

CENTENNIAL FEATURE ARTICLE

Dynamics of Open-Shell Species at Metal Surfaces[†]

Sharani Roy, Neil Shenvi, and John C. Tully*

Department of Chemistry, Yale University, New Haven, Connecticut 06520-8107

Received: December 24, 2008; Revised Manuscript Received: May 3, 2009

A large and fascinating array of possible pathways for energy transfer and chemical reaction are exhibited when open-shell atoms, molecules, or reaction intermediates interact with metal surfaces. The interplay that can occur among phonon excitations, excitation of metallic conduction electrons, electron transfer, spin transitions, and localized molecular electronic transitions is just beginning to be recognized. We outline the challenges to constructing a predictive theoretical understanding of the dynamics of open-shell species at metal surfaces and review recent progress in this area. We emphasize our recent efforts toward including both localized electronic transitions and delocalized electronic friction effects in a consistent computational framework.

I. Mixed Quantum-Classical Dynamics

The interaction of open-shell atoms and molecules with metal surfaces underlies interesting and important chemistry, ranging from useful (catalytic reaction intermediates, materials processing, etc.) to destructive (corrosion by O₂, O-atom erosion in low-earth orbit, etc.). The chemistry of open-shell species can be very complex, however, and relatively little has been done on the theoretical front to understand this complexity, beyond standard molecular dynamics (MD) simulations on the adiabatic ground state potential energy surface (PES). There is growing experimental evidence that this is not adequate; the adiabatic (Born–Oppenheimer) approximation¹ is often violated with severe consequences.^{2–5} There are a number of contributing sources for this substantial nonadiabatic behavior: Multiple PESs can arise from an open-shell electronic configuration. Electron–hole pair (EHP) excitations of metallic conduction electrons are facile. Electron transfer to or from the open-shell species, with the resulting ion stabilized by the image potential, can be implicated. In this paper we examine these issues and illustrate some of them with recent studies of inelastic scattering of the nitric oxide molecule from the (111) face of a gold crystal.

We begin with a brief discussion of strategies for extending conventional MD to account for nonadiabatic electronic transitions between PESs. Classical mechanical MD has been an extraordinarily valuable tool for simulating atomic motions in a wide variety of contexts. In view of the prohibitive computational cost of treating nuclear motion quantum mechanically in full dimensionality, “mixed quantum-classical dynamics” (MQCD) strategies for incorporating the most crucial quantum mechanical effects in an otherwise classical mechanical MD framework have evolved.⁶ Ordinary *ab initio* MD such as direct

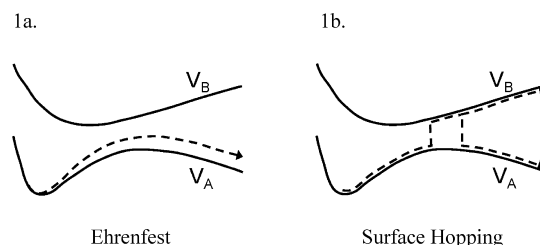


Figure 1. Illustration of mixed quantum-classical dynamics (MQCD) strategies. (a) Ehrenfest (self-consistent-field) approach. (b) Stochastic surface hopping approach.

dynamics⁷ or Car–Parrinello dynamics⁸ can already be considered a MQCD method; electrons are treated quantum mechanically within the adiabatic approximation, and nuclear motion is governed by the forces derived from the adiabatic electronic PES. Here we focus on MQCD approaches beyond the adiabatic approximation (i.e., nuclear motion evolving on multiple PESs). The strategy is to retain classical-like motion of the nuclei but to incorporate the effects of electronic transitions among PESs. The motion of the classical nuclei introduces a time-dependent contribution to the electronic Hamiltonian that produces nonadiabatic transitions among electronic states. In turn, different electronic states exert different forces on the classical particles, thereby altering their trajectories. The two most commonly used approaches for including the feedback between the quantum and classical subsystems are the Ehrenfest^{9–13} and the surface hopping methods,^{14–19} illustrated in Figure 1. With both approaches, the time-dependent Schrödinger equation for the electrons is integrated (at least in principle) along the classical trajectory to obtain the amplitudes of each electronic state as a function of time.⁶ The two methods differ only in how the trajectory is determined. Ehrenfest invokes a self-consistent-field (SCF) approximation, resulting in nuclear motion evolving on a single effective PES, the expectation value of the electronic Hamiltonian with the computed amplitudes. Surface hopping is a stochastic procedure in which nuclear motion “hops” from one PES to another, with hopping prob-

[†] 2008 marked the Centennial of the American Chemical Society’s Division of Physical Chemistry. To celebrate and to highlight the field of physical chemistry from both historical and future perspectives, *The Journal of Physical Chemistry* is publishing a special series of Centennial Feature Articles. These articles are invited contributions from current and former officers and members of the Physical Chemistry Division Executive Committee and from *J. Phys. Chem.* Senior Editors.



Sharani Roy received a B.S. degree in Chemistry from Hansraj College at the University of Delhi, India, in 2000. She earned a M.S. degree in Chemistry at the Indian Institute of Technology (IIT), Delhi where she studied the melting transition in Morse clusters under the supervision of Prof. Charusita Chakravarty. In 2002 she entered the Ph.D. program in Chemistry at Yale University, where she joined Prof. John Tully's research group. Her graduate research has focused on the theoretical study of electronically adiabatic and nonadiabatic interactions of gaseous species with metal surfaces.



Neil Shenvi graduated with an A.B. in Chemistry from Princeton University in 2001 where he worked with Prof. Herschel Rabitz. He earned a Ph.D. in Theoretical Chemistry in 2005 at UC—Berkeley with Prof. K. Birgitta Whaley. His dissertation explored various topics in quantum computation. He is currently a postdoctoral associate at Yale University. He is interested in nonadiabatic dynamics, reduced density matrix theory, and problems that involve “extreme quantum mechanics”, the regime in which classical intuition breaks down completely.

abilities governed by the evolving electronic amplitudes.¹⁵ Both of these approaches are widely used and both have proved quite successful in certain regimes.

II. Electronic Friction

There is a long history of introducing an “electronic friction” to account for energy dissipation via EHP excitations at metal surfaces.^{20–25} Electronic friction can be derived directly from the Ehrenfest MQCD theory by invoking a weak-coupling approximation and taking the Markov (no memory) limit, probably justified for this application to rapidly dephasing EHP transitions. The result is a classical mechanical multidimensional Langevin equation²⁵

$$\mathbf{M} \cdot \ddot{\mathbf{R}} = -\nabla V(\mathbf{R}) - \mathbf{\Omega}(\mathbf{R}) \cdot \dot{\mathbf{R}} + \mathbf{R}(t) \quad (1)$$

\mathbf{R} is the vector specifying the coordinates of each atom and \mathbf{M} is the matrix of atomic masses. The first term on the r.h.s of eq 1 is the gradient of $V(\mathbf{R})$, the PES (i.e., the same force that



John C. Tully received a B.S. from Yale in 1964 and a Ph.D. in Chemical Physics from the University of Chicago in 1968, under the direction of R. Stephen Berry. After a postdoc with Richard Wolfgang, he joined AT&T Bell Laboratories in 1970. At Bell Labs he carried out theoretical research in the area of chemical dynamics, including processes involving multiple potential energy surfaces and molecule-surface interactions. In 1996 he joined the faculty at Yale University where he is currently Sterling Professor of Chemistry and Professor of Physics and Applied Physics.

appears in ordinary MD). The second term is the friction matrix $\mathbf{\Omega}(\mathbf{R})$ dotted into the nuclear velocity vector. For N nuclear degrees of freedom, $\mathbf{\Omega}(\mathbf{R})$ is an $N \times N$ matrix that accounts for the interdependent coupling of each mode to EHP's. The friction also depends strongly on the atomic coordinates \mathbf{R} , i.e., the location of the adsorbate molecule. Explicit expressions for ab initio calculation of $\mathbf{\Omega}(\mathbf{R})$ have been derived and successfully applied,²⁶ so the frictions no longer need to be chosen simply empirically. The random force vector, $\mathbf{R}(t)$, is given by the second fluctuation–dissipation theorem²⁷

$$\langle \mathbf{R}(t) | \mathbf{R}(t') \rangle = kT \mathbf{\Omega}(\mathbf{R}) \delta(t - t') \quad (2)$$

This allows any desired electron temperature to be imposed, including a time-varying temperature to model, e.g., ultrafast laser-induced chemistry at metal surfaces.

The electronic friction approach has been applied successfully to model a number of dynamical processes at metal surfaces.^{28–35} Perhaps the simplest and most convincing of these is the calculation of vibrational lifetimes for adsorbed molecules. For example, the lifetime of the $\nu = 1$ level of the CO molecule adsorbed on Cu(100) has been experimentally measured to be about 2.5 ps. Adiabatic MD simulation, with a realistic CO–Cu interaction potential, exhibits no vibrational energy dissipation at all within a 10 ns integration time.³⁶ Similarly, quantum mechanical perturbation theory within the adiabatic approximation, using the same CO–Cu interactions, predicts a vibrational lifetime of about 1 μ s.³⁶ The lifetime computed by MD with electronic friction, again using the same CO–Cu interactions but including electronic frictions computed a priori by density functional theory (DFT), is 3.3 ps, in good agreement with experiment.³⁷ This short lifetime arises, at least in part, from a small variation of the population of the antibonding π^* orbital of CO as the molecule vibrates.³⁸ A much larger variation in the population of the π^* orbital, formation of a transient negative ion, will be shown below to dominate vibrational relaxation of NO on Au(111).

Bird and co-workers have carried out an informative series of DFT and dynamics calculations of the electronic friction exhibited when a hydrogen atom interacts with the Cu(111) surface.^{34,39,35,40} They demonstrate that the friction (i.e., the

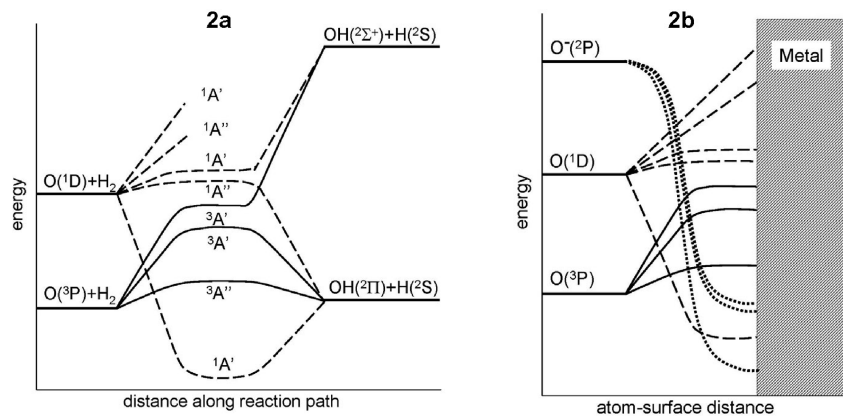


Figure 2. Qualitative representation of the multiple potential energy surfaces (PESs) that can arise when an open shell atom or molecule interacts with a molecule or a metal surface. (a) Interaction of an O atom with the H_2 molecule. (b) Interaction of an O atom with a metal surface.

nonadiabatic coupling) peaks in a relatively small range of atom-surface distances, due to the onset of mixing between the spin up and spin down configurations of the H atom. This is a manifestation of the Kondo effect^{41–43} and will also be revisited below.

As mentioned above, the electronic friction formalism is based on a weak coupling approximation. As a consequence, large amounts of energy can be dissipated only through multiple low-energy electronic excitations. Recent experiments from a number of laboratories cast doubt on this picture. Several groups have constructed various types of nanodevices that involve deposition of a thin metal layer on a semiconductor substrate.^{44–51} They have observed that the energy released by atom or molecule adsorption or exothermic chemical reaction on the metal surface generates electrons with sufficient energy to affect the electrical conductivity of the underlying semiconductor. To do this, electrons must possess sufficient energy to traverse the Schottky barrier at the metal-semiconductor interface, typically 0.5–2 eV. In a different kind of experiment, Wodtke and co-workers have scattered highly vibrationally excited NO molecules from a Au(111) surface.^{52–55} They have observed huge amounts of vibrational relaxation; for initial vibrational state $\nu = 15$ the most probable vibrational state of the scattered molecules peaks at $\nu = 7$ or 8.⁵³ It is conceivable that this can occur by multiple $\Delta\nu = 1$ transitions, as required by a weak coupling or friction theory, if the NO molecule spends sufficient time in the nonadiabatic region. This appears unlikely, however, especially in view of the fact that molecules scatter predominantly near the specular reflection angle, indicating a direct scattering event. Moreover, the Wodtke group has observed the emission of electrons from the surface in these experiments when the clean gold surface was replaced by a cesium-decorated gold surface.^{56,54} In order to escape, an electron must be energized by more than the 1.6 eV work function of their Cs–Au surface.⁵⁷ The production of highly excited electrons in both kinds of experiments is inconsistent with the Brownian motion-type friction picture of many low-energy inelastic events. To explain these experimental observations will require that our current theoretical description of nonadiabatic dynamics at metal surfaces be reformulated, or at least significantly extended.

III. Nonadiabatic Dynamics of Open Shell Species

Many of the issues can be understood by reference to Figure 2. Figure 2a is a schematic representation of the PESs that govern the simple gas phase reaction $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$. There are multiple PESs, but because spin–orbit and Coriolis cou-

plings are very weak, the Born–Oppenheimer (adiabatic) approximation is quite accurate and almost invariably invoked. Thus the reaction of an $\text{O}(^3\text{P})$ atom with H_2 can be assumed to proceed on the lowest triplet $^3\text{A}''$ PES, with no spin–orbit transition to the lower energy singlet state (the PES that correlates with the ground state of the water molecule). Furthermore, at temperatures for which the reaction barriers on the two excited $^3\text{A}'$ states are too high to surmount, it can be assumed that the total reaction probability for $\text{O}(^3\text{P})$ is simply 1/3 of the reaction probability on the lower $^3\text{A}''$ PES. Similarly, the reaction probability of $\text{O}(^1\text{D})$ with H_2 can be taken to be 1/5 of that computed for the lowest of the 5 singlet PESs, ignoring transitions to any of the triplet surfaces that it crosses as well as transitions among the other singlet surfaces. This Born–Oppenheimer (adiabatic) picture is usually quite adequate for thermal energy gas phase reactions. Furthermore, a host of techniques have been developed to address nonadiabatic gas phase processes when needed.⁶ By contrast, at metal surfaces nonadiabatic behavior is the rule rather than the exception, and techniques for addressing this behavior are still rudimentary.

Consider the interaction of an $\text{O}(^3\text{P})$ atom with a metal surface, illustrated schematically in Figure 2b. The potential curves sketched in Figure 2b mirror those of Figure 2a and are not intended to be quantitative, but they display the multiple potential surfaces that exist when an open-shell atom or molecule interacts with a surface. Not shown in the figure, however, are the infinitesimally spaced electronic states of the metallic conduction band. Small energy spacings between electronic states favor nonadiabatic behavior, in this case electron–hole pair (EHP) excitations driven by the motion of the atom or molecule. This is the electronic friction discussed above, and it will definitely remain an important part of the story. For open shell atoms or molecules, additional nonadiabatic mechanisms are rampant, however. Referring to Figure 2b, as the $\text{O}(^3\text{P})$ atom approaches the metal on the lowest triplet PES, it crosses a PES correlating asymptotically with an $\text{O}(^1\text{D})$. This singlet surface can be neglected in the $\text{O}–\text{H}_2$ reaction because spin–orbit coupling is required to flip the spin. This is not the case in the vicinity of a metal; a two-electron exchange in which an electron of one spin is transferred from an occupied level at the Fermi energy and simultaneously an electron of opposite spin is transferred from the O atom to an unoccupied level at the Fermi energy can convert $\text{O}(^3\text{P})$ to $\text{O}(^1\text{D})$. Spin–orbit or magnetic interactions are not required. The spin state of the metal is changed in order that the spin of the entire system is conserved, but for a metal this comes at essentially no energy cost.

Similarly, transitions among the 3 different O-atom triplet components or 5 different singlet components do not require Coriolis coupling; nonadiabatic transitions among all of the $O(^3P)$ and $O(^1D)$ PESs can therefore occur, perhaps quite readily, and quite possibly with major consequences to the dynamics.

We note that the possibility of zero-energy transitions between the different m_s components of $O(^3P)$ by resonant 2-electron exchange is a manifestation of the Kondo effect. Kondo originally addressed the question of how the spin of an isolated spin-1/2 impurity atom (e.g., Co) in a metal (e.g., Cu) is compensated by a surrounding cloud of conduction electrons of opposite spin, analogous to (but very much weaker than) the screening by an image charge.⁴¹ The electronic configuration of spin up impurity with spin down cloud is energetically resonant with that of spin down impurity and spin up cloud. This produces a narrow resonance at the Fermi level, with a width related to the transition rate between up and down impurity spin states, the quantity of interest here.⁴² Proper description of this behavior requires a multiconfiguration electronic wave function; a single determinant mean-field wave function is not adequate. A recent theoretical investigation by Carter and co-workers has revealed valuable insights into the nature of this multiconfiguration state for the case of a cobalt atom interacting with a copper surface.⁴³

A further complication is the possibility of electron transfer either from the valence band of the metal to the molecule, or from the molecule to the conduction band of the metal. Figure 2b includes potential energy curves that correlate asymptotically with the $O(^2P)$ negative ion and are stabilized by the image potential such that they cross many (possibly all) of the neutral states. This opens up the possibility of a single electron hop, in this case from the metal to an unoccupied p orbital of the O-atom. Since the electron can originate from any occupied level below the Fermi energy, the resulting hole can carry away significant energy. Moreover, a subsequent electron hop back into the metal can populate any unoccupied level above the Fermi energy, resulting in an energized electron in the metal. This mechanism may well contribute to the recent observations, described above, of energetic electrons produced by molecular adsorption and chemical reaction at metal surfaces. Furthermore, when an electron hop occurs, the forces exerted on the atom or molecule can be drastically and suddenly altered. Multiple electron transfer events likely underlie the efficient multiquantum vibrational energy transfer observed by the Wodtke group for highly vibrationally excited NO scattered from a gold surface.⁵³

A feature not illustrated in the figure is that all of the excited states sketched are actually resonance states; the energies of these excited states fall within the lower and upper bounds of the conduction band, so they are bound states embedded in a continuum. As such, they are lifetime broadened and should be drawn with finite position-dependent widths. Some methods for computing the lifetimes of such states have been reported, but the methods have serious limitations.^{58–61} It should be noted that the lifetimes do not arise from nonadiabatic interactions. Rather, the localized molecular excited state can be expressed as a linear combination of the delocalized adiabatic states of the metal-molecule system; all of the eigenstates of the electronic Hamiltonian in this energy range are delocalized.

The complexities described above are not merely of academic interest; they can dramatically alter the forces that a molecule experiences, and thereby the rates and pathways of chemical reactions at metal surfaces. At semiconductor surfaces the presence of a band gap usually minimizes the importance of

EHP transitions for thermal energy processes. However, energetic processes such as reactive ion etching and photoinduced processes such as charge injection in photovoltaic cells can directly access the conduction band and be similarly dominated by nonadiabatic behavior. In metallic and semiconductor nanoparticles, the conduction band becomes discrete due to spatial confinement. However, except for extremely small particle sizes, the spacings between energy levels are so small that nonadiabatic effects are still very likely. Achieving the goal of optimizing and controlling the rates and selectivity of chemical reactions at the surfaces of metals, semiconductors and nanoparticles will require an improved understanding of the underlying electronic transformations as well as the ability to carry out accurate and predictive simulations at the molecular level beyond the Born–Oppenheimer approximation.

Electronic friction must remain an important component of a comprehensive theory of the interaction of open shell molecules with metal surfaces. An additional component that is likely to be operative in many situations is the widely invoked transient negative ion mechanism, as introduced by Gadzuk.^{62,63} Consider vibrational excitation of an NO molecule scattering from a metal surface. According to the transient negative ion picture, as the molecule approaches the metal surface on the ground state PES, it encounters an avoided crossing with the PES of the NO^- negative ion. If it passes through the avoided crossing region adiabatically, it will remain in the ground state, thereby becoming a negative ion; that is, an electron will transfer adiabatically from the metal to the molecule. The molecular negative ion will in general have a different equilibrium bond length and force constant than the corresponding neutral molecule. If the intramolecular potential of the molecule changes relatively suddenly when the electron hop occurs, a mixture of vibrational states will be produced in the negative ion, analogous to a Franck–Condon transition in photochemistry. The negatively charged molecule will then reflect from the surface, and as it recedes it will convert back to the neutral state, providing another opportunity for Franck–Condon scrambling of vibrational states. Although this process involves electron transfer, it is not per se a nonadiabatic process. If the electron were removed from the Fermi level of the metal and later returned exactly to the Fermi level, then the system would remain in the electronic adiabatic ground electronic state throughout the entire scattering process. No net electronic excitation would occur, and the energy required to excite vibrations would be taken entirely from the initial translational-rotational energy of the molecule and substrate phonons. However, this is unrealistic; the electron transfer events must inevitably involve some nonadiabatic behavior, resulting in excitation of EHP's. The ground state must change character between neutral molecule and negative ion sufficiently suddenly that the vibrational state of the molecule is altered; the Franck–Condon Principle is a consequence of the sudden approximation. Sudden is the opposite of adiabatic; the more sudden the electron hop, the more serious the breakdown of the Born–Oppenheimer approximation. The importance of this nonadiabatic contribution to the transient negative ion mechanism has not been assessed, however, and it remains difficult to experimentally unravel the role of electronic excitations from other mechanisms of vibrational energy transfer; phonons, hard impact and adiabatic charge transfer.

The transient negative ion mechanism is based on the assumption that nuclear motion evolves essentially on a single PES, neutral or ionic, with relatively sudden switches between them. This is counter to the Ehrenfest assumption of motion on

weighted average PES. The MQCD surface hopping approach appears more natural for describing the distinct electronic transitions that underlie the transient negative ion mechanism, as well as the transitions that occur among the multiple PESs as illustrated in Figure 2b. Moreover, the Ehrenfest method has the deficiency that the electronic states are not resolved into single states even at long times. For example, in the scattering of NO from a metal surface, the final scattered molecule, as computed by Ehrenfest, will have a fractional negative charge, as opposed to the more correct outcome that a fraction of the molecules are neutral and a fraction are negative ions. In fact, for collisions with sufficiently low energy that formation of the negative ion is energetically forbidden, Ehrenfest will still predict some negative ion character. Surface hopping corrects these deficiencies. Thus, our recent goal has been to develop a practical and accurate surface hopping theory of the dynamics of open shell species at metal surfaces. Of course, it remains to be shown how well a surface hopping approach can encompass electronic friction effects. In addition, surface hopping describes nuclear motion classically; important initial steps toward a full quantum mechanical treatment of nuclear motion for nonadiabatic molecule-surface processes have been reported.^{5,64–68} Discussion of progress in this direction is outside the scope of this paper.

An interesting step toward this goal has been reported by Behler and co-workers.^{69,70} They addressed the interaction of oxygen molecules with the Al(111) surface. Using a novel implementation of constrained DFT,⁷¹ they determined that the PES correlating with the ground state $O_2(^3\Sigma_g^-)$ crosses that of the excited $O_2(^1\Delta_g)$. More correctly, the PESs exhibit an avoided crossing, with the off-diagonal coupling resulting from a two-electron exchange interaction, analogous to the Kondo interaction discussed above. Spin–orbit interaction is not required to promote transitions between the surfaces correlating with triplet and singlet O_2 ; the spin state of the metal also changes to retain the overall spin of the system. The adiabatic ground state PES for this system thus switches from triplet O_2 to singlet O_2 character as the molecule approaches the surface. Adiabatic MD simulations on the ground state predict that O_2 will dissociatively adsorb upon virtually every collision with the aluminum surface. This is in striking contrast to the experimental findings of a relatively low sticking probability. Behler and co-workers propose that for the majority of collision events, the $O_2(^3\Sigma_g^-)$ molecule remains in the triplet state after it passes through the crossing with the singlet state; that is, there is a high probability of nonadiabatic transition at the crossing.⁶⁹ They carried out a “fewest switches” surface hopping calculation on the two PESs, with off-diagonal coupling estimated from the difference between the ground state energies obtained with constrained and unconstrained calculations. Their results are in quite good agreement with the experimentally determined sticking probabilities as a function of incident energy.⁷⁰

IV. Surface Hopping at Metal Surfaces

The 2-state model of Behler and co-workers is quite illuminating, and it represents a significant enhancement over conventional adiabatic MD for describing molecular interactions at metal surfaces. It does not allow for the continua of electronic states that arise from the conduction band of the molecule, however. One consequence of this is that electronic friction effects are not included. It might be feasible to tack on electronic friction terms, but such an ad hoc procedure has little justification, and it would not be capable of incorporating the many kinds of dynamical interactions illustrated in Figure 2b. Our

recent efforts have been directed at deriving a consistent surface hopping formulation that is capable, at least in principle, of accurate description of the most critical of these varied dynamical processes, including electronic friction effects.^{72,73}

Let us illustrate our proposed general approach and its associated challenges with reference to the NO–Au(111) system, with the simplifying assumption that only the two molecular states, neutral and negative ion, need be considered. We begin with a discretized version of the widely used Newns–Anderson model,⁷⁴ generalized to interactions that vary with atomic positions, \mathbf{R} . The key feature of the Newns–Anderson model is that electrons are noninteracting. Thus the many-electron Hamiltonian can be expressed as a sum of one-electron terms

$$H_{\text{el}}(\mathbf{R}) = U_0(\mathbf{R}) + \sum_{j=1}^{N_e} E_j(\mathbf{R}) c_j^\dagger c_j \quad (3)$$

where N_e is the number of active electrons of the system, $E_j(\mathbf{R})$ is the j th energy eigenvalue, and c_j^\dagger and c_j are the fermionic creation and annihilation operators for eigenstate j of the following single-electron Hamiltonian

$$H_{\text{el}}^1(\mathbf{R}) = [U_1(\mathbf{R}) - U_0(\mathbf{R})] |a\rangle\langle a| + \sum_{k=1}^M \epsilon_k |k\rangle\langle k| + \sum_{k=1}^M [V_{ak} |a\rangle\langle k| + V_{ka} |k\rangle\langle a|] \quad (4)$$

$U_0(\mathbf{R})$ is the multidimensional “diabatic” PES describing the interaction of the neutral NO molecule with the gold surface, as a function of the coordinates \mathbf{R} of the N, O and Au atoms. $U_1(\mathbf{R})$ is the corresponding diabatic PES for the negatively charged NO^- molecule. $|a\rangle$ is the one-electron wave function (affinity level) of the negative ion, i.e., in the case of NO, the molecular π^* orbital in which the electron resides to form the negative ion. Thus $U_0(\mathbf{R})$ and $U_1(\mathbf{R})$ are the many-electron PESs when the $|a\rangle$ orbital is unoccupied and occupied, respectively. The wave functions $|k\rangle$ are the M (occupied and unoccupied) one-electron states of the metallic conduction band, corresponding to one-electron energies ϵ_k . The conduction band states $|k\rangle$ should properly form a continuum, with the sums in eq 4 replaced by integrals, but in practice we must discretize the continuum. Finally, $V_{ak}(\mathbf{R})$ and $V_{ka}(\mathbf{R})$ are the matrix elements of the off-diagonal interaction

$$V_{ak}(\mathbf{R}) = \omega_k \langle a | V(\mathbf{R}) | k \rangle, \quad V_{ka}(\mathbf{R}) = \omega_k \langle k | V(\mathbf{R}) | a \rangle \quad (5)$$

where ω_k is a weighting factor to account both for the density of electronic states in the conduction band and for the spacing between discrete energy levels at energy ϵ_k , as discussed below.

The independent-electron Newns–Anderson Hamiltonian, eqs 3 and 4, is represented schematically in Figure 3. Figure 3a shows the basis functions; the adsorbate affinity level $|a\rangle$ and the discretized continuum of conduction electron levels $|k\rangle$. The latter are illustrated as M equally spaced levels, but as described elsewhere, in order to best represent the continuum with the fewest number of discrete states, it has proved advantageous to use a more flexible approach to continuum discretization, resulting in unequal spacings.^{75–77} Diagonalizing the one-

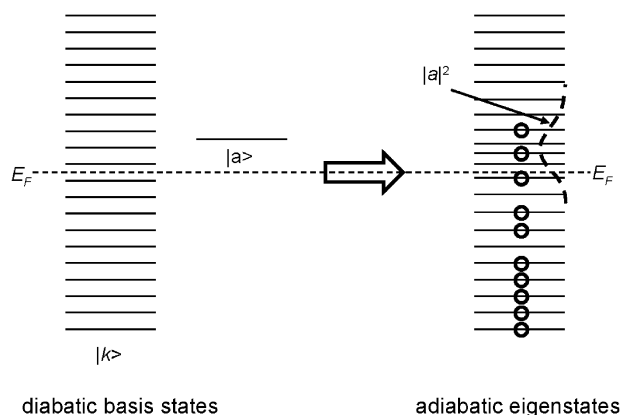


Figure 3. Single-electron energy levels in the Newns-Anderson model. (a) The one-electron diabatic basis functions comprised of the adsorbate affinity level $|a\rangle$ and the conduction band levels $|k\rangle$. (b) Single-electron eigenstates obtained by diagonalization of the single-electron Hamiltonian, eq 4 of the text. The many-electron Newns-Anderson wave function is constructed by populating selected single-electron adiabatic states, as indicated by circles in (b). The many-electron state that is represented in (b) has two one-electron excitations from the ground state.

electron Hamiltonian, eq 4, for fixed positions \mathbf{R} of all the atoms, produces $M + 1$ eigenstates, each of which is a linear combination of the initial basis functions, Figure 3b. The dashed curve in the figure illustrates the magnitude of mixing of the discrete state in each one-electron eigenfunction, peaking near the original energy of the discrete level. The width of the dashed curve represents the lifetime broadening of the discrete state.

The many-electron adiabatic states are obtained by designating the N_e one-electron eigenstates that are filled, leaving the remaining $M - N_e$ eigenstates empty. Thus, the ground state corresponds to filling the N_e lowest energy one-electron eigenstates up to the Fermi level. Excited states are produced by promoting one or more electrons to unoccupied states above the Fermi level. Multiple excitations allow for the creation of multiple EHPs, a necessity for properly describing electronic friction effects. Note, however, that a one-electron excitation does not correspond purely to EHP creation, since each one-electron eigenstate is a linear combination of the $|a\rangle$ and $|k\rangle$ states. Each many-electron eigenstate can thus be denoted by the indices of the occupied orbitals. The ground state is $\langle 1, 2, 3, \dots, N_e \rangle$. $\langle 1, 2, 4, \dots, N_e, N_e + 5 \rangle$ corresponds to promoting an electron from state 3 to state $N_e + 5$, etc. This produces a huge number of many-electron eigenstates. For example, in the NO–Au application discussed below, we typically chose $M = 40$ discrete states to represent the continuum and $N_e = 20$ electrons. There are more than 10^{11} permutations of 20 objects in 41 boxes. Carrying out surface hopping calculations on 10^{11} PESs may seem daunting, but as discussed below, it is actually quite practical.

We employ standard “fewest switches” surface hopping¹⁵ modified to treat multiple independent electrons. The resulting independent-electron surface hopping (IESH) algorithm is discussed in detail in ref 73. To simulate the scattering of the neutral molecule from a 0K surface, we assign the initial electronic state to be the ground state. Nonzero electronic temperature can easily be incorporated by selecting the initial states from a Fermi–Dirac distribution. We assign the initial classical positions and velocities of the surface atoms from a Boltzmann distribution. We assign the initial velocities and positions of the N and O atoms from distributions corresponding to the experimental NO center of mass velocity, rotational state

and vibrational state, with random orientation and random impact site on the surface. We then integrate the classical equations of motion of the atoms subject to the forces on the initial PES. Simultaneously, we integrate the time-dependent Schrödinger equation for the electrons. This is quite feasible because the Hamiltonian is separable into one-electron terms, and each one-electron Hamiltonian is a matrix of dimension $(M + 1)$ by $(M + 1)$ (41×41 in our example). As the molecule approaches the surface and enters into the coupling region where $V_{ak}(\mathbf{R})$ becomes significant, the occupied and unoccupied orbitals that were initially eigenstates of the one-electron Hamiltonian of eq 4 evolve into linear combinations of eigenstates. This nonadiabatic behavior results from the closely spaced nature of the discretized electronic states. Both electron transfer and EHP transitions are incorporated in this way on an equal footing.

Surface hopping is feasible because the nonadiabatic coupling vector is a one-electron operator that can be computed separately for each electron. Surface hops then correspond to single electron transitions from one adiabatic one-electron eigenstate to another. For each electron at each time step, a random number is compared to the standard fewest switches hopping criterion to determine whether a hop occurs between one-electron eigenstates.⁷³ When a hop occurs, the standard surface hopping adjustment of the component of velocity in the direction of the nonadiabatic coupling vector is applied to conserve total energy.¹⁵ No hop and no velocity adjustment are made if the hop is prevented by energy conservation. In our applications to the NO – Au system, large numbers of surface hops occur, often more than 100 for a single scattering event, in contrast to the 2 or 3 hops typically encountered in standard applications of surface hopping. Even with hundreds of surface hops, the system samples only a minuscule fraction of the total number (10^{11}) of many-electron states. This is the whole idea; the power of the Monte Carlo method is that all events do not need to be computed as long as they are sampled at random from the correct distribution. The number of trajectories required to obtain acceptable statistical uncertainty is not governed by the number of electronic states. For example, if the objective were to calculate a sticking probability and 400 of 1000 trajectories resulted in sticking, the probability could be estimated to be 0.40 ± 0.02 . If the number of one-electron states were doubled, the number of many-electron states would increase enormously, but the number of trajectories required to achieve a given confidence level in most cases would be unchanged. This argument must be viewed with caution, of course. As with any nonlinear Monte Carlo search, the possibility of getting trapped in local minima or missing crucial infrequent events must always be examined.

V. Diabatic Interactions for NO–Au(111)

Application of the surface hopping formalism described above requires specification of the diabatic PESs, $U_0(\mathbf{R})$ and $U_1(\mathbf{R})$, and off-diagonal couplings, $V(\mathbf{R})$ of eqs 3–5. Standard ab initio and DFT methods are designed to calculate adiabatic potential energy surfaces, predominantly ground states. Developing robust, accurate and practical methods for providing the required diabatic potential energy surfaces and their off-diagonal couplings is a significant challenge. We have chosen for this application a pragmatic approach that requires only ground state DFT calculations.

We used the Vienna ab-initio simulation package (VASP) plane wave (periodic boundary) DFT code⁷⁸ with the PW91 density functional.⁷⁹ Our results, which are discussed in detail in ref 72, are in close agreement with previously reported

calculations on the NO–Au(111) system.^{80,81} In order to extract the needed diabatic interactions from ground state calculations only, we assumed, as above, that the NO–gold interaction can be adequately represented by the 2×2 diabatic Hamiltonian matrix

$$H = \begin{pmatrix} U_0(\mathbf{R}) & V(\mathbf{R}) \\ V(\mathbf{R}) & U_1(\mathbf{R}) \end{pmatrix} \quad (6)$$

This is an oversimplification, of course, but it encompasses the major electron transfer dynamics. At every choice of atomic positions sampled, we carried out DFT calculations to obtain two quantities, the ground state energy and the effective Bader⁸² charge on the NO molecule. In addition, we repeated the DFT calculations with a small external electric field imposed normal to the plane of the gold surface (both positive and negative directions). From this we calculated the change of the effective charge on the molecule with respect to the electric field strength. We have demonstrated that the ground state energy, charge and variation of charge are sufficient to uniquely specify the three unknown diabatic Hamiltonian matrix elements.⁷² For NO–Au(111), the resulting 3 elements were quite accurately fit to relatively simple analytic forms, similar to those used previously.⁸³ The functional form and fitting parameters are reported elsewhere.⁷² Diagonalization of the 2×2 matrix accurately reproduces the DFT ground state energy and effective charge at all geometries for which we considered the DFT results to be reliable.

This method for computing diabatic potential energy surfaces, as well as their lifetimes and off-diagonal couplings, should prove useful in other applications, not only for providing the necessary input for nonadiabatic dynamics simulations, but also for extracting underlying physical pictures of the interplay between electronic transitions and nuclear motion. However, the method developed here to extract diabatic matrix elements from ground state DFT appears difficult to generalize to situations exhibiting multiple interacting diabatic states, such as those illustrated in Figure 1. For an N -state system the 2×2 matrix will expand to an $N \times N$ matrix with many matrix elements to be determined. We are exploring the use of constrained DFT methods^{71,69} to address these more challenging cases.

Figure 4 is a contour plot of the effective charge on the NO molecule, in the ground state, as a function of its distance from the surface and the N–O separation distance, as computed from the analytical 2×2 diabatic Hamiltonian. The plot shows considerable negative ion character, particularly when the molecule is relatively close to the surface and the NO bond length is extended. It is likely that a vibrationally excited NO molecule will enter and leave the ionic region multiple times in the course of a single thermal-energy scattering event, offering numerous possibilities for electron transfer and nonadiabatic excitation. Note that the more gradual the changeover from neutral to negative ion character, the more likely that electron rearrangements can keep up with the nuclear motion (i.e., the smaller the probability of nonadiabatic transitions). In the adiabatic limit, the transferring electron will originate from the Fermi level and then return to the Fermi level, with no net electronic excitation, in clear disagreement with observations. Conversely, if the switch from neutral to ion and vice versa is sudden, the electron distribution will be unable to accomplish the drastic change exhibited by the ground state, and nonadiabatic behavior will dominate. The NO–Au system appears to be intermediate between these extremes; neither the transient negative ion nor the electronic friction limits are valid.

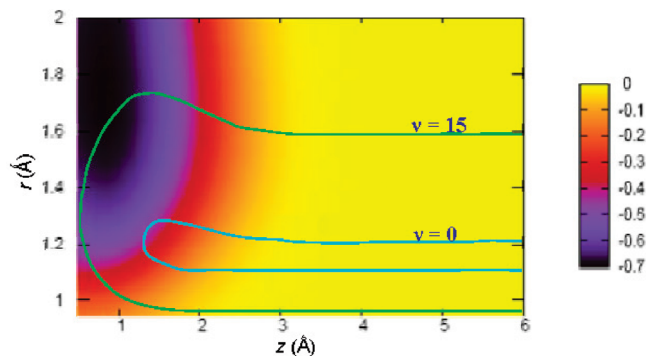


Figure 4. Contour plot of the local charge on the NO molecule in its ground electronic state as computed from the 2×2 diabatic matrix, eq 6 of the text, from ref 72. The NO molecule is oriented perpendicular to the surface over a 3-fold hollow site, with the N end of the molecule toward the surface. The horizontal axis is the distance, z , of the N atom from the $z = 0$ surface plane. The vertical axis is the N–O separation, r . The curves labeled $v = 0$ and $v = 15$ delineate the energy allowed regions for an NO molecule approaching a 0 K gold surface with zero incident translational and rotational energy, and initial vibrational state $v = 0$ and $v = 15$, respectively. Note that a $v = 15$ molecule can access regions of large negative charge, in contrast to a $v = 0$ molecule.

The next step is the construction of the $(M + 1) \times (M + 1)$ Newns–Anderson one-electron Hamiltonian matrix from the 2×2 diabatic matrix. Note that all off-diagonal elements of this matrix are zero except for those in the single row and column connecting with the localized state $|a\rangle$. For the results reported below, the number of electrons, N_e , was taken to be 20 and the number of discrete states, M , representing the continuum was taken to be 40, with 20 below the Fermi level and 20 above. While the density of states of the gold conduction band was assumed to be uniform, the spacings between the discrete states were not taken to be equal. Rather, they were optimized using a strategy reported elsewhere, properly weighted to compensate for the uneven spacings.⁷³ This produced a higher density of discrete states near the Fermi level, as required to properly describe low-energy excitations (i.e., electronic friction). As with the 2×2 matrix, the elements of the $(M + 1) \times (M + 1)$ matrix were fit to analytic forms with parameters chosen to closely reproduce the energies and charges extracted from the DFT calculations.

VI. Dynamics of Scattering of NO from Au(111)

We have now carried out both adiabatic and nonadiabatic (surface hopping) simulations of the scattering of NO from the Au(111) surface.^{73,84} For scattering of NO in its ground vibrational state, both adiabatic and nonadiabatic calculations produce similar trapping (intact sticking) probabilities as a function of incident energy, and these are in relatively good accord with the experimental results of Wodtke and co-workers.⁸⁵ For NO initially excited to $v = 2$, however, the adiabatic results differ significantly from those of the surface hopping simulations, presumably because vibrational energy leads to deeper excursions into the ionic region of Figure 4. The surface hopping results are in better accord with experiment for $v = 2$ as well. Simulations of the scattering of highly vibrationally excited $v = 15$ NO molecules show a striking difference between adiabatic and surface hopping predictions. Moreover, the trapping probability is predicted to be much lower when nonadiabaticity is included. This may appear counterintuitive; EHP excitations offer an additional pathway for the energy dissipation that is required for the molecule to trap. This

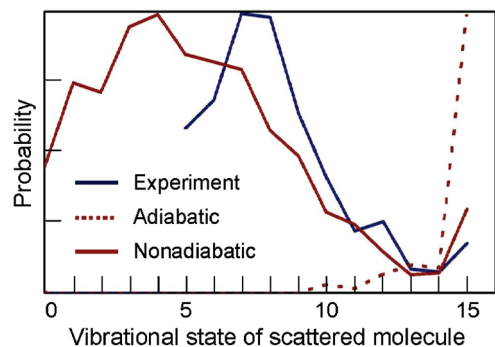


Figure 5. Relative populations of final vibrational states of the NO molecule after scattering from a 300 K Au(111) surface, with initial translational energy = 5 kJ/mol at normal incidence, and initial vibrational state $\nu = 15$. Experimental results are from Wodtke and co-workers, ref 52. Note that there were no experimental measurements of states lower than $\nu = 5$. Adiabatic results are from standard MD simulations on the ground state PES, the lower eigenenergy of the 2×2 diabatic Hamiltonian of eq 6. Nonadiabatic results are from surface hopping simulations, ref 84, as described in the text.

inverse behavior is a result of the contribution of vibrational energy, which greatly exceeds that of the translational energy. In the absence of nonadiabatic behavior, vibration is essentially a spectator in the scattering event; very little vibrational energy is lost, as shown below, because of the time scale mismatch between the high-frequency vibrational motion and low-frequency phonon, translational and rotational motions. By contrast, transfer of vibrational energy to electronic excitations via nonadiabatic coupling is quite facile. The nonadiabatic coupling vector, approximately in the direction in which charge changes most steeply in Figure 4, involves the translational coordinate. Therefore some of the transferred vibrational energy will be channeled into translation, thereby reducing the trapping probability.

The most dramatic difference between the adiabatic and surface hopping simulations can be seen in Figure 5, which shows the final vibrational distribution of scattered NO molecules, for initial vibrational state $\nu = 15$. The adiabatic approximation breaks down severely, predicting minimal vibrational relaxation. This is the expected result; it is consistent with experiments in which vibrationally excited NO was scattered from an insulating surface, LiF.⁸⁶ As discussed above, the large frequency mismatch between the NO stretch and the substrate phonons underlies this result. The surface hopping calculations, by contrast, exhibit very substantial vibrational relaxation, in fairly good accord with experiment.⁵³

As mentioned earlier, the Wodtke group has observed electron emission from a Cs-covered gold surface upon scattering of highly vibrationally excited NO.^{56,54} The electron emission intensity is linearly dependent on the flux of molecules, so it is a single collision event, not heating. The probability of electron emission has a threshold at about $\nu = 8$ and increases thereafter with increasing initial ν . (The energy of the $\nu = 8$ state is 1.88 eV compared to the work function of the Cs-covered gold surface of 1.6 eV.) These experiments demonstrate that a large fraction of the energy lost from vibration can be deposited into a single electron; the relaxation must occur, at least sometimes, by a multiquantum vibrational transition, rather than in a stepwise sequence of single vibrational level transitions. Our calculations only address the clean gold surface, so we cannot make any direct comparisons to the Cs-covered gold experiments. Nevertheless, our surface hopping simulations do predict that multiquantum vibrational transitions, producing energetic electrons, are quite prevalent.

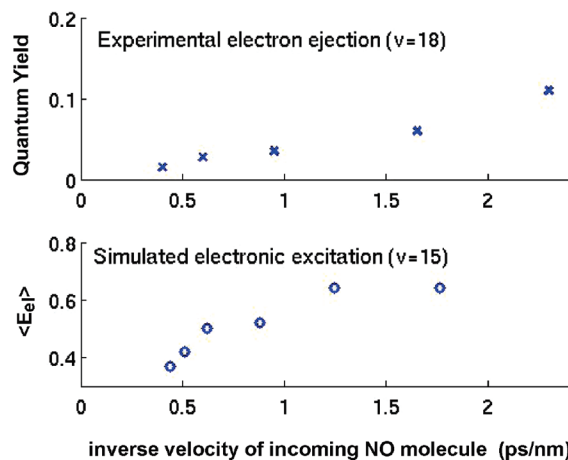


Figure 6. Measures of the dependence of electron excitation probability on the inverse of the incident NO velocity. The experimental results in the upper panel show the relative yield of electrons emitted from a Cs-covered Au(111) surface, for initial NO vibrational state $\nu = 18$, from ref 54. The results shown in the lower panel are the mean energy transferred into electronic excitations as computed by surface hopping for NO($\nu = 15$) scattered from the pure Au(111) surface. Even though the results are for different surfaces and different quantities are plotted, the overall trends are similar. Namely, both exhibit higher nonadiabaticity at lower incident velocities, in contrast to the expectation that nonadiabatic transitions are more prevalent at higher velocities.

The Wodtke group recently published the intriguing observation that the electron emission intensity from the Cs–Au surface depends inversely on the incident translational energy of the NO molecule.⁵⁵ Figure 6a shows their measured yield of emitted electrons as a function of the inverse of the incident velocity. They point out that this is contrary to the expectation that nonadiabatic transitions become more prevalent at higher energies; gradual motion favors adiabatic behavior. As stated above, we have not carried out scattering simulations on the Cs-covered gold surface. However, we have recorded the final electron energy distribution upon scattering of vibrationally excited NO($\nu = 15$) molecules from the clean gold surface. Figure 6b shows the computed mean energy of excitation of the electrons as a function of inverse incident velocity. Although the comparison is between different quantities and different systems, the overall trends are similar. Thus the calculations also show greater nonadiabatic behavior at lower translational energies. The source of this behavior is due to a combination of factors. At lower translational energy, the NO molecule enters the strong coupling region more often and remains longer in this region, enhancing the probability of vibration-to-electronic energy transfer. However, dynamical steering appears to also play an important role in vibrational relaxation.⁸⁴

The surface hopping results summarized above demonstrate, first, that the approach is computationally feasible; a run of 100 scattering trajectories requires about 15 h of computational time on a single processor. Second, the method is capable of reproducing the main experimental trends with acceptable accuracy, especially considering the uncertainties in the diabatic PESs. Finally, the mechanisms underlying the observed behavior are elucidated quite clearly. We note that, for low vibrational excitation where the system does not undergo significant charge transfer, the surface hopping results should approach those of the electronic friction model. We have demonstrated that this is approximately true for the vibrational lifetime of the $\nu = 2$ level of an adsorbed NO molecule, using the same interaction parameters for both calculations.

VII. Challenges

We have described a few steps toward the ultimate goal of a unified theory of the interaction of molecules with metal surfaces. Many challenges remain. The first hurdle is accurate, first-principles calculation of the energies and lifetimes of molecular excited states at metal surfaces. Some promising directions have emerged, notably complex scaling, constrained DFT and embedding methods. The latter of these, a multiconfiguration *ab initio* description of the molecule embedded in a DFT-computed electronic background, is particularly appealing. However, it appears difficult to consistently describe electron transfer states with this formalism; further advances are needed.

Even when methods are developed for reliable and predictive calculation of the kinds of excited electronic PESs illustrated in Figure 1b, as well as the off-diagonal couplings among them, severe challenges will remain. All MQCD methods, including surface hopping, have inaccuracies. The most important of these is not the treatment of nonadiabatic transitions, although improvements would be valuable. Rather, it is the classical mechanical treatment of nuclear motion that underlies MQCD approaches. This precludes accurate description of quantum mechanical tunneling, zero-point motion and quantized vibrations, each of which can significantly affect the rates and pathways of chemical reactions. Full quantum mechanical evolution of the motion of the nuclei, by wave packet, path integral or other approaches, is the ultimate solution. This is a long way off, however; our simulations indicate that at least for NO–Au scattering, it is essential to include the motions, not only of the molecule, but of the surface atoms as well.⁷³ The rigid surface and other reduced-dimensionality assumptions can be very misleading.

These formidable hurdles notwithstanding, there has been significant progress toward the major objective of understanding the underlying principles that govern chemistry at metal surfaces. First-principles calculations that accurately reproduce experimental results would be nice. It is more important, however, to identify and elucidate the qualitative factors that govern chemical events, and to uncover trends that can serve as guidance for future inquiry. Exciting ongoing developments from both experiment and theory are advancing us toward this goal.

Acknowledgment. We are grateful to the Department of Energy Basic Energy Sciences for their generous support of this research through Grant No. DE-FG02-05ER15677.

References and Notes

- Born, M.; Oppenheimer, E. *Ann. Phys.* **1927**, *84*, 457.
- Wodtke, A. M.; Tully, J. C.; Auerbach, D. J. *Int. Rev. Phys. Chem.* **2004**, *23*, 513.
- Hasselbrink, E. *Curr. Opin. Solid State Mater. Sci.* **2006**, *10*, 192.
- Luntz, A. C.; Persson, M. *J. Chem. Phys.* **2005**, *123*, 074704.
- Kroes, G. J. *Science* **2008**, *321*, 794.
- Tully, J. C. *Faraday Discuss.* **2004**, *127*, 463.
- Baldrige, K. K.; Gordon, M. S.; Steckler, R.; Truhlar, D. G. *J. Phys. Chem.* **1989**, *93*, 5107.
- Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.
- McLachlan, A. D. *Mol. Phys.* **1964**, *8*, 39.
- Micha, D. A. *J. Chem. Phys.* **1983**, *78*, 7138.
- Kirson, Z.; Gerber, R. B.; Nitzan, A.; Ratner, M. A. *Surf. Sci.* **1984**, *137*, 527.
- Sawada, S. I.; Nitzan, A.; Metiu, H. *Phys. Rev. B* **1985**, *32*, 851.
- Billing, G. D. *The Quantum Classical Theory*; Oxford University Press: Oxford, 2003.
- Tully, J. C.; Preston, R. K. *J. Chem. Phys.* **1971**, *55*, 562.
- Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061.
- Drukker, K. *J. Comp. Phys.* **1999**, *153*, 225.
- Webster, F. J.; Schnitker, J.; Friedrichs, M. S.; Friesner, R. A.; Rossky, P. J. *Phys. Rev. Lett.* **1991**, *66*, 3172.
- Mead, C. A.; Truhlar, D. G. *J. Chem. Phys.* **1986**, *84*, 1055.
- Doltsinis, N.; Marx, D. *J. Theor. Comp. Chem.* **2002**, *1*, 319.
- Schaich, W. L. *Surf. Sci.* **1975**, *49*, 221.
- d'Agliano, E. G.; Kumar, P.; Schaich, W.; Suhl, H. *Phys. Rev. B* **1975**, *11*, 2122.
- Nourtier, A. *J. Phys. (Paris)* **1977**, *38*, 479.
- Schonhammer, K.; Gunnarsson, O. *Phys. Rev. B* **1980**, *22*, 1629.
- Kasai, H.; Okiji, A. *Surf. Sci.* **1991**, *242*, 394.
- Head-Gordon, M.; Tully, J. C. *J. Chem. Phys.* **1995**, *103*, 10137.
- Tully, J. C.; Gomez, M.; Head-Gordon, M. *J. Vac. Sci. Technol. A* **1993**, *11*, 1914.
- Kubo, R. *Rep. Prog. Phys.* **1966**, *29*, 255.
- Head-Gordon, M.; Tully, J. C. *Phys. Rev. B* **1992**, *46*, 1853.
- Springer, C.; Head-Gordon, M.; Tully, J. C. *Surf. Sci.* **1994**, *320*, L57.
- Kindt, J. T.; Tully, J. C.; Head-Gordon, M.; Gomez, M. A. *J. Chem. Phys.* **1998**, *109*, 3629.
- Kindt, J. T.; Tully, J. C. *J. Chem. Phys.* **1999**, *111*, 11060.
- Li, Y. G.; Wahnstrom, G. *Phys. Rev. Lett.* **1992**, *68*, 3444.
- Diekhoer, L.; Hornekaer, L.; Mortensen, H.; Jensen, E.; Baurichter, A.; Petrunin, V. V.; Luntz, A. C. *J. Chem. Phys.* **2002**, *117*, 5018.
- Trail, J. R.; Graham, M. C.; Bird, D. M.; Persson, M.; Holloway, S. *Phys. Rev. Lett.* **2002**, *88*, 166802.
- Mizielinski, M. S.; Bird, D. M.; Persson, M.; Holloway, S. *J. Chem. Phys.* **2007**, *126*, 034705.
- Head-Gordon, M.; Tully, J. C. *J. Chem. Phys.* **1992**, *96*, 3939.
- Krishna, V.; Tully, J. C. *J. Chem. Phys.* **2006**, *125*, 054706.
- Persson, B. N. J.; Persson, M. *Solid State Commun.* **1980**, *36*, 175.
- Trail, J. R.; Bird, D. M.; Persson, M.; Holloway, S. *J. Chem. Phys.* **2003**, *119*, 4539.
- Bird, D. M.; Mizielinski, M. S.; Lindenblatt, M.; Pehlke, E. *Surf. Sci.* **2008**, *602*, 1212.
- Kondo, J. *Prog. Theor. Phys.* **1964**, *32*, 37.
- Kouwenhoven, L.; Glazman, L. *Phys. World* **2001**, *14*, 33.
- Huang, P.; Carter, E. A. *Nano Lett.* **2006**, *6*, 1146.
- Nienhaus, H.; Bergh, H. S.; Gergen, B.; Majumdar, A.; Weinberg, W. H.; McFarland, E. W. *Phys. Rev. Lett.* **1999**, *82*, 446.
- Nienhaus, H.; Bergh, H. S.; Gergen, B.; Majumdar, A.; Weinberg, W. H.; McFarland, E. W. *Surf. Sci.* **2000**, *445*, 335.
- Gergen, B.; Weyers, S. J.; Nienhaus, H.; Weinberg, W. H.; McFarland, E. W. *Surf. Sci.* **2001**, *488*, 123.
- Ji, X. Z.; Zupero, A.; Gidwani, J. M.; Somorjai, G. A. *Nano Lett.* **2005**, *5*, 753.
- Ji, X. Z.; Somorjai, G. A. *J. Phys. Chem. B* **2005**, *109*, 22530.
- Park, J. Y.; Somorjai, G. A. *ChemPhysChem* **2006**, *7*, 1409.
- Autzen, O.; Wesenberg, C.; Hasselbrink, E. *Phys. Rev. Lett.* **1968**, *19*, 196807.
- Mildner, B.; Hasselbrink, E.; Diesing, D. *Chem. Phys. Lett.* **2006**, *432*, 133.
- Hou, H.; Huang, Y.; Guldung, S. J.; Rettner, C. T.; Auerbach, D. J.; Wodtke, A. M. *J. Chem. Phys.* **1999**, *110*, 10660.
- Huang, Y. H.; Rettner, C. T.; Auerbach, D. J.; Wodtke, A. M. *Science* **2000**, *290*, 111.
- White, D. J.; Chen, J.; Matsiev, D.; Auerbach, D. J.; Wodtke, A. M. *Nature* **2005**, *433*, 503.
- Nahler, N. H.; White, J. D.; Larue, J.; Auerbach, D. J.; Wodtke, A. M. *Science* **2008**, *321*, 1191.
- White, J. D.; Chen, J.; Matsiev, D.; Auerbach, D. J.; Wodtke, A. M. *J. Vacuum Sci. Technol. A* **2005**, *23*, 1085.
- Larue, J. L.; White, J. D.; Nahler, N. H.; Liu, Z.; Sun, Y.; Pianetta, P. A.; Auerbach, D. J.; Wodtke, A. M. *J. Chem. Phys.* **2008**, *129*, 024709.
- Nordlander, P.; Tully, J. C. *Phys. Rev. B* **1990**, *42*, 5564.
- Teillet-Billy, D.; Gauyacq, J. P. *Surf. Sci.* **1990**, *239*, 343.
- Niedfeldt, K.; Carter, E. A.; Nordlander, P. *J. Chem. Phys.* **2004**, *121*, 3751.
- Li, X. S.; Tully, J. C. *Chem. Phys. Lett.* **2007**, *439*, 199.
- Gadzuk, J. W. *J. Chem. Phys.* **1983**, *79*, 6341.
- Newns, D. M. *Surf. Sci.* **1986**, *171*, 600.
- Finger, K.; Saalfrank, P. *Chem. Phys. Lett.* **1997**, *268*, 291.
- Corriol, C.; Darling, G. R.; Holloway, S.; Brenig, W.; Andrianov, I.; Klamroth, T.; Saalfrank, P. *J. Chem. Phys.* **2002**, *117*, 4489.
- Li, S.; Guo, H. *J. Chem. Phys.* **2002**, *117*, 4499.
- Katz, G.; Zeiri, Y.; Kosloff, R. *J. Phys. Chem. B* **2005**, *109*, 18876.
- Saalfrank, P. *Chem. Rev.* **2006**, *106*, 4116.
- Behler, J.; Delley, B.; Lorenz, S.; Reuter, K.; Scheffler, M. *Phys. Rev. Lett.* **2005**, *94*, 036104.
- Behler, J.; Reuter, K.; Scheffler, M. *Phys. Rev. B* **2008**, *77*, 115421.
- Dederichs, P. H.; Blugel, S.; Zeller, R.; Akai, H. *Phys. Rev. Lett.* **1984**, *53*, 2512.
- Roy, S.; Shenvi, N.; Tully, J. C. *J. Chem. Phys.* **2009**, *130*, 174716.
- Shenvi, N.; Roy, S.; Tully, J. C. *J. Chem. Phys.* **2009**, *130*, 174107.

- (74) Newns, D. M. *Phys. Rev.* **1969**, *178*, 1123.
- (75) Burkey, R. S.; Cantrell, C. D. *J. Opt. Soc. Am. B* **1984**, *1*, 539.
- (76) Kazansky, A. K. *J. Phys. B* **1997**, *30*, 1401.
- (77) Shenvi, N.; Schmidt, J. R.; Edwards, S. T.; Tully, J. C. *Phys. Rev. A* **2008**, *78*, 022502.
- (78) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, *54*, 11169.
- (79) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.
- (80) Torres, D.; Gonzalez, S.; Neyman, K. M.; Illas, F. *Chem. Phys. Lett.* **2006**, *422*, 412.
- (81) Zhang, W. H.; Li, Z. Y.; Luo, Y.; Yang, J. L. *J. Chem. Phys.* **2008**, *129*, 134708.
- (82) Bader, R. F. M. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.
- (83) Muhlhausen, C. W.; Williams, L. R.; Tully, J. C. *J. Chem. Phys.* **1985**, *83*, 2594.
- (84) Shenvi, N.; Roy, S.; Tully, J. C. Nonadiabatic Scattering of NO from Au(111): Importance of Dynamical Steering. Manuscript in preparation.
- (85) Wodtke, A. M.; Yuhui, H.; Auerbach, D. J. *Chem. Phys. Lett.* **2005**, *413*, 326.
- (86) Wodtke, A. M.; Huang, Y. H.; Auerbach, D. J. *J. Chem. Phys.* **2003**, *118*, 8033.

JP811393W