Surface Chemistry

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Multiquantum Vibrational Excitation of NO Scattered from Au(111): Quantitative Comparison of Benchmark Data to Ab Initio Theories of Nonadiabatic Molecule–Surface Interactions**

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Predictive theories of molecular interactions at metal surfaces, based on the adiabatic (Born–Oppenheimer) approximation,[1] are becoming increasingly important to the design and understanding of objects of importance to the chemical industry, for example heterogeneous catalysts.[2] It is, however, now well established that the adiabatic approximation, that is the foundation of all conventional theories of chemical dynamics, is not always valid for describing atomic motions at metal surfaces.[3] In particular, electron–hole pair (EHP) transitions can provide a labile pathway for energy flow for processes involving high-frequency molecular vibrations that do not couple efficiently to phonons.[3a–d]

An important early experiment reported vibrational excitation probabilities for NO(v=0→1) scattering from Ag(111) as a function of surface temperature, T_s, and incidence translational energy normal to the surface, $E_{i,\perp}$, between 525 K $\leq T_s \leq$ 800 K and 0.1 eV $\leq E_{i,\perp} \leq$ 1 eV.[3a] The large absolute magnitudes of the excitation probabilities and an observed Arrhenius-like dependence on T_s were considered evidence of Born–Oppenheimer breakdown.

A more qualitatively compelling experiment involved multiquantum vibrational de-excitation of NO(v=15) molecules scattered from Au(111).[3b] This study revealed very efficient multiquantum transfer of molecular vibration to the metal, in contrast to results for the same molecule scattered from an insulator, where vibration was transferred inefficiently.[3b,4] Similar experiments on low work function materials even showed vibrationally promoted exoelectron emission.[3d–f]

Similar to molecular vibration, chemical bond formation can also involve nonadiabatic electronic transitions resulting from nuclear motion.[5] "Chemi-current"[5a] as well as exoelectron emission[5c] induced by surface reactions are clear evidence for such phenomena. Hence, developing ab initio theories of electronically nonadiabatic molecule–surface interactions, that is interactions that underlie such important processes as catalytic reactions, etching, and corrosion, remains one of the greatest challenges to our understanding of chemical transformations at metal interfaces.

A promising approach to developing new nonadiabatic theories involves interaction of experiment and theory in the following way: 1) make necessary simplifying assumptions, which define a model of nonadiabatic interactions, 2) determine the potential(s) and nonadiabatic couplings associated with that model from ab initio calculations (for example using density functional theory, DFT), 3) carry out dynamics calculations (usually this means reduced-dimension quantum calculations or high-dimension calculations with a classical mechanical approximation), and 4) compare predicted results to high quality experimental measurements carried out over as wide a range of experimental conditions as possible.

Here, we present results of two attempts to employ this approach. We first report a new benchmark data set for NO scattering from Au(111), one of the most well-studied systems where electronically nonadiabatic effects have been clearly demonstrated.[3b,6] Specifically, we present experimentally determined absolute excitation probabilities for NO(v=0→1) and NO(v=0→2). We report over eighty excitation probabilities for 300 K $\leq T_s \leq$ 1000 K and 0.11 eV $\leq E_{i,\perp} \leq$ 1.05 eV. This data set goes well beyond what is presently available in the literature. Most importantly, absolute excitation probabilities like those reported here can be quantitatively compared to ab initio predictions. Furthermore, in addition to extending the range of experimental conditions, multiquantum excitation, that is, NO(v=0→2), provides an

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additional criterion against which different ab initio approaches to nonadiabatic molecule–surface interactions can be tested.[3c,g]

Two ab initio theories, based on very different underlying physical pictures of nonadiabatic behavior at metal surfaces, are implemented in high dimension using a classical mechanical approximation for nuclear motion.

The first is electronic friction theory in which motion is assumed to evolve on the ground-state potential energy surface, with nonadiabatic energy transfer through EHP transitions introduced by added position- and mode-dependent frictions and fluctuating forces.[7] In a semiempirical model, Gross and Brenig[8] showed that reasonably chosen forces and frictions could reproduce key experimental observations.[3a] Ab initio implementation of the electronic friction model has been achieved for a number of related applications.[5b,9] Recently, Monturet and Saalfrank[6b] have applied a 2D quantum dynamical version of the electronic friction model, with DFT calculation of frictional terms, achieving qualitative agreement with the experiments of Ref. [3b].

An alternative picture of nonadiabatic dynamics invokes the electron transfer, so-called “harpooning”, mechanism in which an electron from the metallic conduction band can transfer to a localized affinity level of the incident molecule. This sudden electron transfer can populate a distribution of vibrational levels on the negative ion potential energy surface, analogous to a Franck–Condon optical excitation.[10] This is an example of a bound state in a continuum and maps directly onto the Newns–Anderson-independent electron model.[11] This and a closely related model[12] have been successfully applied to the data of Ref. [3a], using a model potential and reasonably chosen empirical parameters.[13]

More recently, this electron-transfer model was applied in an ab initio fashion to vibrational de-excitation of NO(v=15) scattered from Au(111), with Newns–Anderson interaction potentials and couplings computed by DFT.[14] The resulting dynamics were simulated using the independent electron surface hopping (IESH) algorithm,[15] in which the electronic continuum is represented by a discrete set of levels, with transitions amongst electronic states introduced by the surface hopping method.[16] As with the electronic friction calculations of Ref. [6b], the IESH simulations[6a] qualitatively reproduce the experimental results for multiquantum NO vibrational de-excitation,[3b] well within expectations considering the limitations of DFT and the incomplete nature of the experimental data.[17]

Even with such impressive progress, it is unfortunate that both friction-based and electron-transfer models appear to qualitatively reproduce previously available data. Thus prior to this work, even the basic physical picture of the nonadiabatic interactions important for NO collisions at a Au(111) surface remains unclear, a result that is not surprising given the fragmentary data available and the lack of rigorous quantitative comparison between theory and experiment.

Here, we carried out new IESH and electronic friction calculations for the vibrational excitation of NO. Remarkably, we find that the IESH theory originally developed to model vibrational de-excitation of NO(v=15) on Au(111) is in good agreement with our benchmark data over an extraordinary range of experimental conditions. We emphasize that both IESH calculations of vibrational excitation and de-excitation employed the identical DFT-derived Newns–Anderson Hamiltonian. On the other hand, an electronic friction model based on the same many-electron Hamiltonian used in the IESH calculations is not consistent with the data.

These calculations demonstrate that transient negative ion formation plays an important role in the nonadiabatic vibrational energy transfer process as well as the need to go beyond perturbative (electronic friction) approaches to predict molecule–surface interactions. The success of the IESH approach suggests that it may be used to gain deeper insight through comparison with experiment into other aspects of nonadiabatic interactions of molecules at metal surfaces.

To model the nonadiabatic dynamics of NO molecules scattering from Au(111), we used the recently developed IESH method.[14,21] The IESH approach has several advantages. First, we calculate nonadiabatic dynamics based on potential energy surfaces and nonadiabatic coupling strengths obtained from DFT calculations. Second, all electrons are assumed to be non-interacting. Hence, we can independently propagate many one-electron orbitals instead of a single many-electron wave function increasing the algorithm efficiency. Third, motion of the nuclear degrees of freedom is modeled classically and the coupled electron–nuclear dynamics is calculated within the framework of the surface hopping theory.[16] Thus we can perform high-dimensional dynamics calculations including both the NO molecule as well as the Au lattice degrees of freedom.

A set of IESH simulations was performed to study the T_s and E_i dependence of NO vibrational excitation. We calculated excitation probabilities at eight values of T_s from 300 to 1000 K with an interval of 100 K for each value of E_i used in the experiment. The initial states of the NO molecules were chosen to be randomly oriented and non-rotating with initial velocities directed normal to the surface, reflecting a given choice of E_i. The initial vibrational energy of NO was 0.12 eV, representing the vibrational zero-point energy. The metal continuum was represented by 40 metal orbitals appropriately populated by 20 electrons. A detailed description of the construction of the many-electron system Hamiltonian and implementation of the IESH algorithm can be found in Refs. [14,21].

The IESH method is efficient. It takes only 20 to 60 seconds (depending on the choice of E_i and T_s and details of the scattering process) to produce a trajectory on a core of a 2.7 GHz Intel Xeon CPU. This allows us to collect good statistics even for rare events like vibrational excitation. For every simulation point defined by E_i and T_s, we calculated 100000 trajectories and saved the final values of NO vibrational energy for each trajectory. Vibrational energy densities, like that shown in Figure 1, were constructed from these data. As the NO vibrations were modeled classically, we used a standard box binning procedure to obtain the excitation probabilities, rounding the vibrational action (classical analog of the quantum number) to the nearest integer for each

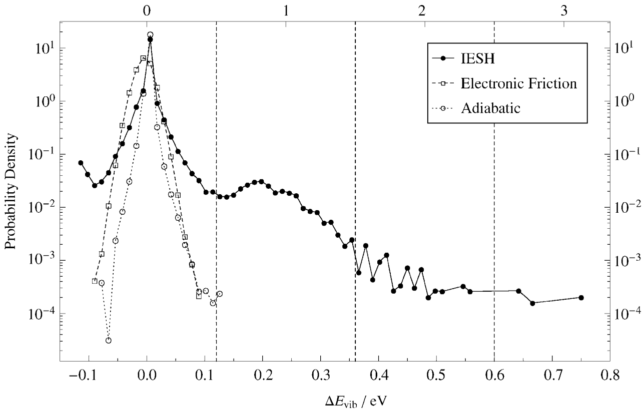

Figure 1. Theoretical calculations of vibrational probability density as a function of the change in vibrational energy, ΔE_{vib}, for $E_i = 0.63$ eV and $T_s = 1000$ K. The zero of the x axis represents the zero-point energy level with 0.12 eV of vibrational energy. Hence, the classical calculation allows loss of vibrational energy resulting in values below the zero-point level. Such trajectories are binned as $v = 0$. Results are shown for adiabatic dynamics (no surface hopping, open circles), electronic friction (open squares), and for IESH (solid circles). Vertical dashed lines show the binning regions for each vibrational state ($v = 0$, 1, 2 and 3), which are indicated on the upper x axis. IESH predicts a much larger vibrational excitation probability than the electronic friction theory or the adiabatic treatment. Note the logarithmic scale.

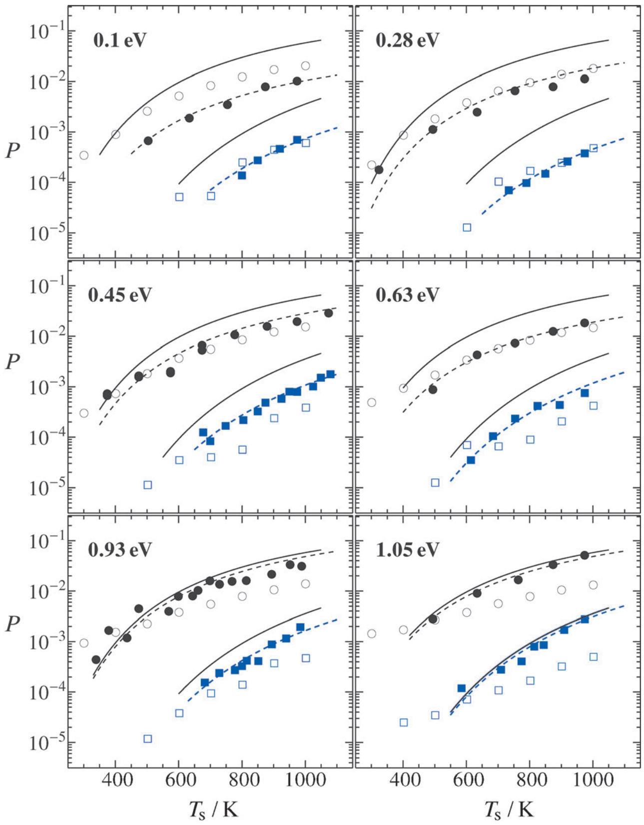

Figure 2. Excitation probabilities (P)for NO/Au(111) as a function of surface temperature, T_s, for six different incidence energies of translation, E_i. Experiment (filled) and IESH theory (empty): circles for NO(v=0→1) and squares for NO(v=0→2). Arrhenius functions fitted to the experimental points are shown as dashed lines. Thermal limits are shown as solid lines.

trajectory.[22] These bins are represented by vertical dashed lines in Figure 1.

The results of both theory (open symbols) and experiment (filled symbols) are presented in Figure 2, where the vibrational excitation probabilities for NO(v=0→1) (black) and NO(v=0→2) (blue) are plotted as a function of T_s at six values of E_i. The experimental vibrational excitation probability is always much larger for NO(v=0→1) than for NO(v=0→2) and for both channels, a higher E_i value leads to an increase in vibrational excitation probability. At all values of E_i, the experimental data follow an Arrhenius dependence on T_s with an activation energy equal to the change of vibrational energy (dashed lines). This is true for both NO(v=0→1) and NO(v=0→2) excitation, with apparent activation energies of one (0.24 eV) and two (0.47 eV) vibrational quanta, respectively.

The absolute excitation probabilities producing NO in both $v = 1$ and 2 are reproduced by the IESH theory over the entire range of conditions for both vibrational channels (see also the Supporting Information). We characterized the agreement between experiment and theory by computing the Pearson χ^2, given by Equation (1), for the N data at each incidence energy.

$$\chi^2 = \frac{1}{N}\sum_{i=1}^{N}\frac{\left(P_i^{\text{obs}} - P_i^{\text{theo}}\right)^2}{P_i^{\text{theo}}} \qquad (1)$$

Here, $P_i^{\text{obs}}$is the ith observed probability from the benchmark data set and P_i^{theo} is the corresponding value predicted by the IESH theory. We find $0.0007 < \chi^2 < 0.03$ for the $v = 1$ channel and $0.00002 < \chi^2 < 0.003$ for the $v = 2$ channel. While improvement is still clearly possible, this is the first time that such good agreement has been obtained between an ab initio theory of nonadiabatic molecule surface interactions and energy transfer data taken over a wide range of experimental conditions. Remarkably, this is achieved with a theory that was originally developed for modeling de-excitation of NO(v=15), using an identical parameterization of the Hamiltonian. This unifies our physical picture of energy transfer for NO scattering on Au over a wide range of vibrational states ($v = 0$–15), surface temperatures (300 K ≤ T_s ≤ 1000 K) and incidence translational energies (0.11 eV ≤ $E_{i,\perp}$ ≤ 1.05 eV). We also note that IESH even predicts population in NO(v=3; Figure 1) although our statistics are not sufficient to evaluate its possible importance.

The most significant deficiency of the IESH results concerns the dependence of the excitation probabilities on E_i, which is somewhat weaker than seen in experiment. The reasons for this (in our view relatively minor) deficiency in IESH remain to be clarified. We do not currently have an established means to evaluate the accuracy of the DFT-derived diabatic states and nonadiabatic couplings. More accurate calculations of these quantities might lead to better agreement with experiment. Furthermore, IESH ignores the existence of different NO spin-states both in the neutral and the anion. What errors this introduces is likewise unclear. All of these issues require future attention. While we do not believe that the classical approximation introduces significant errors over the range of conditions studies here, future quantum versions of IESH are clearly needed to test this. Despite all of these potential concerns, we consider the present level of agreement between theory and experiment to be a remarkable success, indicating the validity of the various assumptions made within the IESH approach.

Calculations for NO/Au(111) scattering were also performed using an electronic-friction model[9b] applied with the same many-electron Hamiltonian that was used in the IESH calculations. Figure 1 shows a comparison at $E_\mathrm{i} = 0.63$ eV and $T_\mathrm{s} = 1000$ K, which is representative of results under other conditions. The extent of vibrational excitation is substantially lower in the electronic friction calculation in comparison to that of IESH. In fact, no trajectory is found, out of the 100000 calculated, that would be binned as $v = 1$ or higher. This absence of vibrational excitation shows that the friction model is insufficient to explain nonadiabatic vibrational excitation in this system. Moreover, its results are very close to ones obtained from the adiabatic model, when surface hopping and electronic friction mechanisms are switched off.

The failure of friction theory arises from the weak coupling assumption. A weak coupling description of a direct scattering process cannot produce vibrational excitation probabilities that approach the thermal limit given by Equation (2).

$$P^{v}_{\mathrm{therm}} = e^{-\frac{v\hbar\omega}{kT_s}}\left(1 - e^{-\frac{\hbar\omega}{kT_s}}\right) \qquad (2)$$

Here, v is the vibrational quantum number, $\hbar\omega$ is the vibrational level spacing, and k is the Boltzmann constant. Thermalization with the surface is an upper limit to the vibrational excitation probability when excitation occurs through an electron-mediated process neglecting translation–vibration coupling.[3c,13,23] This thermal limit is shown as solid lines in Figure 2. The observed vibrational excitation probabilities range between 0.1 and 0.85 of the thermal limit, indicating the need to go beyond the perturbative (electron friction) approach. In contrast, the IESH theory, which describes the strong coupling induced by an electron-transfer event, leads to good agreement with experiment.

The electronic friction calculations of excitation probabilities reported here employ frictions computed via the same DFT-based interactions employed in the IESH simulations. We caution that these frictional terms are not the same as those employed in Ref. [6b]. Nevertheless, IESH predicts excitation efficiencies for NO(v=2 and 1) reflecting the importance of direct overtone NO(v=0→2) excitation,[3c,23] which is confirmed by detailed examination of individual IESH trajectories. In contrast, the weak coupling approximation underlying all friction models—regardless of the way one derives the friction coefficients—requires that the formation of $v = 2$ occurs only through sequential $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ transitions.

As outlined above, the electronic friction and IESH theories are based on different physical pictures of the origins of nonadiabaticity. In fact, IESH encompasses the friction picture in the case of weak coupling. Ab initio calculations of electronic friction for CO on Cu(100) have shown that the dominant contribution to nonadiabatic coupling arises from partial transfer of charge from the surface to the unoccupied antibonding π^* orbital of the molecule, that is, to the affinity level invoked in the harpooning model.[24] Moreover, in the IESH theory, the amplitude of this localized level is spread over many nearby (discretized) continuum levels. Thus, an electronic transition ("surface hop") may result in only a small change in occupation of the localized level; that is, electronic friction effects are encompassed by the IESH theory. The advantage of IESH is that it can also describe strong coupling processes.

Finally, we emphasize the importance of IESH for future work. The remarkable success of this ab initio theory in capturing such a wide range of experimental observations suggests that it can be used (in comparison with experiment) to gain deeper insight into other aspects of nonadiabatic molecule–surface interactions, including translational inelasticity which, as has been pointed out for decades,[13] remains a vexingly difficult problem.

Experimental Section

The equipment and procedures used to make these measurements have been previously described in detail.[18] Supersonic molecular beams were produced using a 10 Hz piezoelectrically driven pulsed valve. The mean translational energy of NO in the molecular beam was adjusted by seeding varying concentrations of NO into a variety of inert carrier gases with different masses. The molecular beam was

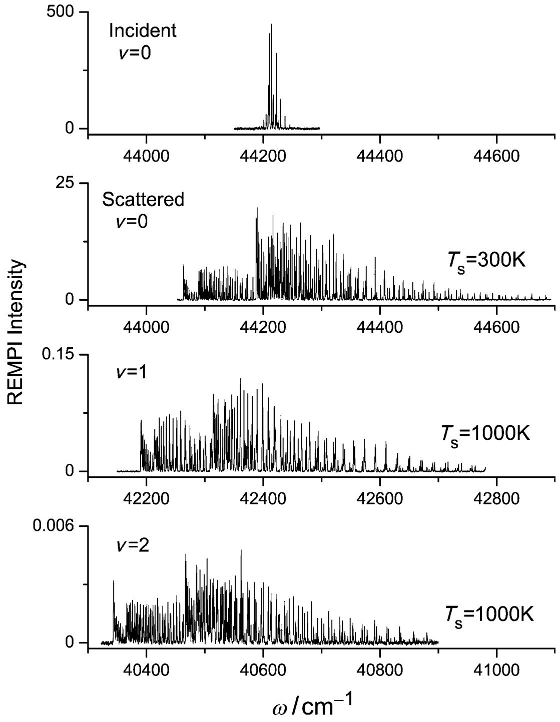

Figure 3. REMPI spectra for incident and scattered NO at $E_\mathrm{i} = 0.63$ eV corrected for differences in laser power and MCP gain. The NO(v=0,1,2) molecules are probed through the γ_{00}, γ_{01}, and γ_{02} bands, respectively. The incident beam is rotationally cold, with significant population in only a few quantum states. The molecules undergo significant rotational and vibrational excitation in the surface scattering process.

skimmed, passed through two stages of differential pumping, and scattered from an Au(111) crystal at near normal incidence. T_s was varied from room temperature to about 1000 K by resistive heating of tungsten wires to which the gold crystal was mounted. Surface impurities were removed by approximately 60 min of Ar ion sputtering. After sputtering, Auger electron spectroscopy revealed no residual carbon (the principal impurity on Au surfaces) up to our detection limit of 0.03 monolayer. The surface was then annealed at around 1000 K for approximately 45 min. The scattered NO molecules were state-selectively ionized with UV laser light used for (1 + 1) resonance-enhanced multiphoton ionization (REMPI) through the $A^2\Sigma^+$ state, often referred to as the γ bands.[19] The ions were collected using ion optics and detected by a dual microchannel plate detector (MCP). Accurate velocity measurements of the NO beams were carried out as in previous work.[20] Briefly, molecular beams of NO(v=0) were "vibrationally tagged" to $v=3$ by exciting them with a 5 ns pulse of 1.8 μm light. State-specific REMPI detection of NO(v=3) was carried out about 15 mm downstream. Arrival time distributions were recorded by varying the delay between the two laser pulses. Knowledge of the flight distance, which was measured independently, led to the velocity distributions of the beams.

To derive the absolute vibrational excitation probabilities, rotationally resolved spectra, like those shown in Figure 3, probing NO(v=0,1,2) molecules were recorded. Absolute excitation probabilities were extracted by comparing the signal of inelastically scattered NO molecules in $v=1$ and 2 to the signal of vibrationally elastically scattered NO molecules in $v=0$. To make this comparison, the entire rotational spectrum was integrated giving the spectral intensity in each vibrational band, and the integrated signal was corrected for various factors such as MCP gain, angular and temporal dilution, and laser power. Angular, temporal, and rotational distributions indicate a direct scattering mechanism for vibrational excitation under all conditions of this work.

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