), but we focus on copper because we have the most detailed experimental data and the most comprehensive comparisons to theory for this system.

For hydrogen on copper, we have detailed quantum state-specific experimental information on the reaction probability at zero coverage, $S_0(T_S, E_i, \theta_i, \phi_i, v_i, J_i, M_i)$ as a function of kinetic energy, E_i, polar angle, θ_i, azimuthal angle, ϕ_i, vibrational state, v_i, rotational state, J_i, and orientation or projection of the rotational angular momentum, M_i. Remarkably, these data are available over the full range of kinetic energies, vibrational states, rotational states, and orientations that are chemically relevant (32, 38–47). In addition, we have information on rotational and vibrational inelastic scattering (32, 48, 49).

Figure 3 illustrates the range of the experimental results available. The experimentally determined S_0 is often expressed in terms of fits of the measurements to a sigmoidal function based on
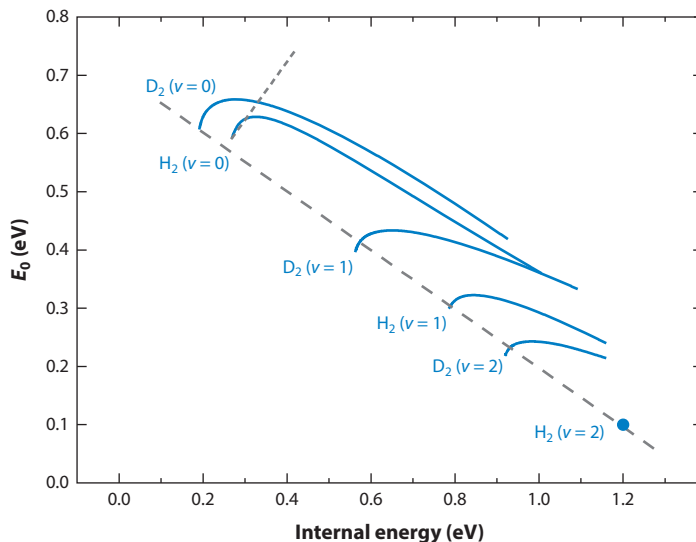
Figure 3

Plot of E_0 as a function of internal energy for H_2/Cu(111) and D_2/Cu(111) as described in the text. The lines correspond to fits to J-dependent E_0 results. The dashed line is a linear fit to the $J = 0$ results and gives a vibrational efficacy of 0.51 ± 0.02. The dotted line on the H_2 ($v = 0$) curve is the initial slope of that curve and gives an initial rotational efficacy of -1. Note that data are available over the full range of internal energies that is relevant to a thermal reaction. Figure reproduced with permission from Reference 41. Copyright 1995, AIP Publishing LLC.

the error function:

$$S_0\{E_i, \theta_i, v_i, J_i, M_i\} = \frac{A(v_i, J_i)}{2}\left\{1 + \textit{erf}\left[\frac{E_i \cos^2(\theta_i) - E_0(v_i, J_i)}{W(v_i, J_i)}\right]\right\}.$$

E_0 is the incidence translational energy at which S_0 reaches half of its high energy limit—it is thus a measure of the barrier to adsorption, one that depends on the molecular quantum numbers. **Figure 3** shows $E_0(v_i, J_i)$ plotted as a function of internal energy. As the vibrational energy increases, E_0 decreases by about half the increase in internal energy. Rotational motion initially inhibits dissociation, but at high J, E_0 decreases by about half the increase in internal energy. Thus, both vibrational energy and rotational energy are about half as effective as translational energy in overcoming the adsorption barrier.

At the present state of the art, none of the standard exchange correlation functionals at the GGA level provides a chemically accurate description of the adsorption barrier for dissociative adsorption of H_2 and D_2 on copper. Of the two functionals most often used, PW91 (50) generally gives values for activation barriers that are too low, whereas RPBE (51) gives barriers that are too high. Correspondingly, six-dimensional (6D) calculations of adsorption probabilities versus collision energy for D_2 on Cu(111) using a PW91-based PES give values that are larger than those found in experiments, whereas calculations using RPBE give values smaller than experiment (52). In response to this problem, Kroes and coworkers (52) developed an adaptation to molecule-metal interactions of the specific reaction parameter (SRP) approach to DFT originally developed for gas-phase problems (53). Essentially, the method involves constructing a new functional as a linear combination of two functionals, for example,

$$E_{XC}^{SRP} = x E_{XC}^{RPBE} + (1 - x) E_{XC}^{PW91},$$

PW91: Perdew and Wang 91 exchange correlation functional

RPBE: revised Perdew-Burke-Ernzerhof exchange correlation functional

SRP: specific reaction parameter exchange correlation functional

and then adjusting the mixing parameter, x, to give optimal agreement with one piece of experimental data, in this case, the adsorption probability for D_2 for a vibrational temperature of 2,100 K. This semiempirical SRP functional successfully reproduced results for many other measurements on this system, such as the variation of E_0 with v and J and the rotational excitation probability (52). The same functional with the same mixing parameter also gave good agreement with reaction probabilities on Cu(100) (37).

Although calculations on the SRP-based PES accurately describe reaction probabilities for Cu(111) and Cu(100), they do not give an accurate description of all the data available. For example, they strongly underestimate the vibrational excitation probability for D_2/Cu(111) and strongly overestimate the orientation dependence of the reaction probability for this system. [Measurements of these quantities for Cu(100) are not yet available.]

Kroes and coworkers argued that these discrepancies do not result from errors in the PES, but rather from the use of the Born-Oppenheimer static surface (BOSS) model, which freezes the surface atoms at their 0-K equilibrium positions. Using ab initio molecular dynamics (AIMD) (54), which allows all degrees of freedom to be computed on the fly (55), they obtained results for the orientation dependence of the reaction probability (56) that are in significantly better agreement with experiment. The deviations from experiment in the vibrational excitation probability are also attributed to the BOSS model (57). It is possible that the remaining discrepancies are somehow related to nonadiabatic electronic excitation, but there is no direct indication that this is the case, nor are we aware of any model that shows how nonadiabatic effects might help to resolve the remaining discrepancies. The use of classical mechanics (in the AIMD calculations) may also contribute to the discrepancies, especially with respect to vibrational excitation. There does not presently appear to be an easy way to check this last point.

Even if nonadiabatic effects do not play a significant role in determining the reaction probability for H_2 and D_2 interactions with copper surfaces, as appears to be the case, they may be important for other aspects of the dynamics. One such area is vibrational energy transfer. Luntz et al. (58) argued that a comparison of reduced-dimensional calculations with data on the vibrational relaxation of H_2 ($v = 1, J = 1$) (59) and D_2 ($v = 1, J = 2$) (60) provides indirect evidence for a nonadiabatic mechanism. This conclusion, however, is controversial. More recently, Muzas et al. (61) found that 6D calculations can qualitatively account for the trends seen in the experimental data. We note that the agreement is only qualitative, and both groups did calculations for Cu(111), whereas the experiments in question were done on Cu(100). Thus, it is probably best to regard the possible role of nonadiabatic effects in vibrational relaxation as an open question.

Nonadiabatic effects may also play a significant, or even dominant, role in the fate of hot hydrogen atoms that result from a dissociative adsorption event. Recently, Alducin and coworkers (62) used a combination of AIMD and the local density electronic friction approximation to study transient hot hydrogen atoms produced in the dissociation of H_2 on Pd(100). Within the approximations they used, they found that nonadiabatic electronic excitation is the dominant mechanism for energy loss in these hot atoms. Unfortunately, there is no experimental evidence available on this point, and it is not even clear how their results could be tested directly. It would be interesting to develop experiments to test this theoretical approach, for example, by measuring the inelastic scattering of fast hydrogen atoms.

2.2. CH$_4$ Dissociation on Metals: Polyatomic Behavior in Surface Chemistry

Methane dissociation at metals is the most deeply studied example of polyatomic surface chemistry. Experiments show that the reaction occurs over an approximately 1-eV activation barrier, varying somewhat from metal to metal (63). Both incidence translation and vibration promote dissociation,

forming adsorbed hydrogen and methyl radicals (64–74). This chemistry disobeys statistical laws of reaction rates. For doubly deuterated methane (CD_2H_2), the reaction probability is five times higher for molecules with two quanta of excitation in one C–H bond compared to molecules with one quantum in each of two C–H bonds (65), despite these two states having nearly identical energies. Bond-selective control of CHD_3 dissociation was also demonstrated—the C–H bond can be selectively dissociated by laser excitation of the C–H stretch (72), and similar behavior is seen in other isotopologs (73, 74). A steric effect has also been reported (75); that is, the reaction probability depends on the direction along which its C–H bonds are vibrating. The barrier to dissociation is found to increase with product surface coverage (76). The reaction probability depends strongly on the surface temperature, increasing by as much as a factor of eight as T_S is increased from 90 K to 473 K, which suggests the importance of surface atom motion (77).

A recent review (29, p. 4) summarized methane's nonstatistical dissociation well:

> Studies of vibrationally mediated [surface] chemistry are showing that the nature of the vibrational excitation, and not just its total energy, can play an important role in determining the rates and pathways of surface reactions. Such . . . behavior results when the timescale for statistical redistribution of vibrational energy within the reaction complex is slower than reaction.

Although there is no doubt about this conclusion, obtaining a full understanding of the vibrational state-specific reactivity is quite challenging (78). Why is CH_4's symmetric C–H stretch (66) much more reactive than the asymmetric stretch is (69)? Why is bending excitation less effective in promoting reaction than the already low-reactivity asymmetric C–H stretch (71, 79)? Beyond this, can we obtain quantitative agreement between experiment and theory for state-specific reaction probabilities?

In recent years, there has been a flurry of theoretical work related to these questions. A major challenge is the large number of degrees of freedom active in this system—15 in the methane molecule and much more if one considers the motion of the surface atoms. Beyond this, the quantum nature of hydrogen atom motion may be important. In short, we demand a high-dimensional treatment absent the classical approximation. The challenges involved have been recently discussed and are beginning to be met (37).

Many approaches have been tried. Quantum dynamics calculations in three and four dimensions on a 15D PES that include all methane degrees of freedom but a frozen nickel surface gave less than satisfactory agreement with experiment (80). 8D quantum dynamics on a 12D PES (neglecting surface motion, translation of CH_4 parallel to the surface, and azimuthal rotation about the surface normal) gave the correct ordering of the reactivity of the vibrational modes: symmetric stretch > asymmetric stretch > bending excitation (81). However, the restriction of impact at a single surface site (with the lowest barrier) greatly overestimated the reaction probability at all incidence energies. Furthermore, the neglect of surface motion meant that the dramatic surface temperature dependence was ignored. DFT calculations show that out-of-plane nickel atom motion lowers the dissociation barrier (81–83).

With 15 molecular degrees of freedom and surface atom motion all influencing reactivity, a brute-force approach is quite challenging, but recently it was attempted using a reactive force field (RFF) to fit DFT data, some of which was derived from AIMD trajectories (82). A full-dimensional PES for methane dissociation on nickel and platinum was obtained, including surface atom motion. In their supplementary material, the authors offered a veiled warning about the PES, stating that the RFFs reported in that work "should be used neither to investigate other reactive processes nor to extend further the range of initial conditions mentioned above without performing additional extensive tests of accuracy for the targeted process/conditions." This reflects

the difficulty of using RFF to accurately and simultaneously describe forces between atoms in molecules with covalent bonds, in which it works well, and metallic bonding, in which problems may arise. Despite these potential problems, the authors were able to understand the mode- and isotope-selective adsorption observed in experiments (72, 73).

Above we mention theories of quantum mechanical nuclear motion in reduced dimensions or, alternatively, theories that employ full-dimensional classical approaches. These give qualitative, but not quantitative, agreement with experiments. To find out if the difficulty lies with the classical approximation, we need full-dimensional quantum calculations. But how can one compute full-dimensional quantum mechanical reactivity?

A promising approach, which appears to capture the full-dimensional nature of the problem and which is fully quantum mechanical, relies on a reaction path Hamiltonian (10, 83–85). Here, only a limited part of the PES needs to be calculated from DFT, namely energy points along the minimum energy path to dissociation as well as the curvature of the PES orthogonal to this path. This dramatically simplifies the polyatomic problem. With the use of a reaction path Hamiltonian, a 15D wave function is expanded in the adiabatic vibrational states of the methane molecule, and close-coupled equations are derived for wave packets propagating on vibrationally adiabatic PESs, with vibrationally nonadiabatic couplings linking these states to each other (10). Sudden models were used to average over the surface impact site and nickel atom lattice vibrations (10). **Figure 4** shows the excellent agreement obtained between experiment and theory.
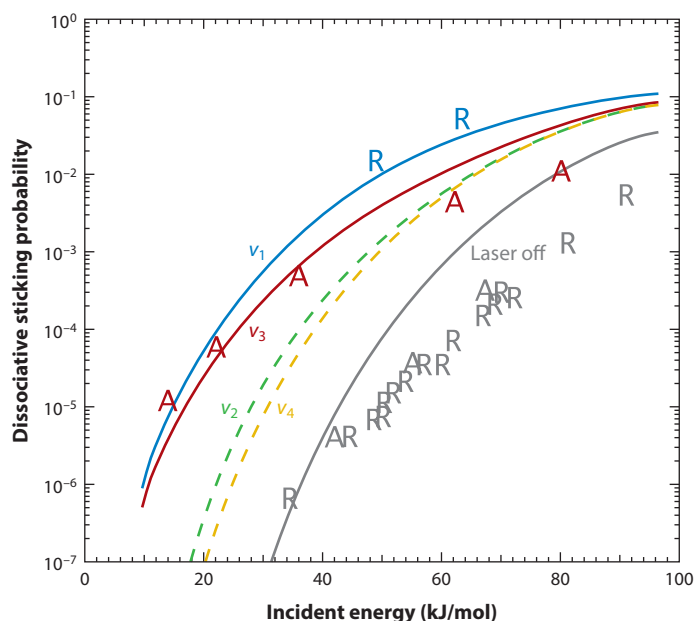
Figure 4

Comparison of experiment (*symbols*) and theory (*lines*) for methane dissociation on nickel. The theory is based on a reaction path Hamiltonian involving 15D quantum dynamics calculations with sudden approximation models introduced to allow for averaging over the impact site and nickel atom out-of-surface motion. The experiments from the groups of Beck (*R*'s) and Utz (*A*'s) employ laser-excited molecular beams to reveal the translational and vibrational promotion of the methane dissociation probability. Shown are the ground vibrational state (*gray*), one quantum symmetric CH stretch (*blue*), one quantum antisymmetric CH stretch (*red*), v_2 bend (*green*), and v_4 bend (*yellow*). Readers are referred to Reference 10, and references therein. Figure reprinted with permission from Reference 10. Copyright 2011, AIP Publishing LLC.

The reactivity results from thermally assisted over-the-barrier processes, and not tunneling. This does not, however, mean that the classical approximation is valid. With these quantum calculations in hand, the classical approximation could be more rigorously tested (84). In general, the classical approximation yields reaction probabilities that are too high. The most troubling problem introduced by the classical approximation is a vibrational ground state that is far too reactive. This effect was found to result from zero-point energy flow to the reaction coordinate possible in the classical approximation (84), a problem that is likely of more general importance (86). By contrast, classical reaction probabilities for vibrationally excited states were in better agreement with quantum results.

These lessons are of great relevance when considering the current increasing interest in AIMD calculations (87–89). Although AIMD allows all degrees of freedom to be involved, it requires a classical approximation. AIMD was used to try to gain insights into the mode selectivity seen in methane dissociation on platinum (87) and nickel (88). Here several hundred classical trajectories were started near the transition state, and the nature of the vibrational, rotational, and translational motion appearing in the methane ejected to the gas phase was analyzed. The authors made use of time reversal to make inferences about mode selectivity in dissociative adsorption experiments and found that the symmetric C–H stretch is most effective in promoting reaction, in qualitative agreement with experiments.

The most ambitious implementation of molecular dynamics came recently when AIMD was used to directly compare state-specific reaction probabilities at various incidence energies of translation (89). As in the quantum classical comparison of Reference 84, the classical AIMD results tend to overestimate the experimental values. Nevertheless, agreement with experiment is remarkably good. We do note that these classical calculations were compared under conditions in which the total energy is much larger than the zero-point energy (84).

2.3. Summary and Key Points

We take stock of the key lessons learned from the dissociative adsorption of molecules for which ET is energetically inaccessible in the following subsections.

2.3.1. Density functional theory.
DFT with the popular PW91 and RPBE GGA exchange correlation functionals does not produce accurate values for the chemical dissociation barrier. A semiempirical SRP functional can give results to chemical accuracy for H_2 on Cu(111) and Cu(100), but the same functional does not work for H_2/Ru. This lack of transferability is a serious failing of the SRP functional at this stage in its development. For CH_4 dissociation, DFT gives reasonably accurate results for the activation barriers but does not give chemical accuracy (1 kcal/mol).

2.3.2. Quasi-classical trajectory method.
For H_2 and D_2 dissociation on copper, the QCT approximation works well for activated dissociative adsorption in which the kinetic energy of the reactive molecules is high. The same is not always true at lower energies, and it is currently difficult to decide in advance if QCT calculations are adequate (36). For CH_4 dissociation, the classical approximation for nuclear motion simply fails. These systems are intrinsically quantum mechanical. That zero-point energy promotes reaction in classical calculations appears to be one of the more important lessons of this area of study. Indeed, it may be a more general problem. If one is interested in modeling activated reactions, in which the zero-point energy is a significant fraction of the barrier height, using QCT may be asking for trouble. For larger polyatomic molecules that

possess more zero-point energy—exactly the situation in which one might wish to employ the classical approximation—one can only fear that this problem is even more severe.

2.3.3. Reduced dimensionality. For hydrogen dissociation, 6D static surface calculations reproduce the main features of the experiments, but inclusion of the motion of surface atoms and coupling to phonons is important for more subtle features such as vibrational excitation and orientation dependence. 4D or lower-dimensional calculations differ significantly from 6D calculations (90). Although 6D or higher-dimensional calculations are required to quantitatively reproduce many of the experimental results, lower-dimensional calculations play a valuable role in establishing an understanding of how the topography of the PES affects experimental results (11). For CH_4, the motion of the surface atoms is critically important for energies near the reaction barrier. The use of a reaction path Hamiltonian and sudden models to average over certain degrees of freedom was quite successful.

2.3.4. Born-Oppenheimer approximation. There is presently no evidence that nonadiabatic electronic excitation has a large influence on the dissociative adsorption of hydrogen or methane. However, this conclusion should be regarded with caution, as a semiempirical approach is used to obtain the PES for hydrogen, and in principle, this might mask nonadiabatic effects—in effect empirically adjusting the barrier height to compensate for errors introduced by the BOA. There is some evidence for the influence of nonadiabatic effects in the vibrational relaxation of H_2 and D_2 and in the dissipation of energy of hot atoms formed in dissociation, but further research that allows more direct comparison of theory and experiment is required.

3. MOLECULAR INTERACTIONS AT METAL SURFACES MEDIATED BY ELECTRON TRANSFER

The previous section describes successes and failures of the provisional model of surface reactivity for some simple surface chemical reactions. DFT-derived PESs are useful but do not give barriers to chemical accuracy (1 kcal/mol) using any of the standard GGA-level exchange correlation functionals. Reduced-dimensional calculations must be approached with some caution and verified by reference to experiment or higher-dimensional calculations. In particular, for some problems, the role of surface atom motion is quite important in influencing reaction barriers and cannot be ignored. Even for light species such as hydrogen, the classical approximation for nuclear motion can be surprisingly good, but with significant provisos—in particular, as a molecule's zero-point energy becomes a substantial fraction of the size of reaction barrier. Importantly, to a very large extent in the examples presented above, the BOA appears to be valid. But are these well-studied examples representative of the breadth of behavior that is possible in molecular interactions and chemical reactions at metal surfaces?

Section 2 focuses on systems for which ET is energetically unfavorable. They lie toward the right-hand side of **Figure 2b**. For systems in which ET is unlikely, such as H_2, N_2 (91), and CH_4 interactions with metals, the electronically adiabatic picture appears reliable. We do note a possible exception: N_2 dissociation on ruthenium has been suggested to be strongly influenced by electronically nonadiabatic effects. However, more work is needed on this system to clarify differences between reported experiments. The interested reader is directed, in particular, to References 92–95.

We now turn our attention to systems in which ET is energetically favorable (i.e., those toward the left-hand side of **Figure 2b**). Perhaps the most basic lesson we have learned over the years in studying molecular interactions at metal surfaces is that ET processes occurring between the

metal and the molecule are intimately involved in the failure of the BOA (31). Furthermore, when ET is involved, DFT may exhibit even more severe problems than those discussed above, even when the BOA might hold. The following examples illustrate these issues.

3.1. CO Interactions with Metals

The lifetime of the first vibrationally excited state of CO on different surfaces can be inferred from the measurements of infrared line widths and time-resolved vibrational spectroscopy. As a typical example, the vibrational lifetime of CO ($v = 1$) on metal surfaces such as Cu(100) ($\sim$2 ps) (96) is nine orders of magnitude shorter than that on an insulator such as NaCl(100) ($\sim$3 ms) (97). This is dramatic, albeit indirect, evidence of the strong nonadiabatic coupling of molecular vibration to the continuum of electronic states in the metal.

Theoretical work treats the vibrational relaxation in an ET model using Fermi's golden rule and perturbations arising from the vibrational kinetic energy operator (98–100). As the bonding of CO with many metals involves the overlap of the electron density from the metal with the molecule's π^* orbital, and because the energy of the π^* orbital is strongly dependent on the CO bond length, CO vibration induces an oscillating ET back and forth between the metal and the molecule. If the electrons cannot adiabatically adjust to this high-frequency vibrational motion, non-Born-Oppenheimer vibrational relaxation exciting electron hole pairs in the metal becomes possible. With this model, one can explain trends in the lifetimes for the different vibrational modes of the CO and other diatomic molecules on Cu(100) and other metals.

Not only do these effects exist, they can be so strong that they dominate the energy transfer between a molecule and the metal upon which it is adsorbed. This has given rise to an important direction of research in which short laser pulses are used to excite electrons in a metal, which are then used to initiate chemical reactions, desorption, and energy transfer to molecular adsorbates (26). In a recent example from this field, the direct measurement of bond cleavage for CO on a metal has been reported (101).

In these examples, chemical binding of the adsorbate to the surface is important. But ET-mediated BOA breakdown can happen even for scattering events in which the transient interaction between the molecule and the surface is extremely short and in which the structures sampled by the scattering molecule are very different than the equilibrium geometry of the adsorbate. Recent studies on the scattering of CO from Au(111) show that the electronically nonadiabatic coupling of vibration to metal electronic degrees of freedom can also be observed in this system in a scattering experiment (102, 103).

3.2. NO on Gold

Vibrationally inelastic scattering of NO from metals has become one of the best-studied examples in nonadiabatic gas-surface interactions (31, 104–105). One reason for this is that stimulated emission pumping allows the preparation of nearly any initial vibrational state in the molecule up to approximately 80% of its bond energy. Originally developed for investigations of gas-gas collisions (106–111), this technique has been extended to applications in gas-surface studies (112) and has been enhanced to allow for orientation of the NO molecule (113).

The fact that one can apply such powerful optical pumping methods to NO provides an opportunity to investigate the energy transfer of highly vibrationally excited molecules with an energy content that is nearly enough to break their chemical bond. Highly vibrationally excited NO ($v = 15$) shows multiquantum vibrational relaxation in scattering from Au(111)—on average, seven quanta of vibration are lost—whereas only little vibrational relaxation is observed for scattering from an insulating LiF surface (114, 115). Such observations clearly show that
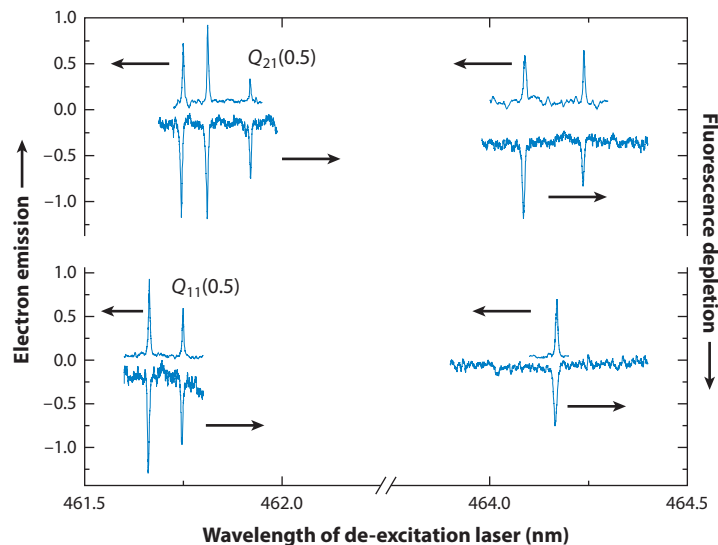
Figure 5

Electron emission resulting from NO ($v = 18$) ($E_{vib} = 3.65$ eV), prepared by stimulated emission pumping, colliding with Cs-covered Au(111) ($\Phi \sim 1.61 \pm 0.08$ eV). The upgoing signals show the electron emission from the surface as a function of the wavelength of the de-excitation laser that dumps molecules, which were initially pumped into $A^2\Sigma^+$ ($v = 3$) via the Q_{21} (0.5) and Q_{11} (0.5) transition, into $X^2\Pi$ ($v = 18$). The downgoing signals show fluorescence depletion spectra taken under identical conditions. The spectra illustrate that electron emission from the surface is strongly enhanced if initial NO molecules are selectively prepared with a vibrational energy that is higher than the work function of the surface. Figure reprinted from Reference 163 by permission from Macmillan Publishers Ltd. on behalf of Cancer Research UK.

molecular interactions at metals are dramatically different than those at insulators. When similar studies were carried out on low–work function surfaces, electron emission was observed as soon as the vibrational energy exceeded the work function (116–119). **Figure 5** demonstrates the correlation of electron emission enhancement and fluorescence depletion upon a change in the de-excitation laser wavelength for preparation of NO ($v = 18$). The kinetic energy distribution of the ejected electron has also been reported (116, 117). These results not only prove that the BOA fails, but also show that nearly all the NO molecule's vibrational energy can be transferred to a single electron, consistent with an ET mechanism.

The electronically nonadiabatic vibrational energy transfer occurring in collisions of NO with an Au(111) surface has become a test bed for new post-Born-Oppenheimer theories of molecular interactions at surfaces. Concerning the multiquantum vibrational relaxation of NO ($v = 15$), molecular dynamics with electronic friction (MDEF) (120, 121) and coupled-channel density matrix (CCDM) with weak vibrational-electronic coupling (120, 121) gave reasonable agreement with experiments, as did independent electron surface hopping (IESH) theory (122–124). All three theories are based on ET mechanisms, but the IESH theory makes no weak coupling approximation, instead using a Newns-Anderson Hamiltonian and electronically nonadiabatic couplings derived from DFT calculations (124). A strong orientation dependence to the vibrational relaxation was also observed—N-first collisions are much more efficient at inducing vibrational energy exchange than are O-first collisions (125, 126). This qualitative observation was predicted theoretically and reflects the orientation-dependent ET of the PES for NO/Au used in the IESH calculations.

MDEF: molecular dynamics with electronic friction

IESH: independent electron surface hopping

Unlike IESH, the models with weak coupling require that vibrational energy is lost or gained one quantum at a time; hence, multiquantum vibrational relaxation is a cascading process of many sequential single-quantum relaxation events. Calculations show that NO ($v = 15$) can relax via this sequential cascade process, giving vibrational state distributions in reasonable agreement with experiment (121).

To better differentiate between these weak coupling theories and IESH, a large benchmark data set was generated for vibrational excitation of NO ($v = 0 \rightarrow 1, 2$) in collisions with Au(111). Here absolute excitation probabilities were obtained over a wide range of surface temperatures and translational incidence energies (127). The IESH theory gave semiquantitative agreement with experiment for both $\Delta v = 1$ and 2 processes—however, somewhat underestimating excitation into $v = 1, 2$ at high E_i and overestimating it at low E_i. In contrast, the weak coupling theories dramatically underestimated the magnitude of the vibrational excitation at all values of E_i. In an extension of this work, NO ($v = 0 \rightarrow 3$) excitation probabilities were also compared to IESH calculations (128). In addition to a less than perfect description of multiquantum vibrational excitation, the IESH theory exhibited an excitation probability that was nearly independent of the incidence translation in contrast to experiment, which showed a strong incidence energy enhancement of the vibrational excitation (127). Although all indications are that the IESH theory is the front-runner in explaining ET-mediated BOA failure, this was the first indication of problems—more were to come.

The most detailed and informative comparison of experiment and theory for this system concerned the scattering of NO ($v = 3$) from Au(111) (129). Here the vibrational relaxation to $v = 1$ and 2 was observed as a function of the incidence energy of translation and compared to IESH and MDEF. Again experiment showed an enhancement of vibrational energy transfer with increasing incidence translational energy (**Figure 6**). Both IESH and MDEF showed the opposite trend.

This led to a detailed analysis of individual trajectories revealing that a large fraction of the trajectories in adiabatic, IESH, and MDEF calculations are multibounce collisions. However, experimentally observed angular distributions were narrow, providing strong evidence of single-bounce scattering (129). Furthermore, state-to-state time-of-flight measurements showed that the translational inelasticity of NO in collisions with Au(111) is consistent with a binary collision (Baule) model, giving powerful evidence against a large probability of multibounce scattering (130, 131). This apparent multibounce artifact in the theory also partially explains the incorrect translational incidence energy dependence exhibited by both IESH and MDEF. The fraction of multibounce collisions increased dramatically with decreasing E_i—at $E_i = 0.1$ eV, up to 90% of the trajectories are multibounce (129). By selecting only single-bounce trajectories from the models, investigators again compared IESH and MDEF to experiment. This procedure improved agreement between IESH and experiment, but MDEF remained unable to describe the $\Delta v = -2$ relaxation. It was concluded that the DFT-based interaction potential used in the IESH and MDEF calculations does not describe the translational inelasticity of NO on Au(111) accurately— the gold surface is too soft and too corrugated—leading to unphysical multibounce trajectories. This work points out how errors in the electronically adiabatic interaction potential can lead to incorrect electronically nonadiabatic dynamics, as unusual regions of phase and configuration space may be accessed that are not relevant to reality.

In passing, we note that the multibounce artifact must also have been present in the first IESH calculation of NO ($v = 15$) on Au(111) (123)—there the incidence energy of translation was 0.05 eV. The good agreement with theory for multiquantum vibrational relaxation may have been fortuitous. Indeed, the first experimental results point in that direction (132).
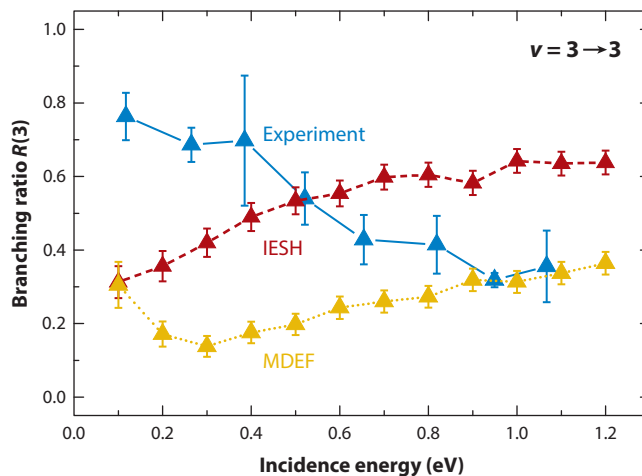
Figure 6

Branching ratio for NO ($v = 3 \rightarrow 3$) scattering from Au(111). The branching ratio is defined as $R(v) = (N(v)) / \sum_{i=1}^{3} N(i)$, where $N(v)$ is the number of molecules scattered into a specific final vibrational state $v_f = 1, 2, 3$. Shown are experimental (*blue*) and theoretical results from independent electron surface hopping (IESH) (*red*) and molecular dynamics with electron friction (MDEF) (*yellow*) calculations. The experiment shows that the fraction of NO ($v = 3$) molecules (the survival probability) decreases with an increasing incidence energy, whereas the theoretical calculations predict the opposite trend. A detailed trajectory analysis by the authors of Reference 129 revealed that the inverse E_i dependence results from an increasing fraction of multibounce collisions in the calculations, which were not in agreement with the experimental observations. Figure reprinted with permission from Reference 129. Copyright 2014, AIP Publishing LLC.

3.3. O₂ on Aluminum

The interaction of O_2 with aluminum has become one of the most intriguing systems to study the underlying assumptions of computational surface chemistry. The experimental results for O_2 dissociation on Al(111) are clear and consistent. Adsorption is translationally (and vibrationally) activated (133). The adsorption process itself involves two reaction channels: The O_2 molecule can either undergo simple dissociative chemisorption or undergo an abstraction reaction in which one oxygen atom binds to the surface and the other is ejected toward the vacuum. Thereby, the abstraction mechanism involves a lower activation barrier than does the dissociative chemisorption. This has been indirectly demonstrated by scanning tunneling microscopy studies showing single isolated oxygen atoms at low or thermal incidence energies, while the fraction of adsorbed oxygen pairs increased at high incidence energy (134, 135). Molecular beam methods allowed the direct detection of the ejected oxygen atom (136).

Theoretical studies on the O_2/Al(111) system showed a much less clear picture. Conventional adiabatic DFT calculations using GGA functionals already fail to reproduce the experimentally observed sticking probabilities owing to the absence of an activation barrier for dissociation (137–141). Several studies showed that the problem is related to the failure of DFT to describe charge transfer that is clearly important for O_2/Al(111) (142, 143). Hellman et al. (143) showed that this problem especially occurs for molecules with medium electron affinities, such as O_2 and NO, whereas DFT calculations give a good description for molecules with high electron affinities, such as F_2 (no barrier at all, charge transfer already at large distances) or very low electron affinities, such as N_2 (no dissociation, charge transfer not important).

Behler et al. (139, 140) showed that the absence of a barrier in DFT for O_2/Al(111) is basically related to the fact that DFT already predicts charge transfer at unreasonably large O_2-surface distances. They were able to avoid this problem by applying locally constrained DFT, which forces the O_2 molecule to stay in its triplet state. When employing this spin-restricted version of DFT, they found a barrier and used this to develop a 6D PES for the O_2/Al(111) system. An extension of the method also included a singlet PES and allowed for surface hopping, which only slightly influenced the results (141, 144, 145), depending on the assumed nonadiabatic coupling.

The apparent success of locally constrained DFT raised the question of whether spin selection rules are important for gas-surface interactions. Libisch et al. (146) suggested that the barrier for O_2 dissociation on Al(111) does not arise from spin conservation rules but comes about when the charge transfer is treated properly, for example, using embedded correlated wave-function methods. The authors used DFT only to calculate the energy of a 5×5 supercell representing the Al(111) surface but calculated the interaction of O_2 to the nearest aluminum atoms by correlated wave-function theory using a 10–14-atom aluminum cluster. The 2D PESs for parallel and perpendicular impacts of the O_2 molecule at different surface sites showed barriers consistent with experimental observations.

The question whether spin selection rules are important in gas-surface interactions or if they simply have to be added to the calculation to avoid the charge transfer problem is still waiting for an answer from experiments. Nevertheless, we point out that DFT-based methods are currently the only possible way to yield a full 6D PES, which is needed for a detailed comparison to experimental data.

3.4. Summary of Key Points

In the following subsections, we take stock of the key lessons learned from the system presented above, one for which ET is energetically accessible.

3.4.1. Density functional theory.
A proper theoretical description of ET remains one of the most important challenges in modern computational surface chemistry. Although DFT has become the workhorse of this field, it is known that it does not accurately handle ET in many cases. This means that large errors in interaction energies can result, for example, in the O_2-Al system in which theory finds no barrier to reaction.

3.4.2. Quasi-classical trajectory method.
Most post-Born-Oppenheimer models employ the classical approximation for nuclear motion. One example of quantum dynamics is available (121) in reduced dimensions, but there is no clear evidence at this point that the classical approximation is better or worse in nonadiabatic cases. A recent paper has shown that a unique classical force exists even outside the BOA (147). The prospect for including electronically nonadiabatic dissipation in on-the-fly dynamics methods is therefore sensible and feasible (148).

3.4.3. Born-Oppenheimer approximation.
The breakdown of the BOA is found to be associated with ET events, a phenomenon typically described poorly by DFT. Theories of electronically nonadiabatic dynamics are still in their infancy, yet post-Born-Oppenheimer protocols implementing ET physics have advanced to a point at which detailed comparisons with experiment are possible. This represents a major step forward in improving the provisional model of surface chemistry, in particular as energy transfer between an adsorbate and the solid is one of the key dynamical features of surface chemistry. Up to now, the most advanced post-Born-Oppenheimer models employed extensive DFT input data—hence, the development of post-Born-Oppenheimer

dynamical theories would also benefit from improved methods for the treatment of ET. New wave-function-based methods that include nonadiabatic electronic transitions offer some promise for the future (146, 149), but they have yet to be rigorously tested against high-level experimental measurements.

4. SUMMARY AND OUTLOOK

4.1. How Good Is the Provisional Model of Surface Chemistry?

Sections 2.3 and 3.4 summarize the successes and failures of key approximations underlying the provisional model of surface reactivity. DFT, the quasi-classical approximation, and models in reduced dimensions all have limitations and must be used with care. Even the BOA breaks down for systems involving ET. Yet we cannot foresee a day when computational chemistry will reach the Diracian ideal of solving the many-body quantum problem from scratch—at least not for any system a chemist might care about. Approximate methods are here to stay, and the limitations they introduce are important to study, understand, and appreciate.

4.2. Challenges for Theory

As of this writing, we still have no general procedure for calculating adsorbate binding energies and surface reaction barrier heights that is chemically accurate—1 kcal/mol or better. (The problem is even worse: We also have no general procedure for measuring such quantities with this accuracy.) This means, among other things, that we may not even obtain the correct binding site for adsorbates [see, e.g., the binding of CO to transition metals (150)]. Although DFT always gives an answer, it is often difficult to judge its accuracy. The problems intensify in systems in which ET is important—here, reaction barriers can simply disappear. Ad hoc adjustments to the DFT approach have been applied with some success, but the underlying basis for such adjustments is not established. It has also become clear that ET, one of the most ubiquitous events in surface chemistry, is intimately associated with the failure of the BOA in surface chemical dynamics. Although progress has been made in understanding how nuclear degrees of freedom are coupled to electron-hole pairs when molecules interact with metal surfaces, this field requires much more effort. Beyond this, as quantum dynamics calculations are still so computationally heavy, we are presently nearly always forced to rely on the classical approximation. The marriage of DFT with QCT in AIMD methods and their variants makes this approach particularly seductive. Yet, even for the simplest case of polyatomic dissociative adsorption, bizarre zero-point reactivity creeps into a classical calculation. This problem is likely even more troublesome as the size of the polyatomic increases.

The advances in computational chemistry made over the past three decades are astonishing, yet the pillars upon which we have built our computational machinery for interactions at surfaces are wobbly. Future work requires deep, and perhaps even speculative, thinking to develop completely new approaches to strengthen or replace the provisional model. Wave-function-based approaches to solving the electron structure problem (post-DFT methods) in surface chemistry are desperately needed and are being developed (149). With regard to the problem of high dimensions and the classical approximation, although on-the-fly methods have shown themselves to be extraordinarily useful, by necessity they impose the classical approximation. Advancing quantum methods for systems with many degrees of freedom is an important direction for future computational surface chemistry, if only to discover where the classical approximation is valid (86). Producing high- or even full-dimensional PESs for surface reactions (151) is a seemingly brute-force approach that may not be fundamentally novel, but innovative thinking will be needed to implement practical

protocols for doing so. On-the-fly calculations and quantum nuclear motion are two concepts that have not presently been married to one another for purposes of studying problems in surface chemistry, yet the approach is known for problems in the gas phase (152). Such spawning methods (152) may even provide new approaches to post-Born-Oppenheimer computations of surface chemistry.

4.3. Challenges for Experiments

Many future experiments are also called for—after all, our computational infrastructure is provisional in nature. Our hope is that this review might inspire more theorists and experimentalists to work together in testing the key aspects of the provisional model. In that spirit, it is illusory to propose specific experiments that are needed for the future. Nevertheless, a few directions for future work occur to us, which we briefly mention.

Up to now, there has been no simple model system of dissociative adsorption, which has been clearly identified to exhibit the breakdown of the BOA. An example in which detailed experimental and theoretical work might be carried out and compared—for instance, at the same level of rigor as the H_2-Cu reaction (52, 57)—would contribute to our understanding of the strengths and weaknesses of the provisional model of surface chemistry. An attractive candidate is the dissociative adsorption of HCl on gold. An electronically adiabatic DFT-based PES was recently reported, and quantum dynamics calculations were performed showing efficient dissociation (153, 154). Experimental studies of inelastic energy transfer revealed the breakdown of the BOA (155–157), yet dissociation has not been observed. Within this context, N_2 dissociation on ruthenium is another interesting system requiring additional study. Although it has been suggested to be strongly influenced by electronically nonadiabatic effects, more work is needed on this system to clarify differences between reported experiments (91–94, 158).

The interactions of atoms with metals are particularly attractive for comparing experiment to theory. Hydrogen atom interactions with metals reveal electron-hole pair excitations measured as chemicurrents on, for example, Schottky diodes (28), a clear sign that the BOA fails. Theoretical studies of such a simple system are attractive and have begun (62, 148, 151) in anticipation of new experimental studies employing photolytic hydrogen atom sources and Rydberg atom tagging.

Hydrogen permeation experiments have been shown to be an excellent tool for studying many dynamical details of recombinative desorption (44). Such experiments can be performed, in principle, for nearly any metal. The hydrogen-copper reaction system has been shown to conform reasonably well to the provisional model. It is logical and interesting to continue studies on as many systems as possible, comparing theory to experiment for different metals and different crystal faces to see how well we can actually do. In the event that the provisional model works well, we will derive a detailed dynamical picture of these simple reactions. Where it does not, we will find where improvements are needed.

4.4. Building the World's Greatest Microscope

The driving spirit of the field of chemical dynamics is the desire to visualize the atomic-scale motion associated with chemical reactions. Accurate atomic-scale dynamics theories derived from the first principles of physics yet employing experimentally validated approximations satisfy such desires in ways that are impossible to fulfill by any other means—one obtains atomic-scale movies with femtosecond time resolution. In a very real sense, atomic-scale dynamics from first-principles theory is the world's greatest microscope. This idea has been clearly demonstrated for simple gas-phase reactions—one beautiful example is the newly discovered roaming reaction, in which

simple bond rupture occurs via trajectories that stray far from the reaction path (159). For surface chemistry, we are still building and testing the "microscope." The number of approximations is greater, and our experimental tools for testing them are more limited. Despite these challenges, we have come further than one might have imagined would be possible.

When considering that computational chemistry for simple gas-phase reactions, such as H + HD $\to$ H$_2$ + D, was still in its infancy in the late 1980s, one realizes the enormous progress made in developing an accurate computational approach to molecular interactions and chemical reactions at metal surfaces. This rapid progress has of course benefitted from the growth and improvement of computer hardware—more importantly, advanced theoretical ideas (e.g., DFT) have utterly changed our view of what is technically possible. It is only a mild overstatement to say that today anything can be calculated. Yet as our implementations of theory apply to ever more complex phenomena, for which direct experimental interrogation can be challenging or impossible, it is important to recall how tenuous the connection is between the first principles of physics and practical computational chemistry. For the time being, we are destined to be working with, in the words of Nate Silver in the epigraph, "simple models that we know to be flawed," but ones in which we can hope to be able to "point out when and where those flaws are likely to occur." In the summer of 2014, during the final stages of writing this article, one of the authors succeeded in outpredicting all others in our department's World Cup betting pool using Silver's "flawed" model. Perhaps there is reason to be hopeful about the usefulness of the provisional standard model of surface chemical reactivity.

DISCLOSURE STATEMENT

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