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ABSTRACT

Recent advances in theoretical characterization of reaction dynamics on metal surfaces are reviewed. It is shown that the widely available density functional theory of metals and their interactions with molecules have enabled first principles theoretical models for treating surface reaction dynamics. The new theoretical tools include methods to construct high-dimensional adiabatic potential energy surfaces, to characterize nonadiabatic processes within the electronic friction models, and to describe dynamics both quantum mechanically and classically. Three prototypical surface reactions, namely, dissociative chemisorption, Eley-Rideal reactions, and recombinative desorption, are surveyed with a focus on some representative examples. While principles governing gas phase reaction dynamics may still be applicable, the presence of the surface introduces a higher level of complexity due to strong interaction between the molecular species and metal substrate. Furthermore, most of these reactive processes are impacted by energy exchange with surface phonons and/or electron-hole pair excitations. These theoretical studies help to interpret and rationalize experimental observations and, in some cases, guide experimental explorations. Knowledge acquired in these fundamental studies is expected to impact many practical problems in a wide range of interfacial processes.

I. SURFACE REACTIONS: WHY AND WHEN DYNAMICS IS IMPORTANT

Chemical reactions occurring at gas-solid interfaces are of great importance. Examples of such reactions include heterogeneous catalysis, corrosion, materials processing, and aerosol chemistry. A typical sequence in such a process involves the (dissociative) adsorption of reactants on the surface, diffusion, reaction, and desorption of products, as schematically depicted in Fig. 1.[1] All these steps are influenced by molecule-surface interaction and energy flow. It is generally believed that the diffusion and reaction steps as well as the desorption are driven by thermal fluctuations, while the initial adsorption step might be significantly influenced by dynamics. This is because the molecular species involved in the former steps are generally in constant contact with the substrate, but the interaction time between the impinging molecule and surface is often short. The assumption of thermal equilibrium simplifies the theoretical treatment of the kinetics because statistical theory, such as the transition-state theory, can be used. Of course, this general rule of thumb is not absolute. For example, molecular adsorption may involve a deep chemisorption well in which the reactant may be partially or completely thermalized with the surface before the reaction occurs. On the other hand, recombinative desorption (RD) could be strongly influenced by post-transition state (TS) dynamics, as discussed below in this review. In general, the importance of dynamics is largely dictated by the time scale of the elementary step relative to that of the intramolecular vibrational redistribution (IVR) in the molecule-surface complex.[2]

Surface reaction dynamics has been an active field for some time, and recent experimental studies demonstrated unambiguously that dynamics does play an important role in surface reactions.[1,3] A good example is the direct dissociative chemisorption (DC) of small molecules such as CH_4 and H_2O on metal surfaces,[4–11] in which reactivity is found to depend on the excitation of reactant modes. Experimental evidence shows that the excitation of a vibrational mode in the impinging molecule can sometimes be more effective

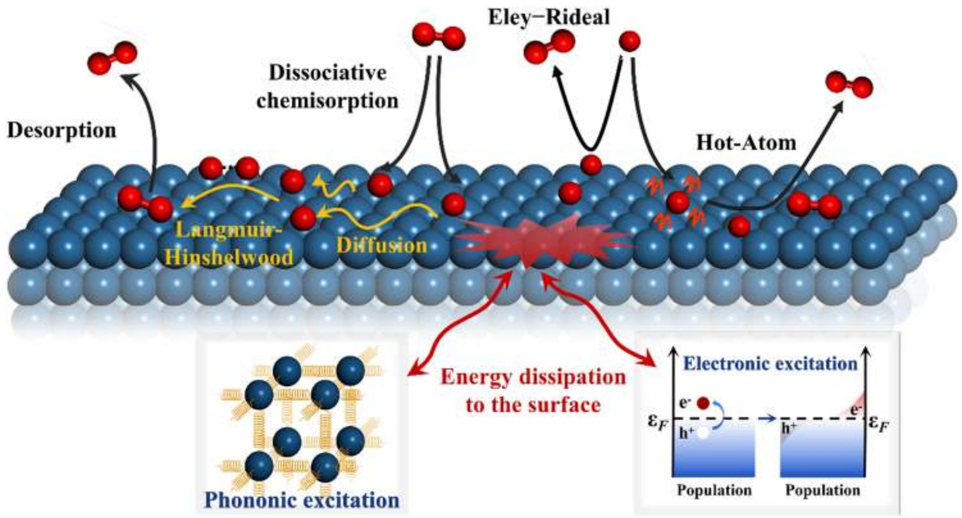

FIG. 1. Schematic diagram of possible elementary surface reactions and energy dissipation processes.

in promoting the reaction than another vibrational mode or the translational mode.[12] Such mode specificity and the related bond selectivity implies that not all forms of energy are equal, thus arguing against the statistical assumption. For these processes, our knowledge of reactivity is incomplete without an in-depth understanding of dynamics.

The foremost motivation for studying dynamics in surface reactions is of course a fundamental one, but knowledge of dynamics may benefit many practical applications. For example, information on site-specific reactivity might aid the design of new and more effective catalysts. Furthermore, a better understanding of dynamics may also allow precise control and manipulation of reactions to achieve better efficiency or to maximize yields of desired products.

In this perspective, we focus on the dynamics of reactions on metal surfaces from a theoretical viewpoint. Although atomic and molecular scattering from surfaces is a prerequisite to surface reactions, it is not the focus here. Neither will the theory of laser driven surface processes[13,14] be discussed. Rather, the review is centered at processes involving the breaking and forming of chemical bonds through collisions. Several excellent reviews on experimental studies of surface dynamics exist.[12,15–19] Theoretical treatments of these processes have also been surveyed before.[20–30] Here, we present a global viewpoint of the field, with an emphasis on recent advances. We note at the outset that many of the theoretical treatments parallel those of gas phase reactions,[31] but the unique surface environment, such as dissipation,[32,33] can greatly complicate the dynamics.

II. KEY ISSUES IN SURFACE REACTION DYNAMICS

In studying surface reaction dynamics, it is both unavoidable and beneficial to compare to those in the gas phase, where many key issues have been investigated in great detail.[31,34–37] While the interaction between the reactant and substrate makes surface dynamics much more complex, many principles governing gas phase dynamics may still be applicable.[38] For example, the vibrational mode-specific and bond-selective reactivity of several polyatomic molecules (e.g., CH_4 and H_2O) has been experimentally observed in both bimolecular reactions in the gas phase[34,36] and DC on metal surfaces.[5–7,9,11] Distinct nonthermal product energy disposals in RD, which can be considered as the reverse of DC via detailed balance, have also been reported,[39–44] in analogs to gas phase reactions. Moreover, molecular dissociative sticking probabilities on metal surfaces have been found to also depend on the initial molecular orientation relative to the surface,[10,45] suggesting a similar steric effect to that identified in bimolecular reactions in the gas phase.[36] The fact that such dynamical signatures survive in these surface processes, i.e., DC and RD, implies that the interaction time between the molecule and surface must be sufficiently short that the thermal equilibrium is not established effectively during the dynamical event.

In many other aspects, however, surface reactions have very different characteristics from their gas phase counterparts. Instead of a single entrance channel typical of a gas-phase reaction, the surface offers multiple impact sites with differing reactivities. The site-dependent reactivity can be viewed as a result of the “chemical shape” of the surface, analogous to the chemical shape of a reactant molecule in a gas phase reaction.[46] Different from the “physical shape” of the surface, which can be probed via nonreactive scattering, this chemical shape is a manifestation of the potential energy surface (PES) near the transition state, which depends on the orientation of the molecule as well as the impact site.[50,51] For example, site-dependent reactivities in both CO oxidation[44] and H_2 DC[47] have been reported with state-of-the-art experimental techniques. Site- and incidence angle-dependences have also known for methane DC on Pt(110)-(1 × 2)[48] and Pt(211).[49–51] Theoretically, it has been predicted that reactivity at a high-barrier site may sometimes be higher than that at a low-barrier site, underscoring the multidimensional nature of the surface chemical shape.[52–54]

Perhaps most importantly, reactions at gas-surface interfaces are always accompanied by energy flow between the molecular species and surface, which can significantly influence many aspects of reaction dynamics. On one hand, the kinetic energy carried by the impinging species can be mechanically transferred to surface atoms upon collision, leading to surface phonon excitations. Such an energy transfer process occurs within the adiabatic Born-Oppenheimer (BO) approximation. On the other hand, surface electrons can also be excited by gas-surface collisions, opening the nonadiabatic energy dissipation channel.

Understanding the dynamics of energy exchange and its relevance to surface reactions on the microscopic scale has been a major goal in past few decades. The relative importance of the two energy dissipation channels is probably system- and process-dependent. In general, energy exchange with surface phonons is often encoded in the dependence of dynamical properties on the incident energy and surface temperature. Even for a light molecule such as H_2, for example, its initial sticking probability (S_0)[55,56] has been found to depend strongly on surface temperature. Energy exchange with surface phonons is essential for dynamical trapping of the molecule, e.g., in the nonactivated chemisorption of H_2 on Pd surfaces.[57,58] For activated DC, on the other hand, lattice motion may be coupled to the reaction coordinate, lowering the DC barrier via surface atom displacements. This molecule-lattice coupling is responsible for the remarkable enhancement of S_0 at low incident energies in DC of methane.[59,60] By contrast, energy dissipation to surface phonons can also remove energy from the reaction coordinate, dynamically lowering the reactivity at high incident energies.[61]

The excitation of electron-hole pairs (EHPs) at metal surfaces has been shown to play a key role in several nonreactive surface processes, such as the inelastic scattering of highly vibrationally excited NO molecules[62–64] and H atoms.[65–67] The former may involve significant charge transfer because of the large electron affinity of NO and thus governed by nonadiabatic transitions between the neutral and anionic NO states near the surface.[68,69] In the latter case, hyperthermal H atoms with high velocities easily reach high electron density regions at and inside the surface and strong nonadiabatic interactions with surface electrons lead to quick loss of their kinetic energies.[70] Analogously, hot H atoms diffusing on metal surfaces have been found to dissipate their kinetic energies more efficiently to EHPs than surface phonons.[71] In addition, hot atom (HA) mediated Eley-Rideal (ER) reactions may be suppressed by energy dissipation to EHPs.[72–74] However, the importance of EHP excitations in the DC of closed-shell molecules such as H_2, HCl, N_2, H_2O, and CH_4[75–83] is more tenuous presumably because the reactions take place sufficiently fast at configurations with relatively low surface electron densities.

An exact treatment of these dissipative channels is difficult because of the large number of degrees of freedom (DOFs) involved. However, many approximate models have been developed to treat these phenomena, as discussed below.

III. THEORETICAL APPROACHES

Given these aforementioned complexities, accurate modeling of the dynamics in surface reactions is by no means a trivial task. Under the BO approximation, the dynamics is governed by a high-dimensional molecule-surface PES, which is intrinsically complex.[27,28] Moreover, dynamics may not be restricted to a single PES when EHP excitations are involved, further complicating the theoretical treatment. Earlier theoretical investigations of surface dynamics relied largely on low-dimensional dynamical models and empirical model Hamiltonians accounting for molecule-surface interactions as well as surface phonons and EHPs.[20,23] Since then, much progress has been made using first-principles approaches. Here, we focus on recent developments, especially those relevant to surface reactions involving polyatomic molecules.

A. Potential energy surfaces

The basic Born-Oppenheimer and static surface (BOSS) approximations[26] represent a good starting point to study surface dynamics because of substantially reduced computational costs. Within these approximations, the PES depends only on molecular DOFs. A semiempirical London–Eyring–Polanyi–Sato (LEPS) function was employed to describe the interaction of a diatomic molecule with a rigid metal surface in the era when first-principles electronic structure calculations were not affordable.[84] This physically inspired PES was adapted from gaseous atom-diatom reactions by incorporating surface periodicity. This LEPS form has been recently improved by adding site-dependent Sato parameters.[85] Stimulated by remarkable advances in density functional theory (DFT), more accurate methods for PES construction have been developed in recent years. In 2000, Busnengo *et al.* proposed the corrugation reducing procedure (CRP) based on symmetric interpolation of thousands of DFT points on a regular grid,[86] which has since become a popular way to construct PESs for various diatom-surface systems.[27] In the CRP framework, the six-dimensional (6D) molecule-surface interaction PES is obtained by subtracting all atom-surface interactions (in three-dimensional, 3D) from the total potential energy. The subsequent interpolation is implemented in the 6 coordinates [illustrated in Fig. 2(a)]. The use of Fourier interpolation over X and Y combined with orientationally and rotationally symmetric interpolation over θ, φ gives the CRP PES the correct periodicity and permutation symmetry. More importantly, the energy range of the strongly repulsive region is dramatically reduced, rendering the interpolation much easier and more accurate. Although an extension of CRP to polyatomic-surface systems is conceptually possible, no attempt has been reported, presumably because of its interpolation nature that scales unfavorably with dimensionality.

Kroes and co-workers[87] adapted the modified Shepard interpolation (MSI) method originally proposed for gas phase reactions.[88] In this approach, the potential energy at a given configuration is represented as a weighted sum of several second-order Taylor expansions at nearby configurations. This method reproduced the dynamics results obtained on corresponding CRP PESs in several H_2-surface systems,[89] although the approximate imposition of translational symmetry by reflection leads to kinks in the PES at the unit cell boundaries.[90] Recently, this problem was solved by introducing redundant coordinates that explicitly take care of the surface periodicity.[91] Although MSI is quite general, it scales poorly with both the size of data set and dimensionality, due apparently to its interpolation nature. Consequently, after a preliminary attempt to the CH_4 + Ni(111) system in 2010,[92] no other high-dimensional PES has been reported.

High-dimensional PESs have also been constructed for polyatomic DC using permutation invariant polynomials (PIPs)[93] by approximating the surface as a pseudoatom.[94,95] However, it is difficult to enforce the surface periodicity and the number of PIPs increases quickly with the system size.

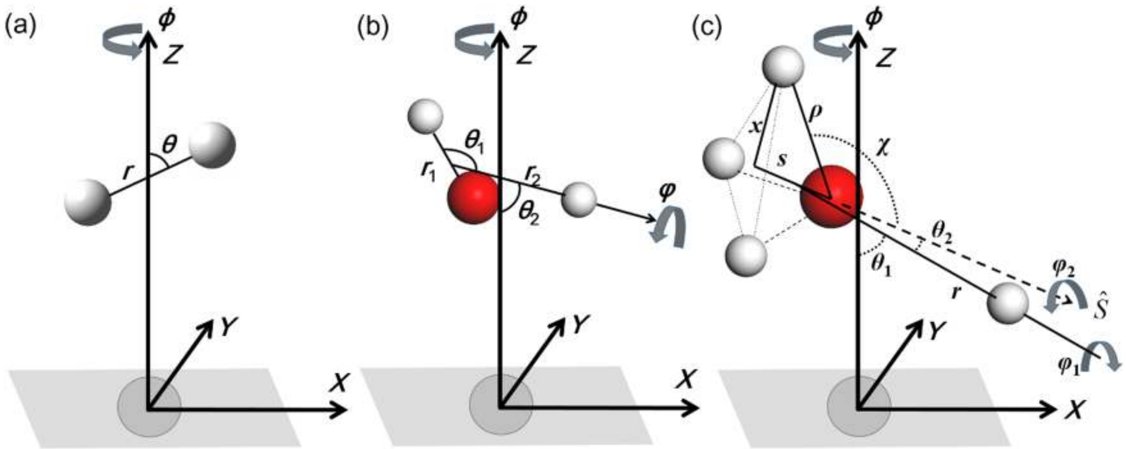

FIG. 2. Coordinate systems used in quantum dynamics calculations for the DC of a diatomic [e.g., H_2 (a)], triatomic [e.g., H_2O (b)], and pentatomic molecule [e.g., CH_4 with C_{3v} symmetry imposed (c)].

Since its introduction for CO adsorption on Ni(111),[96] approaches based on neural networks (NNs) have become widely accepted for developing molecule-surface PESs. NNs provide flexible nonlinear analytical functions that can represent a multidimensional data set with high fidelity. The nonlinear fitting, or "training" in the language of NNs, is quite standard, but the adaptation of symmetry for both surface periodicity and permutation of identical atoms in the molecule presented a challenge. Lorenz *et al.* proposed a set of symmetry-adapted coordinates for the H_2 DC on Pd(100),[97,98] which were later generalized by Reuter and co-workers for different crystal faces and molecular sizes.[99,100] In the application to the H_2 + Cu(111) and H_2 + Pt(111) systems, Ludwig and Vlachos replaced the interpolation within the CRP framework by an NN representation, in which the periodicity of the surface was included by Fourier expansions of the lateral coordinates for each hydrogen atom.[101] Zhang and co-workers recently reported high fidelity NN fits of PESs for HCl, H_2O, and CH_4 DC on various metal surfaces.[102–107] Their PESs were built on data points restricted in a symmetry unique area surrounded by high symmetry surface (i.e., top, bridge, and hollow) sites, and the NN input was based on internuclear distances within the molecule and distances between nuclei in the molecule and high symmetry surface sites. However, none of the aforementioned NN PESs captured the permutation invariance of the system rigorously.

Recently, we proposed a new NN based method that incorporates both the permutation symmetry of the molecule and surface periodicity in a more general and rigorous way. This so-called permutation invariant polynomial neural network (PIP-NN) approach[108] is inspired by the PIP method that has achieved great success in representing the PESs of gas phase reactions.[93] Different from the PIP approach where the PIPs are used as the fitting basis, the PIP-NN approach uses a minimum number of PIPs to enforce the permutation symmetry of the molecule and uses the primitive Fourier expansions of atomic coordinates and the bond distances as the NN input. These symmetry functions (SFs), which differ from the simple symmetrized sums and products of primitive functions used in previous studies,[99,100] were demonstrated to be essential in obtaining an accurate fit of BOSS PESs.[108] Since then, the PIP-NN method has been successfully used for developing high-dimensional PESs for interactions between various molecules and surfaces.[53,109–113]

These aforementioned methods are all limited to rigid surfaces. To describe moving surfaces, surface DOFs need to be included, which drastically increase the dimensionality of the PES. Furthermore, the motion of surface atoms breaks the translational symmetry of the surface. A more efficient strategy is required. One straightforward way to incorporate the surface DOFs is to rely on empirical force fields, such as the embedded atom method (EAM)[114] and embedded diatomics-in-molecule method (EDIM).[115] More recently, the reactive bond order (REBO) force fields[116] have been parameterized by more than 10 000 DFT points to obtain PESs for CH_4 DC on Ni(111) and Pt(111) with reasonable accuracy.[117] To achieve a higher level of accuracy, the atomistic NN (AtNN) approach proposed by Behler and Parrinello[118] seems to be a more promising candidate. In AtNN, the total energy of an N-atom system is given by the sum of atomic energies, i.e., $E = \sum_{j=1}^{N} E_j$, where E_j is the energy of the jth atom, which depends only on its local environment. An individual NN is created for each atom type in the system, which encodes the all possible chemical environments in the system. Immediately, one realizes that this representation scales linearly with the number of atoms and is hence extendable to high-dimensional systems. In addition, it automatically enforces permutation symmetry. The major challenge of the AtNN method is to describe the local environment.[119] To this end, SFs, which are two and three-body expansions that sum over interactions between the central atom and neighboring atoms within a specified cutoff radius, are used.[118,119] The AtNN method has been successfully applied in HCl + Au(111),[120,121] N_2 + Ru(0001),[122] and CO_2 + Ni(100) systems.[123] Gradients can help to improve the efficiency of AtNN fitting.[122,123]

B. Classical and quantum dynamics within the BOSS approximations

Once the PES is available, the nuclear dynamics of a surface reaction can be simulated classically by solving Newton's equation or quantum mechanically by solving the Schrödinger equation. Since the inclusion of surface DOFs significantly increases the complexity, we first review dynamics methods within the BOSS approximations.

The adiabatic dynamics can be described by the quasiclassical trajectory (QCT) method,[124] in which the zero-point vibrational energy (ZPVE) of the reactant is included. The initial coordinates and momenta are sampled from phase space distributions of the vibrational modes. The product ro-vibrational state can be extracted using approximate methods such as the normal mode analysis (NMA) approach.[125,126] Although it is reasonably accurate for scattering and activated DC above the threshold and provides important mechanistic insights, the QCT approach may not be quantitatively accurate due to the unavoidable ZPVE leakage. This can be especially detrimental for polyatomic DC,[127–129] because of the artificially fast IVR within the system. For nonactivated DC processes, it is possible to mitigate this problem by running trajectories on the ZPVE-corrected PES where the distance-dependent ZPVE is added to the PES.[130] In addition, quantum tunneling is absent in QCT calculations, which is often important at low incidence energies.

In principle, only a quantum mechanical (QM) treatment of reaction dynamics can rigorously include quantum effects, but it is numerically demanding and scales poorly with the system size. Earlier quantum dynamics (QD) calculations using either time-independent coupled channel (TICC) or time-dependent wave packet (TDWP) methods have been reported for diatom-surface systems with up to six DOFs. The former, as reviewed by Groß,[21] scales cubically with the number of bases (N_{basis}) and is thus limited to systems with small N_{basis}, such as scattering of H_2 on palladium. The TDWP method is much more powerful as it scales as $N_{basis} \log N_{basis}$ and as a result, has been widely applied to scattering and DC of H_2 on various metals[22,27] and recently extended to heavier diatoms such as HCl.[102] For more details of this approach, the reader is referred to several comprehensive reviews.[22,27]

The WP method has been extended to the more demanding calculations of polyatomic DC.[28,30] Figure 2 depicts the coordinates for QD calculations for diatomic and polyatomic systems on surfaces. Without loss of generality, the Hamiltonian of a molecule-surface system within the BOSS approximations can be written as

$$\hat{H} = \hat{K}_{trans} + \hat{K}_{vib} + \hat{K}_{rot} + \hat{V}(\mathbf{q}), \tag{1}$$

where $\hat{K}_{trans}$ is the kinetic energy operator (KEO) for the center-of-mass translations of the molecule perpendicular (Z) and parallel (X, Y) to the surface and γ is the skew angle between two lattice vectors (not shown in Fig. 2) ($\hbar = 1$ hereafter),

$$\hat{K}_{trans} = -\frac{1}{2M}\left(\frac{\partial^2}{\partial Z^2} + \frac{1}{\sin^2\gamma}\frac{\partial^2}{\partial X^2} + \frac{1}{\sin^2\gamma}\frac{\partial^2}{\partial Y^2} - \frac{2\cos\gamma}{\sin^2\gamma}\frac{\partial^2}{\partial X \partial Y}\right), \tag{2}$$

where M is the molecular mass. On the other hand, $\hat{K}_{vib}$ and $\hat{K}_{rot}$ represent the vibrational and rotational KEOs of the molecule, respectively. The vibrational KEO depends on both the intramolecular radial and angular coordinates, while the rotational KEO depends on angular variables that describe the rotation and orientation of the molecule, as illustrated in Fig. 2. $\hat{V}(\mathbf{q})$ is the PES represented with these $3N_{atom}$ coordinates, where N_{atom} is the number of atoms in the molecule. It should be noted that the Hamiltonian can also be represented in cylindrical coordinates or Cartesian coordinates for the convenience of extracting the product information in an Eley-Rideal reaction.[131,132]

In practice, the wave packet is discretized using basis functions and/or grids. To simulate scattering, an initial wave packet located in the reactant asymptote (at a large Z) is expressed as a product of a Gaussian wave packet in Z, internal state wavefunctions of the reactant, and Fourier bases in surface lattice vectors with the translational periodicity. It is propagated using either the time[133] or Chebyshev propagator.[134] The scattering probabilities can be obtained by projecting the scattering wavefunction onto the asymptotic states. On the other hand, the DC probability can be computed with a flux approach at a dividing surface after the DC transition state[135] or alternatively by summing the scattering probabilities and subtracting from unity.[136]

Comparing to gas phase reactions, WP treatments of surface reactions are more challenging, in at least two aspects. First, the DOFs parallel to the surface can significantly increase the number of basis functions, particularly for heavy molecules. Second, the molecule-surface interaction depends on the azimuthal angle, which is essential to the description of molecular orientation/alignment and thus steric effects. A QD treatment with fixed X and Y coordinates results in the "fixed-site" model,[137] while further neglecting the azimuthal angle arrives at the "flat-surface" model.[138] The latter was applied to study the mode-specific DC of water and methane by us.[11,94,95,139] More recently, Zhang and co-workers proposed an azimuthal angle-averaging approach in which the fixed-site DC probability is well approximated by averaging the flat-surface results obtained at a few azimuthal angles.[103] It was further shown that a weighted average of fixed-site reaction probabilities, obtained with the molecular center sampled at several symmetry and off-symmetry sites, can reproduce well the results obtained with full-dimensional QD calculations for activated DC of H_2 and H_2O on rigid surfaces.[52,104,140] This so-called site-averaging approximation can substantially reduce computational costs, provided that dynamical steering is insignificant.[141–143] Taking advantage of these approximations, several accurate WP calculations for H_2O and CH_4 DC have been reported for up to nine DOFs.[54,105,144]

Despite these advances, it is still difficult to extend the conventional WP methods to higher-dimensional systems. In this regard, the multiconfiguration time-dependent Hartree (MCTDH) method[145] could be a more efficient alternative. The wave packet in the MCTDH framework is expanded in terms of single particle functions which themselves are time dependent and can be optimized. As a result, MCTDH can treat more DOFs than those in the conventional WP framework. The MCTDH method was applied more than 10 years ago to H_2 DC on rigid Cu(100) including all molecular DOFs,[146] but its extension to polyatomic reactions on surfaces has been less successful,[92,147] due largely to difficulties in representing a high-dimensional PES in the sum-of-product form as required in the practical implementation.

In a different approach, Jackson and Nave[148] spearheaded an approximate WP method for DC based on the reaction path

Hamiltonian (RPH).[149] In this RPH-WP approach, the PES is approximated along the reaction coordinate by quadratic potentials for the $(3N - 1)$ generalized normal modes and the initial wave packet is expanded by normal mode vibrational basis functions along the reaction coordinate. An important feature of the RPH-WP model is that nonadiabatic transitions can take place among various vibrational channels, which have been found to be essential in reproducing the experimental observations on mode specificity and bond selectivity of methane DC at various metal surfaces.[148,150–152] For more details, the reader is referred to reviews by Jackson and co-workers.[29,153]

C. Classical and quantum dynamics beyond the BOSS approximations

The BOSS approximations are ideal for describing adiabatic dynamics of light molecules interacting with surfaces. However, neglecting interactions with surface phonons and EHPs renders these calculations inaccurate for most surface reactions. There are several routes to go beyond the static surface limitation. For example, surface phonons can be approximated by a harmonic oscillator which shifts the PES uniformly along a collective surface atom displacement coordinate but retains its chemical shape. This "surface oscillator" (SO) model[61] and various variants account for the energy exchange between the molecule and surface. Such models range from the 1D SO model along the vertical displacement (Z) implemented in low-dimensional QD models[154] to the 3D SO model combined with QCT calculations.[57] One may further enable energy dissipation to the bulk by introducing another ghost oscillator coupled to the SO, whose motion is governed by the generalized Langevin equation (GLE).[155] This generalized Langevin oscillator (GLO) model stems from earlier models in atom-surface collisions advanced first by Adelman and Doll[156] and later by Tully,[157] who treated surface atoms as a harmonic oscillator chain linked by a set of GLEs. Thanks to its simplicity, the GLO model has recently gained much popularity, mostly combined with accurate 6D CRP PESs, for studying diatomic molecule scattering[58,158] and Eley-Rideal reactions[159,160] on metal surfaces. It has been shown to capture the main physics of the molecule-lattice energy transfer.

However, these SO based models are less able to describe the change of local molecule-surface interaction due to surface distortion, which can be considerable for the DC of heavy molecules. To improve, the SO model can be modified by adding a linear coupling as a function of the oscillator coordinate to account for the barrier change in molecular DC.[161] More recently, Jackson and co-workers[59,60,162] identified two key molecule-lattice couplings from the study of CH_4 DC on various metal surfaces. One is referred to as the "electronic coupling," describing a linear dependence of the barrier height on the displacement of the metal atom underneath the molecule. The other is the "mechanical coupling" that describes the change of the transition state location with the displacement of the surface atom normal to surface. In this sense, the SO model can be regarded as a special case of the mechanical coupling with a unit coupling factor. The explicit inclusion of the normal displacement of a surface atom in QD calculations suggested that a sudden approximation of this DOF is sufficient to reasonably reproduce the lattice effects.[162,163] Consequently, Jackson and co-workers proposed a sudden model to correct the dissociative sticking probability obtained within the BOSS framework, with the coupling factors derived from DFT calculations.[162] This sudden model has been successfully applied to RPH[148,150,152,164] and fully coupled QD studies[11,95,143,165,166] of CH_4, H_2O, and CO_2 DC on a variety of metals, which have semiquantitatively reproduced the lattice effects on reactivity at low incidence energies. It can be further improved by including nonlinear electronic coupling terms.[106] Very recently, a modified GLO model was adapted incorporating both types of couplings.[167]

Thanks to the ever increasing computer power, one can now calculate the atomic forces at the DFT level on the fly,[168] thus bypassing difficulties associated with fitting high-dimensional PESs. Furthermore, surface DOFs can be explicitly involved in classical dynamics simulations. This so-called *ab initio* molecular dynamics (AIMD) method, pioneered by Groß and co-workers for studying surface reactions,[169] has become increasingly popular in recent years in studying various reactions where the lattice effects are important[74,170–175] and in some cases, yielded more reliable results than the GLO model.[176] It should be noted that AIMD simulations are perfectly suited for relatively rapid processes with high probabilities but may fall short for long-lived and/or small probability events because of high numerical costs. It might also fail to account long-time energy dissipation to the bulk. The former problem is being gradually solved using the AtNN approach by constructing high-dimensional PESs for the molecule and dozens of surface atoms in the supercell with periodic boundary conditions.[120–123] The latter issue may be overcome by coupling the supercell with the bath via GLEs. Meyer and Reuter[177] recently developed an elegant model that embeds a quantum mechanical (QM) reaction zone in a metal (Me) bath described by a force field. This hybrid QM/Me model allowed a realistic characterization of slow energy dissipation from the adsorbate to bath.

If EHP excitations play a role, the dynamic calculation is much more challenging because of the coupling to an infinite set of continuous electronic states in a metal surface. Fortunately, approximate models have been developed. In the so-called electronic friction model of Head-Gordon and Tully,[178] energy dissipation to EHPs is ascribed to a friction force that captures the response of slowly moved nuclei to fast electronic motion. More specifically, Newton's equation is replaced by GLEs,

$$m_i \frac{\mathrm{d}^2 \mathbf{R}_i}{\mathrm{d}t^2} = -\frac{\partial V(\mathbf{R})}{\partial \mathbf{R}_i} - \sum_j \Lambda_{ij}(\mathbf{R}) \frac{d\mathbf{R}_j}{dt} + F_i(T_e), \qquad (3)$$

where m_i is the mass of the ith atom of the molecule with $\mathbf{R}_i$ being its coordinate vector, $V(\mathbf{R})$ is PES, the electronic friction force is given as a product between the electronic friction tensor $\mathbf{\Lambda}$ and the velocity vector of the atom, and $F_i(T_e)$ denotes the temperature-dependent random fluctuation. The latter is related to the friction through the dissipation-fluctuation theorem. MD simulations with electronic friction based on Eq. (3) are usually abbreviated as MDEF.

A commonly used friction model is based on the local density friction approximation (LDFA),[75] in which each atom of the adsorbate is assumed to be embedded in a homogeneous free electron gas at the metal surface.[179] As a consequence, the friction tensor is reduced to scalar atomic position-dependent friction coefficients, which depend on the local electron density of the substrate, Fermi momentum, and scattering phase-shifts at the Fermi level, all of which can be estimated from Kohn–Sham (KS) states in a static DFT calculation.[179] Combined with the independent atom approximation (IAA) that treats each atom separately,[75] MDEF simulations within LDFA have been extensively used to account for the low-lying EHP excitations in scattering of atoms and molecules from metal surfaces.[32] The LDFA model has also been coupled with the GLO[180] and AIMD models[71,181] to include surface motion. The resulting change in the surface electron density enables the inclusion of both the surface EHP and phonon energy dissipation channels simultaneously.[182]

The validity of the LDFA-IAA model has sometimes been questioned due to the approximations it invokes. The IAA has been improved via the Hirshfeld partitioning of the overall system density to contributions of relevant atoms,[183] which was recently applied to the relaxation of hot atoms and molecules on metal surfaces.[182,184] However, the approximation of the friction tensor by a diagonal form may be rather severe. It is thus desirable to determine the friction tensor from first principles. This can be done using the first-order time-dependent perturbation theory (TDPT)[178,185,186] that fully accounts for the electronic structure of the interacting molecule-surface system. Very recently, two groups reported somewhat different implementations of TDPT that allowed the determination of tensorial friction based on KS orbitals of DFT.[81,187,188] These *ab initio* friction tensors have been fit to analytical forms using NN methods and used in QCT simulations of surface scattering.[81,82] Interestingly, the comparison of TDPT and LDFA results on H_2 + Cu(111)[81] and H_2 + Ag(111)[82] systems indicated that EHP excitations have a rather minor influence on molecular DC, but a more subtle and mode-specific effect on state-to-state scattering.

When charge transfer from the surface to the molecule becomes important, for example, in NO scattering on noble metal surfaces, multiple electronic excited states have to be considered among which explicit nonadiabatic transitions can be simulated by the stochastic wave packet method[68] or independent electron surface hopping (IESH) method.[189] Their relationship with the friction model has been a subject of recent discussion.[190] However, a first-principles characterization of the multidimensional multistate PESs and nonadiabatic couplings between the ground and excited states is still very challenging, which has been done only for few systems.[191,192]

IV. SURFACE REACTIONS

A. Dissociative chemisorption

DC is one of the most studied surface reactions that involve only one molecule. In such a process, the translational and internal energies, as well as the orientation/alignment of the impinging molecule, can in principle affect reactivity, leading to very rich dynamics. There have been numerous experimental and theoretical studies on DC of diatomic molecules, especially H_2 being the simplest benchmark system, as recently reviewed by Kroes and Diaz.[27] Because of its light mass, the energy exchange between H_2 and surface is often neglected and quantitative comparison can thus be made between the dissociative sticking coefficients measured by molecular beam experiments and calculated by 6D QD and QCT results within the BOSS approximations. On Cu(111) and Cu(100), for example, using a specific reaction parameter density functional (SRP-DF) that mixes the generalized gradient approximation (GGA)[193] type of functional, e.g., PW91[194] or PBE[193] and the RPBE[195] DFs, 6D QD and QCT results reproduced measured S_0 in a wide range of incidence energies and quantum state resolved effective barrier heights of H_2 and D_2 with chemical accuracy.[163,196] This success of the SRP-DF has been extended to other weakly activated systems, for example, H_2 + Pt(111).[197,198] However, SRP-DF failed to reproduce the experimental S_0 curve for the nonactivated H_2 + Pd system, which decreases first and then increases with incidence energy.[199] With the help of 6D TICC calculations,[200] the high reactivity at lower energies of H_2 on Pd(100) was attributed to a steering effect, i.e., molecules approaching the surface at low velocities tend to reorient and move to more favorable sites to dissociate.

In some cases, surface motion may be important in H_2 DC. For example, the 6D QD and QCT calculations for H_2 + Cu(111) using the SRP-DF[201] overestimated the rotational alignment parameters as measured by the RD experiments,[202] which are related to the steric effect of DC by detailed balance. Further AIMD simulations involving surface motion[203] significantly improved the agreement with experiments, indicating that the preference for the helicopter orientation (i.e., $m_j = j$, rotation parallel to the surface) in DC is diminished by surface distortion. In addition, Busnengo *et al.* performed classical trajectory calculations for H_2 on Pd(110) using a GLO model,[58] which successfully captured the surface temperature dependence of reactivity that was attributed to a dynamic precursor mediated mechanism. On the other hand, MDEF calculations have suggested that EHP excitations play a minor role in the activated DC of H_2 on Cu(110),[75] Ru(0001),[204] Cu(111),[81] and Ag(111),[82] as evidenced by slight decreases of S_0 in the presence of electronic friction. In contrast, EHP excitations dominate in the relaxation of the hot hydrogen atoms resulted from H_2 DC on Pd(100).[71] AIMD with electronic friction (AIMDEF) simulations indicate that the energy dissipation to EHPs is over five times faster than that to surface phonons.[71] From Eq. (3), one notes that the friction force not only depends on the friction coefficient, which is related to the electron density of the metal surface, but also depends on the atomic velocity. The weak nonadiabatic effect in DC can be understood as the result of lowering velocity as the system climbs up to the DC barrier, even when the friction becomes large.[75] On the contrary, the high velocity of dissociated hot H atoms diffusing close to the surface facilitates the energy dissipation to EHPs.[71] This interplay between the velocity and friction coefficients is the key to understanding nonadiabatic effects in DC and inelastic scattering.[82]

When the molecule becomes heavier, the BOSS approximations become potentially inadequate because of energy exchange with substrate phonons. However, the role played by EHP excitations is much less clear and dependent on the molecular property and the interaction PES. Based on 2D calculations, for example, it was argued that EHP excitations might contribute to the low N_2 DC probability on Ru(0001), even at incidence energies much higher than the DC barrier (~1.8 eV).[205] However, later 6D QCT calculations validated the BOSS approximations and demonstrated that the narrow bottleneck at the transition state is responsible for the low sticking probability, underscoring the importance of the multidimensional PES.[206] Similarly, the different adiabatic multidimensional PES characteristics of the N_2 + W(100) and N_2 + W(110) systems, especially the long-distance molecule-surface interactions, have been found to lead to the higher reactivity of the former than the latter at low energies.[207] In addition, AIMD calculations for N_2 + W(110)[170] and QCT calculations based on a high-dimensional AtNN PES for N_2 + Ru(0001)[122] demonstrated that the inclusion of surface motion in N_2 DC yields better agreement with experimental results because of the significant energy transfer to the lattice. However, MDEF simulations based on LDFA clearly showed that low energy EHP excitations have a very minor effect on N_2 DC.[80,208]

The O_2 DC on Al(111) is a controversial system concerning nonadiabatic effects. It has been long recognized that the conventional GGA based DFT failed to predict an adiabatic DC barrier[209,210] and cannot thus reproduce the observed energy dependence of the sticking probability.[211] To resolve this discrepancy, it was proposed that the apparent barrier may be resulted from a crossing between the triplet and singlet PESs.[212] Indeed, such a barrier was found using a spin-constrained DFT model[213] and subsequent surface hopping simulations including the two states reproduced the experimental S_0 curve.[192] However, recent embedded correlated wavefunction (ECW) calculations challenged this spin-flip picture and showed that an adiabatic barrier appears naturally due to a more reliable description of charge transfer.[214,215] Our recent QCT calculations on a 6D ECW-based PES reproduced the measured thermal and orientation dependent S_0 as a function of incidence energy quite well,[216] supporting the accuracy of the ECW theory in describing the O_2–Al interaction.

As O_2 DC is often highly exothermic, energy dissipation after DC is also an important issue. Interestingly, despite the high density of states at the Fermi level, Meyer and Reuter concluded on the basis of TDPT that the electronic excitation channel only contributes at most ~5% of the total energy dissipation for O_2 DC on Pd(100).[217] Moreover, using the hybrid QM/Me approach[177] enabling the energy dissipation from local phonons to the substrate bulk, the hot oxygen atoms following O_2 DC on Pd(111) were found to be much longer-lived than similar ones on Pd(100). Interestingly, the former randomly walk on the surface with much longer absolute distances but smaller net diffusion lengths.[218]

DC of HCl on Au(111) represents a puzzling system that has recently attracted much interest owing to the strong disagreement between theory and experiment.[78,219] While theory qualitatively captured the observed enhancement by both translational and vibrational excitations of the impinging HCl, the absolute dissociative sticking probabilities obtained by QD[52,220] and QCT[120,121] calculations on PESs and AIMD simulations[78,83,173] were all larger than experimental ones by 1–2 orders of magnitude. This conclusion remains true even when nonadiabatic effects are taking into account by LDFA, implying a negligible role of low-lying EHP excitations.[78,83,121] This substantial discrepancy exceeds the systematic error of DFT and is insensitive to the DF used, suggesting possible errors elsewhere. To resolve this discrepancy, further studies, both theory and experiment, are clearly needed.

Comparing to diatoms, polyatomic molecules possess more internal DOFs and richer dynamic features in DC. Special interest is the influence of various reactant vibrational modes in promoting the reaction. In this respect, the DC of CH_4 and its isotopologs has been extensively investigated. Pioneering quantum state resolved molecular beam experiments by the Beck and Utz groups firmly established that both vibrational and translational energies can promote this reaction.[12,17–19] However, the effects of different vibrational modes and their relative efficacies to translation are different and system dependent. In general, the vibrational efficacy of the symmetric stretch (ν_1) of CH_4 is the largest, followed by that of the antisymmetric stretch (ν_3). The vibrational energy in these modes can be even more effective than the same amount of translational energy in assisting highly activated methane DC, e.g., on Ni(111) and Ni(100).[4,6,8] On the other hand, the efficacies of the bending modes (ν_2 and ν_4) are smaller.[7,221,222] In addition, the efficacies of overtones and combination bands cannot be simply estimated by the sum of the contributing fundamental modes.[222] When methane is isotopically substituted, the excitation of the C–H or C–D stretch not only enhances the overall reaction differently[5,223] but also selectively breaks the corresponding bond.[9,223,224] Using a linearly polarized laser, Yoder *et al.* found that DC probabilities of aligned $CH_4(\nu_3)$ and $CHD_3(\nu_1)$ are the largest (smallest) when the laser polarization is parallel (perpendicular) to the Ni surface plane.[10,45] On Ni(110), the reactivity further depends on the azimuthal alignment of the C–H bond.[45] Mode-specific, bond-selective, and stereodynamics results have been found for methane DC on several metal surfaces,[4–10,45,48,221,222,224–232] offering unambiguous evidence for the strong nonstatistical behavior. The reaction dynamics is further complicated by the remarkable enhancement of the sticking coefficients at low incidence energies at elevated surface temperatures.[230,233–235] These experimental observations posed a challenge for theory.

Earlier reduced-dimensional models treating the CH_3 group as a pseudoatom were incapable of revealing the influence of different vibrational excitations.[59,60,236,237] Jackson and co-workers advanced the RPH-WP approach that naturally includes all vibrational DOFs.[148] Combined with the sudden model for lattice effects,[162] the RPH-WP calculations semiqualitatively reproduced the experimental dissociative sticking coefficients on various transition metal surfaces.[49,150,151,153,238] It was shown that both adiabatic vibrational mode softening and vibrationally nonadiabatic transitions contribute to the mode-specific enhancement of the reactivity.[29] The latter observation suggests that the vibrationally adiabatic picture is inadequate for this surface reaction. The success of the RPH-WP approach indicates that it captures the salient features of the mode-specific and bond-selective DC of polyatomic molecules, despite its approximated nature.

To move beyond the RPH approximation, the DC of methane has been subjected to high-dimensional QD studies on multidimensional PESs. In 2013, Jiang *et al.* developed the first DFT-based high-dimensional global PES for CH_4 + Ni(111) using the PIP method, which includes the vibrational and rotational DOFs of methane but neglects the translation parallel to the surface and the rotation about surface normal.[95] An eight-dimensional (8D) quantum model[239,240] preserving the C_{3v} symmetry of the nonreactive CH_3 group was used to simulate the dynamics. After the lattice effects were corrected with Jackson's sudden model, the calculated sticking probabilities for various vibrational states of CH_4 were found to agree with experiment semiquantitatively.[95] More recently, Shen *et al.* developed thirteen- (13D) and fifteen-dimensional (15D) PESs by NN fitting for methane DC on Ni(111) and Ni(100),[106,107,144] and reported seven-dimensional (7D) to nine-dimensional (9D) QD results which highlighted the importance of the azimuthal angle and site specificity.[54] The alignment effects of CHD_3 on Ni(111) were addressed by QCT calculations using a PIP PES, and the dependence of reactivity on the polarization angle has been attributed to the different quantum probability distributions of the aligned rotational states.[241] The EHP effects within LDFA were found to lead to a small reduction in dissociative probabilities for all vibrational states, hardly changing to the vibrational efficacies.[77]

In the aforementioned studies of methane DC, surface atoms were not explicitly taken into account. Efforts have been made to examine the impact of surface phonons on the DC dynamics. For example, Shen *et al.* investigated bond selectivity in the DC of methane isotopologs on Ni(111) and Pt(111) using a reactive force field for surface DOFs.[117] Kroes and co-workers, on the other hand, included the surface atoms in AIMD studies, focusing on the search for accurate SRP functionals for methane DC on Pt(111)[171,242] and Ni(111).[172] Using the SRP32-vdw functional with 32% of RPBE and 68% of PBE exchange plus the vdW-DF[243] description of nonlocal correlation, AIMD results reproduced dissociative sticking coefficients for CHD_3 on Ni(111), Pt(111), and Pt(211) on a wide range of high incident energies.[172,244] RPH-WP calculations on Pt(211) also reproduced experimental data.[49] As a follow up, Zhou *et al.* constructed a new 15D PES for the CH_4 + Ni(111) system based on a PIP-NN fit of those points computed with SRP32-vdW and QCT results on this PES indeed reproduced AIMD and experimental S_0 values at high incident energies.[111,129,245]

Theoretical studies have also been carried out for DC of other polyatomic molecules. Using a 6D PIP PES and a flat surface QD model, we predicted that symmetric and antisymmetric stretching modes of H_2O show comparable and large vibrational efficacies, followed by the bending modes, all of which are more effective than translation in promoting its DC on Cu(111).[94] Based on the same model, bond selectivity was also predicted in HOD DC on Cu(111).[95] Hundt *et al.*[11] later measured the quantum state-resolved initial sticking probabilities of D_2O on Ni(111) and confirmed that exciting the antisymmetric stretching fundamental and first overtone levels of D_2O significantly enhances the reactivity. These observations were semiquantitatively reproduced by our 6D QD simulations combined with the sudden lattice model, reported in the same publication.[11] Since then, more accurate 9D NN PESs[53,103,165] and 7D–9D TDWP calculations[103–105,143,165,246,247] have been reported, along with RPH-WP calculations,[152] which generally validated the mode specificity and bond selectivity observed in earlier 6D calculations and predicted rotational and steric effects of water DC.[166] Furthermore, the inclusion of the azimuthal angle and site averaging was found to be quite important to obtain the correct absolute S_0.[103,104,247] Given the feasibility of both experiment and full-dimensional BOSS QD characterization, H_2O DC could serve as a candidate for detailed experiment-theory comparison to test the validity of many approximations.[29]

Besides water, mode specificity has also been predicted in the DC of CO_2 on Ni(100),[164,174,248] NH_3 on Ru(0001),[112] and CH_3OH on Cu(111).[113] The mode specificity in CO_2 DC is particularly encouraging, as IVR in this heavier system is expected to be stronger than its lighter counterparts such as CH_4 and H_2O. In the case of methanol, interestingly, activation of the C–O bond seems to be much more strongly enhanced by vibrational excitation, as compared to the quite low C–O dissociation probability at the ground vibrational state, even with the translational energy far exceeding the DC barrier. For example, the vibrational efficacy of the C–O stretch in CH_3OH is more than three times larger than that of the C–H stretch, which can change the branching ratio of C–O/C–H bond cleavage.[113]

The observed mode specificity and bond selectivity can be rationalized (and predicted) based on a simple transition state-based model derived from gas phase reaction dynamics. In this Sudden Vector Projection (SVP) model,[249,250] the efficacy of a reactant mode in promoting reactivity is tied to its coupling strength with the reaction coordinate at the transition state, which in turn is approximated by the projection of the former onto the latter. A large projection would signal strong coupling with the reaction coordinate, facilitating energy flow into the reaction coordinate, thus enhancing reactivity. A small projection, on the other hand, suggests a weak coupling with the reaction coordinate, leading to a spectator mode. Analogously, the energy disposal in the product can be rationalized by SVP by considering the reverse reaction.

The SVP model can be considered as a generalization of the Polanyi rules,[251] which were proposed to predict the relative efficacy of reactant vibrational and translational modes in promoting atom-diatom reactions based on the location of the transition state. In particular, translational energy is more effective in enhancing the reactivity of an early barrier reaction, while the reactant vibrational is more effective in enhancing the reactivity of a late barrier reaction. Instead of the barrier location, the SVP model is based on projections of reactant modes onto the reaction coordinate and thus is more quantitative and able to handle polyatomic systems.

The SVP model has been extensively tested for gas-surface reactions,[28] including the much studied DC of methane[95,223] and water.[252] We note in passing that SVP predictions are not restricted to the molecular vibrational modes; the model can be extended to predict the involvement of translational and surface coordinates as well.[252,253] It also worked especially well for CO_2 DC on Ni(100) where an "early" barrier from physisorption to chemisorption and a "late" barrier from chemisorption to dissociated products influence the mode specificity at low and high incidence energies, respectively.[248] Its success may appear surprising because the presence of the surface can in principle wash out these dynamical features. However, it is important to note that the interaction time between the impinging molecule and surface is typically short such that the molecule cannot be thermalized effectively before it reaches the reactive transition state. As a result, the underlying sudden assumption in the SVP model of slow IVR relative to the collision time is typically fulfilled.[2] Of course, when the reaction becomes indirect, typically involving long-lived intermediates, the SVP model is expected to fail.

We close this subsection by emphasizing entropic effects in DC. As discussed above, the dissociative sticking probabilities of several molecules as plotted in Fig. 3, e.g., for N_2 on Ru(0001),[122,206] CO_2 on Ni(100),[123,174,248] CO on Co(11$\bar{2}$0),[254] and C–O dissociation channel of CH_3OH on Cu(111),[113] are generally very small even with translational energies much higher than their DC barriers, because of their tight transition states. Similar phenomena were also found in the site-specific reactivity of the same molecule, where the reactivity is not always the largest for the lowest barrier site.[52,53,102,143] The tightness of the transition state dictates a narrow reactive cone of acceptance,[46] which can be thought as an entropic effect that affects the reaction rate as the prefactor. This phenomenon may also have a dynamic origin, such as the inefficient energy flow between various molecular modes,[53] and serves as a caveat to the commonly held

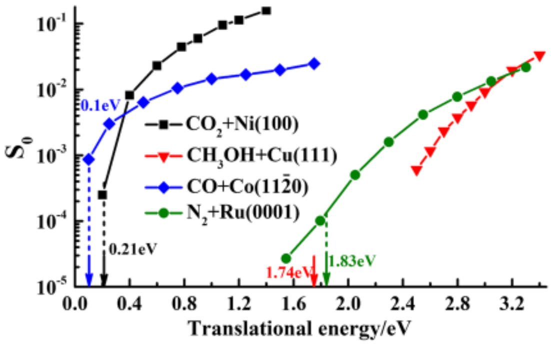

FIG. 3. QCT calculated dissociative sticking probabilities of CO_2 on Ni(100) (black squares, Ref. 123), CH_3+OH on Cu(111) (red triangles, Ref. 113), CO on Co(11$\bar{2}$0) (blue diamonds, Ref. 254), and N_2 on Ru(0001) (green circles, Ref. 122). The corresponding activation barriers are marked by arrows with the same colors.

notion that reactivity is solely determined by the activation barrier height.

B. Eley-Rideal reactions

Bimolecular surface reactions can be loosely classified as the Langmuir-Hinshelwood (LH)[255] and Eley-Rideal (ER)[256] types (see Fig. 1). The former is between two thermalized adsorbates on the surface, while the latter denotes reactions between a gas phase species and an adsorbate. While LH reactions can in general be treated by statistical theories, ER reactions are dominated by dynamics.[15] Within the ER mechanism, the reaction can proceed via a direct ER mechanism, in which the impinging species engages in a single direct collision with the adsorbate. Alternatively, reaction can also take place via the so-called Hot Atom (HA) mechanism,[257] in which the gas phase species hits the surface first before migrating toward the adsorbate. There have been many theoretical studies of ER reactions dynamics,[132,258–263] but until recently, most have used empirical PESs. Two recent advances are worth noting. First is the development of global PESs for ER reactions from DFT calculations, typically for diatomic species.[160,264–268] These PESs allowed QCT studies of the reaction dynamics with a large number of trajectories. The second approach relied on AIMD, which avoids the construction of the PES and includes naturally the surface atoms.[73,74,175,269] This latter approach is ideally suited for reactions involving polyatomic molecules. Most dynamical studies have used QCT because quantum effects are often insignificant for these highly exothermic processes, although there is evidence that a QD treatment may better describe the ER product vibrational state distribution.[132,258]

These theoretical studies of ER dynamics have revealed a surprisingly large role played by the HA mechanism.[160,260–263,268] Furthermore, the direct ER and HA mechanisms may have distinct dynamical signatures. In a recent AIMD study, it was revealed that the CD_4 produced by the D + $CD_3{}^*$ → CD_4 reaction[270] has very different distributions in the CD_4 umbrella vibration, as displayed in Fig. 4.[175] The direct ER reaction proceeds with the impinging H from the top of adsorbed pyramidal CD_3, which results in a necessary inversion of the CD_3 moiety in forming the CD_4 product. This leads to strong excitation in the umbrella mode. The excitation in this mode is much less pronounced in the HA mechanism because the attack of H is from below, causing no CD_3 inversion. In another study, the steric effects in CO oxidation by impinging O atoms[271] were found to force the ER reaction to proceed exclusively via the HA mechanism.[269]

An important issue in ER reactions is the energy exchange with surface phonons and EHPs. In most studies, the surface phonons were treated with approximations, such as the GLO[72,263,268] and DFT based force field[261] models, but more recently they have been explicitly included in AIMD calculations.[73,74,175,269] The two microscopic mechanisms in ER reactions are subjected to very different extents of energy dissipation. In direct ER processes, energy loss of the impinging species is inevitable, but relatively small because the impinging atom is far away from the metal surface when the reaction takes place. However, the HA mechanism necessitates strong interaction of the projectile with the surface, which can induce significant energy exchange with surface phonons and EHPs. Even for light atoms such as H and D, the energy transfer to surface phonons can be significant, driven by the strong attractive force between the hydrogen atom and metal surface. Multiple bouncing for hot atoms near the surface enhances energy loss to the surface.[72–74,175,272] The energy dissipation due to EHP excitations, approximately described using the LDFA model, has also been found to be significant in several ER reactions, due apparently to penetration into high electron-density regions of the surface (sometimes subsurface) by hot atoms and their extensive time spent in these regions.[72–74,175,272] For example, it was found that this nonadiabatic energy loss, which roughly lowers the

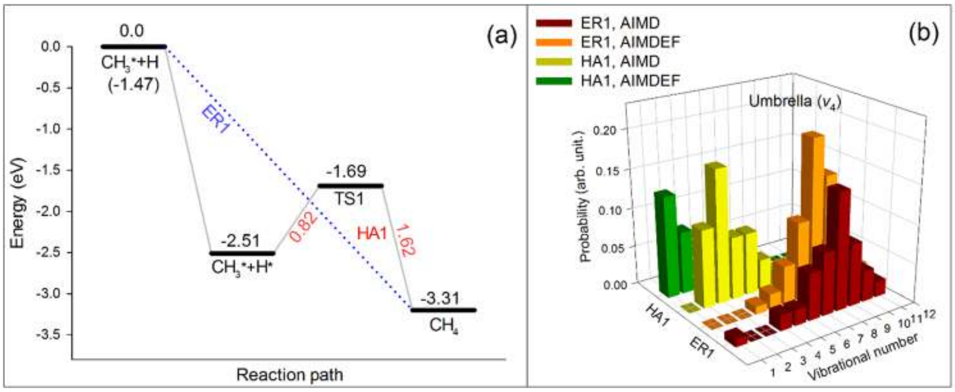

FIG. 4. (a) Energy profiles for ER and HA pathways for the H + $CH_3{}^*$ ER reaction on Cu(111). (b) Distributions of umbrella vibrational modes of the CH_4 products calculated by AIMD and AIMDEF, following the ER and HA pathways, respectively.

HA reactivity by 1/3, improved the quantitative agreement with the measured reaction cross sections for the H(D) + $D^*(H^*)$/Cu(111) recombination process.[74] The large energy loss to surface EHPs of impinging H is consistent with the recent experimental report[66] and theoretical investigations.[70]

C. Recombinative desorption

Dynamics can also be essential after the system surpasses the transition state, particularly in RD. One such example is CO oxidation on metal surfaces, in which hot CO_2 products are produced. This reaction is known to proceed via the LH mechanism between adsorbed CO and O produced from DC of O_2.[39] The experimentally observed translationally and vibrationally hot CO_2 clearly indicates insufficient thermalization,[39,273,274] underscoring the importance of dynamics. Moreover, angle resolved infrared (IR) chemiluminescence measurements revealed that vibrational and rotational temperatures of the desorbed CO_2 are dependent on the desorption angles, shedding light on the structural and orientational information of the transition state.[42,275] It has long been established experimentally that CO_2 products have a bimodal velocity distribution and the two components are associated with different angular distributions.[40,41,44,276,277] By controlling the O density at the step edge, Wodtke and co-workers assigned these two components to reactions taking place at terrace and step sites on Pt surfaces.[44]

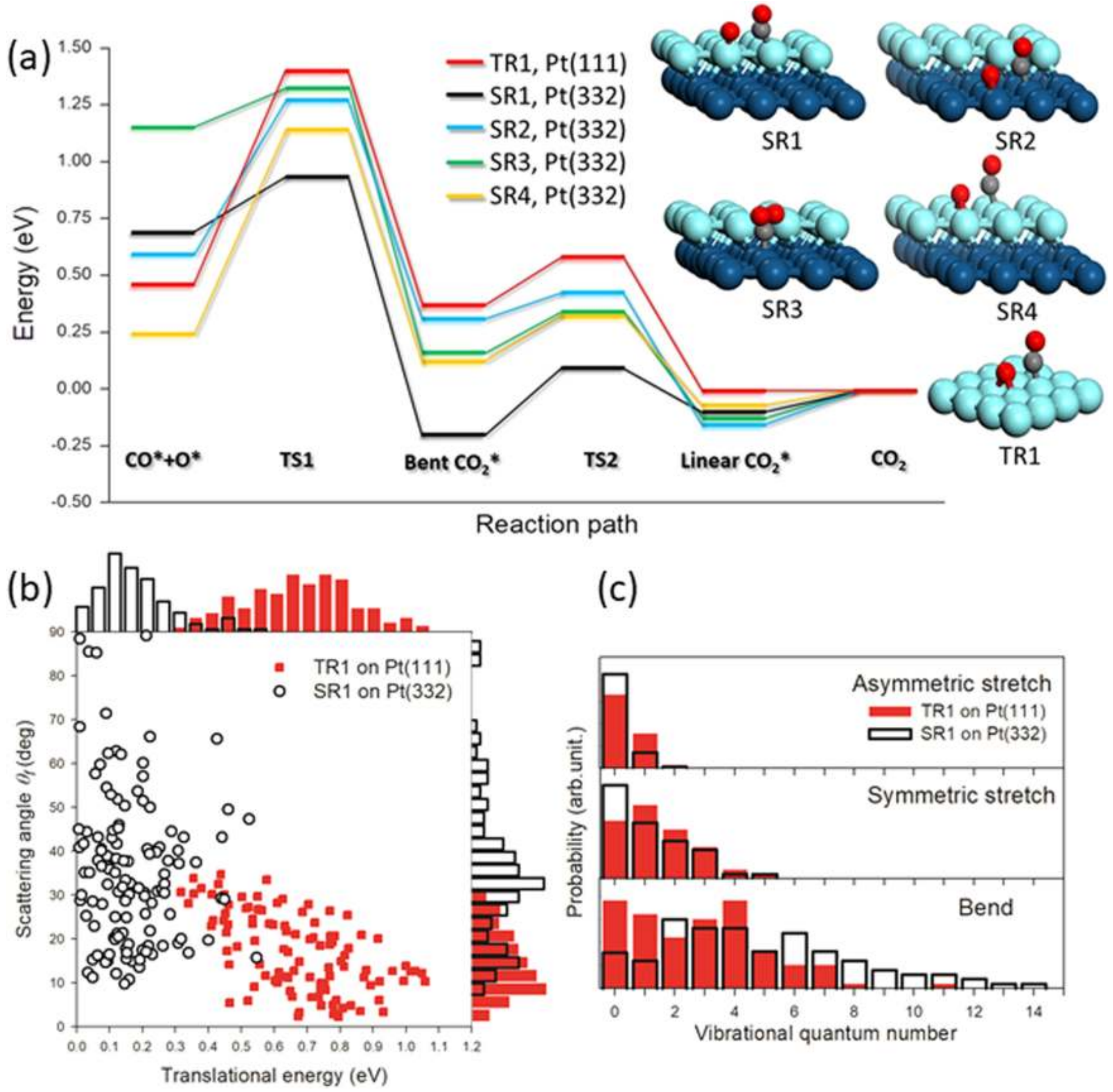

FIG. 5. (a) Energetics of various reaction paths for the oxidation of CO on Pt surfaces (TR1 for the terrace reaction and SRX (X = 1–4) for various step reactions). All energies are referenced to the CO_2 + Pt asymptotic limit. The geometries of various TS1 saddle points are given on the right-hand side. (b) Translational and angular distributions of the CO_2 product. (c) CO_2 vibrational distributions.

A recent theoretical investigation shed light on the dynamical origin of the bimodal distribution of CO_2.[278] As shown in Fig. 5, DFT calculations revealed that the attack of adsorbed CO on Pt surfaces by a nearby O adsorbate via the reactive transition state (TS1) leads to a chemisorbed CO_2 with a bent geometry, which is due apparently to electron transfer to the antibonding orbital of the adsorbate. This chemisorption well is metastable with regard to gaseous CO_2 on Pt(111) but is stable by 0.20 eV on a step site on Pt(332). The chemisorption well is connected to the shallow physisorption well by another transition state (TS2). Further AIMD calculations uncovered that the incipient CO_2 desorbs directly from Pt(111), leading to fast CO_2 near the surface normal. However, nascent CO_2 produced at the step site, which has a lower TS1, is temporally trapped in the chemisorption well. Its final desorption entails slow velocity with a broad angular distribution. In excellent agreement with experimental observations,[44] these theoretical results confirm the assignment and offers insights into the post-transition state dynamics. Furthermore, the AIMD simulations predict strong internal excitation in desorbed CO_2.

It is interesting to note that despite the large (~1 eV) energy release from TS1, the trapping of the incipient CO_2 in the chemisorption well at the step site, as demonstrated by the AIMD dynamics, is in fact predicted by the SVP model,[250] which shows that the reaction coordinate of TS1 is only strongly coupled to the CO_2 vibrational modes with almost no projection onto the translational coordinates. This strong vibrational coupling has previously been noticed in the reverse CO_2 DC reaction.[174,248] As a result, the dynamics after overcoming TS1 channels almost all its energy into the internal DOFs of CO_2, leaving little kinetic energy to overcome the final desorption barrier. The trapping of the chemisorbed CO_2 is supported by experimental evidence based on a transient IR feature in CO oxidation on Pt,[279] which can be assigned to the asymmetric stretching mode of the bent CO_2.

Similar dynamic control of RD has been found in theoretical studies on other surface processes.[280] In addition, it was recently demonstrated that post-transition state dynamics could be responsible for the selectivity in hydrogenation of 1-3-butadiene by a single-atom Pd catalyst anchored on graphene,[281] in which the butene product prefers desorption to the energetically more favorable reorientation.[282] The latter would lead to the complete hydrogenation product butane, contradicting experimental observations.[281]

V. CONCLUSIONS

Recent advances in both experimental and theoretical investigations of surface reactions revealed that dynamics play an important role in many such processes. A thorough understanding of the surface dynamics is essential. As discussed in this perspective, our ability to simulate surface dynamics has been greatly improved in the past few decades, enabled by new theoretical models and methods. Many of these new computational tools have benefited from the availability of efficient electronic structure theory, particularly those based on DFT. The first-principles theory provides not only energies and gradients for either on-the-fly dynamics or construction of global PESs but also other relevant information such as electronic friction. Other theoretical advances include various high-fidelity methods for constructing high-dimensional PESs, quantum and classical trajectory based dynamical methods, as well as approximate ways to treat energy exchange with the substrate.

Our focus here is on dynamics in reactions on metal surfaces. In particular, three types of surface reactions have been identified to have strong dynamic characters. First, the direct DC of molecules is known to show mode specificity, bond selectivity, orientation effects, and site specificity. These nonstatistical effects can now be understood with reasonable accuracy using theoretical methods with differing levels of sophistication. Second, the Eley-Rideal reactions between a gas phase species and an adsorbate have been shown to possess strong stereodynamics when molecular species are involved. Finally, post-transition state dynamics can leave measurable marks in the recombinative desorption. All these reactions can be strongly influenced by energy exchange with the surface phonons and electron-hole pairs.

Despite the progress, our knowledge of surface reaction dynamics is still quite primitive. In our opinion, future theoretical developments need to focus on the following directions. First, the current theoretical models are fundamentally limited by the accuracy of DFT, which is known to be not quantitative. A more accurate characterization of molecule-metal interactions by more advanced electronic structure methods would help to improve the description of surface dynamics. Second, an improved understanding of the energy exchange process during surface reactions is highly desired. While adiabatic energy transfer involving surface phonons can in principle be handled with high-dimensional PESs, nonadiabatic interactions with EHPs require more quantitative theory, preferably based on first-principles treatments. Third, dynamical models also need significant improvements, particularly for simulating quantum-state resolved experiments. While quantum state resolution is achievable with QD models, they are not amenable to large systems, particularly when surface and electronic DOFs are involved. MCTDH or semiclassical characterization of surface phenomena might provide more efficient solutions.

Finally, we emphasize the synergistic relationship between experimental and theoretical studies in this field. In the past, theoretical developments have largely been driven by experimental innovations. In recent years, it has become clear that theory has started to provide a guiding light in experimental exploration. In the coming years, we expect to witness a stronger interplay between the two in our relentless pursuit of a better understanding of surface reaction dynamics, particularly those relevant to practical applications such as catalysis on defects sites, alloys, and clusters.

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