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Electronically non-adiabatic influences in surface chemistry and dynamics†

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Electronically nonadiabatic interactions between molecules and metal surfaces are now well known. Evidence is particularly clear from studies of diatomic molecules that molecular vibration can be strongly coupled to electrons of the metal leading to efficient energy transfer between these two kinds of motion. Since molecular vibration is the same motion needed for bond breaking, it is logical to postulate that electronically nonadiabatic influences on surface chemical reaction probabilities would be strong. Still there are few if any examples where such influences have been clearly investigated. This review recounts the evidence for and against the aforementioned postulate emphasizing reacting systems that have yet to receive full attention and where electronically nonadiabatic influence of reaction probabilities might be clearly demonstrated.

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1 Introduction

Obtaining a predictive theoretical understanding of heterogeneous catalysis is a “grand challenge” of physical chemistry.¹ For well over a century the development of heterogeneous

catalysis has been a trial-and-error effort. Since new catalysts can be so commercially valuable this inefficient approach has been a necessary but acceptable evil. Today we are beginning to understand the fundamental nature of heterogeneous catalysis to a degree of detail that predictions of new catalysts can be made.² These predictions are not always correct, but even so, they already allow computational screening,^{3,4} a process that can dramatically speed up the trial and error development strategy. There is every reason to believe that improving our atomic scale understanding of reactions taking place at surfaces will lead to additional and important practical advances in theoretical predictions of heterogeneous catalysis.

At the most fundamental level, understanding chemical reactions is a problem in quantum physics. Writing about the importance of the discovery of quantum mechanics in 1929, the Nobel Laureate Paul Dirac stated: “*The underlying physical laws necessary for the mathematical theory of... the whole of chemistry are thus completely known*”.⁵ He went on to clarify the nature of the problems theoretical chemists would face up to the present day writing “*and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble*”. Notwithstanding advances in computational capability that Dirac could hardly have imagined, he is still right. The theory of chemistry requires approximate methods for practical computations.

Even for the simplest gas-phase chemical reactions where more exact treatments are possible,^{6–8} approximations are commonly employed; the most important approximation is that of Born and Oppenheimer.⁹ Recognizing that electrons move much faster than nuclei, the Born–Oppenheimer approximation solves the quantum equations of the electrons for stationary nuclei. Repeating this for many nuclear arrangements resembling reactants, products,

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the transition-state, and structures in between, we obtain the electronically adiabatic potential energy surface¹⁰ (PES) and from the PES the atomic scale forces that control and drive the reaction. For simple gas-phase reactions, highly accurate PESs can now be computed and converged calculations of the quantum motion of the nuclei on the PES can be performed.^{11,12} From the experimental side, crossed molecular beams methods and Rydberg atom tagging¹³ yield product-state resolved differential cross-sections, the most highly detailed observables for a simple gas-phase reaction that one can presently measure. Experiments and theory agree quantitatively.^{14–16}

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

There are fundamentally new problems that arise when confronting chemical reactions relevant to heterogeneous catalysis. Surface chemistry involves such a large number of nuclear degrees of freedom that reduced dimensionality approaches are nearly unavoidable. This might involve neglecting the role of surface atom motion,¹⁷ treating the dynamics of a reacting adsorbate in a restricted region of phase space *e.g.* along its reaction path or restricting motion to specific surface sites,¹⁸ or treating only a subset of the reactant molecules degrees of freedom.¹⁹ The large system size also makes it impossible to use the high level quantum chemistry techniques applicable to simple gas phase problems. Instead, we use methods based on DFT^{20–25} most often using exchange correlation functionals at the generalized gradient approximation (GGA) level. While a hierarchy of accuracy in DFT does exist that can be used to guide the theoretician's choice of functional, it has proven difficult to simultaneously obtain accurate results on molecules and solids – see another article in this review for more information.²⁶ Since most work is presently done at the GGA level, comparison with experiment is essential for testing the validity of DFT results. Beyond this, for many systems a complete quantum mechanical description of the nuclear motion is not computationally feasible and the nuclear motion must often be treated in a classical approximation.

Together with the Born–Oppenheimer approximation, these three additional approximations make up what one might call a “provisional model of surface chemical reactivity”. Along with improving computer power, the provisional model has made computations of remarkably complex problems in surface chemistry a technical reality. The potential for deep insights makes this line of research extremely attractive and it is growing in importance and popularity.

At the risk of oversimplifying, it is helpful to understand that perhaps the most fundamental difference between gas phase reactions and those occurring in surface chemistry concerns how energy is exchanged between the reacting atoms and the solid. Consider an example: an HCl molecule colliding at reactive metal surface like Au and dissociating to adsorbed atoms. We already know a little about this reaction: for example, theoretical calculations within the Born–Oppenheimer approximation predict that the reaction must pass over an activation barrier and, furthermore, that both HCl translation and vibration promote reaction.^{27,28} Many simple gas-phase reactions exhibit similar qualitative reaction characteristics, however surface reactions are different in that energy exchange with the solid cannot be ignored. For our HCl reaction at Au, for example, it is not hard to imagine that at least some of the translational energy needed to pass over the reaction barrier will be diverted from reaction and used to excite phonons of the solid.²⁹ There is also clear evidence that vibrational energy of the HCl molecule can be lost to excite electrons of the metal.^{30,31}

We should pause to briefly consider this. Coupling of molecular vibration to metal electronic excitation is a clear-cut breakdown of the Born–Oppenheimer approximation (BOA). But as I have pointed out above, the Born Oppenheimer approximation⁹ is crucial to constructing the provisional model of surface chemistry. Moreover, the fact that vibrational motion is precisely the kind of motion that breaks chemical bonds strongly suggests that energy exchange between a reaction center and electronic excitations of the metal could have an important effect on chemical reaction probabilities at metal surfaces.

This paper reviews evidence for the working hypothesis that electronically non-adiabatic interactions influence surface reaction probabilities (rates). However, so far the evidence for this is far from overwhelming, despite many reasons to believe such effects must be important. There are several possible reasons for this. Not only is it difficult to predict reaction rates with accuracy especially when including the effects of BOA breakdown, it is likewise challenging to make quality experimental measurements of the rates of elementary surface reactions. Hence, there are startlingly few examples where clear and unambiguous experiments can be compared to advanced theories that attempt to treat BOA failure. Furthermore it is not clear which competing ideas presently being discussed and developed to theoretically treat BOA failure are correct – it is even possible that different approaches will be needed for different surface reactions. Finally it is clear that not every reaction will be influenced strongly by BOA failure. Hence, finding the best model systems where these effects are strongest and where quality experiments can be carried out and advanced theory applied is another challenge, yet finding these examples and unleashing the full strength of modern experimental measurement methods upon them to fully characterize these influences is essential to developing the next generation of predictive theory of surface chemistry.³²

In light of these thoughts, this paper goes beyond simply addressing the aforementioned hypothesis and also presents ideas on directions for future research that might help resolve

this important question. In this search for electronically non-adiabatic reactions, it is worth reflecting on J. R. Oppenheimer's casual remark about the nature of science:³³ "The refinement of techniques for prompt discovery of error serves as well as any other as a hallmark of what we mean by science." This simple and crystal clear statement suggests one immediate approach. Make comparisons between detailed and well controlled experimental observations of reactive processes and theoretical calculations that make use of the BOA. In this light, discovering deviations between experiment and theory is not to be seen as a failure of the theory (nor of the theoretician). Rather these deviations are markers on the road signaling that complexity is nearby and that the usual approximations are not working. These are the systems where new ideas and insights are needed, ideas and insights that will deepen our understanding. Thus our search will involve only systems where both experiment and theory touch at the most detailed observables of reactivity. And we will be looking for deviations... (...hopefully, large deviations).

The paper is organized as follows. First I review some of the more compelling evidence for Born–Oppenheimer breakdown in molecular interactions at surfaces; the evidence is clearest in studies of vibrational energy transfer between small molecules and solid metal surfaces. The clarity of this evidence can be traced back to (1) the careful design of experiments employing simple systems and (2) the advances in electronically non-adiabatic theories of molecule surface interactions that can be used to quantitatively compare to experiment. I then move to a brief review of work pointing to the influence of electronically non-adiabatic energy exchange on reactive processes. I emphasize examples where dynamics experiments have been compared to first principles theory. In the final section of the paper I present a more general strategic argument regarding how these effects might be most clearly demonstrated in the future and review work on three simple systems where clear answers are likely to emerge in the near future.

2 Evidence for Born–Oppenheimer failure from energy transfer studies

Evidence is abundant that the Born–Oppenheimer approximation breaks down in energy transfer processes occurring between molecules and metal surfaces. Lifetimes of vibrationally excited CO on Cu could not be theoretically explained without invoking energy transfer from CO vibration to electrons of the metal.^{34–37} Neglecting such electronically nonadiabatic coupling, theoretical lifetimes were 10^9 times longer (ms) than experiment (ps).³⁸ For comparison, experimental measurements of the vibrational lifetime of CO on NaCl (an insulator where electron hole pair excitation is not in resonance with the CO vibration) are in the millisecond range.³⁹

Perhaps the most compelling evidence for BOA failure in vibrational energy transfer studies is the phenomenon of vibrational promotion of electron emission.⁴⁰ In this work, an adlayer of Cs atoms was deposited on a Au(111) crystal surface

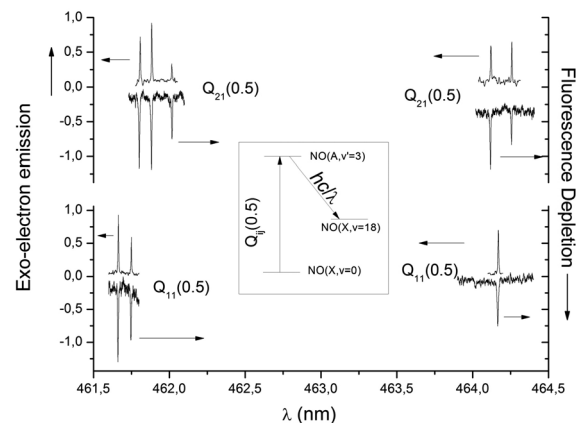


Fig. 1 Electron emission due to NO($v = 18$) collisions with Cs/Au(111) surface. Electron emission (up-going signal) is compared to fluorescence depletion (downward going signal) spectra observed under identical conditions. NO($v = 18$) was produced using the double resonance transition shown in the inset. The wavelength λ is scanned for two excitation transitions ($Q_{21}(0,5)$ – upper panel and $Q_{11}(0,5)$ – lower panel). See ref. 40.

to produce a metal target with a low work function (1.6 eV).⁴¹ Then NO was prepared in high vibrational states whose vibrational energy (3.6 eV) exceeded the surface work function. This experiment relied on stimulated emission pumping spectroscopy a methodology developed over many years in the study of bimolecular collisions of highly vibrationally excited NO^{42–47} and O₂.^{48–51} Exploiting this know-how, it was possible to directly observe the emission of electrons resulting from the vibrational energy transfer from the NO molecule to the solid surface – see Fig. 1. This demonstrated that electron-Volts of NO vibrational energy could be efficiently channeled to electronic excitation of the solid.

The mechanism of this process is only qualitatively understood. Electron kinetic energy distributions showed that the most probable process converts 64% of the vibrational energy into excitation of the emitted electron.^{52,53} Furthermore, the electron emission probability exhibits an inverse velocity dependence,⁵⁴ consistent with a window of opportunity mechanism involving electron transfer from the metal to the molecule, followed by vibrational auto-detachment.⁵⁵

The vibrational auto-detachment mechanism has been studied in detail for NO vibrational energy transfer with noble metal surfaces – see for example these two reviews: ref. 32 and 56. This class of molecule-surface problems is unique in that a wide variety of detailed experiments have been carried out and compared to first principles theories of electronically non-adiabatic interactions.

The first clear evidence of the importance of electron hole pair coupling to NO vibration was found in the temperature dependence of NO excitation at Ag(111).^{57,58} In this case, the population of EHPs in resonance with the vibrational transition from $v = 0-1$, increases according to a pseudo-Arrhenius law with an effective activation energy equal to the vibrational energy spacing between the two quantum states – see ref. 59 for a detailed description of the surface temperature dependence of

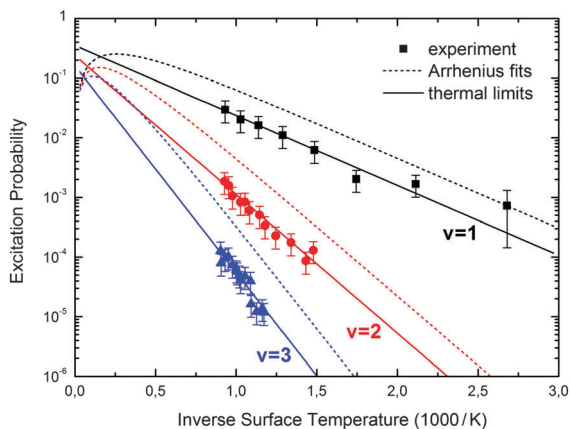


Fig. 2 Arrhenius plots of absolute excitation probabilities for collisional excitation of NO($\nu = 0$) to $\nu = 1, 2$, and 3. Experimental results are shown as symbols: black, $\nu = 1$; red, $\nu = 2$; blue, $\nu = 3$. Solid lines show fits to an Arrhenius expression with the activation energy fixed to the vibrational excitation energy. Dashed lines show the thermal limits. See ref. 60.

electronically nonadiabatic vibrational excitation and de-excitation. This behavior has also recently been demonstrated for NO vibrational transitions to higher vibrational states ($\Delta\nu = +2$ and $+3$)⁶⁰ in collisions at a Au(111) surface where the effective activation energy is doubled and tripled, respectively, compared to that of the $\Delta\nu = 1$. See Fig. 2.

Interactions of highly vibrationally excited NO with Au(111) have also been extensively studied. Here, NO is again prepared in vibrational states with energies of several electron-Volts; however, the work function of the metal target is much higher (5.3 eV) preventing direct detection of emitted electrons. Still the BOA failure can be seen by measuring the vibrational state distribution of the scattered NO molecules.⁶¹ Multi-quantum vibrational relaxation of NO initially prepared in $\nu = 15$ is clearly seen – the most probable process results in loss of 7–8 vibrational quanta of NO, which is a vibrational energy loss of 1.5 eV. When similar experiments are carried out with LiF crystals, which are of course electrically insulating, vibrational energy loss is inhibited.⁶²

The incidence energy dependence of NO's electronically non-adiabatic vibrational energy transfer is simple to understand;⁶³ it is governed by the energetics of a curve crossing between the ground state of the system where NO is neutral and that of the anionic NO state, where an electron has been transferred from the metal to the molecule. The work function of the solid is far larger than NO's electron binding energy; however, as NO approaches the Au solid, the image charge interaction lowers the energy of the anionic state so that it can cross the neutral. Where this crossing occurs depends on the NO vibrational degree of freedom. At low incidence vibrational excitation (e.g. $\nu \sim 2$), translational energy is needed to reach this crossing and vibrational energy transfer is enhanced by incidence translation.⁶⁴ At high incidence vibrational excitation reaching the curve crossing requires little or no translational energy⁶³ and the dependence on translational energy is nearly absent – indeed the incidence energy dependence may even

become inverted.⁵⁴ I note in passing that this is probably the strongest evidence available that does not rely on theoretical simulations that the energy transfer occurs by an electron transfer mechanism.

Attempts to simulate NO interactions and energy transfer with Au(111) from first principles have met with some success. Two approaches have been implemented: (1) electronic friction⁶⁵ (EF) and (2) independent electron surface hopping⁶⁶ (IESH) based on a Newns–Anderson Hamiltonian derived from DFT.⁶⁷ The IESH approach was able to describe the relaxed vibrational distribution of NO($\nu = 16$), measured with an incidence translational energy of 0.05 eV.⁶⁸ This theory also predicted a strong steric effect⁶⁸ that was later confirmed by experiment.^{69–71} These successes were largely matched by EF calculations. Later measurements of vibrational excitation (NO $\nu = 0 \rightarrow 1, 2, 3$)^{60,72} were compared to the predictions of the IESH and EF based approaches. Here only the IESH approach gave good agreement with experiment – EF failed to describe vibrational excitation whatsoever.

More recently, both of these theoretical approaches have been tested against a wider set of experimental data. Here, the development of new experimental methods has played an important role. State-to-state TOF methods have been developed that allow direct observation of translational inelasticity, vibration-to-translation and translational to rotational energy conversion.^{73,74} New approaches to preparing highly vibrationally excited molecules⁷⁵ have made systematic measurements of multi-quantum vibrational relaxation routine. Steric effect measurements of inelastic scattering processes are now possible due to new approaches to preparing oriented molecules.⁷¹ These experimental advances have led to an increasing number of discovered deviations between experiment and theory.

As just mentioned, experiments on vibrational relaxation of NO in collisions with Au(111) reveal a strong steric effect. Evidence for this comes from scattering experiments employing oriented NO molecules^{69–71} or less directly from observations of rotational cooling upon vibrational relaxation.⁷⁶ It is now clear that when the NO molecule approaches the Au(111) surface with its N atom oriented toward the surface, the electron transfer process and thus the vibrational energy transfer can be strongly enhanced.⁷⁰ Although this steric effect was predicted by IESH calculations and is qualitatively consistent with experiment, all attempts to reproduce experimental observations on the steric effect have so far failed – the experimentally observed steric effect is much stronger than that derived from IESH theory. This may reflect the subtle influence of weak forces that re-orient the NO molecule on its approach to the Au(111) surface, forces that are difficult to accurately capture with DFT.

Beyond this, other problems arise. While IESH describes NO($\nu = 0-1$) excitation nearly quantitatively,⁷² it increasingly deviates from experiment as vibrational excitation increases; $\Delta\nu = +2, +3$.⁶⁰

These observations led to extensive experimental studies of vibrational relaxation of NO($\nu = 3 \rightarrow 2, 1$).⁷⁷ Here for the first time, large deviations between experiment and IESH theory were found. Experiment showed that vibrational relaxation probabilities

increased with incidence energy of translation; both IESH and EF theory gave the opposite trend. By analyzing individual trajectories, it was found that multi-bounce collisions in the theory, which were especially important at low translational incidence energy, increased the NO interaction time with the solid and enhanced the energy transfer. Comparisons of experimental translational inelasticity to IESH, EF and even adiabatic theory also showed the interaction potential erroneously predicts too much inelasticity – the gold surface is too soft.⁷⁸ This discrepancy as well as narrow angular distributions seen in experiment strongly suggested that these multi-bounce phenomena are an artifact of the theory. By hand picking the single bounce trajectories ($b = 1$ in Fig. 3) better agreement between experiment and IESH theory was found, whereas EF failed to describe multi-quantum relaxation in the absence of multi-bounce trajectories. This led to the conclusion that the IESH approach is fundamentally sound but that the adiabatic potential energy surface (PES) used in the calculations has errors that introduce artefactual multi-bounce phenomena.^{77,78}

With these new insights an ambitious round of experiments was undertaken to characterize the vibrational relaxation⁷⁸ of highly vibrationally excited NO in collisions with Au(111). Here relaxed NO vibrational distributions were obtained for several incidence vibrational and translational energies. The comparison of experiment to theory at high incidence translational

energies was particularly interesting as the multi-bounce artifacts were absent from the theory under those conditions.⁷⁷ Both electronic friction methods as well as IESH predict substantially less vibrational energy loss than is seen in experiment. Furthermore this deviation increases with incidence vibrational excitation. See Fig. 4.

For incidence vibrational excitation NO($v_i = 3$) agreement is quite good, but deviations are clearly seen for NO($v_i = 11$) and for NO($v_i = 16$) the deviation is quite large. Note that the IESH/EF with and without selection indicate the hand picking (or not) of single bounce trajectories. The right column of comparisons in Fig. 4 shows results from incidence translational energy of 1.0 eV, where multi-bounce effects are unimportant in both the theories.

The growing deviations with incidence vibrational energy are worth emphasizing. For NO($v_i = 16$), the corresponding vibrational energy (3.4 eV) is comparable to the barrier height

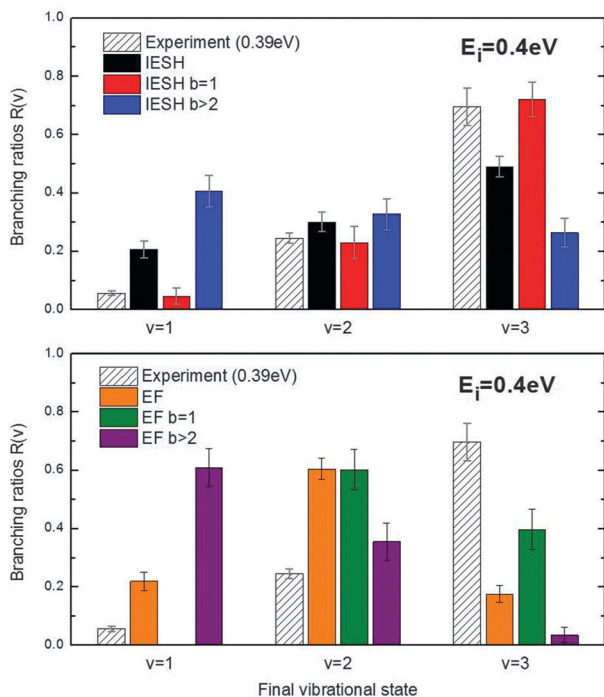


Fig. 3 Comparison of results from state-to-state molecular beam scattering experiments with first principles theoretical simulations. Comparison of IESH (upper panel) and EF (lower panel) theory to experiment for NO($v = 3$) relaxation on Au(111). Both IESH and EF predict too much relaxation. By manually selecting trajectories that exhibit a single bounce with the surface ($b = 1$), better agreement between experiment and IESH theory is found, whereas EF fails to account for multi-quantum vibrational relaxation. The incidence energy of translation is 0.39 eV. See ref. 77.

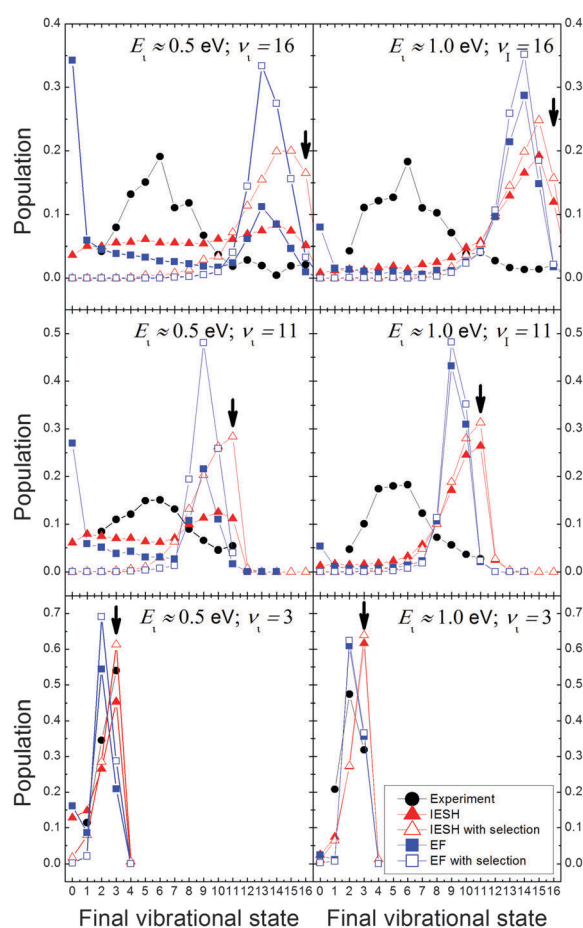


Fig. 4 Final vibrational state distributions for NO(v_i) relaxation against Au(111) at two translational incidence energies. Comparing experiment (black, filled circles) and results of IESH (red, triangles) as well as EF (blue, squares) calculations. Empty symbols indicate the results corrected for multi-bounce events as described in the main text. Vibrationally excited NO is prepared in its electronic ground state with the vibrational quantum number v_i and incidence translational energy $E_i = 0.5$ eV (left panels) and $E_i = 1.0$ eV (right panels), respectively. Arrows indicate the initial vibrational state. See ref. 78.

for NO dissociation on Au(111), 3.5 eV, reported in ref. 79. As we have just seen, errors in the adiabatic PES can have a strong impact on the electronically nonadiabatic energy transfer predicted by theory, the fact that the PES used in the IESH and EF calculations of Fig. 4 does not describe NO dissociation could be the reason for the growing discrepancy with increasing incidence vibrational energy. This is clear if we consider that vibrational energy transfer can be strongly enhanced by trajectories that resemble a failed attempt to traverse the transition state to dissociation, as has been seen for H₂ interactions at Cu(111).⁸⁰ I will return to this line of reasoning later when discussing the relaxation of highly vibrationally excited NO on Ag(111).

3 Dynamical studies of surface reactions: little evidence for Born–Oppenheimer failure

A logical approach to search for and find electronically non-adiabatic influences in surface chemical reactions is to compare experimental reaction probabilities to electronically adiabatic simulations based on first principles. The electronically adiabatic approach to surface chemistry is well developed and if discovered deviations between experiment and theory were large enough and well enough investigated, one might reasonably ascribe them to BOA failure. The most rigorous tests would be to compare theory against experimentally determined reactant quantum state resolved reaction probabilities. This has been done thoroughly for only a few reaction systems, three examples of which are described here in more detail. Other reviews of this topic can be found here.^{32,81–83}

3.1 Hydrogen dissociation on metals

One of the most important is dissociative adsorption of H₂ and its isotopomers on metals.^{82,84–86} Of these, H₂ dissociation on Cu has been most extensively studied. For this system, we do have detailed quantum state-specific experimental information on the reaction probability at zero coverage, $S_0(T_s, E_i, \theta_i, \phi_i, v_i, J_i, M_i)$ and how it depends on a host of incidence conditions: kinetic energy E_i , polar angle, θ_i , azimuthal angle, ϕ_i , vibrational state, v_i , rotational state, J_i , and orientation or projection of the rotational angular momentum, M_i .^{87–98} In addition we have information on rotational and vibrational inelastic scattering of H₂ from copper.^{80,91,99}

The reaction is activated both by incidence translation and vibration. The characteristic incidence kinetic energy needed for reaction, E_0 , has been derived from experiment and its dependence on many other reaction parameters has been obtained. As the vibrational energy increases, E_0 decreases by about half the increase in internal energy. Rotational motion initially inhibits dissociation – E_0 increases, but at high J , E_0 decreases by about half the increase in internal energy. Thus, both vibrational energy and rotational energy are about half as effective as translational energy in overcoming the adsorption barrier.⁹⁰

These effects have been captured by electronically adiabatic simulations, with the caveat that these calculations are not

strictly speaking first principles. Since standard exchange correlation functionals at the GGA level do not provide a chemically accurate description of the adsorption barrier for dissociative adsorption of H₂ and D₂ on Cu. Kroes and coworkers¹⁰⁰ developed an adaptation to molecule–metal interactions of the specific reaction parameter (SRP) approach to DFT¹⁰¹ originally developed for gas-phase problems. Essentially the method involves constructing a new functional as a linear combination of two functionals, and adjusting the mixing of the two to give optimal agreement with one piece of experimental data, in this case the adsorption probability for D₂ for a vibrational temperature of 2100 K. This semi-empirical SRP functional then successfully reproduced results for many other measurements on this system like the variation of E_0 with v and J and the rotational excitation probability.^{100,102} See Fig. 5. The same functional with the same mixing parameter also gave good agreement with reaction probabilities on Cu(100).⁸⁶

This approach does not reproduce all relevant data. For example they strongly underestimate the contribution of vibrational excitation to the so-called gain peak in the measured TOF distribution of H₂ scattering from Cu(111) at high incidence

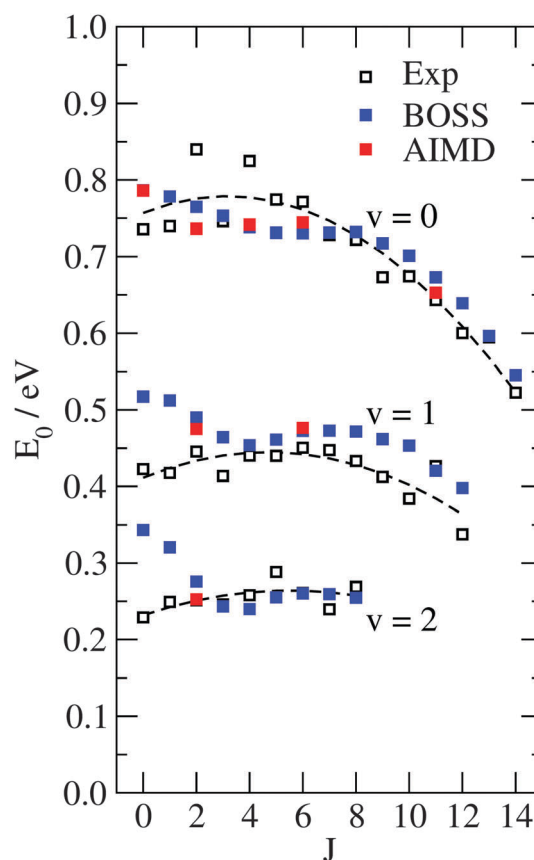


Fig. 5 Experimental (empty squares) and theoretical (blue and red for BOSS and AIMD, respectively) E_0 values are plotted as a function on J . E_0 values have been estimated from FPC fits of the BOSS data and from LGS fits of the AIMD data. The dashed lines are quadratic fits of the experimental E_0 values, for $v = 0, 1$, and 2 as indicated in the figure. Reprinted from Nattino *et al.*, *J. Chem. Phys.*, 2014, **141**, 124705, with the permission of AIP Publishing. See ref. 102.

energies⁸⁰ and strongly overestimate the orientation dependence of the reaction probability for this system.

Kroes and coworkers argued that these discrepancies are not due to errors in the PES, but rather to the use of the Born Oppenheimer static surface (BOSS) model that freezes the surface atoms at their 0 K equilibrium positions. Using *ab initio* molecular dynamics (AIMD),¹⁰³ which allows all degrees of freedom to be computed “on the fly”¹⁰⁴ they obtain results for the orientation dependence of the reaction probability¹⁰⁵ that are in better agreement with experiment. The deviations from experiment in the vibrational excitation probability is also attributed to the static surface model.¹⁰⁶

It is still possible that the remaining discrepancies are somehow related to nonadiabatic electronic excitation, but there is no direct indication that this is the case, nor is there any work that shows how nonadiabatic effects might help to resolve the remaining discrepancies. At present, there doesn't appear to be an easy way to check this last point.

Other questions concern the importance of electronic non-adiabaticity. While hydrogen recombination reaction occurring through a Langmuir–Hinshelwood mechanism appears to be a dramatic and convincing success for the provisional model of surface chemical reactivity, it is worth noting that recent theoretical studies suggest that H Atom recombination through an Eley–Rideal mechanism may be strongly influenced by EHP excitation.¹⁰⁷

Nonadiabatic effects may also play a significant or even dominant role in the fate of the hot H atoms that result from a dissociative adsorption event. Recently, Alducin and coworkers used a combination of AIMD and the local density electronic friction approximation to study transient hot H atoms produced in dissociation of H₂ on Pd(100).¹⁰⁸ Within the approximations they use, they find that nonadiabatic electronic excitation is the dominant mechanism for energy loss in these hot atoms.

3.2 Methane dissociation on metals

Methane dissociation at metal surfaces is another well studied system using electronically adiabatic theory and state resolved experiment. Experiments show that the reaction occurs over an approximately 1 eV activation barrier, varying somewhat from metal to metal.¹⁰⁹ Both incidence translation and vibration promote dissociation forming adsorbed H and methyl radicals.^{110–120} This chemistry disobeys statistical laws of reaction rates, a topic that has recently been reviewed.¹²¹ For doubly deuterated methane (CD₂H₂), the reaction probability is 5x higher for molecules with two quanta of excitation in one C–H bond compared to molecules with one quantum in each of two C–H bonds,¹¹¹ despite the fact these two states have nearly identical energies. Bond selective control of CHD₃ dissociation was also demonstrated – the C–H bond can be selectively dissociated by laser excitation of the C–H stretch¹¹⁸ and similar behavior is seen in other isotopologues.^{119,120} A steric effect has also been reported,¹²² *i.e.* the reaction probability depends on the direction along which its C–H bonds are vibrating. Suggesting the importance of surface atom motion, it is observed that the reaction probability depends strongly on

surface temperature, increasing by as much as a factor of 8 as T_s is increased from 90 K to 473 K.¹²³

Theoretical simulations of this reaction have also made substantial progress.^{86,124,125} A major challenge is the large number of degrees of freedom active in this system – 15 in the methane molecule and much more if one considers the motion of the surface atoms. Beyond this, the quantum nature of H-atom motion may also be important.

A promising approach, which appears to capture the full dimensional nature of the problem and which is fully quantum mechanical relies on a reaction path Hamiltonian.^{18,126–128} Here, only a limited part of the PES needs to be calculated from DFT, namely energy points along the minimum energy path to dissociation as well as the curvature of the PES orthogonal to this path. This dramatically simplifies the polyatomic problem. Using a reaction path Hamiltonian, a 15D wave function is expanded in the adiabatic vibrational states of the methane molecule, and close-coupled equations are derived for wave packets propagating on vibrationally adiabatic potential energy surfaces, with vibrationally nonadiabatic couplings linking these states to each other.¹⁸ Sudden models were used to average over surface impact site and Ni atom lattice vibrations.¹⁸ Fig. 6 shows the excellent agreement obtained between experiment and theory.

To briefly summarize, in two quite different systems presenting different theoretical challenges, the application of electronically adiabatic first principles simulations succeeded in reproducing central characteristics of sophisticated quantum-state resolved experiments. While deviations between experiment

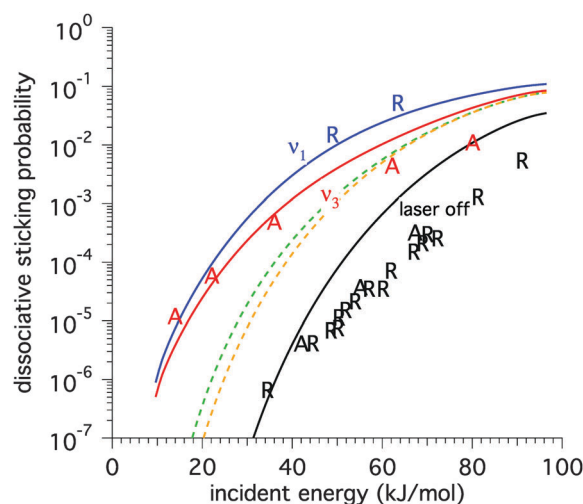


Fig. 6 Comparison of experiment (symbols) and theory (lines) for methane dissociation on Ni. The theory is based on a reaction path Hamiltonian involving 15D Quantum dynamics calculations with sudden approximation models introduced to allow for averaging over impact site and Ni atom out of surface motion. The experiments employ laser excited molecular beams to reveal the translational and vibrational promotion of the methane dissociation probability. Ground vibrational state (black), one quantum symmetric CH stretch (blue), one quantum anti-symmetric CH stretch (red), v_2 bend (green) v_4 bend (yellow). Reprinted from B. Jackson and S. Nave, *J. Chem. Phys.*, 2011, **135**, 114701, with the permission of AIP Publishing. See ref. 18 and references therein.

and theory remain, no compelling case can be made attributing these to BOA failure.

It is worth mentioning that other reaction systems have also been recently investigated – water dissociation on Ni is of particular current interest¹²⁹ as it has been suggested that electronic non-adiabaticity may be important here.¹³⁰ Further study promises deeper insights.

Turning now to a system with more complex electronic structure also reveals ambiguous conclusions: for O₂ dissociation on aluminum, π -bonding is involved and the issue of spin is central. Experiments for O₂ dissociation on Al(111) show clearly that the reaction is translationally and vibrationally activated.¹³¹ The reaction involves two channels: the O₂ molecule can either undergo simple dissociative chemisorption or it can undergo an abstraction reaction where one O-atom is left bound to the surface and the other is ejected towards the vacuum. The abstraction mechanism involves a lower activation barrier than does dissociative chemisorption. This has been indirectly demonstrated by STM studies showing single isolated O-atoms at low or thermal incidence energies while the fraction of adsorbed oxygen pairs increased at high E_i.^{132,133} Furthermore, molecular beams methods allowed the direct detection of the ejected O-atom.¹³⁴

Applications of electronically adiabatic density functional theory on the O₂/Al(111) system are less clear. DFT calculations using GGA functionals fail to reproduce the experimentally observed sticking probabilities, as the calculated potential energy surface exhibits no activation barrier for dissociation.^{135–139} This has been explained as a failure of the adiabatic approximation – a diabatic approach may be needed to accurately describe the influence of electron transfer on the reaction probability. Several studies suggested that the problem is related to failure of DFT to properly describe electron transfer,^{140,141} which is likely to be important for O₂/Al(111). An alternative but not necessarily unrelated explanation imposes spin selection rules – the O₂ dissociation is constrained to react on a triplet PES^{137,138} using a locally constrained DFT (LC-DFT). By forcing the O₂ molecule to have a local spin-1, a barrier to dissociation was found. In this way a 6D PES for the O₂/Al(111) system was derived both for the lowest triplet and singlet state and the translational activation seen in experiment could be captured by the theory.^{139,142,143}

The phenomenon of local O₂-spin raises issues of electronic non-adiabaticity in an interesting and peculiar way. Considering the O₂ metal surface system as a whole, it is clear that in the absence of magnetic coupling and spin-orbit interaction, the total electronic spin of the system remains conserved. If we consider O₂ initially in its ³ Σ ground state removed far from the aluminum surface, the total spin is 1 (assuming an even number of Al atoms). As the O₂ molecule begins to interact with the metal at closer distances, O₂ conversion to the local ¹ Δ state (or indeed ¹ Σ state) is possible *via* a two electron transfer process, where one spin-up electron jumps to the O₂ molecule forming a transient anion and one spin-down electron jumps back. Here, the total spin remains 1, but the spin on the molecule is now 0. If this local singlet-O₂ configuration is lower in

energy than the local triplet-O₂ configuration when O₂ is close to the Al surface, then an O₂-local spin-transition must occur in order that the system remains on the ground electronic state. Now, if such two electron transfer processes are not likely on the time-scale of O₂ approach, this local triplet to singlet transition will not take place. Then, the O₂(³ Σ) state will become an excited electronic state of the system as the O₂ molecule approaches the surface. This is one possible explanation of the entrance channel barrier in the dissociative adsorption of O₂ on Al; that is, the activated dissociative adsorption of O₂ on Al is due to an electronically nonadiabatic effect related to local spin conservation.

However, an alternative explanation has been recently proposed: namely that the barrier to O₂ dissociation on Al arises simply when one uses an electronic structure method that treats electron transfer properly. Using an embedded correlated wave function method, which is claimed to treat electron transfer better than DFT, 2D PESs were calculated for parallel and perpendicular impact of the O₂ molecule at different surface sites revealing activation barriers consistent with experimental observations.¹⁴⁴

In summary, despite highly suspicious behavior certainly suggestive of BOA failure, the O₂ Al system still holds mysteries. Specifically, we do not know if spin changing two-electron transfer processes between molecules and metals are possible.

3.3 Chemicurrents: direct evidence of Born–Oppenheimer failure in surface chemistry

Comparing theory to experiment is expected to give the clearest and most useful evidence of Born–Oppenheimer failure in surface chemistry. The previous sections show that this has not yet been a fruitful endeavor. Despite this, there is direct experimental evidence for Born–Oppenheimer failure in surface reactions, which is obtained from detection of chemicurrents and related phenomena. This topic has been reviewed before^{83,145} and the current state of the field is discussed elsewhere in this issue;¹⁴⁶ I only touch on it briefly here, due to its central relevance to the topic of this paper.

The chemicurrent experiment deviates strongly from methods so far presented. Instead of single crystal metal samples cleaned and prepared in ultrahigh vacuum, these experiments involve complex devices fabricated under less well controlled conditions. Fig. 7b shows an example of such a device: a Schottky diode capable of detecting a chemicurrent. Here, a few nm thick film of metal is deposited on a semiconductor wafer with electrical leads. This is often done in a clean room, it may involve wet chemical treatment (*e.g.* HF treatment of the native oxide film common to silicon surfaces) and later the device is introduced to an ultrahigh vacuum surface science apparatus for chemicurrent measurements. It is common that the metal film is evaporated on the device *in situ*.

Fig. 7a shows the idealized electronic structure of the device and the proposed mechanism of chemicurrent formation for the example of H atom adsorption at a silver surface. According to current understanding, when an H atom adsorbs to the thin metal film, hot electron hole pairs are created. The hot

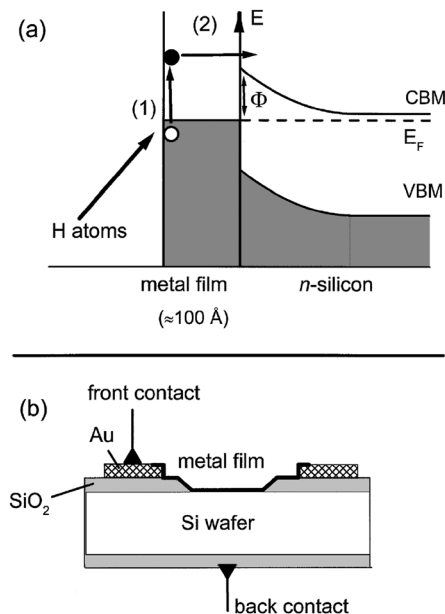


Fig. 7 From electron-hole pair creation at Ag and Cu surfaces by adsorption of atomic hydrogen and deuterium. Reprinted figure with permission from H. Nienhaus *et al.*, *Phys. Rev. Lett.*, 1999, **82**, 446–449. Copyright (1999) by the American Physical Society. See ref. 147.

electrons are believed to travel elastically through the thin film (ballistic transport) and the fraction that possess enough kinetic energy to pass the Schottky barrier then enter the conduction band of the silicon semiconductor.¹⁴⁷ This separation of electrons and holes results in a current that can be measured directly as long as the Schottky diode is held at low enough temperature and kept in the dark. Analogous measurements have been made on different but similar metal-insulator-metal (MIM) devices^{148,149} and catalytic nanodiodes.^{150,151}

Since the first observation of chemicurrents involving H adsorption on copper and silver films,¹⁴⁷ chemicurrents have been studied for a variety of adsorption systems and as a function of adsorption energy. Even weakly exoergic processes, releasing energy down to 0.2 eV yielded detectable signals.¹⁵²

Although chemicurrents represent strong evidence of the importance of BOA failure in surface chemistry and cannot be ignored, attaining an atomic scale understanding of chemicurrent phenomena is far more challenging. For example, even in the first reported examples, chemicurrents on Ag were found to be more than thirty times stronger than those on copper. This was attributed to supposed differences between the two devices, which led to differential trapping of ballistic electrons at the metal/semiconductor interface.¹⁴⁷ Hence a proper theory of chemicurrents may need to account for complex electron transport phenomena through interfaces that may not have been clearly characterized experimentally.

The ubiquity of chemicurrents is also puzzling – for example, even Xe adsorption on silver yields a detectable chemicurrent.¹⁵² There is no independent confirmation that rare gas scattering or adsorption from any metal surface results in electron hole pair excitation, despite the fact that these systems have been

studied for decades; see for example.¹⁵³ This suggests that additional mechanisms of chemicurrents other than that shown in Fig. 7a are important, a topic that has recently attracted increased scrutiny.^{146,154}

4 Outlook

I have given a brief review of a few of the best examples of elementary chemical reactions at surfaces including those that are most amenable to electronically adiabatic theories of surface chemistry. The aim was to find large deviations between experiment and theory that might be attributable to BOA failure. Comparisons of experiment to theory reveal that electronically adiabatic theories do remarkably well for two systems: hydrogen dissociation on copper and methane dissociation on nickel. Considering an example with more complex electronic structure – oxygen dissociation on aluminum – deviations between experiment and theory are clearly seen, but their interpretation is ambiguous. Here it is possible that electronically nonadiabatic influences give rise to a reaction barrier *via* a local O₂-spin conservation rule. Others disagree concluding that an improved electronically adiabatic theory not suffering the weaknesses of DFT related to proper characterization of electron transfer would explain experiment.

I have also reviewed experimental studies showing incontrovertible evidence that BOA failure can be a profoundly important influence on molecular energy transfer at surfaces. Furthermore, chemicurrents have given us clear qualitative observations of BOA failure in surface reactions that, despite the complexities of such experiments, cannot be explained away – these experiments clearly show Born–Oppenheimer failure can be important even if it is not certain that all reports of chemicurrents involve electron hole pair excitation. In light of this we ask the question: how shall the field proceed to find better examples of simple chemical reactions at surfaces that are strongly influenced by Born–Oppenheimer failure and can serve as test beds for theoretical analysis and developments of new approaches to atomic scale simulations of surface chemistry?

While this review is not intended to be comprehensive, it is nevertheless striking how few systems have been studied with both modern quantum state resolved experimental methods and advanced dynamical theories that go beyond the Born–Oppenheimer approximation. Up to now, the community has worked first (and this is probably always the case in experimental science) on those systems that are most technically feasible. Perhaps, these systems are simply not the best ones to demonstrate and characterize Born–Oppenheimer failure. It begs the question: is there a logical way to proceed systematically in the search for Born–Oppenheimer failure in surface chemistry.

Consider that Born–Oppenheimer failure has been studied most thoroughly by experiment and theory in energy transfer studies. It appears to me sensible to start our search from these systems, where energy transfer is clearly influenced by BOA failure and try to adjust experimental conditions to induce, observe and study reaction. To demonstrate this strategy, I present two

examples of systems where Born–Oppenheimer failure has been found in energy transfer studies and suggest ways to extend them to problem of chemical reaction.

4.1 NO scattering from noble metals: something is still missing

Earlier in this paper I reviewed work on the vibrational energy transfer of NO with noble metals; here, both experimental and theoretical methods have been developed to study this important example of Born–Oppenheimer failure. It is clear that the N–O stretch vibration is strongly coupled to EHPs of the Au and according the spirit of this section, NO dissociation on a noble metal would appear to be an excellent candidate reaction to observe the influence of electronic non-adiabaticity. There is also indirect evidence that the dissociation reaction is playing a role in the vibrational relaxation.

As discussed previously, Fig. 4 shows how the predictions of two theories of electronically nonadiabatic vibrational energy transfer between NO(v) and Au(111) (IESH and EF) increasingly deviate from experiment as the incidence energy of vibration is increased. In the discussion of this figure above, I speculated that this growing deviation may be due to the fact that NO dissociation is ignored in the adiabatic PES used in these dynamical simulations. The energy of the NO($v = 16$) molecule (translational + vibrational) is 4.3 eV, which may be compared to the calculated barrier for NO dissociation on Au(111) (3.6 eV⁷⁹). Access to the dissociation transition state is energetically possible and there is precedence in the literature that when the transition state is accessed, “failed reaction” can lead to efficient vibrational relaxation.⁸⁰ If the dissociative part of the PES is playing an important role, one would expect that these influences are even more important on metal surfaces where the dissociation barrier is lower than for NO on Au(111). Thus pursuing the dissociation of NO on Au at higher incidence energies, both translational and vibrational is one promising direction.

We might also consider changing to another noble metal where we might assume that many of the physical properties are only somewhat different from Au. For example, if we were to compare NO($v_i = 11$, $E_{\text{vib}} = 2.4$ eV) at a translational incidence energy of 0.5 eV and compare the total energy ($V + T = 2.9$ eV) to the NO dissociation barrier heights on Au(111) (3.6 eV) and Ag(111) (3.1 eV) we might expect to see a stronger influence of the chemical transition state for Ag compared to Au.

Fig. 8 shows measurements of multiquantum vibrational relaxation of NO($v_i = 11$, $E_{\text{vib}} = 2.4$ eV, $E_{\text{trans}} = 0.5$ eV) after collisions on Au(111) and Ag(111).¹⁵⁵ The vibrational relaxation is dramatically enhanced on Ag(111) in comparison to Au(111). When first reported, relaxation of highly vibrationally excited NO occurring in collisions with Au(111) surfaces exhibited the largest vibrational inelasticity seen in molecule–surface collisions and no system has since been found exhibiting a greater vibrational inelasticity. In Fig. 8, one sees that the relaxation probability and the average vibrational energy loss are much higher when scattering from Ag(111).

The explanation for this is not yet certain. However, one reasonable hypothesis is that the lower barrier to dissociation

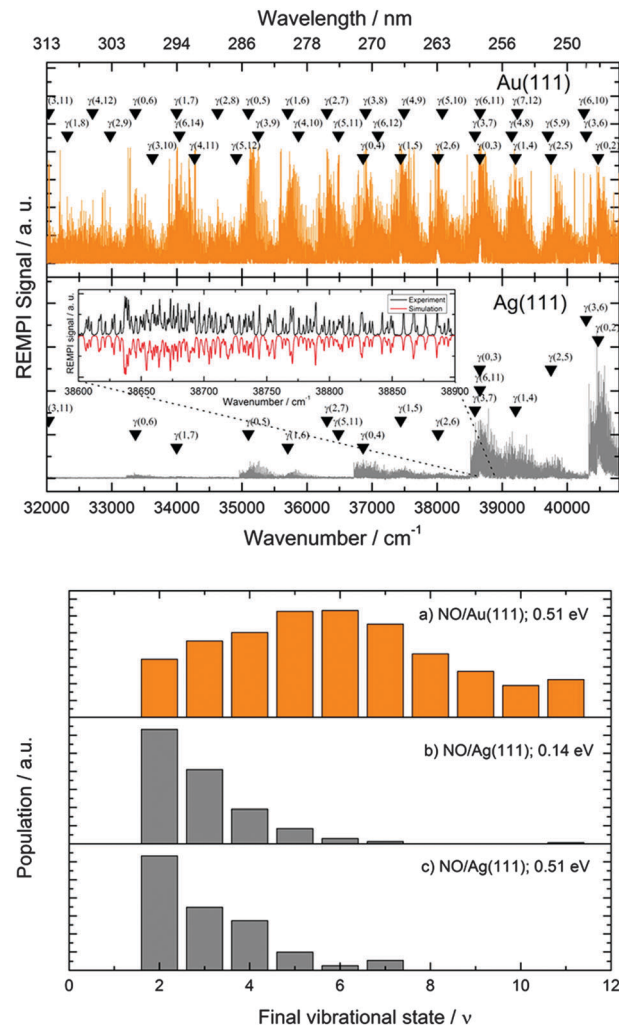


Fig. 8 Comparison of multiquantum vibrational relaxation of NO($v_i = 11$) on Au(111) and Ag(111). (upper panel) REMPI spectra of NO($v_i = 2–11$) scattered from Au(111) at 300 K and from Ag(111) at 670 K. The incidence translational energy is in both cases is 0.51 eV. The triangles mark the band heads within the γ band system. The numbers in the parentheses (v, v') indicate the vibrational quantum number in the electronically excited $A^2\Sigma$ state (v') and the electronic ground state $X^2\Pi$ state (v). Vibrational bands starting at high vibrational states in the electronic ground state are missing when scattering NO($v_i = 11$) from Ag(111). The enlargement of a small section of the spectrum in the inset shows the good agreement between experiment and spectral simulation used in the assignment process. (lower panel) Relaxed vibrational state distributions of NO($v_i = 11$) scattered from (a) Au(111) with $E_{\text{inc}} = 0.51$ eV and $T_{\text{surf}} = 300$ K, (b) $E_{\text{inc}} = 0.14$ eV and (c) $E_{\text{inc}} = 0.51$ eV. See ref. 155.

for NO on Ag(111) enhances the multiquantum vibrational relaxation. Future work to decide this question would include theoretical calculations based on a PES that accurately describes the dissociation transition state, implemented with state of the art electronically nonadiabatic dynamics such as IESH or EF.

4.2 HCl dissociation on Au(111): an intriguing challenge for the future

Dissociation of HCl on Au(111) is a possible system to investigate the validity of the BOA in an elementary surface chemical reaction.

The recombination of adsorbed H and Cl on Au(111) was reported already more than 20 years ago.¹⁵⁶ Here both Eley–Rideal and Langmuir–Hinshelwood mechanism were clearly identified using REMPI based detection in combination with molecular beam time-of-flight techniques. Inelastic energy transfer studies showed evidence that the HCl vibration and translation are coupled to the electronic degrees of freedom of the metal.^{29–31} With the constant progress in computing power and improved algorithms for solving quantum mechanical equations of motion, the dissociation of HCl on Au(111) could recently be treated by adiabatic dynamical theory. Here, a full 6D potential energy surface was fitted to more than 60 thousand DFT-derived energy points and quantum scattering calculations were performed for both HCl and DCl isotopes under the frozen lattice approximation.^{27,28,157}

The calculations employed: (1) the Born–Oppenheimer approximation (BOA), (2) density functional theory at the generalized gradient approximation level (DFT-GGA) and (3) a reduced dimensionality approximation – static surface approximation (SSA).

These calculations show that the dissociative adsorption of HCl on Au(111) occurs over an activation barrier. The barrier is lowest (0.65 eV above the reactant asymptote) over a bridge site; the barrier is higher at other surface sites (about 0.75 eV above the hollow site and 0.85 eV above the top site).²⁷ Quantum dynamics calculations of reaction probabilities for HCl($\nu = 0, 1$ and 2) were performed for HCl propagating normal to the Au(111) surface; these calculations showed that both vibration and translation enhance the reaction probability. The translational and vibrational efficacies were nearly equal; hence, the reaction probability depended on total reactant energy.

Recent experiments using a hot-nozzle technique similar to that used to study the dissociation of hydrogen on copper^{89,90,93} confirm the qualitative aspects of the theoretical predictions; specifically, evidence for translational and vibrational activation are clearly seen.¹⁵⁸ Here, initial sticking probabilities, S_0 , were measured for different molecular beam dosing conditions. The accumulated Cl on the Au surface was detected by Auger electron spectroscopy. The molecular beams were formed using a variable temperature SiC nozzle, employing molecular beams of HCl seeded in various carrier gases to control the HCl kinetic energy. Additionally the incidence angle is varied – this is useful since it is believed that only the normal component of kinetic energy promotes reaction.

The vibrational and translational enhancement of the reaction can be seen in Fig. 9. The red and black circles with error bars indicate the experimentally derived initial sticking probabilities (reaction probabilities) for HCl dissociation on Au(111). The abscissa indicates the normal component of incidence translational energy in each experiment. For the black data points the nozzle temperature has been varied from 295 to 1060 K and the incidence angle was fixed at 90°. The red points were obtained by varying the incidence angle at a fixed nozzle temperature of 1060 K. For the black points, both HCl translational and vibrational excitation increase from left to right, whereas for the red points only the normal component of translational energy changes, while the vibrational excitation remains at the highest level obtainable in this work. The fact that both sets of data

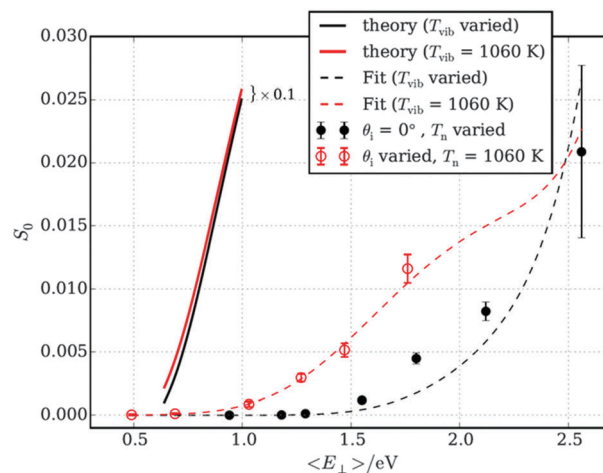


Fig. 9 Vibrational and translational activation of HCl dissociation on Au(111): comparison of hot-nozzle experiment and electronically adiabatic theory. Data points are shown with error bars. The dashed lines are the result of a fit to the data that yields translational and vibrational dependence of the reaction probability; this involves a convolution over the measured translational and vibrational energy distributions of the HCl produced in the hot nozzle experiment. The solid lines are the expected result based on theoretical calculations of the vibrational and translational activation of this reaction. Reactivity is dramatically overestimated by theory. See text for more detail and ref. 158.

increase with $\langle E_{\perp} \rangle$ directly shows that the reaction is translationally activated while the fact that the red points always lie higher than the black points indicates the reaction is also vibrationally activated.

The translational and vibrational activation of the reaction can be modelled with a vibrational state specific sticking function, S_0^{ν} , where the translational incidence energy dependence is described by a simple error function, with the shape from left to right of a rising step.

$$S_0^{\nu} = \frac{A_{\nu}}{2} \left[1 + \text{Erf} \left(\frac{E - E_{0\nu}}{W_{\nu}} \right) \right]$$

Here, $E_{0\nu}$ is the translational energy where reactivity reaches its half height, A_{ν} is the asymptotic reactivity at high incidence translational energy and W_{ν} is inversely related to the step-steepness of the rise in reactivity. The dashed lines in Fig. 9 are fits to the data using this model for the vibration state specific translational activation. Here $S_0^{\nu=0}$ and $S_0^{\nu=1}$ are averaged over the vibrational population and translational energy distributions produced by the hot nozzle molecular beam. Both the vibrational population distribution and the translational energy distributions could be measured independently.

In this way, one can obtain the initial sticking probabilities for HCl molecules in $\nu = 0$ and 1. However, due to the large number of fit parameters (six) it is difficult to find meaningful values without imposing constraints. The dashed lines in Fig. 9 show the results obtained by fitting with the reasonable constraints: $A_0 = A_1 = 1$ and $W_0 = W_1$. The best fit parameters obtained are $E_{00} = 3.98$ eV, $E_{01} = 1.7$ eV and $W_0 = W_1 = 0.51$ eV.

Also shown in Fig. 9 (solid red and black curves) are the expected sticking when these theoretical reaction probabilities²¹ are averaged over experimental vibrational population and translational energy distributions as just described. It is immediately obvious that the observed reaction probabilities are dramatically smaller than those expected from theory. Although there are significant uncertainties in the experimental results, the disagreement with theory is so large that we must consider possible deficiencies in the calculations. Specifically we ask: which assumptions of the theory are most likely to be in error?

First, it is possible that the calculated barrier height to dissociation obtained from DFT-GGA is too low. Using the PW91 functional – the same as was used in ref. 28 – for N₂ dissociation on ruthenium gave a 0.6 eV lower dissociation barrier height than that obtained when the RPBE functional was used.¹⁵⁹ Clearly, if the barrier were higher than $E_b = 0.65$ eV, it could help explain the reduced reactivity seen in experiment. It appears to us at least possible that this is not a major problem with the calculations.

Consider the experimental reactivity for HCl($\nu = 0$), which can only be promoted by HCl translation. A binary collision model suggests that 52% of the E_i would excite phonons in solid gold,^{29,30} which could mean that only 48% of the E_i is available to promote reaction. If correct, we would expect an HCl($\nu = 0$) reaction threshold at $E_b/0.48 = 1.4$ eV, similar to what is seen experimentally (black circles of Fig. 9). This argument implies that neglect of energy transfer from the reacting system to the solid's phonons leads to incorrect results.

The large vibrational enhancement of reactivity is also not captured by the theory. In fact, the difference is stark. Experiment shows that HCl($\nu = 0$) hardly reacts within the energy range studied – reaction practically requires vibrational excitation to $\nu = 1$. Within the spirit of the Polanyi rules,¹⁶⁰ this suggests that the transition state to reaction is late and that this might not be accurately described at the DFT-GGA level of theory with a PW91 functional. One way things could go wrong has to do with charge transfer. A transition state with an electronic structure similar to the HCl[−] anion would certainly be late; the bond length of HCl[−] anion is severely extended with respect to that of neutral HCl.^{161,162} Furthermore, calculations at the DFT-GGA level are notoriously poor at describing electron transfer accurately at metal surfaces.^{136,163,164} Hence, if electron transfer were to play an important role in this reaction, it is plausible that the transition state structure is poorly represented by the DFT-GGA calculations of ref. 28.

Finally, we note that our analysis suggests that the absolute reactivity of HCl($\nu = 0$) is dramatically overestimated by the electronically adiabatic theory of ref. 28. One possible direction to pursue the solution to this problem involves the possible influence of electronic friction near the transition state. We know that when frictional dissipation is important near the transition state of a reaction, for example in condensed phase chemical reactions, Transition State Theory predicts rates that are too large and one must instead employ Kramers' theory of rates in a Brownian fluid¹⁶⁵ to capture the friction induced reduction in reaction rate. Electronically nonadiabatic coupling of the HCl

vibration to the electronic degrees of freedom of the metal may also result in electronic friction near the transition state. By analogy to the above mentioned reaction rate theories, it is reasonable to suspect that such frictional effects would also act to reduce the reaction probability compared to an electronically adiabatic calculation. Previous studies have indeed shown that the HCl stretching vibration – surely involved in motion through the transition state – is coupled to gold electron-hole pairs.^{30,31} If electronic friction in the transition state suppresses the bond dissociation, initial HCl vibrational excitation might be particularly helpful (even necessary) to promote reaction. This might explain why the reactivity of HCl($\nu = 0$) is so much smaller than that of HCl($\nu = 1$); frictional dissipation nearly completely suppresses reaction of the former, while the latter may still overcome this suppressing influence albeit with a still small reaction probability.

Up to now we have emphasized systems where large deviations between experiment and theory are found. We argue that these large deviations are sign posts on the road to a deeper understanding. But for at least one simple reaction we are now reaching the goals set out in the introduction of this manuscript, a subject with which it is appropriate to close.

4.3 H-adsorption at a metal: a success story

The strategy suggested above is, simply put, to attempt to identify systems where chemical reactions are clearly influenced by BOA failure and to study these with detailed and well controlled dynamical experiments as rigorous tests of electronically non-adiabatic theoretical simulations. Theoretical studies suggest that hydrogen adsorption is an excellent place to pursue these goals.^{108,166–169} Indeed, this is now perhaps the only system known, where the reaction (sticking) probability is dominated by electronically nonadiabatic interactions and where theoretical simulations have successfully described dynamical experiments.^{167,168,170,171} This allows us an extraordinary ability to visualize the sticking process.

Fig. 10 shows experimental observations of the translational energy loss of H atoms colliding at a metal and an insulating surface. These results rely on a new experimental approach to the study of atomic scattering from solid surfaces,¹⁷¹ where nearly mono-energetic incident beams of H atoms are formed by laser-photolysis and scattering-angle resolved, translational energy loss spectra derived from Rydberg-atom neutral time-of flight measurements.¹⁷² Those measurements show that collisions of H atoms at metal surfaces (open symbols) are strongly inelastic. By contrast, H atom collisions at an insulator (closed symbols) are nearly elastic. For the insulator, the small inelasticity can be understood as a simple binary collision between a light and heavy atom where linear momentum is conserved. The situation for H atom energy transfer with the metal is clearly different and results predominantly from electronic excitation of the solid.

To understand this more deeply, theoretical simulations were developed and performed. Following the lead of others,¹⁷³ a potential energy surface (PES) for H-atoms interacting with fcc Au(111) was reported based on fitting the analytic form of the energy from effective medium theory (EMT) to *ab initio*

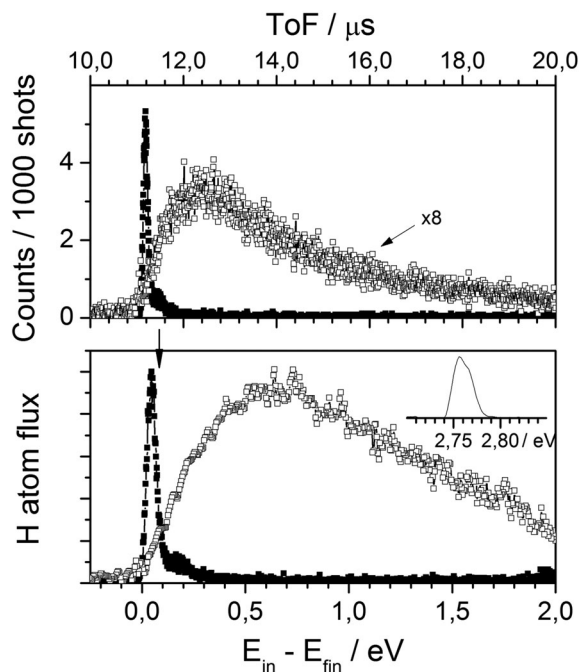


Fig. 10 Translational inelasticity for H atom collisions with an insulator and a metal. Upper panel: Measured TOF spectra for H-atoms scattered from Au(111) (\square) and solid Xe (\blacksquare). The channel width is 8 ns for Au and 4 ns for Xe. Lower panel: Corresponding kinetic energy loss spectra obtained by Jacobian transformation of the TOF data. The inset shows the kinetic energy distribution of the incident H-atom beam. The vertical arrow marks the expected energy loss for a binary collision between an H and a Xe atom. The experimental conditions are $E_i = 2.76$ eV, $\theta_i = 45^\circ$, $\theta_s = 45^\circ$ and $\phi_i = 0^\circ$ with respect to $[10\bar{1}]$ direction. See ref. 171.

energies calculated with density functional theory.^{170,174} The fit used input from configurations of the H-Au system with Au atoms at their lattice positions as well as configurations with the Au atoms displaced from their lattice positions derived from a single AIMD trajectory at finite temperature. The EMT PES reproduces DFT energies in full dimension, not only for the configurations used as input but also for a large number of additional configurations derived from *ab initio* molecular dynamics (AIMD) trajectories not employed in the fitting. Adiabatic molecular dynamics simulations on this PES reproduce the energy loss behavior of AIMD.^{167,168} EMT also provides expressions for the background electron density, which compare favorably to those from DFT. This provided the basis to develop a self-consistent approach to simulate mechanical as well as electron-hole pair excitation and investigate the effect of each on the motion of the incident H-atoms.¹⁷⁵

For H atoms with energy of 2.7 eV colliding with Au, electron-hole pair excitation was by far the most important energy loss pathway, giving an average energy loss ~ 20 times that of the adiabatic case. Similar translational inelasticity was also found using adiabatic AIMD trajectories with electronic friction subsequently imposed on the adiabatic trajectories, an approach termed “post-friction”.¹⁶⁸ Using the EMT-PES based molecular dynamics approach, atomic scale, simulations involving hundreds of Au atoms extending over several

picoseconds could be performed, shedding light on H atom adsorption process.

The increased energy loss due to coupling to electron hole pairs significantly enhances the probability of H-atom adsorption.¹⁷⁰ The mostly likely outcome for H-atoms that are not scattered also depends strongly on the energy transfer mechanism; for the nonadiabatic case, more than 50% of the H-atoms which do not scatter, are adsorbed on the surface while for the adiabatic case more than 50% pass entirely through the 4 layer simulation slab (see Table IV of ref. 170), a result that is a dramatic example of how wrong simulations can be if they neglect electronic non-adiabaticity.

This approach was also successful in reproducing the observations of experiment. This is shown in Fig. 11. The solid black line shows the theoretical prediction neglecting electronic excitation. The narrow energy loss distribution, peaking near the expected value for a binary collision of H with Au (56 meV – shown as a vertical arrow), clearly fails to capture the observed magnitude of the H atom translational energy loss (open squares). The gray solid line shows the simulated energy loss distribution when electronic excitation is included in the MD simulations. Here, the theoretical energy loss distribution captures the experimental result remarkably well. The inset to Fig. 11 shows how the translational inelasticity depends on the incidence energy and compares to the electronically nonadiabatic MD simulations. At all incidence energies, agreement between experiment and theory is good and the energy loss is dominated by electronic excitation. We note that the fractional energy loss,

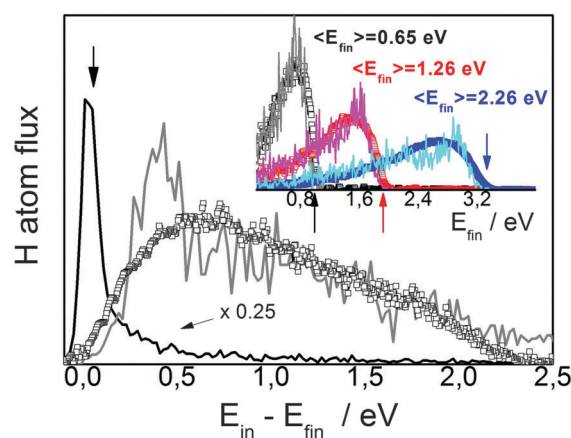


Fig. 11 H atom scattering from Au(111) – comparison of experimentally obtained kinetic energy loss spectrum to theoretical simulations. Theoretical energy loss found when neglecting (solid black line), and including (solid gray line) electronic excitation. Experimental energy loss for $E_{in} = 2.76$ eV are shown as open squares. The vertical arrow marks the expected energy loss for a binary collision between an H and an Au atom. The inset shows the incidence energy dependence, E_{in} , of the experimentally derived translational inelasticity (open squares) and comparison to theory (solid lines): $E_{in} = 3.33$ eV (blue), 1.92 eV (red), 0.99 eV (black). Colored arrows mark the three incidence energies. Also shown are the average final translational energies, $\langle E_{fin} \rangle$. The scattering angles are $\theta_i = 45^\circ$, $\theta_s = 45^\circ$ and $\phi_i = 0^\circ$ with respect to $[10\bar{1}]$ direction. In all cases the scattered H atoms remain unthermalized with the solid, emerging with a substantial fraction of their incidence translational energy. See ref. 171.

$(E_{\text{in}} - E_{\text{fin}})/E_{\text{in}} = 0.33 \pm 0.01$, is nearly independent of E_{in} , meaning that electron hole pair excitation remains important even at reduced incidence energies.

The good agreement between experiment and theory is evidence for the validity of the assumptions made in the MD simulations. Furthermore, the ability of the simulations to reproduce these experiments lends weight to the predictions made in ref. 170. Most interesting among these are the predictions that electron hole pair excitation increases the sticking probability and determines the adsorption mechanism, which occurs predominantly by a penetration-resurfacing motif. Here, H atom adsorption occurs by initial population of subsurface binding sites (where electronic excitation is most efficient in regions of high electron density) followed by migration to the strongest binding sites, which are at the surface. This work also invalidates a prior alternative hypothesis, one where multiple electronically adiabatic collisions resulting from a conversion of normal to parallel H atom momentum lead to sticking.¹⁷³ Inspection of individual trajectories shows that such adsorption behavior occurs only when electronic excitation is included in the simulations.¹⁷⁰ Movies of representative adsorption trajectories are included in the ESI† of this paper.

5 Conclusion

Advancing our understanding of surface chemistry, especially that occurring at metals requires better understanding of how electronic excitations of the solid influence the chemical reaction. This understanding is slowly emerging as experimental methods advance to be able to deliver detailed dynamical observations. As experiment discovers unexpected behavior, theory must extend to find quantitative explanations. This fruitful interplay between experiment and theory is however still at an early stage. Future efforts promise important new advances in this still evolving field of study.

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