

**First-principles Insights into Adiabatic and Nonadiabatic Vibrational Energy Transfer  
Dynamics during Molecule-Surface Scattering: The Importance of Surface Reactivity**

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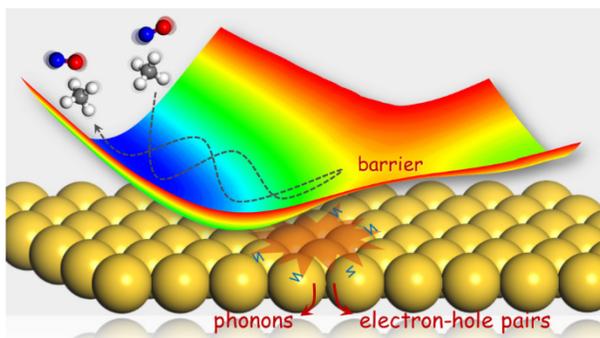
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## Abstract

Energy transfer is ubiquitous during molecular collisions and reactions at gas-surface interfaces. Of particular importance is vibrational energy transfer due to its relevance to bond forming/breaking in surface reactions. In this Perspective, we review recent first-principles studies on vibrational energy transfer dynamics during molecular scattering from metal surfaces at the state-to-state level and insights these studies provided into experimental observations. Taking several representative systems as examples, we highlight the intrinsic correlation between vibrational energy transfer in nonreactive scattering and surface reactivity, and how it operates in both adiabatic and nonadiabatic energy transfer pathways. Adiabatically, the presence of a dissociation barrier softens a bond in the impinging molecule and increases its coupling with other molecular modes and with surface phonons. In the meantime, the stronger interaction between the molecule and the surface also changes the electronic structure at the barrier, resulting in an increase of nonadiabatic effects. We further discuss future prospects towards a more quantitative understanding of this interplay between energy transfer and the potential energy surface.

TOC graphic



Energy transfer between molecules and surfaces is an unavoidable companion of a plethora of physical and chemical processes at gas-solid interfaces that are essential in heterogeneous catalysis, corrosion, crystal growth, material fabrication, and many other important interfacial applications. It is therefore crucial to understand how energy transfer influences various collisional and reactive processes in gas-surface encounters. To this end, quantum state resolved experimental studies on the molecular scattering, adsorption/desorption, and reactions at surfaces have been reported in recent years,<sup>1-4</sup> which have provided unprecedented details on the energy partitioning in these elementary processes. While these experiments shed light on the system before and after the collision with the surface, what happens in between often remains elusive. Indeed, experiment alone is often insufficient to determine the relative importance of energy transfer in various channels. This is where theory comes in to bridge the gap between experimental observations and an atomic-level understanding of the underlying mechanisms and dynamics.

An accurate simulation of the energy transfer dynamics during the interaction of molecules with solid surfaces, especially with metal surfaces, remains a challenge. Ideally, one would like to treat on an equal footing both the discrete quantum states of the gas-phase molecule and the continuous states of the solid substrate with numerous degrees of freedom (DOFs). A pragmatic strategy often starts with the Born-Oppenheimer (BO) approximation, assuming that the nuclear dynamics evolves adiabatically on a single potential energy surface (PES). Within the BO approximation, the adiabatic PES is the lowest eigenvalue of the electronic Hamiltonian, which depends parametrically on the nuclear coordinates. Due to the huge number of electrons in the metal, the electronic structure of gas-surface systems is typically characterized by density functional theory (DFT). Based on molecule-surface PESs calculated on the fly<sup>5-6</sup> or fitted to DFT points,<sup>7-8</sup> the nuclear motion for both the molecular and surface DOFs can be further determined.

This adiabatic treatment allows the intramolecular vibrational energy redistribution (IVR) and/or energy exchange between molecules and surface phonons.

On metal surfaces, one often has to go beyond the BO approximation, since electronically nonadiabatic channels are also present via either hot electron-hole pair (EHP) excitations near the Fermi level or electron/spin exchange with the molecule.<sup>9</sup> An exact quantum mechanical description of the nuclear dynamics coupled with a dense manifold of electronic states is still extremely difficult,<sup>10-11</sup> if not impossible. Mixed quantum-classical methods have been developed to treat electronic DOFs quantum mechanically but nuclear DOFs classically, with varying levels of success.<sup>10-19</sup> Depending on the specific problems at hand, these nonadiabatic theories may differ in their description of the nonadiabatic coupling and response, *e.g.*, in either an electronic friction (EF)<sup>20-21</sup> or surface hopping (SH)<sup>22</sup> framework. Although the agreement with experimental observations has not always been quantitative, these theoretical approaches have offered valuable first-principles insights into nonadiabatic phenomena in diverse gas-surface dynamical problems.<sup>23</sup>

Reflecting the rapid progress of the field, there have recently been several excellent and comprehensive reviews summarizing theoretical and computational efforts in various aspects of chemical dynamics at gas-surface interfaces.<sup>11, 18, 23-29</sup> In this Perspective, we focus on the latest theoretical advances in understanding vibrational energy transfer during molecular-surface scattering. Although such processes often coexist with and complement to reactive events,<sup>29</sup> only nonreactive processes are considered here, because the breaking and forming of chemical bonds complicate the energy transfer dynamics. As we stress in more detail below, however, the propensity for vibrational energy transfer is inextricably correlated with the reactivity of the surface, as bond breaking can be considered as excessive vibrational excitation. For nonreactive scattering where the energy is below the reaction threshold, the presence of a dissociation barrier

still cases a long shadow on the dynamics, as it softens the corresponding bond and increases the coupling among different molecular modes and with the surface phonons. The breaking and forming of bonds at the barrier also significantly perturbs the electronic structure, leading to a potential increase of nonadiabatic effects near the reaction barrier.

Through several benchmark molecule-surface systems, we strive in this Perspective to demonstrate that recent progress in theoretical models has enabled a more advanced understanding on how vibrational energy flows in between different modes and/or into/from the translational/diffractive, rotational, phononic, and electronic DOFs at gas-surface interfaces. One of the key questions we will emphasize is the relative importance of the two vibrational energy transfer channels. While the adiabatic channel is present in almost all collisional processes, the nonadiabatic channel might or might not be significant.

Let us start with the simplest and lightest molecule,  $H_2$ , whose energy transfer mechanisms on metal surfaces have been extensively investigated, serving as a benchmark for understanding more complicated systems.<sup>23,26</sup> Given its light mass and high vibrational frequency, the scattering of  $H_2$  from a surface typically results in energy flow from its vibrational mode to its translational/diffractive and rotational DOFs, as the influence of the lattice motion is expected to be small.<sup>30</sup> On metal surfaces, it is important to recognize that the  $H_2$  molecule can always dissociate, although the barrier depends on the metal. Within the BO and static surface (SS) approximation, early low-dimensional calculations with model PESs have already revealed that ro-vibrationally inelastic transitions of  $H_2$  in surface scattering are enhanced by the elongation of the H-H bond as the molecule approaches the dissociation barrier.<sup>31-33</sup> The extent of bond elongation depends on the curvature of the PES along the reaction path and the location of the barrier.<sup>32-33</sup> This relationship between the topography of the PES and efficiency of energy transfer

qualitatively explained experimental observations on the ro-vibrationally inelastic scattering of H<sub>2</sub>.<sup>34-35</sup> Interestingly, this correlation is also closely related to the enhancement of dissociation by initial vibrational excitation of H<sub>2</sub> on Cu(111) where a “late” dissociation barrier exists with a large curvature near the barrier.<sup>36</sup>

This mechanism was later confirmed by quantum dynamics (QD) and quasi-classical trajectory (QCT) simulations on more accurate DFT-interpolated PESs including all six DOFs (6D) of H<sub>2</sub> on rigid surfaces.<sup>37-39</sup> For example, 6D QCT calculations by Muzas *et al.* on H<sub>2</sub> scattering from Cu(111) using a DFT based PES revealed that scattering near the top site is responsible for vibrational deexcitation,<sup>38</sup> which was attributable to the large PES curvature near this especially “late” barrier. More recently, 6D QD and QCT calculations by del Cueto *et al.* on H<sub>2</sub> scattering from a Co(0001) surface, which has an earlier and smaller barrier than the Cu(111) surface, identified a correlation between the extension of the H-H distance in the barrier region and the alignment change of the rotational angular momentum ( $\Delta m_j \neq 0$ ).<sup>40</sup> This correlation indicates an increased anisotropy of the PES as the molecule accesses the dissociative channel, facilitating energy exchange among the vibrational, translational, and rotational DOFs of the impinging molecule.

On the other hand, the importance of nonadiabatic energy transfer from the vibrational DOF to EHPs during H<sub>2</sub> scattering from metals is still being debated. As a close-shell molecule with a large negative electron affinity, H<sub>2</sub> scattering processes are unlikely to involve significant electron transfer and thus amenable to an EF treatment. In this weak coupling limit, the electronic response of the metal substrate to nuclear dynamics can be effectively replaced by a frictional force counterbalanced by a random fluctuation term, augmenting the interatomic force provided by the adiabatic PES, leading to a generalized Langevin equation (GLE) for classical dynamics of the

adsorbate nuclear DOFs.<sup>25</sup> The frictional force is given by the atomic velocity vector multiplied with an electronic friction tensor (EFT,  $\Lambda$ ), whose elements (or coefficients in simplified models) characterize the effective electron-nuclear couplings.<sup>20-21</sup>

Luntz and Persson first computed friction coefficients from DFT along the reaction path of the dissociative adsorption of H<sub>2</sub> on Cu(111) within a two-dimensional model.<sup>41</sup> The differences between their low-dimensional adiabatic and nonadiabatic dynamics calculations suggested a nonadiabatic mechanism for vibrational deexcitation of H<sub>2</sub> and D<sub>2</sub> on Cu(111).<sup>42</sup> However, this claim was disputed by Juaristi *et al.*, who investigated the 6D dynamics using a local density friction approximation (LDFA) model and found the nonadiabatic channel is of minor importance in H<sub>2</sub> dissociation on Cu(110).<sup>12</sup> Approximating the EFT with a diagonal tensor in Cartesian coordinates, the LDFA results in an isotropic scalar friction coefficient for each atom that is simply dependent on the embedded electron density of at the atomic position on the bare surface. Similarly, Muzas *et al.* found that EHP excitations play a minor role in the vibrational deexcitation of H<sub>2</sub> and D<sub>2</sub> scattering from Cu(111).<sup>38</sup> They also attributed the experimentally observed isotopic effects<sup>43-</sup><sup>44</sup> to an adiabatic mechanism, in which the impinging H<sub>2</sub> reaches closer to the top site than D<sub>2</sub> at a given incidence energy due to bond softening, leading to more significant vibrational energy loss than the latter.<sup>38</sup> These results underscore the importance of multidimensional nature of the PES in describing the vibrational energy transfer.

A potential source of error in the LDFA approach is the approximation of the EFT with its diagonal elements and the neglect of the anisotropy of the friction. To address this issue, first principles approaches have recently been developed to determine full-rank EFTs using time-dependent perturbation theory based on Kohn-Sham orbitals,<sup>45-46</sup> often referred as orbital dependent friction (ODF).<sup>47</sup> These EFTs account for the influence of electronic structure of the

molecule-surface system on different nuclear DOFs and can be used to describe the dynamics within the GLE framework. Based on *ab initio* molecular dynamics (AIMD) with on-the-fly computed ODF, Maurer *et al.* first predicted more nonadiabatic energy loss in vibration than in translation during H<sub>2</sub> scattering from Ag(111), resulting in a noticeable impact on the final energy distributions of scattered molecules.<sup>48</sup> This work has motivated the development of neural network (NN) representations of the EFT for diatomic molecules on rigid surfaces by the Meyer group<sup>47, 49</sup> and the Jiang group<sup>50</sup>, respectively. 6D QCT-EF simulations using the analytical EFTs revealed system-dependent mode-specific nonadiabatic effects on the state-to-state scattering of H<sub>2</sub> from Cu(111)<sup>47</sup> and Ag(111),<sup>50-51</sup> as shown in Fig. 1. These detailed simulations revealed that the nonadiabatic vibrational energy loss to EHPs depends on the magnitude of the diagonal EFT element of the molecular vibration ( $\Lambda_{rr}$ ,  $r$  is the H-H distance) and the associated nuclear velocity during a scattering event. The former increases as the molecule climbs up to the barrier region, during which the latter concurrently decreases. But the nuclear velocity in this process depends on the potential energy landscape and the initial vibrational excitation. In comparison, ODF elements along the reaction coordinate for H<sub>2</sub> dissociation on Cu(111) are about twice those on Ag(111). In addition,  $\Lambda_{rr}$  of ODF is larger than that of LDFA, especially on Cu(111) (Fig. 1a). On the other hand, H<sub>2</sub> can more easily reach the barrier region on Cu(111) than on Ag(111), due to a lower dissociation barrier on Cu(111). As a result, the nonadiabatic effect for vibrational relaxation of H<sub>2</sub>( $v=2 \rightarrow v=1$ ) was predicted to be much stronger on Cu(111) than on Ag(111), and more prominent with ODF than with LDFA, as shown in Fig. 1b and 1c. By increasing the internuclear stretching velocity via initial vibrational excitation, the nonadiabatic effect became noticeable for vibrational relaxation of H<sub>2</sub>( $v=3 \rightarrow v=2$ ) on Ag(111) with ODF (Fig. 1c). These results offer

guidance for searching highly nonadiabatic gas-surface processes, which still await experimental confirmation.

For diatomic molecules heavier than  $H_2$ , more sophisticated models are often required because energy exchange with surface phonons cannot be ignored. A reasonable approach proposed by Martin-Gondre *et al.* is to approximate the energy dissipation to the lattice vibration by the generalized Langevin oscillator (GLO) model<sup>52</sup> that allows the rigid surface to move as a whole, much like a 3D surface oscillator coupled with an extra 3D ghost oscillator approximating a thermal bath.<sup>53</sup> A combination of the LDFA and the GLO approach has practical advantages because it can be conveniently integrated with any molecule-surface BOSS PES with high accuracy to consider both adiabatic and nonadiabatic energy transfer. Recently, the AIMD method has become a popular choice as the motion of surface atoms can be included realistically, avoiding the phenomenological treatment in the GLO model.<sup>5-6</sup> The electronic friction force can also be calculated on-the-fly via the LDFA scheme, in the so-called AIMD with electronic friction (AIMD-EF) approach.<sup>54</sup> To further avoid unphysical phonon reflections at the periodic boundaries of the supercell, the AIMD supercell can be embedded in a phononic bath consisting of thousands of metal (Me) atoms described by empirical force fields, resulting in an AIMD/Me model.<sup>55</sup> Successful applications of these methods have been reviewed in more detail elsewhere.<sup>11, 18</sup>

To overcome the inability of the GLO model to include individual surface atoms or the high computational cost of the AIMD method, more recent efforts have been devoted to developing machine learned high-dimensional PESs explicitly incorporating molecular and surface DOFs. In this regard, an atomistic concept has proven to be essential, in which the total potential energy of the system is expressed as the sum of atomic contributions so that the PES scales linearly with the total number of atoms and is thus well-suited for including surface DOFs. An added benefit is that

the permutation invariance of identical atoms is automatically enforced. In practice, each atomic energy can be represented by some empirical functions with a few adjustable parameters to approximate interatomic interactions within a local environment. Such physically inspired force fields (FFs) for specific gas-surface systems can be parameterized in terms of a small number of DFT points.<sup>56-60</sup> A successful example is the H atom scattering from metals and graphene, in which the effective medium theory based FFs helped to uncover the energy transfer mechanisms.<sup>56-57</sup> However, these FFs do not always have the flexibility to provide a faithful representation of the DFT data.<sup>61</sup> Integrating this concept with NNs, the well-known Behler and Parrinello neural network (BPNN) model<sup>62</sup> and a similar embedded atom neural network (EANN) model<sup>63-64</sup> enable much more accurate representations of molecule-surface PESs than physically inspired FFs. Both methods use atomic NNs to map atomic structures to atomic energies, but differ in their atomic descriptors used to distinguish the atomic structures in the local environment. The EANN method is a powerful platform that is not restricted to representing scalar properties such as the potential energy.<sup>65</sup> Indeed, it has been extended to learn electron density surface for estimating the LDFA friction coefficients<sup>66</sup> and to learn the ODF tensor in a fully symmetry-adapted way,<sup>67</sup> both with moving surface atoms. These atomistic NN methods have revolutionized our ability to construct molecule-surface PESs and related properties and have allowed low-cost QCT simulations (with or without EF) to achieve good statistics for rare and long-time events.<sup>68</sup>

One first application of atomistic NN PESs is the scattering of HCl from Au(111), in which the energy transfer between this “heavy” molecule and the surface phonons cannot be ignored. It has been observed experimentally that about half of the HCl translational energy is lost after scattering<sup>69-70</sup> and the vibrational energy transfer is enhanced with the increasing incidence translational energy and initial vibrational excitation.<sup>71</sup> Adiabatic QCT calculations on an early

60-dimensional BPNN PES for this system<sup>72</sup> based on RPBE points found the scattering is direct, and corresponding results qualitatively reproduced the significant translational energy loss of HCl to the lattice and the increase of vibrational excitation probabilities with increasing incidence energy.<sup>73</sup> The latter signals an adiabatic energy transfer mechanism, in which the loss of translational energy is increasingly channeled to the vibrational DOF as the incidence energy increases. Much like the H<sub>2</sub> case discussed above, this can be rationalized by the enhanced translation-to-vibration coupling by visiting the vicinity of the transition state for dissociative chemisorption,<sup>71</sup> again underscoring the correlation between energy transfer and the surface reactivity.

Quantitatively, however, QCT calculations on this PES overestimate the vibrational excitation probabilities and underestimate the energy loss to the surface. In the meantime, the predicted dissociation probabilities are much higher than experiment.<sup>74</sup> These discrepancies suggest that the PES probably allows for the molecule to access (and overcome) the dissociation barrier more easily than it should, due presumably to inaccuracies introduced by the density functional. Indeed, the agreement between experiment and theory is somewhat improved by a new BPNN PES based on a meta-GGA (MS-RPBE1) functional<sup>75</sup> and AIMD with the specific reaction parameter van der Waals (vdW) corrected functional (SRP32-vdW-DF1).<sup>76</sup> The MS-RPBE1 functional predicts a “later” transition state than the RPBE functional, which leads to lower vibrational excitation and dissociation probabilities.<sup>75</sup> The vdW correction significantly increases energy transfer from the molecule to the surface phonons.<sup>76</sup> These improvements underscored the uncertainty introduced by DFT in simulating molecule-surface dynamics.

Interestingly, experimental evidence suggested a transition from an electronically adiabatic at low surface temperature to a nonadiabatic mechanism at high surface temperature in the vibrational

excitation of  $\text{HCl}(\nu=1)$  and  $\text{HCl}(\nu=2)$ .<sup>71, 77</sup> However, the introduction of nonadiabatic effects in the QCT calculations at the LDFA level was found to contribute only a very small fraction of energy loss to EHPs.<sup>73, 76</sup> This marginal impact by EHPs can be rationalized by the limited interaction time in this direct scattering process and lack of access to regions with high surface electron densities because of the large size of the chlorine atom.<sup>73</sup> More advanced nonadiabatic models beyond LDFA (*e.g.*, ODF) may be necessary to better describe the nonadiabatic vibration-to-EHP energy transfer in this system.

The relative importance of adiabatic and nonadiabatic energy dissipation in CO scattering from Au(111) has also been examined on novel NN-based PESs. Experimental studies of low energy  $\text{CO}(\nu=2)$  scattering from Au(111) observed unexpected slow vibrational relaxation, evidenced by the detection of  $\text{CO}(\nu=2)$  and  $\text{CO}(\nu=1)$  after long ( $\sim 10^2$  ps) delays.<sup>78</sup> Interestingly, the scattered  $\text{CO}(\nu=1)$  molecules were found to also have a fast component, with a characteristic angular distribution signaling direct scattering. Although the CO vibrational frequency is sufficiently high that adiabatic energy dissipation to the lattice is an unlikely multi-phonon process,<sup>79-80</sup> it is known that adsorbed  $\text{CO}(\nu=1)$  decays on Cu surfaces within a few ps,<sup>81</sup> due to coupling with the metal EHPs.<sup>19</sup> Given the fast decay rate on Cu surfaces, the observation of the long lifetime of vibrationally excited CO molecules on the Au surface was hence surprising. One possible explanation, which is supported by DFT calculations, is that the CO molecule only physisorbs on Au(111), so the nonadiabatic vibrational energy dissipation is inefficient as the adsorbed molecule is far from the surface and has poor access to the surface electron density.<sup>82</sup> However, this model does not explain the observed fast  $\text{CO}(\nu=1)$  component, which must experience rapid energy dissipation.

To understand the scattering, trapping, diffusion, and desorption of the vibrationally excited CO molecule on Au(111), we have constructed a 60-dimensional BPNN PES based on DFT data.<sup>83</sup> (A more accurate and higher dimensional fit was later developed using EANN.<sup>84</sup>) Our PES identified not only a physisorption well, as in an earlier study,<sup>82</sup> but also a chemisorption well, with comparable well depths. The chemisorbed CO with a C-down configuration is much closer to the surface, thus amenable to strong nonadiabatic coupling with EHPs. Indeed, QCT-EF studies on the PES identified not only the trapped CO undergoing extensive diffusion on the Au(111) while retaining its vibrational excitation, but also strong vibrational dissipation for trajectories that enter the chemisorption well. These observations provided a plausible explanation of the experimentally observed fast and slow components of the CO( $\nu=1$ ) product.<sup>83</sup> The former presumably corresponds to fast vibrational energy loss to EHPs when the impinging CO( $\nu=2$ ) enters the chemisorption well, followed by rapid scattering. The latter might be attributable to CO( $\nu=2$ ) initially trapped in the physisorbed well, which loses its vibrational energy either slowly in the physisorption well or by accessing the chemisorption well during the long diffusion on the surface. The coexistence of chemi- and physisorption wells for CO on Au(111) was also instrumental in explaining the temperature dependence of the vibrational decay rates.<sup>85</sup>

The emergence of high-fidelity NN-based high-dimensional PESs has played a decisive role in elucidating the vibrational relaxation mechanism for NO scattered from Au(111) and LiF(001). In this classic system, detailed experimental studies have revealed efficient multi-quantum vibrational relaxation of highly vibrationally excited NO( $\nu$ ) in scattering from Au(111).<sup>86</sup> In contrast, the scattering of such NO( $\nu$ ) from LiF(001) was found to be largely vibrationally elastic.<sup>87</sup> For a long time, it was generally believed that electronically adiabatic vibrational relaxation of small molecules on solid surfaces is inefficient given the mismatch between molecular vibration

and surface phonon frequencies.<sup>79-80</sup> Consequently, it was argued that the large vibrational energy loss of NO( $\nu$ ) on Au(111) is most likely caused by the electron-mediated nonadiabatic channel, which is however effectively turned off on the insulating LiF(001). Indeed, NO-surface scattering has become a poster child for nonadiabatic vibrational energy transfer at gas-surface interfaces,<sup>13, 15, 86-96</sup> as discussed in several recent reviews.<sup>2, 4, 97</sup>

Because of its large electron affinity, NO is known to undergo extensive charge transfer near the metal surface. The resulting anionic NO species near the surface suggests that the influence of the EHPs may not be perturbative. In this strong coupling limit, an independent electron surface hopping (IESH) model developed by Tully and coworkers,<sup>94</sup> which characterizes nonadiabatic effects via probabilistic transitions between electronic states in the SH framework,<sup>14</sup> seems to be more appropriate. As multiple electronic state PESs and their nonadiabatic couplings are extremely difficult to determine from first principles for metallic systems, the practical application of the IESH model for describing the hopping of independent electrons relied on either empirical models<sup>92</sup> or a Newns-Anderson diabatic Hamiltonian parametrized by limited ground state DFT data.<sup>93</sup> The IESH simulations reasonably reproduced the multi-quantum vibrational relaxation of NO( $\nu=15$ ) at a low incidence energy on Au(111), via the nonadiabatic channel.<sup>13</sup> Importantly, such multi-quantum relaxation was found absent in the adiabatic QCT calculations on the ground state PES (namely, the lowest eigenvalue of the diabatic Hamiltonian).<sup>13</sup> The IESH results also agreed with experimental vibrational excitation probabilities of NO( $\nu=0 \rightarrow 1$  and 2), which were predicted by neither adiabatic QCT simulations nor EF models.<sup>15</sup> These results led to the conclusion of a dominant role of nonadiabatic vibrational energy transfer in NO( $\nu$ ) scattering from Au(111) due to strong vibration-to-electron couplings. While including the nuclear-electronic coupling in a first-principles manner, it is noted that this IESH model used insufficiently flexible pair-wise

functions to represent the diabatic potentials and their couplings and limited DFT data in parameterization, which could compromise the accuracy of the IESH model. Indeed, it failed to capture some more recent observations, such as the incidence energy<sup>90-91</sup> and orientation<sup>96</sup> dependence of vibrational relaxation and translational inelasticity of NO( $\nu=3$ ).<sup>91</sup> These failures were attributed to the inaccuracy of the ground state PES in the IESH model<sup>90</sup>, which is “too attractive” and non-dissociative.

Recently, the NO( $\nu$ )/Au(111) scattering dynamics have been revisited with the assistance of a global 60-dimensional BPNN PES fitted to thousands of DFT data at the PW91 level,<sup>66</sup> which is much more accurate than the ground state PES used in the previous IESH model. QCT simulations on this new PES have significantly improved the agreement with observed translational energy distribution and the incidence energy dependence of vibrationally (in)elastic probabilities for NO( $\nu=3$ ) scattering from Au(111) over those based on the IESH model. Detailed analysis of trajectories suggested that the new BPNN PES is less attractive than that the IESH ground state PES in the entrance channel, thus less favorable for the impinging NO to reach the surface and for multi-bounce trajectories.<sup>66</sup> This feature enabled more facile (adiabatic) vibrational energy transfer with the increasing incidence energy, in qualitative agreement with the experimental observation.<sup>90</sup> More importantly, this BPNN PES (and an equally accurate EANN PES fitted to the same dataset<sup>98</sup>) have predicted a large amount of adiabatic vibrational energy transfer of the impinging NO( $\nu=15$  or 16) to the lattice vibration and molecular rotation/translation,<sup>66</sup> in sharp contrast to previous theoretical results on the ground state PES of the IESH model.<sup>13</sup> This is surprising as the conventional wisdom, as observed in NO on LiF(001), suggests that adiabatic vibrational energy transfer to substrate phonons is unlikely.

To understand the difference between the metal and salt surfaces, Fig. 2 displays the corresponding potential energy landscapes of the two systems on DFT based EANN PESs for NO on Au(111) and on LiF(001), along with two representative trajectories.<sup>98</sup> In the LiF case (Fig. 2a), the PES is purely repulsive and the NO vibrational DOF is barely coupled to any other DOFs, as the NO molecule does not dissociate on the ionic surface. On the other hand, the highly-vibrationally excited NO molecule can readily access the region near the dissociation barrier ( $\sim 3$  eV) on Au(111) (Fig. 2b) and the coupling between the vibrational mode with the other DOFs is strong near the barrier. As a result, the NO bond gradually softens as it approaches the barrier region, enabling its coupling to both the translational/rotational DOFs and surface phonons. Such coupling is apparently responsible for the substantial vibrational energy loss that accounts for almost half of the experimental observation, underscoring the importance of the adiabatic channel. Interestingly, we observed that NO molecules at a low vibrational state of (*e.g.*,  $\nu=1$ ) mostly experience vibrationally elastic scattering on both Au(111) and LiF(001), because the dynamically relevant region of the PES is qualitatively similar in both cases.<sup>98</sup> In particular, NO( $\nu=1$ ) molecules do not have sufficient energy to access the barrier region on Au(111) where the PES is endowed with strong intermodal coupling. These insights highlight again that the synergic effect of the initial vibrational excitation of the impinging molecule and potential energy landscape in determining the efficacy of vibrational energy transfer.

The EANN PES of NO+Au(111) has been further combined with a symmetry-adapted tensorial EANN representation of the EFT calculated from DFT,<sup>67</sup> allowing first-principles simulations of both adiabatic and nonadiabatic energy exchanges between NO and the surface in the EF framework.<sup>99</sup> State-to-state QCT calculations with ODF resulted in the best agreement up-to-date with experiments with respect to vibrational elastic scattering and single quantum

vibrational relaxation of low initial vibrational states NO( $\nu=2, 3$ ), exhibiting significant improvement over the adiabatic dynamics results and these with LDFA. These results suggest that part of nonadiabatic effects in this system may be adequately described by the EF theory, as long as the friction coefficients are reliably computed. On the other hand, the inclusion of ODF-EFT does not seem to improve the description of multi-quanta vibrational energy loss, particularly in the case of high initial vibrational states such as  $\nu=11$  and  $\nu=16$ , for which the width and shape of the final NO vibrational state distribution are well described, but the average number of lost vibrational quanta remains unchanged as in the adiabatic model and much smaller than in experiment.<sup>98</sup> It was pointed out that the Markov approximation intrinsically invoked in the ODF EFT calculations<sup>21</sup> excluded the high-lying EHP excitations above 1.5 eV that could be excited by such high vibrational states. This limitation would hence miss a large fraction of vibrational loss to EHPs. By analysis of the friction spectrum and rescaling of the ODF tensor, the overall vibrational state distribution shifts lower, improving the quantitative agreement with the experiment. This finding is both surprising and promising, as it suggests that a full account of memory effects could potentially extend the applicability of the EF model to describe cases involving strong nonadiabatic effects without resorting to the explicit inclusion of multiple crossing states and their couplings. Unfortunately, calculations with the scaled ODF tensor still failed to resolve the significant overestimation of trapping at high incidence energies.<sup>99</sup> This is likely due to the absence of strong nonadiabatic effects that arise from transient charge- and/or spin-transfer between the metal and NO molecule, which could result in non-negligible changes in effective potential energy landscape, thus beyond the mean-field description within the EF framework.<sup>100</sup> In such cases, SH based methods would likely be required. However, the failures of IESH discussed above indicate that such methods need to be integrated with more realistic first-

principles determined charge transfer states,<sup>101</sup> which remains very challenging for metallic systems.

Comparing with diatomic molecules, the energy transfer dynamics of polyatomics at surfaces are expected to be more complex given the additional vibrational DOFs. It is of particular interest to understand how energy flows from one vibrational mode of polyatomic molecules to another when interacting with metal surfaces. If the vibrational mode is strongly coupled with the reaction coordinate in dissociative chemisorption, it can be expected that vibrational excitation could impact the reactivity. In the past two decades, extensive quantum-state resolved experimental and theoretical studies have indeed demonstrated that vibrational energy in different modes of polyatomic molecules such like methane and water have different abilities in promoting their dissociative adsorption on metal surfaces, revealing remarkable mode specificity, bond selectivity, and steric effects.<sup>24, 60, 102-112</sup> In some cases, the vibrational efficacy is higher than translational excitation.<sup>1, 103, 113</sup> Such non-statistical dynamics cannot be described by conventional transition-state theory and suggest IVR among multiple vibrational modes is incomplete. However, ample reviews on this topic can be found,<sup>1, 3, 23-25, 27</sup> so it is not discussed here.

The aforementioned vibrational enhancement of reactivity requires slow IVR, as the randomization of vibrational energy within the impinging molecule will diminish the effectiveness of mode specificity. Hence, it is important to understand energy flow within a polyatomic molecule as it collides with the surface. Vibrational excitation/relaxation of a polyatomic molecule upon collision at a metal surface can occur in a simple mechanical process, governed by the BO PES. For example, the umbrella vibrational ( $\nu_2$ ) mode of  $\text{NH}_3$  can be excited in collisions with the Au(111) surface at the incidence energies exceeding a certain energetic threshold and the vibrational excitation probabilities are independent of surface temperature.<sup>114</sup> QCT and QD

calculations on model potentials have confirmed a facile translational to vibrational energy transfer via an adiabatic mechanism occurring upon the impulsive collision of the “light” hydrogen end of  $\text{NH}_3$  with the surface.<sup>114-115</sup> However, much less is known about how the vibrational energy in one mode flows to another when colliding with the surface. This IVR induced by the molecule-surface interaction has been recently investigated by Beck and coworkers in state-to-state experiments of  $\text{CH}_4$  scattering from Ni(111) and graphene covered Ni(111).<sup>116-117</sup> It was found that the vibrational energy initially deposited in the antisymmetric stretching ( $\nu_3$ ) mode of  $\text{CH}_4$  ( $1 \nu_3$ ) can be efficiently transferred to the symmetric stretching ( $\nu_1$ ) mode in the encounter with Ni(111) and the resulting  $\nu_1/\nu_3$  ratio in scattered molecules is about  $\sim 0.4$ , roughly independent of incidence energy.<sup>116</sup> However, this IVR channel is absent when Ni(111) is covered by graphene.<sup>117</sup>

As a full-dimensional QD description of the state-to-state scattering of  $\text{CH}_4$  is prohibitively difficult, approximate models have been proposed to shed light onto the vibrational energy transfer in polyatomic molecule-surface systems. Using a reaction path Hamiltonian-based wavepacket method,<sup>107</sup> the inelastic scattering probabilities of  $\text{CH}_4$  on Ni(111) and graphene/Ni(111) at fixed sites have been calculated by Jackson and coworkers.<sup>117</sup> A clear correlation between the elongation of one of the C–H bonds of methane with the magnitude of the  $\nu_3 \rightarrow \nu_1$  transition was revealed, as shown in Fig. 3a, which can be understood as follows. The  $\nu_3$  and  $\nu_1$  normal modes of  $\text{CH}_4$  are linear combinations of the four local C-H vibrations differing only by the relative phases of the C-H stretching motion.<sup>118</sup> As it approaches the Ni(111) surface, one C-H bond elongates at the point of closest contact with an attempt to dissociate, while the other three C-H bonds are merely perturbed. In this frustrated dissociation process, the four C-H vibrations are no longer equivalent and the  $\nu_3$  and  $\nu_1$  modes are mixed with each other (but barely with bending modes). This distortion of the molecule is the largest on the top site, where the lowest barrier lies, leading to the most

efficient vibrational energy transfer between the two modes (at most  $\sim 30\%$   $\nu_3 \rightarrow \nu_1$  transition probability). In addition, the puckering of a Ni atom, which has been found to enhance the dissociative adsorption, also significantly increases the C–H bond length and the transition probability. On the contrary, since the graphene/Ni(111) surface is catalytically inactive (*i.e.*, without a dissociation channel), none of C-H bonds is elongated at all so that the  $\nu_3 \rightarrow \nu_1$  transition probability of CH<sub>4</sub> on this surface is negligibly low ( $\sim 1.5\%$ ). These findings qualitatively explain the contrasting behaviors observed in experiments, correlating the propensity for vibrational energy transfer with the catalytic activity of a surface, much like the NO( $\nu$ ) scattering from the Au and LiF surfaces discussed above.

To understand the general mechanism associated with the collision-induced IVR, we performed state-to-state quantum scattering calculations of a similar and simpler system, namely H<sub>2</sub>O from Cu(111), based on a fully-coupled 6D QD method<sup>119</sup> on a first-principles determined BO PES<sup>120</sup> that explicitly includes all internal DOFs of H<sub>2</sub>O. Comparing with the CH<sub>4</sub> scattering experiments on Ni(111), even stronger vibrational energy transfer from the antisymmetric ( $\nu_3$ ) to symmetric ( $\nu_1$ ) stretching modes was predicted for H<sub>2</sub>O( $1 \nu_3$ ) scattering from Cu(111).<sup>119</sup> The  $\nu_3 \rightarrow \nu_1$  transition probability is comparable to the survival probability of  $1 \nu_3$  itself, as shown in Fig. 3b, rendering the  $\nu_1/\nu_3$  branching ratio being close to unity (0.7~1.2) in the energy range of interest. Moreover, a similar  $\nu_1/\nu_3$  ratio was found no matter whether the initial energy is deposited into the  $1 \nu_1$  or  $1 \nu_3$  state of H<sub>2</sub>O, manifesting a memory-loss effect.<sup>121</sup> Such an efficient vibrational energy transfer between stretching modes in CH<sub>4</sub> and H<sub>2</sub>O in scattering from metal surfaces can be rationalized via a local mode picture in the sudden limit.<sup>119</sup> Like CH<sub>4</sub>, the  $1 \nu_1$  and  $1 \nu_3$  normal modes of the free H<sub>2</sub>O can be represented equally by linear combinations of the two local O-H

vibrations, differing by a phase in the coefficients. As the water molecule approaches the Cu(111) surface and attempts to dissociate, one of the O-H bonds will strongly interact with the surface and becomes elongated and softened (*i.e.*, the reactive O-H bond), while the other remains essentially a spectator. In the strongly interacting region, the original  $1 \nu_1$  and  $1 \nu_3$  normal modes lose the initial coherence of the two local O-H vibrations, but both contribute to either the reactive OH bond or the spectator OH bond. As the molecule eventually scatters back, the  $1 \nu_1$  and  $1 \nu_3$  normal modes re-emerge with almost equal weights as linear combinations of the two local O-H vibrations with scrambled phases. This mechanism explains a similar  $\nu_1/\nu_3$  ratio, namely  $\sim 1.0$ , no matter if the initial excitation is in the  $\nu_1$  or  $\nu_3$  mode. Analogously, this mechanism accounts for the  $\nu_1/\nu_3$  ratio of  $\sim 1/3$  for CH<sub>4</sub> scattering from on Ni(111), because  $\nu_3$  is triply degenerate. In addition, this mechanism can reconcile the absence of the  $\nu_3 \rightarrow \nu_1$  transition in CH<sub>4</sub> scattering from graphene/Ni(111), in which the surface is inert for CH<sub>4</sub> activation and unable to convert the normal modes into a local C-H vibrations and back, thus preventing surface-induced IVR. In contrast to the H<sub>2</sub>O case, the stretching vibrational modes of the partially deuterated HOD molecule become well separated and intrinsically localized. The initial energy deposited in the  $1 \nu_{\text{OH}}$  or  $1 \nu_{\text{OD}}$  mode of HOD is thus more difficult to flow into the other mode,<sup>121</sup> consistent with this local mode picture. This is clearly shown in our theoretical results (Fig. 3c).

Finally, we note that the nonadiabatic channel for vibrational energy transfer involving polyatomic molecules is much less explored than diatoms. In several LDFA calculations,<sup>122-124</sup> the coupling of the molecule with EHPs during surface scattering is found to be weak and with little impact to the vibrational mode specificity, chiefly because the bulkiness of the molecule prevents a close contact with the surface electron density. This is further exacerbated by the short interaction time in direct scattering.

In summary, recent advances in theoretical investigations of vibrational energy transfer in surface scattering processes have benefited greatly from our improved capabilities to describe both the interaction potentials and dynamics. In particular, the emergence of machine learned high-dimensional PESs enabled more efficient and more accurate studies of collision dynamics, which shed valuable light on adiabatic energy flow within the impinging molecule and between the projectile and the surface. In addition, the development of new and first-principles methods for computing electron friction tensors have greatly advanced our ability to explore the nonadiabatic dissipation channels. Combining with new experimental observations, these recent developments have significantly advanced our understanding of surface physics and chemistry.

An important theme, as demonstrated by the examples discussed in this Perspective, is the strong correlation between the vibrational energy transfer at gas-surface interfaces and the potential energy landscape accessible by the impinging molecule. Both the energy landscape from the entrance channel to the barrier and the initial velocity of the molecule (both direction and magnitude) determine how a scattering trajectory evolves on the PES. Importantly, a reactive surface has a superior capability to a non-reactive one for facilitating vibrational energy flow, as the former possesses regions where the vibration of the impinging molecule is strongly coupled with other molecular modes and surface phonons due to the presence of a reactive barrier. Both the adiabatic and nonadiabatic channels of vibrational energy transfer are affected as the molecule accesses the barrier region and elongates the corresponding bond. This origin of strong nonadiabatic effects is presumably attributable to the rapidly changing electronic structure near the barrier. This correlation is valid for not only the energy transfer from molecular vibration to translation/rotation, surface phonons and electron-hole pairs, but also the energy redistribution in different intramolecular vibrational modes.

Despite the uncovering of this general principle, a quantitative theoretical description of vibrational energy transfer at gas-surface systems still faces challenges. First, the accuracy of the BO PES is crucial for describing adiabatic vibrational energy transfer, which largely relies on accuracy of the electronic structure method, specifically the density functional used in DFT. More efforts are necessary in developing chemically accurate functionals for general use and/or more advanced methods beyond DFT.<sup>23, 125-126</sup> Second, the current ODF calculation remains very time-consuming even with some approximations for numerical convenience (*e.g.*, the first-order perturbation, broadening in approximating the delta function). More efficient and robust algorithms for calculating EFTs with improved accuracy and convergence behavior are in progress.<sup>127-128</sup> Third, to accurately capture strong nonadiabatic vibrational energy transfer like in NO+Au(111), first-principles determinations of diabatic states in global configuration space need be explored. One promising approach is the constrained DFT (CDFT)<sup>129-130</sup> that imposes constraints on the charge density and/or magnetic moments during the SCF calculation. This approach was previously applied in computing the triplet state PES for O<sub>2</sub>+Al(111),<sup>130</sup> which however was not generally available in standard electronic structure codes. Very recently, we found that the CDFT implementation<sup>131</sup> in CP2K,<sup>132</sup> with some modifications, can generate physically reasonable neutral and ionic states for NO+Au(111), as shown in Fig. 4. Specifically, the predicted neutral and ionic states at a stretched NO distance ( $r = 1.6 \text{ \AA}$ ) and their couplings agree well with these predicted by an earlier two-state model Hamiltonian invoked in the IESH method, where the diabatic states were estimated using the dipole-induced energy shift of the ionic state in an infinitesimal electric field.<sup>93</sup> One might extend the powerful NN-based approaches to fit global diabatic states from a large number of CDFT data, which can be combined with IESH or similar approaches achieving the correct detailed balance at equilibrium<sup>10</sup> to enable a more

accurate modelling of vibrational energy transfer of NO and CO scattering from metal surfaces. Finally, full-dimensional and fully coupled quantum calculations for polyatomic state-to-state scattering from metal surfaces remain a daunting task. The multi-configuration time-dependent Hartree approach has shown promise in gas phase reactions,<sup>133</sup> but its progress in gas-surface systems is rather limited.<sup>134-135</sup> More recent calculations based on non-equilibrium ring-polymer molecular dynamics<sup>136-137</sup> and semi-classical corrections of the QCT method<sup>138-139</sup> have suggested alternative directions for developing approximate methods achieving quantum accuracy. We expect ample future opportunities for advancing theory towards a predictive understanding of vibrational energy transfer dynamics in various gas-surface systems. In combination with state-resolved experiments, such first-principles studies will serve as a sensitive probe of the molecule-surface interaction potential and the relevant dynamics.

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## References

- (1) Juurlink, L. B. F.; Killelea, D. R.; Utz, A. L., State-resolve Probes of Methane Dissociation Dynamics. *Prog. Surf. Sci.* **2009**, *84*, 69-134.
- (2) Golibrzuch, K.; Bartels, N.; Auerbach, D. J.; Wodtke, A. M., The Dynamics of Molecular Interactions and Chemical Reactions at Metal Surfaces: Testing the Foundations of Theory. *Annu. Rev. Phys. Chem.* **2015**, *66*, 399-425.
- (3) Chadwick, H.; Beck, R. D., Quantum State-resolved Studies of Chemisorption Reactions. *Annu. Rev. Phys. Chem.* **2017**, *68*, 39-61.
- (4) Park, G. B.; Krüger, B. C.; Borodin, D.; Kitsopoulos, T. N.; Wodtke, A. M., Fundamental Mechanisms for Molecular Energy Conversion and Chemical Reactions at Surfaces. *Rep. Prog. Phys.* **2019**, *82*, 096401.
- (5) Groß, A., Ab Initio Molecular Dynamics Study of Hot Atom Dynamics after Dissociative Adsorption of H<sub>2</sub> on Pd(100). *Phys. Rev. Lett.* **2009**, *103*, 246101.
- (6) Nattino, F.; Díaz, C.; Jackson, B.; Kroes, G.-J., Effect of Surface Motion on the Rotational Quadrupole Alignment Parameter of D<sub>2</sub> Reacting on Cu(111). *Phys. Rev. Lett.* **2012**, *108*, 236104.
- (7) Jiang, B.; Li, J.; Guo, H., High-Fidelity Potential Energy Surfaces for Gas-Phase and Gas-surface Scattering Processes from Machine Learning. *J. Phys. Chem. Lett.* **2020**, *11*, 5120-5131.
- (8) Zhou, X.; Zhang, Y.; Yin, R.; Hu, C.; Jiang, B., Neural Network Representations for Studying Gas-surface Reaction Dynamics: Beyond the Born-Oppenheimer Static Surface Approximation. *Chinese J. Chem.* **2021**, *39*, 2917-2930.
- (9) Tully, J. C., Chemical Dynamics at Metal Surfaces. *Annu. Rev. Phys. Chem.* **2000**, *51*, 153-178.
- (10) Dou, W.; Subotnik, J. E., Nonadiabatic Molecular Dynamics at Metal Surfaces. *J. Phys. Chem. A* **2020**, *124*, 757-771.

- (11) Alducin, M.; Díez Muiño, R.; Juaristi, J. I., Non-adiabatic Effects in Elementary Reaction Processes at Metal Surfaces. *Prog. Surf. Sci.* **2017**, *92*, 317-340.
- (12) Juaristi, J. I.; Alducin, M.; Díez Muiño, R.; Busnengo, H. F.; Salin, A., Role of Electron-hole Pair Excitations in the Dissociative Adsorption of Diatomic Molecules on Metal Surfaces. *Phys. Rev. Lett.* **2008**, *100*, 116102.
- (13) Shenvi, N.; Roy, S.; Tully, J. C., Dynamical Steering and Electronic Excitation in NO Scattering from a Gold Surface. *Science* **2009**, *326*, 829-832.
- (14) Carbogno, C.; Behler, J.; Reuter, K.; Groß, A., Signatures of Nonadiabatic O<sub>2</sub> Dissociation at Al(111): First-principles Fewest-switches Study. *Phys. Rev. B* **2010**, *81*, 035410.
- (15) Cooper, R.; Bartels, C.; Kandratsenka, A.; Rahinov, I.; Shenvi, N.; Golibrzuch, K.; Li, Z.; Auerbach, D. J.; Tully, J. C.; Wodtke, A. M., Multiquantum Vibrational Excitation of No Scattered from Au(111): Quantitative Comparison of Benchmark Data to Ab Initio Theories of Nonadiabatic Molecule-surface Interactions. *Angew. Chem. Int. Ed.* **2012**, *51*, 4954-4958.
- (16) Bünermann, O.; Jiang, H.; Dorenkamp, Y.; Kandratsenka, A.; Janke, S. M.; Auerbach, D. J.; Wodtke, A. M., Electron-hole Pair Excitation Determines the Mechanism of Hydrogen Atom Adsorption. *Science* **2015**, *350*, 1346-1349.
- (17) Rittmeyer, S. P.; Meyer, J.; Juaristi, J. I.; Reuter, K., Electronic Friction-based Vibrational Lifetimes of Molecular Adsorbates: Beyond the Independent-atom Approximation. *Phys. Rev. Lett.* **2015**, *115*, 046102.
- (18) Rittmeyer, S. P.; Bukas, V. J.; Reuter, K., Energy Dissipation at Metal Surfaces. *Adv. Phys. X* **2018**, *3*, 1381574.
- (19) Novko, D.; Tremblay, J. C.; Alducin, M.; Juaristi, J. I., Ultrafast Transient Dynamics of Adsorbates on Surfaces Deciphered: The Case of CO on Cu(100). *Phys. Rev. Lett.* **2019**, *122*, 016806.
- (20) Hellsing, B.; Persson, M., Electronic Damping of Atomic and Molecular Vibrations at Metal Surfaces. *Phys. Scr.* **1984**, *29*, 360-371.
- (21) Head-Gordon, M.; Tully, J. C., Molecular Dynamics with Electronic Frictions. *J. Chem. Phys.* **1995**, *103*, 10137-10145.
- (22) Tully, J. C., Molecular Dynamics with Electronic Transitions. *J. Chem. Phys.* **1990**, *93*, 1061-1071.
- (23) Kroes, G.-J., Computational Approaches to Dissociative Chemisorption on Metals: Towards Chemical Accuracy. *Phys. Chem. Chem. Phys.* **2021**, *23*, 8962-9048.
- (24) Nave, S.; Tiwari, A. K.; Jackson, B., Dissociative Chemisorption of Methane on Ni and Pt Surfaces: Mode-specific Chemistry and the Effects of Lattice Motion. *J. Phys. Chem. A* **2014**, *118*, 9615-9631.
- (25) Guo, H.; Farjamnia, A.; Jackson, B., Effects of Lattice Motion on Dissociative Chemisorption: Toward a Rigorous Comparison of Theory with Molecular Beam Experiments. *J. Phys. Chem. Lett.* **2016**, *7*, 4576-4584.
- (26) Kroes, G.-J.; Diaz, C., Quantum and Classical Dynamics of Reactive Scattering of H<sub>2</sub> from Metal Surfaces. *Chem. Soc. Rev.* **2016**, *45*, 3658-3700.
- (27) Jiang, B.; Yang, M.; Xie, D.; Guo, H., Quantum Dynamics of Polyatomic Dissociative Chemisorption on Transition Metal Surfaces: Mode Specificity and Bond Selectivity. *Chem. Soc. Rev.* **2016**, *45*, 3621-3640.
- (28) Shen, X.; Zhang, D. H., Recent Advances in Quantum Dynamics Studies of Gas-surface Reactions. *Adv. Chem. Phys.* **2018**, *163*, 77-116.
- (29) Jiang, B.; Guo, H., Dynamics in Reactions on Metal Surfaces: A Theoretical Perspective. *J. Chem. Phys.* **2019**, *150*, 180901.
- (30) Bonfanti, M.; Somers, M. F.; Díaz, C.; Busnengo, H. F.; Kroes, G.-J., 7d Quantum Dynamics of H<sub>2</sub> Scattering from Cu(111): The Accuracy of the Phonon Sudden Approximation. *Z. Phys. Chem.* **2013**, *227*, 1397-1420.
- (31) Jackson, B., Spectral Grid Study of Ro-vibrational Coupling in Hydrogen-metal Scattering. *J. Phys. Chem.* **1989**, *93*, 7699-7702.

- (32) Darling, G. R.; Holloway, S., Translation-to-vibrational Excitation in the Dissociative Adsorption of D<sub>2</sub>. *J. Chem. Phys.* **1992**, *97*, 734-736.
- (33) Kroes, G.-J.; Wiesenekker, G.; Baerends, E. J.; Mowrey, R. C., Competition between Vibrational Excitation and Dissociation in Collisions of H<sub>2</sub> with Cu(100). *Phys. Rev. B* **1996**, *53*, 10397-10401.
- (34) Rettner, C. T.; Auerbach, D. J.; Michelsen, H. A., Observation of Direct Vibrational Excitation in Collisions of H<sub>2</sub> and D<sub>2</sub> with a Cu(111) Surface. *Phys. Rev. Lett.* **1992**, *68*, 2547-2550.
- (35) Hodgson, A.; Samson, P.; Wight, A.; Cottrell, C., Rotational Excitation and Vibrational Relaxation of H<sub>2</sub> ( $\nu=1, J=0$ ) Scattered from Cu(111). *Phys. Rev. Lett.* **1997**, *78*, 963-966.
- (36) Rettner, C. T.; Auerbach, D. J.; Michelsen, H. A., Role of Vibrational and Translational Energy in the Activated Dissociative Adsorption of D<sub>2</sub> on Cu(111). *Phys. Rev. Lett.* **1992**, *68*, 1164-1167.
- (37) Díaz, C.; Pijper, E.; Olsen, R. A.; Busnengo, H. F.; Auerbach, D. J.; Kroes, G.-J., Chemically Accurate Simulation of a Prototypical Surface Reaction: H<sub>2</sub> Dissociation on Cu(111). *Science* **2009**, *326*, 832-834.
- (38) Muzas, A. S.; Juaristi, J. I.; Alducin, M.; Muiño, R. D.; Kroes, G. J.; Díaz, C., Vibrational Deexcitation and Rotational Excitation of H<sub>2</sub> and D<sub>2</sub> Scattered from Cu(111): Adiabatic Versus Non-Adiabatic Dynamics. *J. Chem. Phys.* **2012**, *137*, 064707.
- (39) Sementa, L.; Wijzenbroek, M.; Kolck, B. J. v.; Somers, M. F.; Al-Halabi, A.; Busnengo, H. F.; Olsen, R. A.; Kroes, G.-J.; Rutkowski, M.; Thewes, C., et al., Reactive Scattering of H<sub>2</sub> from Cu(100): Comparison of Dynamics Calculations Based on the Specific Reaction Parameter Approach to Density Functional Theory with Experiment. *J. Chem. Phys.* **2013**, *138*, 044708.
- (40) del Cueto, M.; Zhou, X.; Muzas, A. S.; Díaz, C.; Martín, F.; Jiang, B.; Guo, H., Quantum Stereodynamics of H<sub>2</sub> Scattering from Co(0001): Influence of Reaction Channels. *J. Phys. Chem. C* **2019**, *123*, 16223-16231.
- (41) Luntz, A. C.; Persson, M., How Adiabatic Is Activated Adsorption/Associative Desorption? *J. Chem. Phys.* **2005**, *123*, 074704.
- (42) Luntz, A. C.; Persson, M.; Sitz, G. O., Theoretical Evidence for Nonadiabatic Vibrational Deexcitation in H<sub>2</sub>(D<sub>2</sub>) State-to-State Scattering from Cu(100). *J. Chem. Phys.* **2006**, *124*, 091101.
- (43) Watts, E.; Sitz, G. O., State-to-state Scattering in a Reactive System: H<sub>2</sub>( $\nu=1, J=1$ ) from Cu(100). *J. Chem. Phys.* **2001**, *114*, 4171-4179.
- (44) Shackman, L. C.; Sitz, G. O., State-to-state Scattering of D<sub>2</sub> from Cu(100) and Pd(111). *J. Chem. Phys.* **2005**, *123*, 064712.
- (45) Askerka, M.; Maurer, R. J.; Batista, V. S.; Tully, J. C., Role of Tensorial Electronic Friction in Energy Transfer at Metal Surfaces. *Phys. Rev. Lett.* **2016**, *116*, 217601.
- (46) Maurer, R. J.; Askerka, M.; Batista, V. S.; Tully, J. C., Ab Initio Tensorial Electronic Friction for Molecules on Metal Surfaces: Nonadiabatic Vibrational Relaxation. *Phys. Rev. B* **2016**, *94*, 115432.
- (47) Spiering, P.; Meyer, J., Testing Electronic Friction Models: Vibrational De-excitation in Scattering of H<sub>2</sub> and D<sub>2</sub> from Cu(111). *J. Phys. Chem. Lett.* **2018**, *9*, 1803-1808.
- (48) Maurer, R. J.; Jiang, B.; Guo, H.; Tully, J. C., Mode Specific Electronic Friction in Dissociative Chemisorption on Metal Surfaces: H<sub>2</sub> on Ag(111). *Phys. Rev. Lett.* **2017**, *118*, 256001.
- (49) Spiering, P.; Shakouri, K.; Behler, J.; Kroes, G.-J.; Meyer, J., Orbital-dependent Electronic Friction Significantly Affects the Description of Reactive Scattering of N<sub>2</sub> from Ru(0001). *J. Phys. Chem. Lett.* **2019**, *10*, 2957-2962.
- (50) Zhang, Y.; Maurer, R. J.; Guo, H.; Jiang, B., Hot-Electron Effects During Reactive Scattering of H<sub>2</sub> from Ag(111): The Interplay between Mode-specific Electronic Friction and the Potential Energy Landscape. *Chem. Sci.* **2019**, *10*, 1089-1097.
- (51) Maurer, R. J.; Zhang, Y.; Guo, H.; Jiang, B., Hot Electron Effects During Reactive Scattering of H<sub>2</sub> from Ag(111): Assessing the Sensitivity to Initial Conditions, Coupling Magnitude, and Electronic Temperature. *Faraday Disc.* **2019**, *214*, 105-121.
- (52) Tully, J. C., Dynamics of Gas-surface Interactions: 3d Generalized Langevin Model Applied to Fcc and Bcc Surfaces. *J. Chem. Phys.* **1980**, *73*, 1975-1985.

- (53) Martin-Gondre, L.; Alducin, M.; Bocan, G. A.; Díez Muiño, R.; Juaristi, J. I., Competition between Electron and Phonon Excitations in the Scattering of Nitrogen Atoms and Molecules off Tungsten and Silver Metal Surfaces. *Phys. Rev. Lett.* **2012**, *108*, 096101.
- (54) Blanco-Rey, M.; Juaristi, J. I.; Díez Muiño, R.; Busnengo, H. F.; Kroes, G.-J.; Alducin, M., Electronic Friction Dominates Hydrogen Hot-atom Relaxation on Pd(100). *Phys. Rev. Lett.* **2014**, *112*, 103203.
- (55) Meyer, J.; Reuter, K., Modeling Heat Dissipation at the Nanoscale: An Embedding Approach for Chemical Reaction Dynamics on Metal Surfaces. *Angew. Chem. Int. Ed.* **2014**, *53*, 4721-4724.
- (56) Janke, S. M.; Auerbach, D. J.; Wodtke, A. M.; Kandratsenka, A., An Accurate Full-Dimensional Potential Energy Surface for H–Au(111): Importance of Nonadiabatic Electronic Excitation in Energy Transfer and Adsorption. *J. Chem. Phys.* **2015**, *143*, 124708.
- (57) Jiang, H.; Kammler, M.; Ding, F.; Dorenkamp, Y.; Manby, F. R.; Wodtke, A. M.; Miller, T. F.; Kandratsenka, A.; Bünermann, O., Imaging Covalent Bond Formation by H Atom Scattering from Graphene. *Science* **2019**, *364*, 379-382.
- (58) Xiao, Y.; Dong, W.; Busnengo, H. F., Reactive Force Fields for Surface Chemical Reactions: A Case Study with Hydrogen Dissociation on Pd Surfaces. *J. Chem. Phys.* **2010**, *132*, 014704.
- (59) Shen, X. J.; Lozano, A.; Dong, W.; Busnengo, H. F.; Yan, X. H., Towards Bond Selective Chemistry from First Principles: Methane on Metal Surfaces. *Phys. Rev. Lett.* **2014**, *112*, 046101.
- (60) Moiraghi, R.; Lozano, A.; Peterson, E.; Utz, A.; Dong, W.; Busnengo, H. F., Nonthermalized Precursor-mediated Dissociative Chemisorption at High Catalysis Temperatures. *J. Phys. Chem. Lett.* **2020**, *11*, 2211-2218.
- (61) Wille, S.; Jiang, H.; Bünermann, O.; Wodtke, A. M.; Behler, J.; Kandratsenka, A., An Experimentally Validated Neural-network Potential Energy Surface for H-atom on Free-standing Graphene in Full Dimensionality. *Phys. Chem. Chem. Phys.* **2020**, *22*, 26113-26120.
- (62) Behler, J.; Parrinello, M., Generalized Neural-network Representation of High-dimensional Potential-energy Surfaces. *Phys. Rev. Lett.* **2007**, *98*, 146401.
- (63) Zhang, Y.; Hu, C.; Jiang, B., Embedded Atom Neural Network Potentials: Efficient and Accurate Machine Learning with a Physically Inspired Representation. *J. Phys. Chem. Lett.* **2019**, *10*, 4962-4967.
- (64) Zhang, Y.; Hu, C.; Jiang, B., Accelerating Atomistic Simulations with Piecewise Machine-learned Ab Initio Potentials at a Classical Force Field-like Cost. *Phys. Chem. Chem. Phys.* **2021**, *23*, 1815-1821.
- (65) Zhang, Y.; Ye, S.; Zhang, J.; Hu, C.; Jiang, J.; Jiang, B., Efficient and Accurate Simulations of Vibrational and Electronic Spectra with Symmetry-preserving Neural Network Models for Tensorial Properties. *J. Phys. Chem. B* **2020**, *124*, 7284-7290.
- (66) Yin, R.; Zhang, Y.; Jiang, B., Strong Vibrational Relaxation of NO Scattered from Au(111): Importance of the Adiabatic Potential Energy Surface. *J. Phys. Chem. Lett.* **2019**, *10*, 5969-5974.
- (67) Zhang, Y.; Maurer, R. J.; Jiang, B., Symmetry-adapted High Dimensional Neural Network Representation of Electronic Friction Tensor of Adsorbates on Metals. *J. Phys. Chem. C* **2020**, *124*, 186-195.
- (68) Zhou, X.; Zhang, Y.; Guo, H.; Jiang, B., Towards Bridging the Structure Gap in Heterogeneous Catalysis: The Impact of Defects in Dissociative Chemisorption of Methane on Ir Surfaces. *Phys. Chem. Chem. Phys.* **2021**, *23*, 4376-4385.
- (69) Cooper, R.; Rahinov, I.; Yuan, C.; Yang, X.; Auerbach, D. J.; Wodtke, A. M., Efficient Translational Excitation of a Solid Metal Surface: State-to-state Translational Energy Distributions of Vibrational Ground State HCl Scattering from Au(111). *J. Vac. Sci. Technol. A* **2009**, *27*, 907-912.
- (70) Rahinov, I.; Cooper, R.; Yuan, C.; Yang, X.; Auerbach, D. J.; Wodtke, A. M., Efficient Vibrational and Translational Excitations of a Solid Metal Surface: State-to-state Time-of-flight Measurements of HCl( $\nu=2$ ,  $J=1$ ) Scattering from Au(111). *J. Chem. Phys.* **2008**, *129*, 214708.

- (71) Geweke, J.; Shirhatti, P. R.; Rahinov, I.; Bartels, C.; Wodtke, A. M., Vibrational Energy Transfer near a Dissociative Adsorption Transition State: State-to-state Study of HCl Collisions at Au(111). *J. Chem. Phys.* **2016**, *145*, 054709.
- (72) Kolb, B.; Luo, X.; Zhou, X.; Jiang, B.; Guo, H., High-dimensional Atomistic Neural Network Potentials for Molecule–surface Interactions: HCl Scattering from Au(111). *J. Phys. Chem. Lett.* **2017**, *8*, 666-672.
- (73) Liu, Q.; Zhou, X.; Zhou, L.; Zhang, Y.; Luo, X.; Guo, H.; Jiang, B., Constructing High-dimensional Neural Network Potential Energy Surfaces for Gas–surface Scattering and Reactions. *J. Phys. Chem. C* **2018**, *122*, 1761-1769.
- (74) Shirhatti, P. R.; Geweke, J.; Steinsiek, C.; Bartels, C.; Rahinov, I.; Auerbach, D. J.; Wodtke, A. M., Activated Dissociation of HCl on Au(111). *J. Phys. Chem. Lett.* **2016**, *7*, 1346-1350.
- (75) Gerrits, N.; Geweke, J.; Smeets, E. W. F.; Voss, J.; Wodtke, A. M.; Kroes, G.-J., Closing the Gap between Experiment and Theory: Reactive Scattering of HCl from Au(111). *J. Phys. Chem. C* **2020**, *124*, 15944-15960.
- (76) Füchsel, G.; Zhou, X.; Jiang, B.; Juaristi, J. I.; Alducin, M.; Guo, H.; Kroes, G.-J., Reactive and Nonreactive Scattering of HCl from Au(111): An Ab Initio Molecular Dynamics Study. *J. Phys. Chem. C* **2019**, *123*, 2287-2299.
- (77) Ran, Q.; Matsiev, D.; Auerbach, D. J.; Wodtke, A. M., Observation of a Change of Vibrational Excitation Mechanism with Surface Temperature: HCl Collisions with Au(111). *Phys. Rev. Lett.* **2007**, *98*, 237601.
- (78) Shirhatti, P. R.; Rahinov, I.; Golibrzuch, K.; Werdecker, J.; Geweke, J.; Altschäffel, J.; Kumar, S.; Auerbach, D. J.; Bartels, C.; Wodtke, A. M., Observation of the Adsorption and Desorption of Vibrationally Excited Molecules on a Metal Surface. *Nat. Chem.* **2018**, *10*, 592-598.
- (79) Lucchese, R. R.; Tully, J. C., Trajectory Studies of Vibrational Energy Transfer in Gas-surface Collisions. *J. Chem. Phys.* **1984**, *80*, 3451-3462.
- (80) Misewich, J.; Zacharias, H.; Loy, M. M. T., State-to-state Molecular-beam Scattering of Vibrationally Excited NO from Leaved LiF(100) Surfaces. *Phys. Rev. Lett.* **1985**, *55*, 1919.
- (81) Ryberg, R., Vibrational Line Shape of Chemisorbed CO. *Phys. Rev. B* **1985**, *32*, 2671-2673.
- (82) Lončarić, I.; Alducin, M.; Juaristi, J. I.; Novko, D., CO Stretch Vibration Lives Long on Au(111). *J. Phys. Chem. Lett.* **2019**, *10*, 1043-1047.
- (83) Huang, M.; Zhou, X.; Zhang, Y.; Zhou, L.; Alducin, M.; Jiang, B.; Guo, H., Adiabatic and Nonadiabatic Energy Dissipation During Scattering of Vibrationally Excited CO from Au(111). *Phys. Rev. B* **2019**, *100*, 201407(R).
- (84) Hu, C.; Lin, Q.; Guo, H.; Jiang, B., Influence of Supercell Size on Gas-surface Scattering: A Case Study of CO Scattering from Au(111). *Chem. Phys.* **2022**, *554*, 111423.
- (85) Borodin, D.; Rahinov, I.; Shirhatti, P. R.; Huang, M.; Kandratsenka, A.; Auerbach, D. J.; Zhong, T. L.; Guo, H.; Schwarzer, D.; Kitsopoulos, T. N., et al., Following the Microscopic Pathway to Adsorption through Chemisorption and Physisorption Wells. *Science* **2020**, *369*, 1461-1465.
- (86) Huang, Y.; Rettner, C. T.; Auerbach, D. J.; Wodtke, A. M., Vibrational Promotion of Electron Transfer. *Science* **2000**, *290*, 111-114.
- (87) Wodtke, A. M.; Huang, Y.; Auerbach, D. J., Interaction of NO( $\nu=12$ ) with LiF(001): Evidence for Anomalously Large Vibrational Relaxation Rates. *J. Chem. Phys.* **2003**, *118*, 8033-8041.
- (88) Huang, Y.; Wodtke, A. M.; Hou, H.; Rettner, C. T.; Auerbach, D. J., Observation of Vibrational Excitation and Deexcitation for NO( $\nu=2$ ) Scattering from Au(111): Evidence of Electron-hole Pair Mediated Energy Transfer. *Phys. Rev. Lett.* **2000**, *84*, 2985.
- (89) Bartels, N.; Kruger, B. C.; Auerbach, D. J.; Wodtke, A. M.; Schafer, T., Controlling an Electron-transfer Reaction at a Metal Surface by Manipulating Reactant Motion and Orientation. *Angew. Chem. Int. Ed.* **2014**, *53*, 13690-13694.
- (90) Golibrzuch, K.; Shirhatti, P. R.; Rahinov, I.; Kandratsenka, A.; Auerbach, D. J.; Wodtke, A. M.; Bartels, C., The Importance of Accurate Adiabatic Interaction Potentials for the Correct Description of

Electronically Nonadiabatic Vibrational Energy Transfer: A Combined Experimental and Theoretical Study of NO( $\nu=3$ ) Collisions with a Au(111) Surface. *J. Chem. Phys.* **2014**, *140*, 044701.

(91) Kruger, B. C.; Bartels, N.; Bartels, C.; Kandratsenka, A.; Tully, J. C.; Wodtke, A. M.; Schafer, T., NO Vibrational Energy Transfer on a Metal Surface: Still a Challenge to First-principles Theory. *J. of Phys. Chem. C* **2015**, *119*, 3268-3272.

(92) Li, S.; Guo, H., Monte Carlo Wave Packet Study of Vibrational Deexcitation of NO Scattered from a Metal Surface. *J. Chem. Phys.* **2002**, *117*, 4499-4508.

(93) Roy, S.; Shenvi, N. A.; Tully, J. C., Model Hamiltonian for the Interaction of NO with the Au(111) Surface. *J. Chem. Phys.* **2009**, *130*, 174716.

(94) Shenvi, N.; Roy, S.; Tully, J. C., Nonadiabatic Dynamics at Metal Surfaces: Independent-electron Surface Hopping. *J. Chem. Phys.* **2009**, *130*, 174107.

(95) Monturet, S.; Saalfrank, P., Role of Electronic Friction During the Scattering of Vibrationally Excited Nitric Oxide Molecules from Au(111). *Phys. Rev. B* **2010**, *82*, 075404.

(96) Bartels, N.; Golibrzuch, K.; Bartels, C.; Chen, L.; Auerbach, D. J.; Wodtke, A. M.; Schafer, T., Dynamical Steering in an Electron Transfer Surface Reaction: Oriented NO( $\nu=3$ ,  $0.08 < E_i < 0.89$  eV) Relaxation in Collisions with a Au(111) Surface. *J. Chem. Phys.* **2014**, *140*, 054710.

(97) Wodtke, A. M., Electronically Non-adiabatic Influences in Surface Chemistry and Dynamics. *Chem. Soc. Rev.* **2016**, *45*, 3641-3657.

(98) Yin, R.; Jiang, B., Mechanical Vibrational Relaxation of NO Scattering from Metal and Insulator Surfaces: When and Why They Are Different. *Phys. Rev. Lett.* **2021**, *126*, 156101.

(99) Box, C. L.; Zhang, Y.; Yin, R.; Jiang, B.; Maurer, R. J., Determining the Effect of Hot Electron Dissipation on Molecular Scattering Experiments at Metal Surfaces. *JACS Au* **2021**, *1*, 164-173.

(100) Coffman, A. J.; Subotnik, J. E., When is Electronic Friction Reliable for Dynamics at a Molecule–Metal Interface? *Phys. Chem. Chem. Phys.* **2018**, *20*, 9847-9854.

(101) Wu, Q.; Zhou, L.; Schatz, G. C.; Zhang, Y.; Guo, H., Mechanistic Insights into Photocatalyzed H<sub>2</sub> Dissociation on Au Clusters. *J. Am. Chem. Soc.* **2020**, *142*, 13090-13101.

(102) Beck, R. D.; Maroni, P.; Papageorgopoulos, D. C.; Dang, T. T.; Schmid, M. P.; Rizzo, T. R., Vibrational Mode-specific Reaction of Methane on a Nickel Surface. *Science* **2003**, *302*, 98-100.

(103) Smith, R. R.; Killelea, D. R.; DelSesto, D. F.; Utz, A. L., Preference for Vibrational over Translational Energy in a Gas-surface Reaction. *Science* **2004**, *304*, 992-995.

(104) Killelea, D. R.; Campbell, V. L.; Shuman, N. S.; Utz, A. L., Bond-selective Control of a Heterogeneously Catalyzed Reaction. *Science* **2008**, *319*, 790-793.

(105) Yoder, B. L.; Bisson, R.; Beck, R. D., Steric Effects in the Chemisorption of Vibrationally Excited Methane on Ni(100). *Science* **2010**, *329*, 553-556.

(106) Hundt, P. M.; Jiang, B.; van Reijzen, M.; Guo, H.; Beck, R. D., Vibrationally Promoted Dissociation of Water on Ni(111). *Science* **2014**, *344*, 504-507.

(107) Jackson, B.; Nave, S., The Dissociative Chemisorption of Methane on Ni(100): Reaction Path Description of Mode-selective Chemistry. *J. Chem. Phys.* **2011**, *135*, 114701.

(108) Nattino, F.; Migliorini, D.; Kroes, G.-J.; Dombrowski, E.; High, E. A.; Killelea, D. R.; Utz, A. L., Chemically Accurate Simulation of a Polyatomic Molecule-metal Surface Reaction. *J. Phys. Chem. Lett.* **2016**, *7*, 2402-2406.

(109) Jiang, B.; Liu, R.; Li, J.; Xie, D.; Yang, M.; Guo, H., Mode Selectivity in Methane Dissociative Chemisorption on Ni(111). *Chem. Sci.* **2013**, *4*, 3249-3254.

(110) Zhang, Z.; Liu, T.; Fu, B.; Yang, X.; Zhang, D. H., First-principles Quantum Dynamical Theory for the Dissociative Chemisorption of H<sub>2</sub>O on Rigid Cu(111). *Nat. Comm.* **2016**, *7*, 11953.

(111) Shen, X.; Zhang, Z.; Zhang, D. H., Communication: Methane Dissociation on Ni(111) Surface: Importance of Azimuth and Surface Impact Site. *J. Chem. Phys.* **2016**, *144*, 101101.

- (112) Jiang, B., Rotational and Steric Effects in Water Dissociative Chemisorption on Ni(111). *Chem. Sci.* **2017**, *8*, 6662-6669.
- (113) Maroni, P.; Papageorgopoulos, D. C.; Sacchi, M.; Dang, T. T.; Beck, R. D.; Rizzo, T. R., State-resolved Gas-surface Reactivity of Methane in the Symmetric C-H Stretch Vibration on Ni(100). *Phys. Rev. Lett.* **2005**, *94*, 246104.
- (114) Kay, B. D.; Raymond, T. D.; Coltrin, M. E., Observation of Direct Multiquantum Vibrational Excitation in Gas-surface Scattering: NH<sub>3</sub> on Au(111). *Phys. Rev. Lett.* **1987**, *59*, 2792-2794.
- (115) Liu, L.; Guo, H., Theoretical Study of Vibrational Excitation of Ammonia Scattered from Cu Surface. *Chem. Phys.* **1996**, *205*, 179-190.
- (116) Werdecker, J.; van Reijzen, M. E.; Chen, B.-J.; Beck, R. D., Vibrational Energy Redistribution in a Gas-surface Encounter: State-to-state Scattering of CH<sub>4</sub> from Ni(111). *Phys. Rev. Lett.* **2018**, *120*, 053402.
- (117) Werdecker, J.; Chen, B.-J.; Van Reijzen, M. E.; Farjamnia, A.; Jackson, B.; Beck, R. D., State-to-state Methane-surface Scattering as a Probe of Catalytic Activity. *Phys. Rev. Res.* **2020**, *2*, 043251.
- (118) Child, M. S.; Halonen, L., Overtone Frequencies and Intensities in the Local Mode Picture. *Adv. Chem. Phys.* **1984**, *57*, 1-58.
- (119) Zhang, L.; Jiang, B., Efficient Vibrational Energy Redistribution between Stretching Modes: State-to-state Quantum Scattering of H<sub>2</sub>O from Cu(111). *Phys. Rev. Lett.* **2019**, *123*, 106001.
- (120) Jiang, B.; Ren, X.; Xie, D.; Guo, H., Enhancing Dissociative Chemisorption of H<sub>2</sub>O on Cu(111) via Vibrational Excitation. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 10224-10227.
- (121) Zhang, L.; Jiang, B., State-to-state Quantum Dynamics of H<sub>2</sub>O/HOD Scattering from Cu(111): Mode- and Bond-selective Vibrational Energy Transfer. *J. Chem. Phys.* **2020**, *153*, 214702.
- (122) Jiang, B.; Alducin, M.; Guo, H., Electron-hole Pair Effects in Polyatomic Dissociative Chemisorption: Water on Ni(111). *J. Phys. Chem. Lett.* **2016**, *7*, 327-331.
- (123) Luo, X.; Jiang, B.; Juaristi, J. I.; Alducin, M.; Guo, H., Electron-hole Pair Effects in Methane Dissociative Chemisorption on Ni(111). *J. Chem. Phys.* **2016**, *145*, 044704.
- (124) Luo, X.; Zhou, X.; Jiang, B., Effects of Surface Motion and Electron-hole Pair Excitations in CO<sub>2</sub> Dissociation and Scattering on Ni(100). *J. Chem. Phys.* **2018**, *148*, 174702.
- (125) Kroes, G.-J., Toward a Database of Chemically Accurate Barrier Heights for Reactions of Molecules with Metal Surfaces. *J. Phys. Chem. Lett.* **2015**, *6*, 4106-4114.
- (126) Gerrits, N.; Smeets, E. W. F.; Vuckovic, S.; Powell, A. D.; Doblhoff-Dier, K.; Kroes, G.-J., Density Functional Theory for Molecule-metal Surface Reactions: When Does the Generalized Gradient Approximation Get It Right, and What to Do If It Does Not. *J. Phys. Chem. Lett.* **2020**, *11*, 10552-10560.
- (127) Jin, Z.; Subotnik, J. E., A Practical Ansatz for Evaluating the Electronic Friction Tensor Accurately, Efficiently, and in a Nearly Black-box Format. *J. Chem. Phys.* **2019**, *150*, 164105.
- (128) Box, C. L.; Stark, W. G.; Maurer, R. J. Ab Initio Calculation of Electron-phonon Linewidths and Molecular Dynamics with Electronic Friction at Metal Surfaces with Numeric Atom-centered Orbitals **2021**.
- (129) Wu, Q.; Van Voorhis, T., Direct Optimization Method to Study Constrained Systems within Density-functional Theory. *Phys. Rev. A* **2005**, *72*, 024502.
- (130) Behler, J.; Delley, B.; Reuter, K.; Scheffler, M., Nonadiabatic Potential-energy Surfaces by Constrained Density-functional Theory. *Phys. Rev. B* **2007**, *75*, 115409.
- (131) Holmberg, N.; Laasonen, K., Efficient Constrained Density Functional Theory Implementation for Simulation of Condensed Phase Electron Transfer Reactions. *J. Chem. Theory Comput.* **2017**, *13*, 587-601.
- (132) Kühne, T. D.; Iannuzzi, M.; Ben, M. D.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schütt, O.; Schiffmann, F., et al., Cp2k: An Electronic Structure and Molecular Dynamics Software Package - Quickstep: Efficient and Accurate Electronic Structure Calculations. *J. Chem. Phys.* **2020**, *152*, 194103.
- (133) Welsch, R.; Manthe, U., Loss of Memory in H + CH<sub>4</sub> → H<sub>2</sub> + CH<sub>3</sub> State-to-state Reactive Scattering. *J. Phys. Chem. Lett.* **2015**, *6*, 338-342.

- (134) van Harrevelt, R.; Manthe, U., Multiconfigurational Time-dependent Hartree Calculations for Dissociative Adsorption of H<sub>2</sub> on Cu(100). *J. Chem. Phys.* **2004**, *121*, 3829.
- (135) Krishnamohan, G. P.; Olsen, R. A.; Kroes, G.-J.; Gatti, F.; Woittequand, S., Quantum Dynamics of Dissociative Chemisorption of CH<sub>4</sub> on Ni(111): Influence of the Bending Vibration. *J. Chem. Phys.* **2010**, *133*, 144308.
- (136) Liu, Q.; Zhang, L.; Li, Y.; Jiang, B., Ring Polymer Molecular Dynamics in Gas–surface Reactions: Inclusion of Quantum Effects Made Simple. *J. Phys. Chem. Lett.* **2019**, *10*, 7475-7481.
- (137) Marjollet, A.; Welsch, R., Nuclear Quantum Effects in State-selective Scattering from Ring Polymer Molecular Dynamics. *J. Chem. Phys.* **2020**, *152*, 194113.
- (138) Rodriguez-Fernandez, A.; Bonnet, L.; Crespos, C.; Larregaray, P.; Diez Muino, R., When Classical Trajectories Get to Quantum Accuracy: The Scattering of H<sub>2</sub> on Pd(111). *J. Phys. Chem. Lett.* **2019**, *10*, 7629-7635.
- (139) Zhang, L.; Chen, J.; Jiang, B., Vibrational State-to-state Scattering of Water from Cu(111): Comparison of Quantum and Quasiclassical Methods with Normal Mode and Adiabatic Switching Sampling. *J. Phys. Chem. C* **2021**, *125*, 4995-5005.

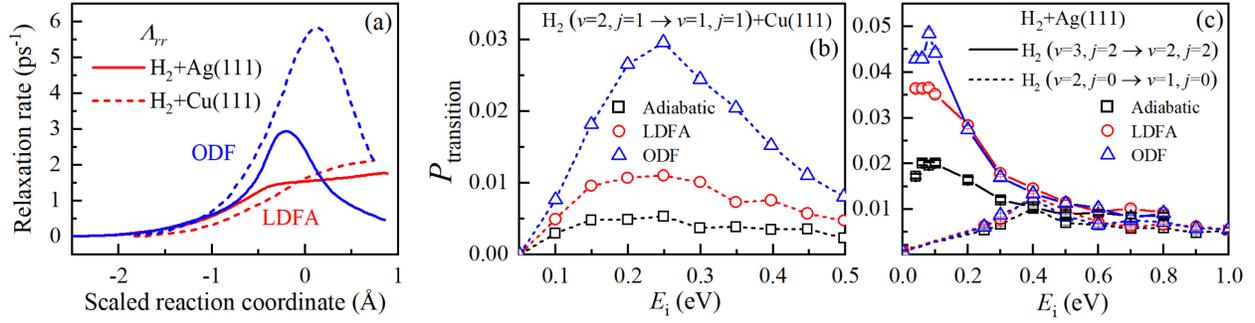


Fig. 1. (a) Comparison of LDFA (red lines) and ODF (blue lines) friction coefficients with respect to the vibrational coordinate ( $A_{rr}$ ) for the H<sub>2</sub>+Cu(111) (dash lines) and H<sub>2</sub>+Ag(111) (solid lines) systems. (b) Transition probabilities ( $P_{\text{transition}}$ ) of H<sub>2</sub>( $\nu=2, j=1 \rightarrow \nu=1, j=1$ ) scattering from Cu(111) and (c) H<sub>2</sub>( $\nu=3, j=2 \rightarrow \nu=2, j=2$ ) (solid lines) and H<sub>2</sub>( $\nu=2, j=0 \rightarrow \nu=1, j=0$ ) (dash lines) scattering from Ag(111), as a function of the incident energy ( $E_i$ ) obtained from adiabatic (blue squares), LDFA (red circles) and ODF (blue triangles) MD simulations. These figures are adapted from Refs. 47, 50, and 51 with permission.

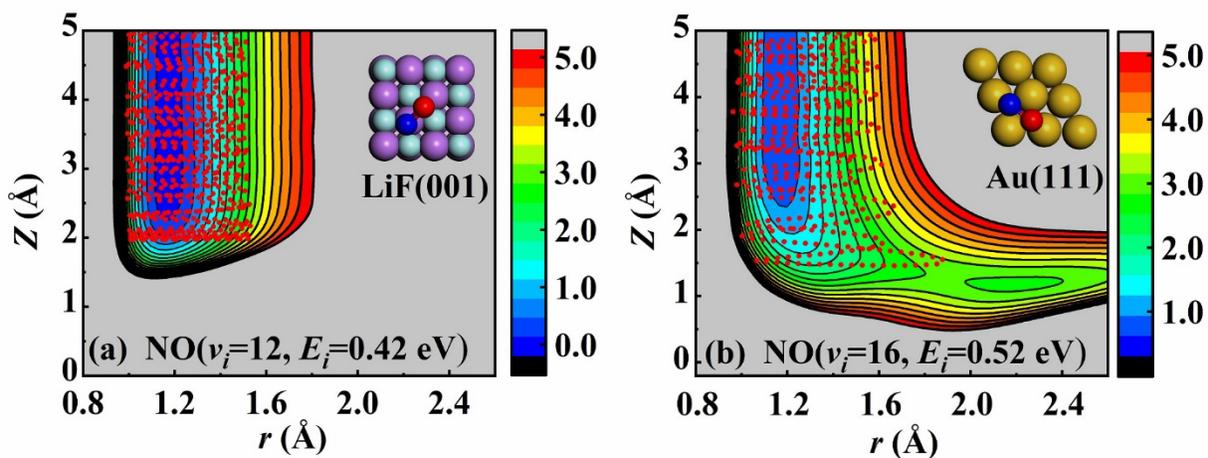


Fig. 2. Contour plots of (a) the NO+LiF(001) and (b) the NO+Au(111) PESs as a function of the N-O distance ( $r$ ) and the center of mass height ( $Z$ ) of NO above the surface, with other coordinates fixed at the adsorption state on LiF(001) and at the dissociation transition state on Au(111), respectively. Red dotted lines are for the representative trajectory of each system. Reproduced from Ref. 98 with permission.

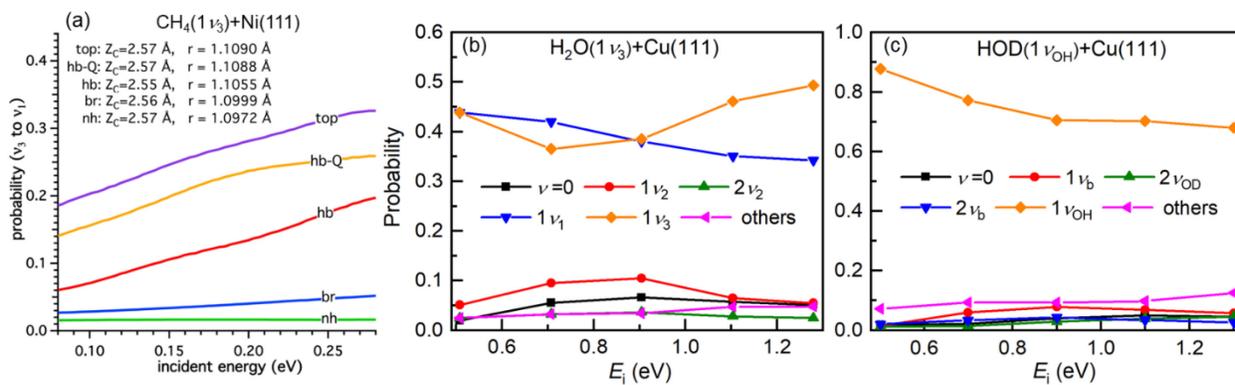


Fig. 3. (a) Transition probabilities of  $\text{CH}_4$  from  $1\nu_3$  to  $1\nu_1$  during scattering from Ni(111) at a fixed top site (top), bridge site (br), half-bridge site (hb), near-hollow site (nh), and half-bridge site with a vertical displacement of the Ni atom closest to the molecule (hb-Q) as a function of  $E_i$ , where  $Z_c$  and  $r$  correspond to the height of the C atom and the longest C-H bond length at the turning point of collision. Reproduced from Ref. 117 with permission. (b) Survival probabilities of  $\text{H}_2\text{O}(1\nu_3)$  and transition probabilities to other vibrational states during scattering from Cu(111) as a function of  $E_i$ . (c) Same as (b) except for  $\text{HOD}(1\nu_{\text{OH}})$ . Both (b) and (c) are reproduced from Ref. 121 with permission.

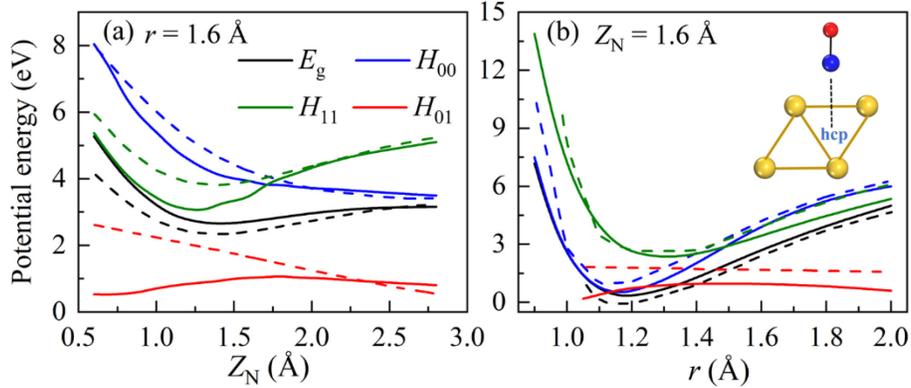


Fig. 4. (a) Potential energy curves of the ground state ( $E_g$ , black), NO neutral diabatic state ( $H_{00}$ , blue), NO anion diabatic state ( $H_{11}$ , green), and off-diagonal coupling of two diabatic states ( $H_{01}$ , red) of the NO+Au(111) system, as a function of N-surface distance ( $Z_N$ ) with the N-O distance ( $r$ ) elongated to 1.6 Å. (b) Same as (a) but as a function of  $r$  with  $Z_N = 1.6$  Å. NO lies perpendicular to the surface with the N atom pointing towards the surface at the hcp site. Color scheme for atoms: N (blue), O (red), and Au (gold). Solid lines are results obtained by CDFT calculations based on Bader charge analysis, in which the revPBE functional is used and Au(111) is modeled by a four-layer slab in a  $6 \times 6$  supercell. Dashed lines are results in the two state diabatic Hamiltonian in the IESH method digitized from Fig. 2 in Ref. 93. In each case, the energy is relative to that of a clean surface plus a free NO molecule in equilibrium, respectively.