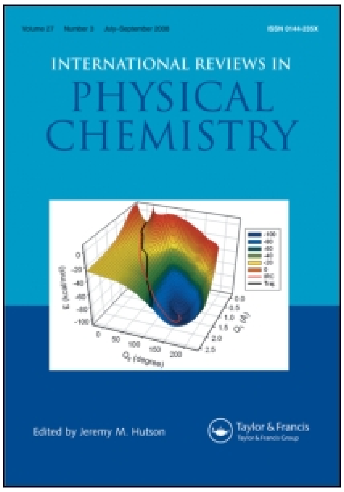

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Electronically non-adiabatic interactions of molecules at metal surfaces: Can we trust the Born-Oppenheimer approximation for surface chemistry?

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Electronically non-adiabatic interactions of molecules at metal surfaces: Can we trust the Born–Oppenheimer approximation for surface chemistry?

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When neutral molecules with low levels of vibrational excitation collide at metal surfaces, vibrational coupling to electron-hole pairs (EHPs) is not thought to be strong unless incidence energies are high. However, there is accumulating evidence that coupling of large-amplitude molecular vibration to metallic electron degrees of freedom can be much stronger even at the lowest accessible incidence energies. As reaching a chemical transition-state also involves large-amplitude vibrational motion, we pose the basic question: are electronically non-adiabatic couplings important at transition states of reactions at metal surfaces? We have indirect evidence in at least one example that the dynamics and rates of chemical reactions at metal surfaces may be strongly influenced by electronically non-adiabatic coupling. This implies that theoretical approaches relying on the Born–Oppenheimer approximation (BOA) may not accurately reflect the nature of transition-state traversal in reactions of catalytic importance. Developing a predictive understanding of surface reactivity beyond the BOA represents one of the most important challenges to current research in physical chemistry. This article reviews the experimental evidence and underlying theoretical framework concerning these and related topics.

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1. Introduction

Almost all discussions of chemical reaction dynamics begin with the Born–Oppenheimer approximation (BOA) (Born and Oppenheimer 1927), the assumption that the light, fast-moving electrons adjust instantaneously and completely to the slower motions of the more massive atomic nuclei. The BOA underlies the concept of the potential energy surface (PES), $V(\mathbf{R})$, the electronic and nuclear repulsion energy of the system at the fixed set of nuclear positions, $\mathbf{R}$ (Eyring and Polanyi 1931). Often referred to as the adiabatic or Born–Oppenheimer potential energy surface, $V(\mathbf{R})$ is the centerpiece of chemical reaction theory. Stable molecular conformations correspond to the local minima of $V(\mathbf{R})$. The properties of $V(\mathbf{R})$ in the vicinity of each local minimum determine the stability of the conformation and its vibrational and rotational motions. Chemical reactions are governed by the pathways that lead from one stable minimum to another. The minimum energy path connecting two stable conformers is often identified as the 'reaction coordinate'. The saddle point or position of maximum energy along the minimum energy path is the 'transition state', the focus of the widely used 'transition state theory' or 'activated complex theory' of chemical reaction rates (Glasstone *et al.* 1941). The actual quantum mechanical or classical mechanical time-dependent trajectory that the system follows as an inelastic collision or chemical reaction evolves is the focus of the field of chemical dynamics. All of these concepts, which initially grew out of studies of the dynamics of simple gas-phase encounters, have been fruitfully carried over to the field of gas–surface interactions. These ideas permeate almost all theoretical descriptions of inelastic scattering of molecules from surfaces, energy accommodation, adsorption and desorption, molecular dissociation, surface diffusion, catalytic reactions, etching and deposition, and so on.

Situations in which the BOA is not valid have been widely documented. The validity of the BOA rests on the following factors: (1) the rearrangement of the electron cloud associated with a change of nuclear positions must be gradual; that is, non-adiabatic coupling must be small; (2) the electronic states of the system must be widely separated in energy; and (3) the velocities of the nuclei must be sufficiently small to permit the electrons to adjust completely to their motions. These conditions are often not met in high-energy collisions (condition 3), in situations involving electron transfer (1), and in photochemical reactions (2). However, there are a number of experimental demonstrations of the breakdown of the BOA even in thermal energy collisions of ground state molecules in the gas phase, for example when low lying excited spin–orbit states are available (Hepburn *et al.* 1981; Dagdigian and Campbell 1987).

It can be anticipated that breakdowns of the BOA will be even more frequent in chemical processes at metal surfaces than in gas-phase reactions. The stronger attraction of a molecule to a surface, proportional to the inverse third power of distance compared to the inverse sixth power in the gas phase, can lower the energies of more polarizable excited electronic states, bringing them nearer in energy to the ground state. More dramatically, positively or negatively charged molecules at surfaces are stabilized by an image potential proportional to the inverse first power of the distance, frequently resulting in the crossing or avoided crossing of ionic and neutral potential energy surfaces. Metals also bind electrons more weakly (work functions are generally less than 5 eV) than most gas-phase molecules (ionization potentials are generally more than 8 eV). Finally, metal surfaces exhibit a continuum of electronic states, the conduction band, for which there is no energy separation *whatsoever* between electronic states. Electron-hole pair (EHP) transitions between electronic levels in the conduction band can provide a mechanism for energy transfer with an adsorbate molecule (Metiu and Gadzuk 1981) and perhaps even call into question the applicability of the concept of motion evolving on a PES.

In this article, we review the growing evidence that understanding the dynamics of reactions at metal surfaces requires insights and approaches that go beyond the BOA. We first present a theoretical exposition of the BOA and how it must be viewed within the context of heavy-atom motion near metal surfaces. This has the advantage of defining many important terms and concepts early in the review as well as providing an overview of those few but important efforts that have already been undertaken to advance theory beyond the confines of electronic adiabaticity. We then discuss in a more or less historical fashion the experimental evidence accumulated thus far that points to problems with the electronically adiabatic approach to surface reactivity.

2. Theoretical approaches to the problem of non-adiabatic electronics

There have been a number of theoretical efforts to incorporate non-adiabatic transitions into the description of chemical dynamics at surfaces. In order to efficiently present and contrast these approaches, we first summarize the underlying principles. The total non-relativistic quantum mechanical Hamiltonian for a system of interacting adsorbate and substrate atoms is:

$$H = -\frac{\hbar^2}{2}\sum_{\alpha} M_{\alpha}^{-1}\nabla_{R_\alpha}^2 - \frac{\hbar^2}{2}\sum_{i} m_e^{-1}\nabla_r^2 + V(\mathbf{r},\mathbf{R}) = -\frac{\hbar^2}{2}\sum_{\alpha} M_{\alpha}^{-1}\nabla_{R_\alpha}^2 + H_{el}(\mathbf{r};\mathbf{R}), \quad (1)$$

where **r** and **R** denote the positions of the electrons and nuclei, respectively, M_α is the mass of nucleus α and m_e is the electron mass. Note that, in principle, **r** includes all of the electrons in the system and **R** denotes the positions of both adsorbate and substrate atomic nuclei. $V(\mathbf{r},\mathbf{R})$ includes all interparticle interactions: electron–electron repulsions, electron–nuclear attractions and nuclear–nuclear repulsions. $H_{el}(\mathbf{r};\mathbf{R})$ is the entire Hamiltonian of the system with the exception of the kinetic energy operator for the nuclei, and can be viewed as the Hamiltonian that governs the electrons when the nuclei are fixed at position **R**. The conventional adiabatic (Born–Oppenheimer) electronic wave functions $\Phi_j(\mathbf{r};\mathbf{R})$ are the eigenfunctions of $H_{el}(\mathbf{r};\mathbf{R})$ for a fixed **R**:

$$H_{el}(\mathbf{r};\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}) = E_j(\mathbf{R})\Phi_j(\mathbf{r};\mathbf{R}). \quad (2)$$

$E_j(\mathbf{R})$ is the adiabatic or Born–Oppenheimer PES corresponding to electronic state j, as described in the introduction, with $j = 0$ denoting the ground state PES. The ground and excited state electronic wave functions $\Phi_j(\mathbf{r};\mathbf{R})$, for any fixed **R**, constitute a complete set that spans the space of the electrons. Thus, we can express the exact molecular wave function $\Psi(\mathbf{r},\mathbf{R})$ as

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_i \Phi_i(\mathbf{r};\mathbf{R})\Omega_i(\mathbf{R}). \tag{3}$$

Substituting equation (3) into the time-dependent Schrödinger equation using the Hamiltonian of equation (1), multiplying from the left by $\Phi_j^*(\mathbf{r};\mathbf{R})$ and integrating over electronic coordinates $\mathbf{r}$, we obtain the standard set of coupled Schrödinger equations for the wave functions $\Omega_j(\mathbf{R})$ describing nuclear motion on each potential energy surface, $E_j(\mathbf{R})$:

$$\begin{aligned}&-\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla_{R_\alpha}^2\Omega_j(R) + E_j(R)\Omega_j(R) - E\Omega_j(R)\\ &\quad = -\frac{\hbar^2}{2}\sum_i D_{ji}(R)\Omega_i(R) + \hbar^2\sum_{i\neq j} d_{ji}(R)\cdot\nabla_{R_\alpha}\Omega_i(R),\end{aligned} \tag{4}$$

where the first- and second-derivative matrix elements are defined as

$$\mathbf{d}_{ij}(\mathbf{R}) = -\sum_\alpha M_\alpha^{-1}\int\left\{\Phi_i^*(\mathbf{r},\mathbf{R})\left[\nabla_{R_\alpha}\Phi_j(\mathbf{r},\mathbf{R})\right]\right\}d\mathbf{r}, \tag{5}$$

$$D_{ij}(\mathbf{R}) = -\sum_\alpha M_\alpha^{-1}\int\left\{\Phi_i^*(\mathbf{r},\mathbf{R})\left[\nabla_{R_\alpha}^2\Phi_j(\mathbf{r},\mathbf{R})\right]\right\}d\mathbf{r}. \tag{6}$$

The BOA is obtained by setting the right-hand side of equation (4) equal to zero, resulting in

$$\left[-\frac{\hbar^2}{2}\sum_\alpha M_\alpha^{-1}\nabla_{R_\alpha}^2 + E_j(\mathbf{R}) - E\right]\Omega(\mathbf{R},t) = 0. \tag{7}$$

Note that the first term on the right-hand side of equation (4) contains a diagonal term involving $D_{jj}(\mathbf{R})$. This term is frequently included in equation (7) as a correction to $E_j(\mathbf{R})$. We omit it here for simplicity; it is of the same order of magnitude as the neglected off-diagonal $D_{ij}(\mathbf{R})$ terms.

The final result when the BOA is valid, equation (7), is that nuclear motion (in other words all fundamental aspects of chemical bond making and breaking) is governed by a Schrödinger equation with the potential energy function given by $E_j(\mathbf{R})$. $E_j(\mathbf{R})$, in turn, is obtained from equation (2) for each required nuclear geometry $\mathbf{R}$.

This review explores the question of the extent to which the BOA is valid or invalid during the interaction of molecules with metal surfaces. There is no easy general answer to this. The *Massey Criterion* provides a simple and often helpful guide in the case of two interacting electronic states; the criterion for validity of the BOA is

$$\frac{\hbar\mu\dot{\mathbf{R}}\cdot\mathbf{d}_{12}}{|E_1 - E_2|} \ll 1, \tag{8a}$$

where $\mathbf{d}_{12}$ is the non-adiabatic coupling defined in equation (5), μ is the reduced mass along the direction of $\mathbf{d}_{12}$, and $\dot{\mathbf{R}}$ is the nuclear velocity.

In the vicinity of an isolated avoided crossing resulting from a 2×2 'diabatic' Hamiltonian matrix with elements H_{ij}, this expression takes the more usual form

$$\frac{\hbar \dot{R} \left| \partial H_{11}/\partial R - \partial H_{22}/\partial R \right|}{4H_{12}^2} \ll 1. \tag{8b}$$

These expressions apply only to cases involving two electronic states, however, and are not of direct use when a continuum of electronic states is involved, as is the case for a molecule in the vicinity of a metal surface.

In cases for which the BOA, equation (7), is valid, the first stage in describing nuclear motion is the construction of an accurate PES $E_j(\mathbf{R})$. In most studies, empirical or semi-empirical approximations to $E_j(\mathbf{R})$ have been used, sometimes quite successfully. However, *ab initio* methods, particularly those based on density functional theory (DFT), are now becoming feasible and allow more accurate determinations of the PES (Gross 2002). In addition, recent advances in Car–Parrinello and 'direct dynamics' methods have made it possible, in classical mechanical molecular dynamics simulations, to compute the classical forces 'on the fly' as the trajectory is unfolding (Car and Parrinello 1985). This represents a significant step forwards and will play an increasingly important role in molecular dynamics simulations of gas–surface interactions. In cases for which the BOA is not valid and equation (7) must be replaced by equation (4), however, Car–Parrinello and direct dynamics methods are not applicable. Equation (4) requires the calculation of more than one potential energy surface $E_j(\mathbf{R})$, as well as the derivative couplings of equations (5) and (6) that govern non-adiabatic transitions between PESs. Furthermore, electronic transitions are quantum mechanical in nature; it is not clear to what extent nuclear motion can be treated classically when the BOA is not valid.

A potential solution to the latter problem is to abandon classical mechanics and solve equation (4) quantum mechanically. This is a daunting task, even when the BOA is valid and equation (7) applies. The numerical solution of equation (7) requires propagation of the multidimensional wave packet $\Omega_j(\mathbf{R})$. Time-dependent propagation methods have improved significantly over the past few years, to the point that it is now feasible to tackle problems with six active nuclear degrees of freedom. There have been several studies of a diatomic molecule (six degrees of freedom) interacting with a rigid surface on a single PES. These studies have been very valuable in elucidating the dynamics of inelastic scattering and dissociative adsorption at surfaces (Nielsen *et al.* 1990; Gross 1998; Kroes 1999). However, the required simplification that the surface is rigid, that is that the substrate atoms do not move, has so far prevented the study of molecule–surface energy transfer by fully quantum mechanical simulation, except under the imposition of reduced dimensionality. Furthermore, no rigorous quantum treatments of EHP excitations or other non-adiabatic effects have been achieved. An interesting step in this direction has been proposed by Baer and Kosloff (1997), who introduce a 'surrogate Hamiltonian' that represents the continuum of EHP excitations by a finite set of effective electronic levels.

2.1. *Friction models*

Classical mechanical-based 'friction' models have been applied to describe exchange of energy between molecular motion and EHP's at metal surfaces

(D'Agliano *et al.* 1975; Brako and Newns 1980; Li and Wahnstrom 1992; Head-Gordon and Tully 1995). While most have used empirical friction parameters, more rigorous treatments have been developed. One of these, termed 'molecular dynamics with electronic friction' (MDEF), rests on a weak coupling approximation (Head-Gordon and Tully 1995; Tully 2000). With this approximation, a classical mechanical multidimensional Langevin equation is derived,

$$\mathbf{M}\ddot{\mathbf{R}} = -\nabla V(\mathbf{R}) - \underline{\underline{\Omega}} \cdot \dot{R} + \mathcal{R}(t) \tag{9}$$

For N degrees of freedom, the friction $\underline{\underline{\Omega}}$ is an $N \times N$ matrix that accounts for the coupling of each mode to EHPs. The electronic friction depends strongly on the atomic coordinates, that is the orientation of the adsorbate molecule and its distance from the surface. Explicit expressions for *ab initio* calculation of $\underline{\underline{\Omega}}$ have been derived. The random force, $\mathcal{R}(t)$, is obtained by using the 2nd fluctuation–dissipation theorem,

$$\langle \mathcal{R}(t) R(0) \rangle = kT\underline{\underline{\Omega}}\delta(t) \tag{10}$$

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

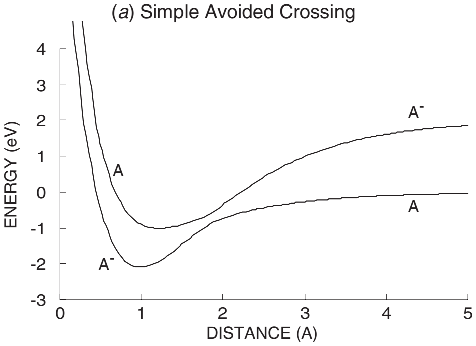
This approach was applied, with EHP frictions computed at the Hartree–Fock level, to compute the lifetimes of the four vibrational modes of CO adsorbed on Cu(100). The computed vibrational lifetimes are in fairly good accord with measured lifetimes (Tully *et al.* 1993). In particular, the lifetime of the C–O stretch was computed to be about 3 ps, in agreement with the measured value of 2 ps. The lifetime of the bending mode (frustrated rotation) was computed to be about 1 ps, in agreement with the value obtained from a lineshape analysis of 1 ps. The CO-surface stretch was computed to have a significantly longer lifetime, about 20 ps. No direct measurement of this lifetime has been reported, but the reported lifetime of the CO-surface stretch on Pt(111) is 22 ps. The in-plane frustrated translational mode is also predicted to be weakly coupled to EHPs.

Perhaps the most important outcome of this study was the predicted mode selectivity of EHP coupling. Two modes, the C–O stretch and the bend, were calculated to have very short lifetimes dominated by EHP relaxation. The other two modes were calculated to have much longer lifetimes dominated by phonons. Persson and Persson (1980a,b) have provided insight into the short lifetime of the internal CO stretching mode. When the molecule is adsorbed, the antibonding π^* orbital of the CO molecule broadens into a resonance, with a tail that dips below the Fermi level. Thus there is some electron occupation of this orbital ('back bonding'). As the molecule vibrates, the position and width of the π^* orbital fluctuates, causing electrons to flow onto and off the molecule. Indeed, by examination of the HOMO and LUMO orbitals from the Hartree–Fock calculations of EHP coupling, it is clear that the Persson and Persson picture is qualitatively correct.

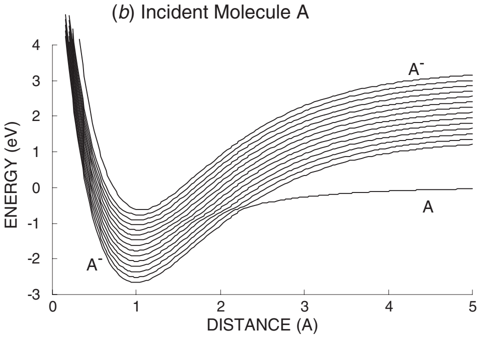
2.2. *Electron transfer and a warning concerning friction models*

Because of the (up to now) dominant importance of friction-like models (in particular, MDEF) in our attempts to treat electronically non-adiabatic dynamics at surfaces, it is worth making some statements about their known limitations. The MDEF theory allows full-dimensional classical treatment of the motions of all adsorbate and substrate atoms, responding self-consistently to the excitation and de-excitation of EHPs. In addition, all input to the theory is computable, at least in principle, by *ab initio* methods. However, as discussed above, the theory rests on a 'weak coupling approximation'. As a result, it is suspect in cases for which non-adiabatic couplings are strong, such as at avoided crossings or when electron hops occur. As is presented below, there is now growing evidence that, at least in some cases, large-amplitude vibrational motion associated with passing over a chemical transition state may strongly couple to electrons in the metal. The latter may be fairly common as a result of the image potential stabilization of ions near metal surfaces. Figure 1(*a*) is a schematic illustration of the potential energy curves for a molecule such as nitric oxide approaching a metal surface. At large distances *z* from the surface, the lowest potential energy curve corresponds to the molecule in its

(*a*) Simple Avoided Crossing



(*b*) Incident Molecule A



(*c*) Scattered Molecular Anion A-

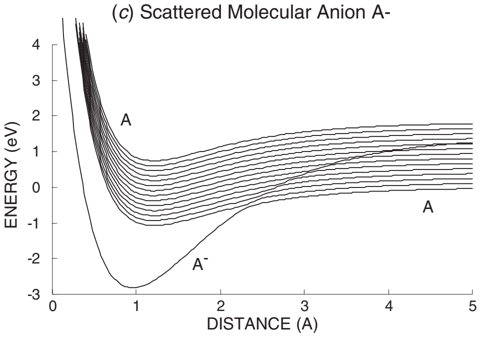


Figure 1. Schematic one-dimensional models of the electronically non-adiabatic mechanisms that are possible in the case of electron transfer.

neutral ground state. There will also be higher potential energy curves, not shown, corresponding to excited states of the neutral molecule. In addition, the figure shows an 'ionic' potential curve describing the interaction of the molecular negative ion with the surface, which at large z is displaced upwards in energy from the ground state curve by $\phi - E_a$, where ϕ is the work function of the metal and E_a is the electron affinity of the molecule. As the molecule approaches the surface, the energy of the lowest neutral state begins to decrease because of the attractive interaction with the surface. The energy of the molecular ion generally decreases much faster, however, because of the z^{-1} image attraction between the ion and the metal. At some distance z_c, the energy of the molecular ion may cross below that of the neutral. The adiabatic (Born–Oppenheimer) potential energy surfaces will not cross, however, but will exhibit an 'avoided crossing' as indicated in figure 1(*a*). In the region near the crossing point the adiabatic states are a mixture of ionic and neutral configurations. As the neutral molecule approaches the surface, the adiabatic pathway is to remain on the same (lowest) adiabatic potential energy surface; that is, the adiabatic pathway exhibits an electron jump from the surface to the molecule. If the molecule moves through the crossing region rapidly, however, there may not be time for the drastic rearrangement of electron density that results from an electron transfer event to occur, and the system will remain with at least some probability in its neutral state; thus a non-adiabatic transition to the excited potential energy surface will occur. This is the reason for the appearance of the nuclear velocity in the Massey criterion, equation (8). Note that the attractive gas–surface potential will accelerate the incoming molecule so that, even in the limit of zero incident velocity, the BOA may be invalid.

Figure 1(*a*) describes an isolated avoided curve crossing as occurs typically in gas-phase collisions, for example between an alkali atom and a halogen atom, or perhaps in collisions of molecules with insulator or semiconductor surfaces. Collision of a molecule with a metal surface poses additional complexity, as illustrated in figures 1(*b*) and 1(*c*). The neutral molecule approaches the metal surface on a potential energy surface similar to that of figure 1(*a*). However, instead of a single ionic potential energy surface, there is a continuum of surfaces. The continuum is indicated in figure 1(*b*) by closely spaced, discrete curves. The lowest member of the continuum corresponds, as before, to the energy of removing an electron from the Fermi level of the metal and placing it on the molecule. But at absolute zero Kelvin, an electron can be removed from any energy level below the Fermi level as well, giving rise to ionic curves of the same shape but shifted to higher energy. At non-zero temperature there is some electron population above the Fermi level, resulting in a downward creep and smearing of the low-energy edge of the continuum. As the neutral molecule approaches the surface, the neutral PES will enter the ionic continuum and an electron hop may occur. The process will be adiabatic only if the electron hop occurs at the instant the bottom of the continuum is reached. But this is prohibited by the uncertainty principle; there must always be some non-adiabatic penetration into the continuum prior to the electron jump. There has been very little discussion in the literature, however, about the extent of this non-adiabatic behaviour and its consequences.

After the molecule scatters from the repulsive part of the gas–surface potential and begins to recede from the surface, in the above example, its ground state will initially correspond to the negative ion. We represent this in figure 1(*c*) as an isolated potential energy curve. For illustration purposes we have removed the continuum of higher energy ionic states. This amounts to the questionable assumption that any excited conduction electrons or holes that might have been formed during the approach and hard collision phases of the scattering process have become delocalized or have moved far enough away from the impact site that they no longer play a role. Now, as the molecule recedes from the surface, it enters a continuum of neutral PESs, as shown in figure 1(*c*). The lowest of these corresponds to transfer of the electron from the molecule to the Fermi level of the metal. The higher levels correspond to transferring the electron to empty levels above the Fermi level. As in the incoming phase, there will inevitably be some non-adiabatic behaviour in the outward phase as well, leaving behind an excited conduction electron.

As illustrated in figure 1, the non-adiabatic excitation of electrons will be accompanied by loss of translational energy of the scattered molecule. However, the electron binding energy of a diatomic molecule often depends sensitively on its internuclear separation. This is certainly the case for the nitric oxide molecule, as will be discussed later. In addition, image stabilization of the ion may depend upon the molecular orientation, particularly for molecules with large dipole moments or strongly orientated bonding. This provides a mechanism for non-adiabatic transfer of vibrational and rotational energy. This mechanism can modify the widely discussed Franck–Condon mechanism for vibrational energy transfer in collisions of molecules with metal surfaces (Gadzuk 1983; Newns 1986). Referring again to figure 1(*a*), the molecule in its ground vibrational state approaches the metal surface on the ground state (neutral) PES. If it passes through the avoided crossing region adiabatically, it will remain in the ground state, thereby becoming a negative ion. The molecular negative ion will in general have different equilibrium bond lengths and force constants 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 result 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 mixing of vibrational states. Although this process involves electron transfer, it is not *per se* a non-adiabatic 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 of the surface 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, according to the arguments given above in discussing figures 1(*b*) and 1(*c*), the electron transfer events will inevitably involve some non-adiabatic behaviour, resulting in excitation of EHPs. The ground state must change character from neutral molecule to negative ion and back to neutral sufficiently suddenly that the vibrational state of the molecule is altered. (The Franck–Condon principle is a consequence of the sudden approximation.) The more sudden the electron hop, the more serious the breakdown of the BOA. The importance of this non-BOA behavior has not been assessed, however, and it remains difficult to unravel the role of electronic excitations from other mechanisms of vibrational energy transfer; phonons, hard impact and adiabatic charge transfer.

Although effects of electronic excitations can be included phenomenologically in simulations of molecule–surface dynamics, there have been only a few attempts at quantitative and predictive theoretical treatments. One of these is the MDEF approach discussed above, in which *ab initio* expressions were obtained for the strengths of the coupling of EHPs to translational, vibrational and rotational motions. A related *ab initio* study of EHP friction upon scattering of a hydrogen atom with a metal surface has been carried out recently (Trail *et al.* 2002). As the projectile is an atom, this work does not address vibrational energy transfer, but the approach might be extendable to molecules. Furthermore, the method allows calculation of the energy distribution of excited electrons in the metal. This is a valuable observable that is crucial to experimental findings discussed below. Both of these methods are perturbative, however; they are frictional theories that apply to cases for which the electron density changes relatively gradually in response to nuclear motion. It is not clear how these approaches can be extended to describe the sudden and drastic change of electron density that accompanies a charge transfer event.

Li and Guo (2002) have reported a non-perturbative treatment of electron-induced vibrational energy transfer at metal surfaces. They introduce hops between neutral and negative ion states of the molecule via a Monte Carlo wave packet solution to the Liouville–von Neumann equation. This is a restricted dimension calculation with empirical parameters, but it represents a promising alternative to friction models that is capable of introducing multiple-quantum vibrational transitions, shown experimentally to be important, as discussed below.

In the following sections of this review, we present the results of a number of fascinating experiments that have been designed to assess the range of validity of the BOA in gas–surface dynamics. Most of these experiments have examined non-reactive, vibrationally inelastic processes for which quantitative, state-to-state measurements can be carried out and definitive conclusions can be extracted. They have direct bearing, however, on the dynamics of chemical reactions at surfaces where bond breaking is preceded by large-amplitude vibrations. Most recently, these vibrationally inelastic scattering experiments have been extended to include very high vibrational states of diatomic molecules, where the amplitude of vibration is comparable to bond-breaking events and electronically non-adiabatic effects appear to be crucial. An important conclusion arising from the review of experimental evidence is the need for more advanced theoretical approaches to the electronically non-adiabatic nature of chemistry at metal surfaces.

3. First evidence of Born–Oppenheimer breakdown

Perhaps the first evidence for the breakdown of the BOA for adsorbates at metal surfaces arose from the study of infrared reflection–absorption line-widths of adsorbates on metals, a topic that has been reviewed by Hoffmann (1983). In the simplest case, we consider the mechanism of vibrational relaxation operative for a diatomic molecule that has absorbed an infrared photon, exciting it to its first vibrationally excited state. Although the interpretation of spectral line-broadening experiments is always fraught with problems associated with distinguishing homogeneous from inhomogeneous effects, some simple adsorbate systems seem to exhibit sufficiently rapid vibrational relaxation that the homogeneous contribution to line-width resulting from relaxation of the adsorbate to the surface is observed.

Persson and Persson (1980a,b) suggested a simple model for understanding the line-broadening of CO on metals. Here it was recognized that CO binds to many metals by 'back-bonding', where electron density from the metal flows into the π^* C–O anti-bonding orbital, creating a strong coupling between the M–CO bond and the C–O motion. Thus, as the CO bond vibrates, electron charge is expected to oscillate in and out of the π^* orbital. This temporal and spatial oscillation of charge can be treated as a short-range vibrational damping mechanism for CO vibration resulting in the excitation of metallic electrons. This model makes predictions that line-widths increase with degree of back-bonding, an expectation that has been borne out, at least qualitatively, by experiment (Hoffmann 1983).

More recently, the application of sub-picosecond, time-resolved pump–probe methods revealed the timescale for vibrational relaxation of a diatomic molecule at a metal surface directly (see, for example, Beckerle *et al.* 1991; Morin *et al.* 1992; Cavanagh *et al.* 1995). In comparison to vibrational relaxation on NaCl salts (Huan-Cheng and Ewing 1990), which occurs on the millisecond timescale, another relaxation mechanism is clearly at play. MDEF theory of vibrational relaxation gave agreement with observed picosecond timescales for CO on copper (Head-Gordon and Tully 1992).

Gas–surface scattering experiments have long played an important role in the investigation of the nature of the interactions of molecules with metal surfaces. One of the most significant experimental findings was also one of the simplest (Rettner *et al.* 1985, 1987). Here, a molecular beam of nitric oxide (NO) was allowed to collide with a crystalline Ag(111) metal surface. The NO was seeded in a light carrier gas to control the incidence energy of the sample and the surface temperature could also be varied. A pulsed laser beam was used to probe the population in selected quantum states of the scattered NO molecules. By varying the surface temperature and incidence energy while probing the scattered population in selected rotational levels of NO($v=1$), the nature of the vibrational coupling to the metal surface could be observed.

Observed angular distributions were quasi-specular and scattered rotational distributions were strongly dependent upon the incidence energy, both observations indicating the direct nature of the interaction. The most important observation of the work was the approximately Arrhenius surface temperature dependence of the vibrational excitation probability, exhibiting an effective activation energy close to the vibrational excitation energy of the scattered molecule. The authors also showed that the population of excited EHPs at an energy resonant with the NO($0-1$) vibrational spacing exhibited the same temperature dependence as that observed in the experiment. While still indirect, the implication was obvious: recombination of hot EHPs was responsible for vibrational excitation of the scattered molecules. This was the strongest evidence available at the time that thermally excited electrons could interact strongly enough with nuclear motion to induce changes in vibrational state in a molecule at the metal surface.

Much theoretical work went into trying to understand these results more completely. Newns (1986) constructed a simple one-dimensional model that incorporated the idea of electrons hopping in and out of the π^*–anti-bonding orbital of NO as the means by which hot EHPs could transfer energy to the NO molecule. Using reasonable assumptions, he was able to quantitatively reproduce the experimentally observed surface temperature and incidence energy dependence.

However, others reached more ambiguous conclusions. Gates and co-workers developed a two-dimensional model based on coupling NO vibration to surface phonons, but ignoring the possible role of EHPs, and successfully captured the essential experimental results (Gates and Holloway 1994; Gates *et al.* 1994). Gross, Brenig and co-workers also showed that it was not necessary to invoke hot EHPs to reproduce these experimental observations (Gross *et al.* 1991; Gross and Brenig 1993a,b). In these models, the PES was important in coupling NO vibration to surface phonon motion. Taking into account the softening of the NO bond upon bonding to Ag, model calculations could account for most of the characteristics of the vibrational exchange.

In the meantime other experiments have improved our range of observational results. For example, Watts *et al.* (1997) carried out experiments very similar to the NO/Ag(111) experiments described above. An important difference in this work was the substitution of Cu(110) for the Ag(111). Despite the chemically distinct metal surface, nearly identical results were obtained to those using Ag(111) (Rettner *et al.* 1985, 1987), in particular with regard to the surface temperature and incidence energy dependence. While it is not unlikely that the bond softening of NO is similar on Ag(111) and Cu(110), there is no *a priori* reason to believe that these two metals would exhibit the same incidence energy and surface temperature dependence in vibrational excitation experiments. More importantly, there has not been a theoretical attempt to explain why these two chemically distinct systems behave so similarly within the context of electronically adiabatic models.

However, the similarity between metals is a characteristic of the electron-mediated vibrational energy transfer models. Here, only the population of excited EHPs at the energy of vibrational excitation must be calculated, a quantity that is fairly similar for many metals. Unless the role of surface electronic states is included, only differences in the density of electronic states near the Fermi level are expected to distinguish one metal from another.

Theoretical advances were also forthcoming. By comparing different models, some involving EHPs and others without, Gross and Brenig (1993a,b) were able to make predictions about the incidence energy dependence of vibrational de-excitation, a characteristic of the interactions that had not yet been experimentally investigated. According to their work, observation of strong incidence energy dependence to the vibrational de-excitation probability would be an expected characteristic of electron-mediated vibrational energy transfer.

Experiments to measure the vibrational de-excitation of NO scattered from a metal surface are much more challenging than those already described. Both a source of vibrationally excited molecules and a means of detecting the results of the scattering interaction are required, necessitating the use of at least two lasers in harmony with an ultra-high vacuum surface scattering apparatus. Furthermore, it might be thought that simply laser exciting NO($v = 0 \rightarrow 1$) would suffice to produce a vibrationally excited sample. This approach fails, however, because of a trivial background problem. When an attempt is made to detect the vibrationally relaxed sample in $v = 0$, ambient NO in the experimental chamber obscures the results.

These problems were overcome recently. By using overtone excitation of NO($v = 0 \rightarrow 2$) as the means of preparing a sample of vibrationally excited molecules, both excitation to $v = 3$ and de-excitation to $v = 1$ resulting from collisions with a Au(111) surface could be observed without difficulty (Huang *et al.* 2000a,b). The authors systematically investigated the incidence energy and surface temperature dependence of vibrational excitation and de-excitation. Strong incidence energy dependence of the vibrational de-excitation (figure 2) was indeed observed, providing

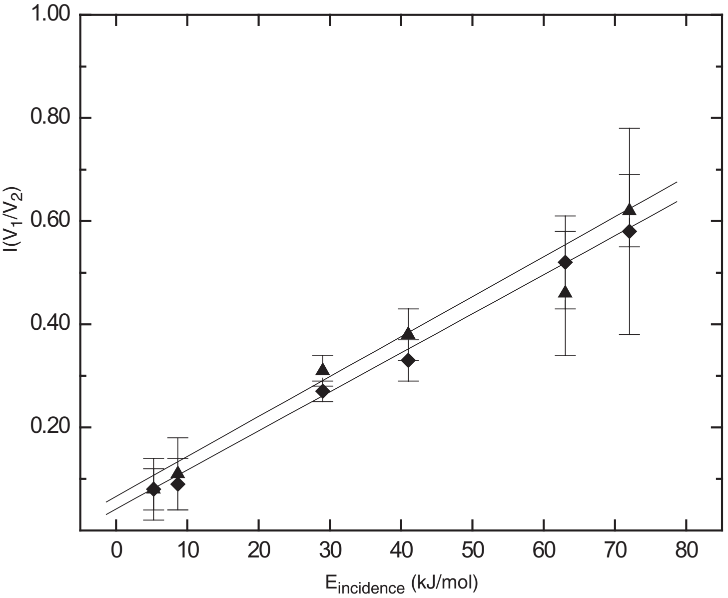


Figure 2. Incidence kinetic energy dependence of the relaxation probability for NO($v=2$) scattering from Au(111). Relaxation of NO($v=2\rightarrow1$) $T_s=480\,\text{K}$ (▲) and $T_s=300\,\text{K}$ (◆). Unbroken lines are linear fits to the data. The strong incidence energy dependence was taken as evidence for electronically non-adiabatic influences. (From Huang *et al.* 2000a.)

additional evidence of the importance of electron-mediated vibrational energy transfer.

In light of the accumulated evidence, it seems likely that the scattering of NO from metals does induce electronic transitions, representing a fundamental breakdown of the BOA. Clearly this falls in the category of electronically non-adiabatic phenomena that we set out to understand. But there is a broader question. Is the Born–Oppenheimer breakdown significant within a broader chemical context?

This question has been the subject of theoretical study using MDEF (Tully *et al.* 1993; Springer *et al.* 1994; Head-Gordon and Tully 1995; Kindt *et al.* 1998). Using this model, the researchers tried to investigate important chemical processes at metal surfaces to deduce the role of electronic non-adiabaticity. In particular, they have investigated the importance of EHP excitation in scattering, sticking and surface mobility of CO on a Cu(100) surface (Tully *et al.* 1993; Kindt *et al.* 1998). Those studies indicated that the magnitude of energy transferred by coupling to the electron bath was significantly less than that coupled to phonons. Thus the role of EHP excitation in determining the sticking probability was found to be small in this work (Kindt *et al.* 1998). In a similar way, coupling of EHPs to molecular rotation and translation was found to be weak and the dominant interactions controlling exchange of these degrees of freedom with the surface were associated with phonons. These results are also not inconsistent with the results presented above. Indeed, the largest interactions of EHPs were with the molecular vibrations (Tully *et al.* 1993).

It might therefore seem that electronically non-adiabatic interactions are important for vibrational energy transfer but perhaps for little else. This alone might be of some significance to chemistry. The rate at which vibrational energy contained in molecular adsorbates comes to thermal equilibrium with the metal surface is undoubtedly of importance to an understanding of surface reactions. But there are more fundamental questions that we have so far ignored. Up to this point we have taken for granted that vibrational exchange with electronic degrees of freedom is a good indicator of Born–Oppenheimer breakdown. Specifically, we assume that observation of vibrational transitions in NO from $v = 0$ to $v = 1$ tells us something about the validity of the BOA in surface chemistry.

Clearly, this view can provide only a general guide to this important question. There are fundamental differences between the nuclear motions associated with a surface reaction when compared to molecules making transitions between their lowest vibrational states. Surface chemical reactions—indeed all reactions—are characterized by large-amplitude nuclear motion, which is accompanied by a profound reorganization of the electrons binding the nuclei together. An obvious example is the dissociative adsorption of a diatomic molecule, which requires vibrational excursions comparable to, indeed greater than, the equilibrium bond length. During these large-amplitude excursions, substantial electronic reorganization is expected including: (1) bonding electrons becoming non-bonding or anti-bonding electrons between the diatomic, (2) orbital population transfer to form bonding interactions with the metal, and (3) charge transfer from or to the metal to create charged atomic species on the surface. Reactions such as dissociative adsorption are characterized by 'multiple assaults on the summit', involving large-amplitude nuclear motion that might by coupled to the electron bath in a very different way from molecules that remain near their equilibrium geometries.

To add to this, bond stretching can, and does, have a dramatic influence on the ability of a molecule to bind electrons. Dissociation of many closed-shell molecules, for example HCl, transforms two atoms cohabitating in a fashion that repels electrons into a non-interacting pair of 'electron attractors'. The electron affinity of HCl is indeed negative, whereas the combined electron affinities of H and Cl atoms exceeds 3 eV. This picture suggests that molecules subjected to the rigours of large-amplitude vibrational motion typical of reacting systems might undergo the kind of electron hopping envisioned by Newns (1986) with much greater alacrity than molecules residing near their equilibrium structures. In the following section we review the present evidence available on electronically non-adiabatic effects for large-amplitude heavy-atom motion near a metal surface.

4. Born–Oppenheimer breakdown in surface reactions

Experimental probes of Born–Oppenheimer breakdown under conditions where large-amplitude vibrational motion occurs are now becoming available. One approach to this problem is to compare theoretical predictions and experimental observations for reactive properties that are sensitive to the Born–Oppenheimer PES. Particularly useful in this regard are recombinative desorption and Eley–Rideal reactions. In both cases, gas-phase reaction products may be probed by modern state-specific detection methods, providing detailed characterization of the product reaction dynamics. Theoretical predictions based on a Born–Oppenheimer PESs should be capable of reproducing experiment. Observed deviations between experiment and theory may be attributed to Born–Oppenheimer breakdown.

An interesting body of work merits the reader's attention concerning the Eley–Rideal reaction of H-atom abstraction of chlorine atoms adsorbed on gold (Jackson *et al.* 1994; Rettner 1994; Rettner and Auerbach 1994; Rettner *et al.* 1996).

$$\mathrm{H(g) + Cl - Au(111) \rightarrow HCl(g)} \quad \Delta \mathrm{E} \sim -230\,\mathrm{kJ/mol}.$$

The energetics of the Eley–Rideal reaction ($\Delta\mathrm{E} \sim -230\,\mathrm{kJ/mol}$) are well established (Kastanas and Koel 1993). Here, the highly exoergic reaction forming gas-phase HCl was probed by time-of-flight velocity measurements (Rettner 1994; Rettner and Auerbach 1994), scattering angular distributions (Rettner 1994; Rettner and Auerbach 1994) and state-selective laser spectroscopy (Jackson *et al.* 1994; Rettner 1994; Rettner and Auerbach 1994).

Despite the large exoergicity, less than about 100 kJ/mol appears as HCl translation, rotation or vibration. On average, 60 kJ/mol appears as HCl translation, 30 kJ/mol appears as HCl vibration (peaks in $v = 1$) and 10 kJ/mol as rotation (Rettner 1994). Thus, on average, over half of the available energy is transferred to the solid. It was argued by Rettner (1994) that despite possessing similar energetics, the Eley–Rideal reaction is qualitatively different from the gas-phase reaction:

$$\mathrm{H + Cl_2 \rightarrow HCl + Cl} \quad \Delta\mathrm{E} \sim -195\,\mathrm{kJ/mol},$$

where the vibrational population distribution of HCl peaks in $v = 3$ (Anlauf *et al.* 1972). Strong coupling of HCl vibration to metal electronic motion was mentioned as the most likely explanation of the apparent absence of HCl product vibrational excitation (Rettner 1994). Note also that, at least for low coverage, Cl bound to Au will possess an excess negative charge ($\mathrm{Cl^-}$) that must be transferred to the metal surface when HCl departs (Rettner 1994), clearly indicating the possible importance of electronically non-adiabatic effects in this system.

It should also be mentioned that a theoretical model using an empirical LEPS PES has been used successfully to reproduce the vibrational population distribution of the products of this surface reaction (Jackson *et al.* 1994). This approach confines itself to the assumptions of the BOA and underscores one of the major questions remaining in this field: Do we just need better Born–Oppenheimer potential surfaces or do we need a different theoretical approach?

Luntz and colleagues have recently carried out an impressive study that follows in the spirit of the Eley–Rideal work (Diekhoner *et al.* 2002). Specifically, laser-assisted recombination of N-atoms desorbing to form gas-phase N_2 on Ru(0001) was investigated. Experimental measurements of state-selectively detected N_2 recoiling from the surface recombination event were obtained using resonance-enhanced multiphoton ionization and ion time-of-flight methods. In this way translational energy distributions of individual rovibrational states could be obtained experimentally. In addition, N_2-vibrational population distributions could be derived.

This reaction is an interesting test of the modern approach to chemical reactivity. DFT calculations have been used to construct a PES for this reaction (Murphy *et al.* 1999). The transition state for this reaction occurs at an N–N separation of ~ 1.85 Å. Furthermore, the energy release from the transition state to products is very large (250 kJ/mol). From the point of view of Polanyi and his famous characterization of reactive PESs, N-atom recombination from a Ru surface is an early barrier reaction (Polanyi 1972); that is, the transition state resembles the reactants. Early barrier reactions are well known to channel large amounts of the reaction exoergicity into product vibration. For example, the famous chemical-laser reaction, $F + H_2 \rightarrow HF(v) + H$, is such a reaction producing a highly inverted HF vibrational distribution (Parker and Pimentel 1969; Polanyi and Tardy 1969; Schafer *et al.* 1970; Chapman *et al.* 1998). Luntz and co-workers carried out a classical trajectory calculation on this Born–Oppenheimer PES and found that the properties of this early barrier reaction do indeed include an inverted N_2 vibrational distribution that peaks near $v = 6$ and extends to $v = 11$ (figure 3(*a*)). In marked contrast to these theoretical predictions, the experimentally observed N_2 vibrational distribution is

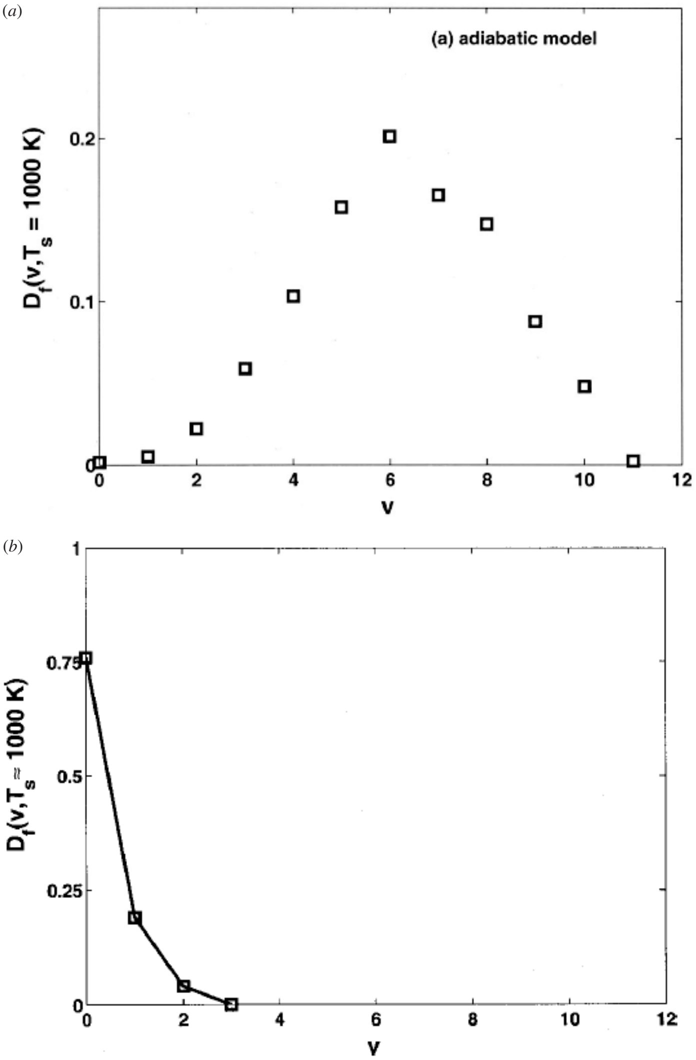


Figure 3. Vibrational population distributions of N_2 formed in associative desorption of N-atoms from ruthenium. (*a*) Predictions of a classical trajectory-based theory adhering to the Born–Oppenheimer approximation. (*b*) Experimentally observed distribution. The qualitative failure of the electronically adiabatic approach provides some of the best available evidence that chemical reactions at metal surfaces are subject to strong electronically non-adiabatic influences (see Diekhoner *et al.* 2002).

skewed towards low values of *v* (figure 3(*b*)). Diekhoner *et al.* (2002) also used the electronic friction theory of Tully and Head-Gordon (Head-Gordon and Tully 1995) in an attempt to model electronically non-adiabatic influences to the reaction, first using the friction coefficients as adjustable parameters (Diekhoner *et al.* 2002) and later using friction coefficients calculated with quantum chemical techniques (Luntz and Persson, in press). Of course, the more meaningful results came from the *ab initio* calculations of friction, which showed dramatically larger friction coefficients than Tully's work for CO on Cu. More importantly, the friction was seen to increase significantly for configurations near the transition state of the reaction. Unfortunately, while the *ab initio* accounting of friction did result in a strong coupling of N_2 vibration to EHP excitation, qualitatively consistent with experiment, the theoretically predicted effect was too small to lead to good agreement with experiment (Luntz and Persson, in press). The results imply that we require new theoretical methods capable of going beyond the weak coupling approximation of the molecular dynamics with electronic friction theory.

One of the most significant recent insights in surface chemical dynamics is the idea that the principle of detailed balance may be used to infer the properties of a dissociative adsorption reaction from measurements on an associative desorption reaction (Rettner *et al.* 1991; Michelsen *et al.* 1993). This means, for example, that the observation of vibrationally excited desorption products is an indicator that the dissociative adsorption reaction must be vibrationally activated, or vice versa, the observation of vibrationally cold desorption products indicates little vibrational promotion of dissociative adsorption. In this spirit, it is valuable to think carefully about the Luntz work from the point of view of detailed balance.

The picture of the reaction that emerges is interesting, suggesting that the newly forming diatomic molecule whose bond is still dramatically stretched exhibits a tendency to release enormous amounts of vibrational energy into metal electron degrees of freedom during vanishing short times; in fact, more energy than can be described by a friction theory. This explains, at least qualitatively, the observation that the reaction probability for dissociative adsorption of N_2 to ruthenium approaches only about 1% even when the available energy significantly exceeds the Born–Oppenheimer predicted reaction barrier (Diekhoner *et al.* 2001). Apparently, in the course of approaching the transition state, the reaction is subject to strong energy-transfer phenomena from vibrational to metal-electron motion, an energy drain that naturally suppresses reaction. If this picture is correct, one must pity the N_2 molecule as it confronts the ruthenium surface. Not only does it have an uphill battle to reach the transition state but also upon its approach it is confronted with unprecedented energy loss channels that rob it of its reactive energy! On the other hand, if the surface were at an elevated temperature, rapid transfer of energy from excited EHPs to the adsorbate could possibly replenish energy lost as the molecule climbs the reaction barrier. In the limit of very efficient energy transfer, the adsorbate degrees of freedom will remain equilibrated at the surface temperature throughout the transition state region, thereby fulfilling the condition for validity of transition state theory. In this limit, reaction probabilities are determined by the topography of the PES at the transition state; the specific modes and pathways of energy transfer become irrelevant.

Recently, similar evidence has been found from detailed comparisons between experiment and theory of the reaction of molecular oxygen with aluminium surfaces. Molecular beam experiments yielding the dissociative reaction probability in this

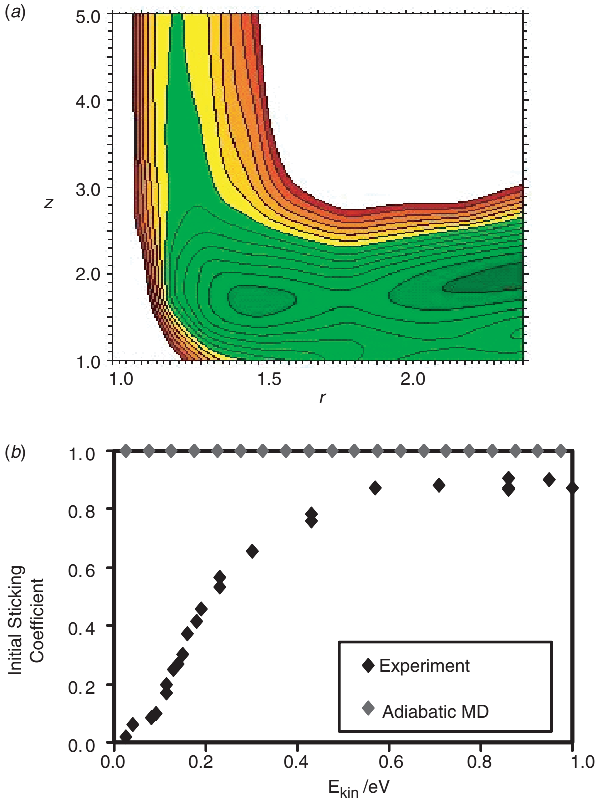


Figure 4. The reaction of oxygen on aluminium. (*a*) Recent density functional theory calculations of the electronically adiabatic potential energy surface show no barrier to dissociative adsorption (Behler *et al*., submitted). (*b*) Experimental investigations of the incidence energy dependence of the reaction probability suggest that the reaction is activated by translational energy (Österlund *et al*. 1997). This is another example where the predictions of the potential energy surface calculated within the BOA would make incorrect predictions about the reaction.

system were found to rise dramatically with O_2 incidence energy (figure 4(*b*)), reaching a value near unity only at incidence energies above ~0.6 eV (Österlund *et al*. 1997). Experimental data like this are often taken to indicate the presence of a substantial activation barrier on the electronically adiabatic PES, assuming that the BOA holds. It was therefore particularly startling when recent calculations of the BOA adiabatic PES using DFT showed the complete absence of any barrier (Behler *et al*. 2004; see figure 4(*a*)). Behler *et al*. pointed out that one difficulty with using the BOA approximation is in the treatment of the system's proper spin state. These workers calculated a spin-restricted adiabatic PES, where O_2 is forced to remain in its triplet state and cannot exchange spin with the metal. In this case, a substantial potential barrier is indeed present; however, the triplet barrier is substantially larger than the observed incidence energies where reaction is efficient. To reconcile this, Behler *et al*. invoked the possibility of excited electronic states that correlate either with $O_2(^1\Delta)$ or with O_2^-, which cross the triplet potential at an energy below its barrier. While not able to account quantitatively for the incidence energy dependence of the reaction probability, this work again points to the fact that important chemical realities are overlooked when one uses the BOA in the treatment of reactions at metal surfaces.

This work and also the nitrogen on ruthenium work are consistent with the observation made on the H/Cl/Au Eley–Rideal chemistry and, taken together, the implications of these three pieces of work are quite fundamental in nature, suggesting that an accurate theory of surface reactions cannot be constructed without accounting for strong coupling between the reaction coordinate and the metal's electron bath.

In the next section we describe more direct experiments that indicate the nature of the interactions when molecules in states of large-amplitude heavy-atom motion interact with metals surfaces.

5. Experiments with state-selected highly vibrationally excited molecules

The work we have reviewed so far suggests that molecules that undergo large-amplitude vibrational motion typical of passing through a transition state may interact much more strongly with metallic electrons than do vibrational ground-state molecules. Yet studies of the sort so far described are admittedly indirect. A proper theoretical treatment of surface chemistry involves many degrees of freedom and, with technology available in the foreseeable future, it will remain necessary to carry out reduced dimensionality calculations. The BOA is in fact an example of one way to reduce the number of (electronic) degrees of freedom. Thus, in some sense we should not be surprised when energy transfer to and from the 'missing degrees of freedom' turns out to be important. However, there are other missing degrees of freedom, in particular phonons. Do molecules passing over transition states interact with phonons in important ways that have yet to be fully understood? In addition to the class of questions associated with ignoring certain degrees of freedom, we must also ask more mundane questions about some of the work described in the last section. Specifically, is the Born–Oppenheimer PES accurate enough? In light of these considerations, it is clearly useful to attempt more direct kinds of experiments that test the important ideas emerging from the study of surface chemistry.

One implication of the N_2/Ru work is that molecules in high states of vibrational excitation, which are in the process of bond formation, exchange energy with metallic electrons in a remarkable way. Recombining N-atoms that are expected to form N_2 in vibrational states as high as $v = 11$ (with more than 200 kJ/mol of vibrational energy) are observed primarily in $v = 0$. The time available for this to take place is on the order of 10s of fs. Such efficient, rapid and large-scale energy transfer may at first glance appear outlandish. Direct observation of such chemically interesting behaviour is necessary to support this line of reasoning.

Experiments designed to probe these ideas have been carried out for NO in high vibrational states ($v \leq 18$) colliding with Au(111) surfaces. Before considering the results of these experiments, let us first look at how vibration might lead to unusual interactions with metal electrons. Molecules in these high vibrational states undergo nuclear excursions that influence their electronic properties. In contrast to the $v = 0$ state, whose vibrational amplitude is on the order of 0.1 Å, the $v = 15$ state of NO exhibits vibrational amplitudes close to the magnitude of the bond length [$R_e = 1.15$ Å, $R_{min}(v = 15) = 0.8$, $R_{max}(v = 15) = 1.6$]. *Ab initio* quantum chemical calculations (Cornelius McCarthy *et al.* 1998) of NO and NO^- can be used to discover the bond length dependence of the energetics of electron binding (denoted as the vertical electron binding energy) to NO (Huang *et al.* 2000a,b). Such analysis reveals that the vertical electron binding energy to NO is a strong function of the internuclear separation. This idea harkens back to ideas originally put forward by Dennis Jacobs when considering the scattering of NO^+ and NO^- from metal surfaces (see, for example, Qian *et al.* 1995 and references therein). This viewpoint leads us to realize that with respect to electron transfer, highly vibrationally excited NO has a 'split personality'. Near its outer turning point, it may attach an electron, releasing more than 2 eV of energy. Near the inner turning point, the molecule exhibits repulsion energy towards electrons of a similar magnitude.

This insight has important implications for any electron hopping induced vibrational energy transfer model. Consider the one put forward by Newns (1986). In the one-dimensional Newns' model, two electronic states of the system are important. The ground state represents the interaction of a neutral NO molecule with the metal surface. This interaction is relatively weak, resulting in a shallow physisorption well. The excited electronic state of the system is formed by removing an electron from the Fermi level of the metal and attaching it to the NO molecule. The interaction of the ion with its image charge lowers this state's energy as the molecule approaches the surface. The point at which the two curves cross is influenced strongly by the work function of the metal and the electron binding energy to the molecule. For NO near its equilibrium bond length (1.15 Å), the electron binding energy is very small and a barrier to the crossing associated with electron hopping results. By comparison, when the molecule is stretched, approaching the outer turning point of a high vibrational state, the much larger vertical electron binding energy eliminates the Newns-like barrier. This means that electron transfer from metals to stretched molecules may be much more facile than when the molecule is near its equilibrium bond length.

These considerations suggest a possible mechanism for energy transfer between metallic electrons and large-amplitude vibration in NO, where an electron is transferred from the metal to the molecule when the bond is stretched near the outer turning point to vibration (see figure 5). The newly formed NO^- will then compress the bond as vibration continues. This has the effect of raising the potential energy of the electron far above the Fermi level as the vertical binding energy of the electron to the molecule is reduced and may even become negative. The electron may then detach from the NO^- and enter unoccupied energy levels of the metal far above the Fermi level.

This model, which is a two-dimensional extension of the one-dimensional Newns picture, leads to two dramatic predictions, both of which are seen in experiment. First, it predicts that vibrational energy exchange will be possible at low incidence energies, in contrast to electron-mediated vibrational energy transfer in low vibrational states (Rettner *et al.* 1985, 1987; Watts *et al.* 1997). Second, it implies that large amounts of vibrational energy may be converted to metallic electron excitation as the range of electronic excitation depends so strongly on internuclear vibration.

Such experiments have recently been successfully carried out (Hou *et al.* 1999a,b,c; Huang *et al.* 2000b; Wodtke *et al.* 2003). Using stimulated emission pumping (Hamilton *et al.* 1986; Yang *et al.* 1993; Silva *et al.* 2001), highly vibrationally excited NO was prepared in states as high as $v = 15$ and state-to-state scattering experiments were carried out on a Au(111) surface. By seeding the NO in a

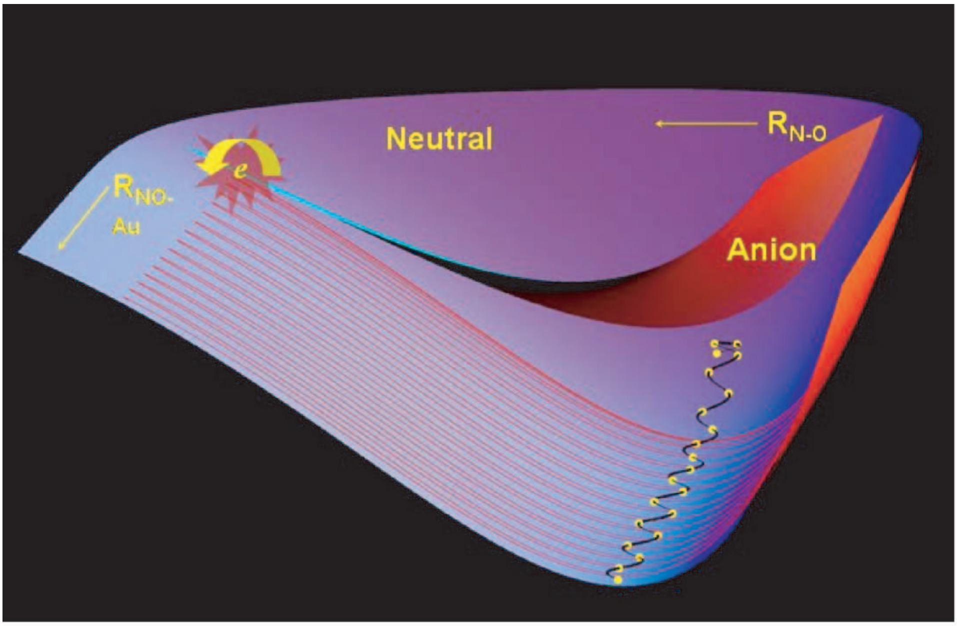


Figure 5. The emerging picture of electronically non-adiabatic interactions of NO molecule scattering at a metal surfaces. Transition from the ground electronic state to an anionic state that is strongly attractive to the metal surface can be accomplished by high translational energy when vibrational excitation is low (black trajectory). When vibrational motion is highly excited, even low translational energies allow transition to the anionic state (red trajectory). (From Hou *et al.* 1999a, b, c; Huang *et al.* 2000b; Wodtke *et al.* 2003.)

heavier carrier gas, it was possible to lower the incidence energy to 5 kJ/mol. State-selective laser detection methods were used to make measurements from which the scattered vibrational state distribution could be derived.

The scattered vibrational population distribution is remarkable. First, only a small fraction of the prepared population remains in the initial vibrational state, indicating that the survival probability is at most a few per cent. At this low incidence energy, similar experiments carried out with NO($v=2$) scattering from Au(111) were unable to detect vibrationally inelastic processes; that is the vibrational survival probability is near unity (Huang *et al.* 2000a).

Even more remarkably, vibrational relaxation of NO($v=15$) on Au(111) is characterized by an unprecedented multiquantum vibrational relaxation. Specifically, the most probable vibrational scattering channel releases more than 1.5 eV. Vibrational relaxation events exchanging as many as 10 vibrational quanta were observed. It seems likely that even more vibrational quanta can be exchanged with significant efficiency, but background problems prevented the observation of these channels. Thus the reported vibrational population distribution terminates below $v=5$.

Recently, Monte-Carlo wave packet calculations using the electron transfer mechanism described above have been able to reproduce these experimental results, at least qualitatively (Li and Guo 2002). This work also investigated the idea of an electron being transferred to and from the metal at different average internuclear separations. By analysing the results of the calculation, it was possible to deduce that, on average, the electron transferred to the molecule at a significantly larger NO bond distance than when the electron transferred back. Although there may still be important aspects of this energy transfer process that are not fully understood, this result is in clear conceptual agreement with the ideas put forward above.

Angular distributions of the scattered products were also measured in this work by translating the probe laser in front of the Au(111) surface. These were found to be sharply peaked and rotational distributions were strongly dependent upon incidence energy. These observations indicate a direct, near-specular scattering mechanism. The timescale of interaction for specular scattering events is similar to that of surface chemical reactions, such as the time required for recombining N-atoms on Ru near the transition state to reach the asymptotic limit. In light of these observations, the interpretations of Luntz and co-workers regarding the electronically non-adiabatic effects in Haber–Bosch chemistry appear to be supported (Diekhoner *et al.* 2002).

Further evidence for strong coupling between large-amplitude vibration and metallic electrons was found by carrying out similar experiments with an insulator surface (Huang *et al.* 2000b; Wodtke *et al.* 2003). In this work vibrational relaxation of NO($v = 12$) was investigated on a LiF crystalline surface. Incidence energy and surface temperature were varied to help reveal the nature of the energy transfer mechanism. The experiments revealed a large survival probability ($>80\%$) for the initially prepared high vibrational state under all conditions used in that work. Of the small fraction of all collisions that led to vibrational energy transfer, loss of a single vibrational quantum was the most prevalent process. In dramatic contrast to the results on a metallic surface, here little vibrational energy transfer is observed. Also different from electron-mediated processes operative in collisions at metals, here little or no dependence on incidence energy is seen. Angular distributions are consistent with vibrationally elastic trapping and desorption of NO($v = 12$) (see figure 6).

Despite the lack of vibrational energy transfer observed on the insulator surface in comparison to metals, these experiments do suggest that vibrational energy transfer to phonons may be substantially more efficient for molecules in large-amplitude states of vibrational motion than present theory is capable of explaining. Examination of all of the data does reveal that at the lowest incidence energies and surface temperatures, substantial (30%) loss of the population from the initial vibrational state is observed. Furthermore, under these conditions of surface temperature and incidence energy, angular distributions of scattered molecules approach a $\cos(\theta)$-form, typical of trapping/desorption. In addition, rotational distributions of scattered molecules were found to be pseudo-Boltzmann with rotational temperatures approaching that of the surface.

Based on a knowledge of the binding energy of NO to LiF, the residence time of the NO($v = 12$) molecules on the surface under these conditions is estimated to be in the picosecond range (Wodtke *et al.* 2003). Observing 30% population loss in a few picoseconds represents a rate of vibrational relaxation that is many orders of magnitude faster than has been reported for diatomic molecules relaxing from $v = 1$ on salt crystals (Huan-Cheng and Ewing 1990), suggesting that further theoretical and experimental work is needed to fully understand how large-amplitude vibrational motion couples to solid phonons.

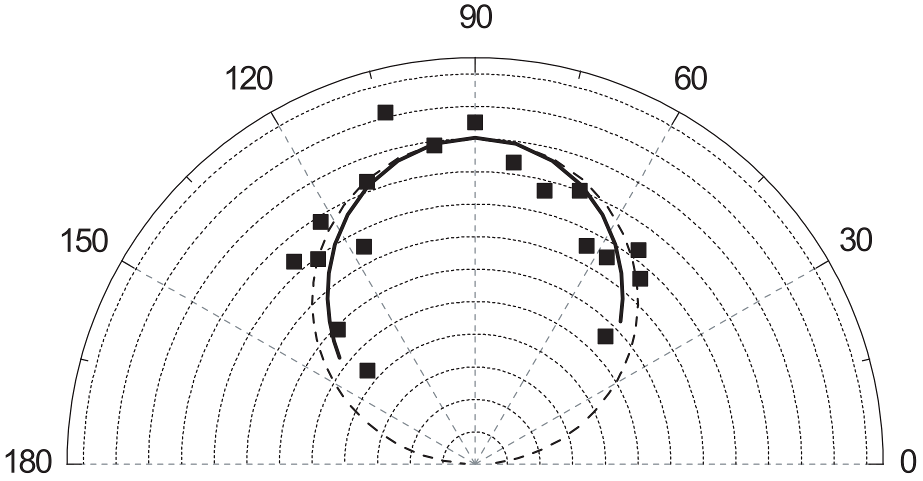


Figure 6. Trapping followed by desorption of highly vibrationally excited molecules on an insulator Polar plot of the angular distributions for NO($v=12$) vibrationally elastic scattering from LiF(001) for a surface temperature of 300 K and kinetic energy of incidence 5.3 kJ/mol. Also shown are the $\cos(\theta)$ function (dashed line) and $\cos^{1.3}(\theta)$ function (unbroken line). The molecular beam is incident at the angle indicated 90°. The data are consistent with vibrationally elastic trapping and desorption. The measured survival probability under these conditions was greater than 80% for $v=12$. (From Huang *et al.* 2000b; Wodtke *et al.* 2003.)

6. Detecting excited metal electrons produced in non-adiabatic dynamics

As we have seen for vibrational energy transfer, it is also observed that dissipation of chemical energy released in exothermic reactions at metal surfaces may occur adiabatically by creation of excited phonons or non-adiabatically by excitation of the electronic system of the metal or the reactants. It is, of course, of great interest to gain an understanding of the nature and magnitude of the electronic excitations that take place during electronically non-adiabatic chemistry at metal surfaces. It is only now becoming possible to carry out experiments that probe this important class of issues. Additionally, theoretical efforts capable of making predictions about the resulting electronic excitation have begun. In this way, we can foresee that it will soon be possible to understand the ways in which chemical interactions at surfaces result in electronic excitations, something that is of great relevance not only to catalysis but also to chemical signalling and molecular sensing. Likewise, it may soon be possible to understand to what degree electronic excitations in metals might be used to influence chemical reactions.

The experiments presented so far have not provided direct evidence of excited electrons. Such experiments are clearly desirable in light of the accumulating indirect evidence that large-amplitude heavy-atom motion of adsorbates near metal surfaces may exchange electron volts of energy with metal electrons. In the past decades, the only direct experimental evidence for such non-adiabatic reactions has been exoelectron emission into vacuum and surface chemiluminescence, which are observed in a special class of very exothermic reactions (see, for example, the work of Ertl and colleagues; Bottcher *et al.* 1990, 1991, 1993a,b, 1994, 1996; Greber *et al.* 1993; Grobecker *et al.* 1994a,b; Jacobi *et al.* 1995).

A novel experimental approach using Schottky diodes with ultrathin metal films has made direct measurement of reaction-induced hot electrons and holes possible (see, for example, Nienhaus *et al.* 1999a,b; Gergen *et al.* 2001a; Nienhaus 2002). Here, a sufficiently exothermic reaction on the thin metal film is thought to create hot charge carriers (EHPs) that travel ballistically from the metal film towards the Schottky interface and are detected as a chemicurrent in the diode. This work has been reviewed by Nienhaus (2002). Similar results have been found with metal–insulator–metal (MIM) devices that also show 'chemicurrents' for many exothermic surface reactions (Nienhaus *et al.* 1999a,b, 2000; Gergen *et al.* 2001a,b).

Interestingly, the efficiency for producing chemicurrents scales with the reaction exoergicity (Gergen *et al.* 2001a). A theoretical treatment of such devices, where the excitation of the electron is calculated using a forced oscillator model, was able to reproduce the 1% efficiency with which H-atom adsorption on Cu(111) produced excited metallic electrons above the Shottky barrier ($\sim$0.7 eV) (Trail *et al.* 2002). A new theoretical approach based on analogies with theories of X-ray core-level spectroscopy has given qualitatively similar results (Gadzuk 2002).

Although the body of evidence for non-adiabatic electronic effects in processes involving large-amplitude nuclear motion is growing and is rather persuasive, more direct evidence is needed. Many very basic questions remain. In particular, can we make measurements relevant to and theoretical predictions of the excited electrons that are part and parcel of the phenomenology we have been describing? When large amounts of vibrational energy are transferred to the electronic degrees of freedom, is more than one electron involved? What is the mechanism for coupling between heavy atom adsorbate motion and electronic degrees of freedom? Such direct measurements of the electronic excitation will become possible in the near future.

7. Conclusions

There is an accumulating and persuasive body of evidence suggesting that the validity of the BOA may be suspect for large-amplitude vibrational motion including motion over chemical transition states in reactions at metal surfaces. It is now clear that at least for some reactions at metals, including reactions of significant catalytic importance, theories of chemical reactivity that go beyond the BOA are required. It is perhaps too early to say whether the evidence that has been found so far represents an interesting conversation piece within the field of heterogeneous catalysis or whether it is just a hint of a more general and significant chemical reality. The future will undoubtedly lead to studies similar in method to those presented here applied to a wider variety of chemical reactions. New experimental methods designed to probe more electronically non-adiabatic effects in heterogeneous reactions will no doubt be developed. Initial forays into the theory of non-Born–Oppenheimer chemical reactivity have already met with some success. Doubtless more successes await the dedicated theorist. At the root of this field of research lies the fundamental question: Do we have a correct picture of heterogeneous reactivity? Improving our understanding of chemical reactivity at metal surfaces represents one of the great remaining challenges in physical chemistry.

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