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Chemisorbed-Molecule Potential-Energy Surfaces and Electronically-Stimulated Processes

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ABSTRACT

Three topics illustrate some central physics of processes produced by UV-laser and low-energy electron stimulation. First, a multi-dimensional ground-state potential energy surface (PES) for $\text{NH}_3:\text{Pd}(111)$, computed using *ab initio* local-density functional theory, allows dramatically different dynamics depending on poorly-known excited-state forces. We use quantum-resolved experimental data to argue that stimulated desorption is dominated by a direct path off the surface, following placement of the wavepacket on a molecule-surface hard wall accessed by internal molecular motion. This illustrates the questionable relevance of one-dimensional models for understanding molecule-surface dynamics. Second, we study the image-charge model of excited state forces experienced by ions produced, for example, by hot carrier attachment. *Ab initio* results show that this model *totally* fails at molecule-surface distances typical of chemisorption. Finally, we present a purely-electronic adiabatic model of excited state PESs and use it to argue that, if significant covalent interactions occur between an adsorbate and a surface, hot carrier attachment does *not* simply produce singly-charged ions. Instead, attachment creates excitations of the molecule-surface bond occur and, in some cases, may result in *multiply*-charged ions.

1. INTRODUCTION

Understanding dynamical processes involving chemisorbed molecules is of importance for catalysis, epitaxial materials-growth, and processes involving surface electronic excitations, such as "desorption induced by electronic transitions" (DIET) [1], non-thermal materials processing, and photodesorption [2]. Knowledge of potential energy surfaces (PESs) is central to understanding laser-stimulated processes. Little is currently known concerning the ground state PESs of chemisorbed molecules; less is known about excited-state PESs. The role of *multi*-dimensionality has only been explored in a limited sense. Therefore, dynamical studies [3] have unfortunately had to rely on *model* excited-state PESs, sometimes not even proposed with chemisorbed molecules in mind [4]. Although these potential surfaces have been accepted as "conventional wisdom", our results suggest that they have no validity for chemisorbed molecules on metal surfaces.

In this report, three topics illustrate the need for accurate PESs. First, for the $\text{NH}_3:\text{Pd}(111)$ system, we present the two-dimensional PES where the molecule-surface distance is coupled with the H-N-H angle internal to the molecule. Using clusters of up to 18 Pd atoms, this surface was computed with the local-density-functional DMol computer code [5]. We note three very different dynamical models for desorption, all of which are possible on this PES but only one of which agrees with quantum-state resolved experimental data from a related system, Pt(111). Next we use similar calculations to study the excited-state forces on a molecular ion placed 2.1-3.2 Å above a metallic surface. We find that the image-charge model predicts forces up to an order of magnitude too large. Finally, we present a simple electronic-structure model in order to develop physical insight into the excited-state dynamics of molecules that have a

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significant covalent interaction with the substrate. We believe our adiabatic model applies to almost all adsorbed molecules. For hot-electron and hot-hole attachment processes, proposed to be important mechanisms for laser photon-stimulated desorption (PSD) [2,3], we find results, reported below, that in many ways contradict the conventional thinking used in recent studies [3]. For the NO:Pt(111) system, we have derived semi-empirical parameters for our model. We point out that hot-electron attachment actually produces the *doubly* negative ion with substantial probability because the singly negative ion is not locally a stationary state, being mixed heavily in the ground and lowest excited state of the metal-molecule bond.

Below, we first provide some technical details concerning the calculations and the NH₃:Pt(111) experiments. We then examine the ground and excited state results in more detail before making a summary of our major conclusions.

2. TECHNICAL DETAILS

The DMol program [5] solves the Kohn-Sham equations [6] for the ground state energy and charge density, using a local-density-functional exchange and correlation potential of the form derived by von Barth and Hedin [7]. Calculations are of the LCAO form; our work used the "double-numerical plus polarization-function" bases and the fine mesh for numerical integration. (The double numerical bases exceed double-zeta Gaussian bases in completeness [8].) With metal clusters, a finite Fermi temperature (or "smearing parameter") is necessary to achieve a convergence of 10⁻⁶ Hartree (1Hy = 27.21 eV). Tests showed that the results reported below do not depend on this parameter even though it is finite (0.1 eV).

Local-density functional theory has a long history in the study of metals. We tested the DMol code for its ability to study ammonia as well. Comparison of the DMol results with gas-phase ground-state properties revealed high accuracy: an N-H bondlength within 0.02 Å and an H-N-H bond angle within 1.2° of experimental results. In addition, the calculated inversion barrier was within 0.03 eV of experiment.

We used Pd metal clusters of from 9 to 18 atoms to study NH₃:Pd(111). (Because DMol does not yet contain relativistic corrections, we used Pd to compare with experimental data from NH₃:Pt). The Pd₁₈ calculations allow comparison of hollow (h), bridge (b), and atop (a) sites all on the same cluster, with all Pd atoms nearest to ammonia being fully coordinated. We fixed the Pd positions in the geometry appropriate to a bulk-terminated (111) surface; however, inward and outward relaxation of the three Pd atoms about h-NH₃ on Pd₁₈ showed negligible change in chemisorption energy. We conducted studies of the convergence of binding energy and ground state geometry with increasing cluster size. Details will be reported elsewhere.

Two-photon resonance-enhanced multi-photon ionization (REMPI) through the C' state was used to detect neutral ammonia desorbed from Pt(111) under electron bombardment. These experiments provide quantum-state resolved translational energies and yields, as well as excitation threshold information. Experimental details are reported elsewhere [9]; the experimental results are presented in Section 3, below.

3. THE GROUND-STATE POTENTIAL ENERGY SURFACE OF NH₃:Pd(111)

The threshold for ammonia desorption, < 10 eV, correlates with excitation of the highest-

occupied $3a_1$ molecular orbital. For the two types of adsorbed ammonia on Pt(111), this level is found ~ 8 eV below the Fermi level for the low-coverage α -NH₃ and 5.5 eV below for the high-coverage β -NH₃ adlayer. Ionization of the $3a_1$ level in gas-phase ammonia excites only the ν_2 vibrational mode, also known as the umbrella or inversion mode. This is because the $3a_1$ excitation places the molecule on a PES with ~ 0.7 eV of potential energy and the planar geometry lowest in energy [10]. Indeed, our REMPI experiments detected excitations *only* in the umbrella mode of desorbed ammonia, consistent with the threshold assignment. Unlike molecules such as CO and NO, ammonia contains no low-lying molecular orbitals that can accept charge-transfer screening from the metal. In fact, the lowest bound-to-bound excitations in gas-phase ammonia place an electron in a Rydberg level. (On the surface the Rydberg levels experience substantial overlap with the lower-energy metal orbitals. Because of orthogonality requirements, their energies are thus raised and screening involves polarization of metal charge.) Therefore, we expect excited ammonia on the surface to closely approach a positive ion in charge.

In Fig. 1, we show a two-dimensional ground-state PES of chemisorbed ammonia. Because only ν_2 internal excitations are observed in the desorbate, the degrees of freedom chosen for Fig. 1 are the position of the N-atom above the surface plane of Pd atoms and the angle made between the N-H bonds and the normal to the surface, z . (This is equivalent to hydrogen motion in the umbrella vibration; the N-H bond length is fixed, as negligible relaxation effects occur with z -N-H angle). At large distances from the surface, we observe the symmetric double wells of upright and inverted ammonia with an inversion barrier approaching at large distances the calculated value of 0.28 eV (cf. the experimental value of 0.25 eV [11]). As the molecule approaches the surface, we find that *all geometries bind*; however, the upright molecule binds most strongly and is thus closer to the surface at equilibrium. This factor breaks the symmetry of the gas-phase, causing an increase in the ν_2 frequency on the surface (as observed [12]) and, at sufficiently close distances, the complete loss of the double-well structure (with z -N-H angle). The ground state wavepacket, ϕ_0 , is centered at the position labeled #1, and the curve representing $1/e$ of the maximum in ϕ_0^2 is drawn.

The topology presented in Fig. 1 is common to all three adsorption sites. On the 18-atom Pd cluster, the binding energy of the atop site (1.1 eV) is greater than that of the hollow and bridge sites (both ~ 0.8 eV), as summarized in Table 1. The notation (x,y) is used to denote $x(y)$ atoms in the first(second) metal-layer of the cluster. Note that Table 1 also shows pronounced cluster-size effects. The difference in binding energies between sites narrows significantly between the 18 atom cluster, used to study all three sites, and the smaller clusters of 9 Pd atoms, used to model h-NH₃ and b-NH₃, and 10 atoms, used for a-NH₃. (The "n/a" in Table 1 indicates that these clusters are not appropriate to study these sites.) Thus, it is not clear that convergence to the extended surface has been obtained even at 18-atoms. In addition, notice in Table 1 the steady decrease in the Pd-N distance with increasing binding. This affects the dynamics because the hard wall of the inverted molecule does not change its location appreciably with cluster size; thus, as cluster size increases, there is a steady decrease in the need for inward motion in the excited state in order to achieve sufficient potential energy on the hard wall for desorption (see below). (For computational efficiency, Fig. 1 corresponds to the hollow site on Pd₉. We checked key regions of the PES for all three sites on Pd₁₈ and found no qualitative changes; however, Figure 1 should not be assumed to quantitatively apply to the extended surface and is used here only for illustration.)

Pd Cluster:	18(12,6)	10(7,3)	9(6,3)
E_a	1.13	0.99	n/a
E_b	0.80	n/a	0.54
E_h	0.78	n/a	0.41
z_a	2.13	2.18	n/a
z_b	2.10	n/a	2.16
z_h	2.11	n/a	2.35

Table 1: Calculated adsorption energies, $E(\text{eV})$, and heights above the surface plane, $z(\text{\AA})$, at hollow (h), bridge (b), and atop sites (a). (For cluster notation, see the text.)

Figure 1: The ground-state PES of NH_3 in a three-fold hollow on the 9-atom Pd cluster plots the molecule-substrate distance vs. the distance of the N atom to the hydrogen plane ($-r_0 \cos \theta$, where θ is the z-N-H angle and r_0 is the N-H bondlength of 1.9 au). The numbers on the figure refer to positions referred to in the discussion.

Assuming motion in the excited-state is completely unknown, several very different dynamical pictures are possible, all of which can cause desorption from the PES of Fig. 1:

1) **The one-dimensional Antoniewicz model [4]** -- If the dynamics of a positively-charged ammonia ion were dominated by attractive image-charge forces, direct inward motion to the hard wall at position #2 would leave the molecule, upon de-excitation, with enough potential energy to desorb directly by accelerating in the +z-direction. (This dynamics has been explored by Gadzuk for NO:Pt(111) [3].) We find that this scenario does *not* occur for the NH₃:Pt(111) system: The timescale for inversion, estimated from the ν_2 frequency, is ~ 17 fs; this is too fast to be ignored compared with translation. The observation of desorbate ν_2 vibrational "temperatures" of 950 ± 50 K (NH₃ populations of 1.0:0.26:0.09 for ν_2 of 0:1:2), shows that motion in this mode must be considered. The isotope effect between the NH₃ and ND₃ yield is ~ 3 , which is anomalous for a one-dimensional model [13]. However, if motion in the inversion mode is critical to desorption, the isotope effect may be explained because of the slower speed at which the deuterated molecules move internally (a point noted by Zhu and White in their discussion of data from the NH₃:GaAs(100) system, which also shows an anomalous isotope effect [14]). Finally, while the REMPI experiments detect an NH₃ desorbate tumbling energy (in temperature, ~ 350 K) consistent largely with the sudden release of the zero point kinetic energy of the rocking mode on the surface (720 cm^{-1} [12]), the spinning energy of the desorbate, ~ 650 K, is totally at odds with the negligible zero-point energy of a nearly free rotor, indicated by computation on the upright molecule (rotational barrier of ~ 0.006 eV for the hollow site) and consistent with experimental observations [15]. This pronounced rotational heating, together with an observed rotational isotope effect of ~ 3 , require near inversion of the molecule during the desorption dynamical process.

2) **Mode-to-mode vibrational energy transfer** -- If the excitation moved the ground-state wavepacket towards position # 3, and we had sufficient total energy in the umbrella motion to desorb, coupled-oscillator dynamics results. However, this would require a transfer of the energy to the molecule-surface mode. We have run a classical-trajectory test of this model using the PES of Fig. 1 and find very slow mode-to-mode energy transfer, as is obvious from the frequency mismatch between the slow molecule-surface stretch and the fast umbrella motion. This makes it improbable for sufficient energy to be concentrated in the single mode required for desorption, before damping due to the metal removes sufficient energy to prevent desorption. (Other modes, such as the N-H stretch, do not contribute because they are not vibrationally excited and are not consistent with the threshold of the $3a_1$ excitation. Even if they were excited, the frequency mismatch would be worse.) In addition, we observe the *same* desorbate translational energies and vibrational temperatures for NH₃ and ND₃, which is unexpected from this mechanism. Finally, we observe *weak* correlation between the translational energies of the desorbates and the excitation of the internal ν_2 mode. This at most weak mode coupling makes this mechanism, proposed by Zhu and White as a possible explanation of the isotope effect observed on the GaAs surface [14], not supported by the quantum-resolved data from the Pt(111) surface.

3) **Direct desorption on the two-dimensional PES** -- If the excitation lives sufficiently long and inversion forces dominate the excited-state motion, the system finds itself in region #4 of Fig. 1, on the hard wall of the molecule-surface interaction of the *inverted* molecule. The indicated trajectory, which follows the trough of the inverted molecule off the surface, was calculated assuming the excitation drops the wavepacket where indicated with no kinetic energy. Using gas-phase

frequencies, we estimate ($t \sim \pi/\omega$) that inversion takes ~ 17 fs for NH_3 and ~ 22 fs for ND_3 . A reasonable excitation lifetime of 5 fs would then produce our observed isotope effect of ~ 3 . Since we calculate that the image-charge forces experienced by the molecule are *much* smaller than the classical prediction of $e^2/4z^2$ (see next section), this scenario agrees with our *ab initio* calculations as well. However, this scenario also offers immediate understanding of the experimental observations: Those molecules that desorb follow trajectories down the well of the inverted molecule, causing weak vibrational-translational coupling and isotope-independent translational and vibrational energies. In addition, as the molecules approach inversion, an increase occurs in the corrugation of the rotational PES (peak-to-trough differences are as large as 0.3 eV for inverted ammonia on Pd_{18}). This causes them to “spin-up”, thus explaining the rotational heating.

In summary, by considering the *multi*-dimensional aspects of the PESs, we can understand the quantum-resolved experimental data from this system. At the same time, the data strongly indicates which of the above dynamical scenarios is appropriate. Thus chemisorbed ammonia constitutes another case where multi-dimensionality is the key aspect of the analysis, the first example of which was $\text{NO}:\text{Pt}(111)$ [16] (there, data suggests that *rotation* allows the molecule to find a translational hard-wall).

4. IMAGE-CHARGE FORCES AT CHEMISORPTION DISTANCES

The above discussion has indicated the importance of knowing the excited-state forces, at least approximately. The case of ammonia should be one of the simplest because, as noted, the absence of charge-transfer screening makes excited chemisorbed ammonia close to a positive ion. The “conventional wisdom”, used in semi-quantitative studies (e.g., Ref. [3]), suggests that the excited-state PES with respect to the surface should then have the image-potential form, $V_+^{ic}(z) = V_0(z) - e^2/4z + \epsilon^*$, where V_0 is the ground-state potential, ϵ^* is the energy to make the excitation, and z is here the distance of the ion from the image plane (being a constant, ϵ^* does not affect the forces).

Many workers have noted that chemisorbed molecules have several components to their binding [17-20]. Molecules with no orbitals close to the Fermi level, such as water and ammonia, have been described as being bound “electrostatically”. This does not mean, however, that a dipole-image-dipole model is correct, for as noted by Müller and Harris for the $\text{H}_2\text{O}:\text{Al}$ system [17], this can explain only a small fraction ($\sim 10\%$) of the observed total binding energy. We find this also true for chemisorbed ammonia. Ref. [17] also noted that there would always be some fractional charge transfer from the lone pair orbitals of such molecules to the surface, as supported by observed work function changes [21]. Indeed, Fisher [21] proposed several tenths of an electron transfer, out of the σ -donating $3a_1$ orbital, to explain workfunction and photoemission-level shifts for $\alpha\text{-NH}_3$. Because the $3a_1$ orbital is so deep, however (near the bottom of the metal valence bands), we expect that only a fraction of the chemisorption bond is due to this weak covalency.

To investigate the magnitude of the $3a_1$ -surface interaction, we performed the following computational experiment: We *inverted* the molecule, thus removing whatever direct interaction there is with the $3a_1$ orbital and the surface, and computed the binding energy and equilibrium position. We found, for $\alpha\text{-NH}_3$ on Pd_{10} , that the inverted molecule was bound by 0.7 eV, compared with 1.0

eV for the upright molecule. *Thus about 2/3 of the binding is "electrostatic"*. (Since the atop site has stronger transfer integrals between the lone-pair electrons and the Pd 4d atomic orbitals than do hollow or bridge sites, we consider 2/3 a lower bound for the other sites.)

In summary, we find ammonia bound substantially at all sites and in all orientations. We have even demonstrated substantial binding for the planar molecule, which has no dipole moment. (Our results contrast markedly with some earlier theoretical work, which found repulsive interactions at hollow sites on other metals such as Cu [22]. We note that some of these results did not include correlation; our results agree with more recent local-density results which also found binding at all sites on Cu [23], though weaker than we found on Pd.)

What is the origin of this binding? Note that compared with the size of the metal atoms, ammonia is a small object having an internal charge distribution much more complex than a simple dipole. In addition, at all three sites, its equilibrium distance from the surface is about the same, ~ 2.1 Å for the N-down orientation. This distance is not large compared with the sum of covalent radii of Pd and N (2.03 Å). Thus there must be substantial overlaps between the metal and ammonia charge distributions. Such overlaps necessarily cause charge rearrangement, principally on the metal because it is much more polarizable than the molecule. These redistributions in turn can cause attraction, with strength increasing with substrate polarizability. Since the latter also increases with the density of states at the Fermi level, this explains the greater binding we observe for ammonia on Pd compared with a recent similar theoretical study of ammonia on Cu [23]. Pending a detailed analysis of the charge distribution changes upon chemisorption, we postpone answering this question in more detail.

The above computational experiment on inverted ammonia allows us to study the image-charge question for a relatively pure positive ion. By eliminating the small covalency and σ -donation, we also removed the related questions of changes in metal-adsorbate bond polarization and dative bonding upon ion formation. Knowing from the gas-phase work that a positive charge will not induce charge-transfer screening due to virtual-orbital lowering, we thus obtain a "best" case for the image charge model, since the above effects reduce the image force on the ion.

We make the ion by placing a proton on the N-nucleus of the inverted molecule, at the atop site above a Pd₁₀ cluster. In Table 2, we observe the calculated force on the ion vs. the image charge model. We obtain the force by first computing the total energy of the cluster for a finite number of ion heights above the surface, obtaining $V_+(z)$. We then repeat the calculation for the neutral molecule, obtaining $V_0(z)$. The image potential at each point is $-e^2/4z$, where z is the distance to the image plane. The image charge model then predicts the total ion energy to be $V_+^{ic}(z) = V_0(z) - e^2/4z$ (we omit the constant ϵ^*). We obtain the force from $\Delta E/\Delta z$; thus the forces in the table are actually an average force between the distances shown in the first column. The position of the image plane is taken at one-half the metal layer spacing above the surface layer of atoms, or at 1.12 Å above the top Pd nucleus. (However, the failure of the model is so pronounced that changing exact image plane placement will not really help.)

From Table 2, observe that the real forces on the ion are fully an *order of magnitude* lower than those of the image charge model in the region of 2.40-2.56 Å (in italics), which, bracketing the equilibrium distance of 2.45 Å, is the region of interest for dynamics! At closer distances, the image charge model even has the wrong direction for the force. Note that the real forces only con-

verge to the image charge model at a distance greater than $\sim 3 \text{ \AA}$. Finally, note that beyond that distance, the cluster calculation forces exceed the image model. This is because the image charge is constrained by the cluster size to be closer to the ion than appropriate for a real metal surface.

Height ($\text{\AA}$)	$\Delta V_+/\Delta z$	$\Delta V_+^{ic}/\Delta z$
2.08-2.24	+1.485	-0.145
2.24-2.40	+0.483	-0.692
2.40-2.56	-0.090	-0.891
2.56-2.72	-0.421	-0.925
2.72-2.88	-0.588	-0.878
2.88-3.04	-0.688	-0.810
3.04-3.20	-0.751	-0.730

Table 2: *Ab initio* forces (in eV/bohr) are compared with the image-charge model (V^{ic}), as a function of N-height above the plane of surface atoms. Ground-state equilibrium is at $2.45 \text{ \AA}$.

The total failure of the image charge model may be blamed on two factors: First, at only ~ 2.0 - $2.5 \text{ \AA}$ from the surface, the image charge model suggests the charge is almost entirely contained on the nearest neighbor Pd atom(s). This, of course, would have a large kinetic energy cost, meaning that the real "image charge" spreads out more in space, thus reducing the force induced on the adsorbate. Secondly, near equilibrium we have a balance of two large forces, the attractive part and the hard-wall repulsion. Ion formation, in redistributing molecular and surface electron density, changes the hard-wall position. Since this factor is exponentially rising, even small changes in position have a large effect. We have demonstrated the hard-wall effect by calculation and will report it elsewhere.

Having shown that one component of "conventional wisdom" fails totally even in the ideal case of a "purely" electrostatically-bound adsorbate, we now turn to what happens with laser induced hot-carrier processes in the case of an adsorbate that has appreciable covalent interaction with the substrate.

5. THE ADIABATIC MODEL OF CHEMISORBED MOLECULES

Our model is based on what we believe to be a new application of the adiabatic approximation. Due to the relative weakness of the covalent portion of the chemisorption bond, the timescale for substrate relaxation (the inverse of several eV) is much faster than the timescale for charge fluctuations between the metal and the adsorbed molecule. In this limit, the substrate adiabatically follows changes in adsorbate charge. When this is true, the ground-state ($i = 0$) and lowest-excited state wavefunctions ($i > 0$) of the adsorbate-substrate complex may be written in product form:

$$\Psi_i = \sum_q C_q^i \chi_q^M \chi_q^A$$

where the χ 's are the *fully relaxed* metal (M) and adsorbate (A) wavefunctions for the case of the metal of charge $-q$ and the adsorbate of charge q , the C's are expansion coefficients, to be determined, and $\mathcal{A}$ is the antisymmetrizer operator. Just as in the derivation of the Born-Oppenheimer approximation [24], the smallness parameter, which tests the validity of this form of the wavefunction, is obtained by substituting Ψ_0 into the Schrödinger equation. For our adiabatic approximation, this parameter is the ratio of the metal-adsorbate transfer integral, t , to the energy cost of electronically *locally* exciting the metal (see below) or the molecule while q is fixed. We believe this condition is met by almost all metal-molecule systems.

A detailed derivation of the above equation may be found elsewhere [25]. We find that the expression is rigorous for all adsorbates at distances from the surface at which the transfer integral to the surface becomes very small compared with other interactions; thus, this theory has relevance for atomic and molecular scattering. However, the theory is only relevant for adsorbates in cases where the *covalent portion* of the chemisorption bond is small, say $\ll 1$ eV. This approximation provides a tremendous simplification of the description of the chemisorption bond and the lowest lying excited states. The physical insights yielded by this approximation we shall find, in retrospect, to be rather simple.

Consider the NO:Pt(111) system, that has been examined in several desorption studies [3,16], and where the total chemisorption bond is ~ 1 eV. *Ab initio* work by Bagus and Paccioni [20] on a system which bears some similarity, CO:Pt(111), has shown that only a *fraction* of the total chemisorption bond strength is due to covalency. We use their work to estimate that for NO:Pt(111), the covalent bondstrength E_c is $\sim 1/2$ eV, with the remainder of the bond caused by electrostatic interactions, such as " σ -donation", rehybridization, and correlation [20]. The small value of E_c suggests that t is small, perhaps $\sim E_c$, but we cannot be sure of this without further computation using our model. As reported elsewhere [25], we have studied the possible range of t given reasonable variations in the uncertainty of the empirically derived parameters (see below). We find that in all cases $t < 0.5$ eV, thus suggesting validity of the model for the NO:Pt(111) system.

There are several arguments for why only *local* substrate excitations enter the validity of our model: 1) As the charge on the molecule changes, the hole or electron transferred to the metal is localized by the presence of the charged molecule itself, and its wavepacket does not delocalize beyond the distance of a few atoms; 2) The overall neutral entity of the charged molecule and its "image charge" are screened out by the substrate over a small distance, so that the metal, beyond a few interatomic distances, is unaffected by the presence of the adsorbate; 3) *Ab initio* cluster calculations at the CI level [20], and even those reported above by us, show that all low-energy properties of the adsorbate are well-determined as cluster size approaches ten metal atoms, so that no long-range properties of the metal significantly affect the essential nature of the metal-molecule bond; and 4) The adiabatic model is consistent with the timescale-separation arguments made above. Since local excitations of the metal are clearly much more energetic than delocalized excitations (as seen in the energy gaps between orbitals of the same symmetry in cluster calculations with a small (~ 10 -20) number of metal atoms), we propose that the condition for validity of the adiabatic approximation is met even with metallic substrates.

The Hamiltonian matrix in the adiabatic approximation, $\langle \mathcal{A}\chi^M_{-q0}\chi^A_{q0} | H | \mathcal{A}\chi^M_{-q'0}\chi^A_{q'0} \rangle$, is a configuration interaction (CI) model of Ψ_0 . Let ϵ_q be the total energy of the fully-relaxed system

when the molecular charge is frozen as q (thinking of the system total energy when the molecular charge is restricted to a single value is similar to the "constrained local-density functional" methods used to compute the screened hole-hole interactions in high-temperature superconductors [26]). Making the approximations that 1) the t are independent of q and may be neglected in cases of multiple electron hops, and 2) that multiply-charged molecular configurations are too high in energy to be important for testing our model, our Hamiltonian matrix is then

$$\bar{H} = \begin{bmatrix} \varepsilon_{-1} & t & 0 \\ t & \varepsilon_0 & t \\ 0 & t & \varepsilon_1 \end{bmatrix}$$

In order to find t for the real system of NO:Pt(111), we use semi-empirical parameters for the matrix elements. We find that the above Hamiltonian may be recast in Hubbard-like form, which allows empirical input to estimate one of the parameters, the screened electron-electron interaction, U . (Auger experiments on chemisorbed CO have shown $U \sim 0.2$ eV for valence holes [27]. We believe that chemisorbed NO is similar and that these values are *upper* bounds for the U between *electrons* in the chemisorption bond [28].)

In the adiabatic approximation, the wavefunction bases are the differently charged configurations of the adsorbate and the relaxed metal. If the adsorbate charge q is restricted to $-1 \leq q \leq 1$, the diagonal energies can then be redefined using $\varepsilon_{+1} = e_0$, $\varepsilon_0 = \varepsilon + e_0$, and $\varepsilon_{-1} = 2\varepsilon + U + e_0$, for zero, one, and two electrons in the adsorbate molecular orbital of energy ε , which is bonding to the metal, and where e_0 is a reference energy. The CI Hamiltonian matrix can now be written in a more symmetric form by taking $e_0 = -\varepsilon$ and defining $\delta \equiv (\varepsilon_{-1} - \varepsilon_1)/2 = \varepsilon + U/2$, obtaining

$$\hat{H} = \begin{bmatrix} (\frac{U}{2} + \delta) & t & 0 \\ t & 0 & t \\ 0 & t & (\frac{U}{2} - \delta) \end{bmatrix}$$

Finite δ causes the adsorbate to have fractional charge. Diagonalization of the above matrix yields the covalent portion of the binding energy, E_c (the negative of the lowest eigenvalue, E_0); the energies of the lowest lying excited states, E_1 and E_2 ; and the fractional charge on the adsorbate in the ground state, $Q \equiv \sum_q q |C_q^0|^2$. The eigenfunctions Ψ_i contain information about the low-lying excited states of the system.

In order to estimate Q , we analyzed the shift in N-O stretch vibration frequency. We find that the shift due to damping on ps timescales by substrate electron-hole pair creation (~ -100 cm^{-1}) almost cancels the shift due to coupled N-O and Pt-NO vibrations ($\sim +100$ cm^{-1}) [29]. We expect that the shift due to rehybridization within the molecule is small, because the shallowest orbitals which must change in order to produce rehybridization, the 5σ and 1π , are deep in energy (~ 9 eV

below the Fermi energy). Thus we conclude (as has also been found for CO:Pt [20]) that the largest cause of the observed shift upon chemisorption is due to fractional-charge transfer into the strongly-antibonding 2π molecular orbital. The 2π lies close to the Fermi energy and interacts with the substrate to produce the covalent portion of the chemisorption energy. By scaling the frequency shift using gas-phase data from species such as NO and NO⁻, we estimate $Q \sim 1/3$ - $1/2$ electron for NO:Pt(111), meaning a *mean* 2π occupancy of 1.3-1.5 electrons.

Fixing E_c at $1/2$ eV and Q at $1/2$ e⁻, we solve the Hamiltonian matrix for t as a function of U . We find that the *simultaneous observation of small E_c and fractional Q* necessitates a small value for t , supporting the validity of our model. (This is because fractional Q means that at least two configurations are sufficiently close in energy to be mixed by t ; however, when this is true, large t necessary implies a large value for E_c .)

Is the restriction of the Hamiltonian matrix to only three levels valid? Note that for NO, all positive ions beyond +1 involve ionization from the deep (> 8 eV) levels. Certainly these states mix only slightly in the chemisorption bond. Because U is small, the doubly-negative state is not as high in energy as would be true in the gas-phase. In fact its energy is somewhat in doubt and it could contribute somewhat to the bond. However, the qualitative results do not change with some mixing from this level. However, the triply negative state, having the 2π orbital filled, cannot be screened efficiently by the metal (just as the U in Cu, at 8 eV is much larger than the U in Ni, at ~ 2 eV, because the 3d shell closes). Thus this configuration must be much higher in energy and may be excluded.

We now turn to hot carrier processes. Inverse photoemission and electron attachment add an electron to the ground state; thus, to trace the effect we operate on Ψ_0 with a^* . Meanwhile, photoemission and hole attachment is represented by an operation with a . If

$$\Psi_0 = C_{-1}^0 \chi_{-1} + C_0^0 \chi_0 + C_1^0 \chi_1$$

then

$$a^* \Psi_0 = C_{-1}^0 \chi_{-2} + C_0^0 \chi_{-1} + C_1^0 \chi_0$$

and

$$a \Psi_0 = C_{-1}^0 \chi_0 + C_0^0 \chi_1 + C_1^0 \chi_2$$

where we have used the shorthand of χ_q for $\mathcal{A}\chi_q^M - q\chi_q^A$. Note that $a^*\Psi_0$ and $a\Psi_0$ are *not stationary states* of the adsorption site, because they are not eigenstates of the Hamiltonian. To observe the effect of attachment processes, we compute the matrix elements R where $R_i \equiv \langle a^*\Psi_0 | \Psi_i \rangle$ or $\langle a\Psi_0 | \Psi_i \rangle$, for all i . Since the χ_q are orthogonal, this projection is easily carried out. For the case of hot electron or hole processes, the cross-sections by Fermi's golden rule are then given by

$$\sigma_i(E) \propto |R_i|^2 \rho(E) \delta(E - E_i)$$

The energy-conserving δ -function determines which excited states of energy E_i are possible to populate, given the spectral density of the hot electrons or holes, $\rho(E)$.

Note that attachment populates (energy permitting) two configurations ignored in our original analysis, namely the doubly-charged χ_{+2} . As discussed above, χ_{+2} may be ignored if we are only considering relatively-low-energy processes. Because χ_{-2} is undoubtedly the next higher excitation after Ψ_2 , to a fair approximation $\Psi_3 \sim \chi_{-2}$.

Inverse photoemission therefore populates the *doubly-negative* state of NO as well as other states that represent the lowest excitations of the Pt-NO bond. We have argued that the π^* resonance may in fact be $\sim \chi_{-2}$, and ascribe its FWHM (~ 1 eV) principally to vibrational broadening caused by changing the mean 2π occupancy by almost *two* electrons [25]. Although separated by $\sim 1/4$ eV, these vibrational peaks are unresolved in inverse photoemission [30], suggesting experimental and lifetime broadening approaching the peak separation. In addition, resonant photoemission experiments [31] concluded that the lifetime was *less* than the lifetime of a carbon 1s hole (again, a few inverse tenths of an eV). Thus the doubly-negative ion is short-lived on molecular-motion timescales. Finally, we suggest that the lower spectroscopic features, up to ~ 1 eV in energy, are unobserved due to their superposition with the unfilled portion of the substrate d-bands. Because all of these low-lying excited states decay predominantly by hot carrier *emission*, the timescale is governed by the product of t (the matrix element) and the density of states into which a hot electron or hole may be ejected at the appropriate energy.

Our local density of excited states for NO:Pt(111) thus has the following features: several low-energy excitations and a higher broader feature which we assign to the π^* . (The latter has the greatest computed inverse-photoemission intensity [25].) If we broaden our local DOS to reflect lifetime, these same rough qualitative features may be found in results from other many-body models, such as the Newns-Anderson Hamiltonian, with t (there called V) in the weak-coupling range (see e.g., Brenig and Schönhammer [32]). This result cannot, of course, be obtained from single-particle models, such as local-density functional approaches.

We now consider the relevant PESs for electron-attachment dynamics of NO:Pt(111). We find [25] that destructive phase interference prohibits substantial population of Ψ_2 which is mostly $q = +1$, so that, for a wide energy spectrum of hot electrons, most amplitude goes into two states: Ψ_1 , which has antibonding phase between the neutral and negative configurations, and Ψ_3 , which, except for some relatively small mixing of the lower energy configurations, is *doubly negative*. The latter state sits ~ 1.5 eV above the Fermi level of the substrate (if it is the π^*) and, being dou-

bly charged, may be expected to have inward forces which are much larger than those shown in Table 2 for a singly-charged ion. All of these excited states decay by hot-carrier emission. The decay of Ψ_3 proceeds by hot-electron emission to Ψ_0 or Ψ_1 (the amplitudes can be numerically determined from the coefficients of the Ψ_i [25]).

With hole attachment, both the first and second excited states (Ψ_1 and Ψ_2) have substantial intensities. The second excited state is largely $q = +1$ and decays to the ground and first excited states. *Thus excitation of the covalent portion of the chemisorption bond is produced by both types of hot carriers.*

Note that the degree of antibonding character in the first excited state depends critically on the parameter U in the Hamiltonian. With $U = 0$, this state is *non*-bonding as far as the covalent interaction is concerned, with a covalent energy of exactly zero, independent of distance. With $U > 0$, the energy of this state rises monotonically. Thus the repulsive excited-state forces on the molecule increase with increasing U . (It would be interesting to compare Auger-determined U 's for different substrates and sites.) Even at $U = 0$, however, we believe that the first excited state has a weakly-repulsive potential energy surface due to the molecule finding itself closer to the surface, by the loss of covalent attraction, than the distance where the attractive electrostatic interactions and the repulsion due to closed shells are balanced.

Let us now summarize the differences found between our adiabatic model and the image charge PES used for example in Ref [3]: 1) The Antoniewicz mechanism [4] of NO^- motion is irrelevant for $\text{NO}:\text{Pt}$ because the singly-negative ion is *not* locally a stationary state. This is because the observed fractional negative charge on the molecule *necessarily* means that the $q = -1$ configuration is heavily mixed in both the ground and first excited state (with bonding and antibonding phases with respect to the neutral configuration, respectively). 2) We find that hot-electron attachment can cause a direct transition from the ground to the doubly-negative state. This is because the system already has appreciable $q = -1$ amplitude in the ground state; adding an electron to this configuration thus produces transition amplitude for the -2 ion. The excited state forces on this ion, expected to be larger than those in Table 2, may have important dynamical consequences (although the ion lifetime is rather short, $\sim 10 \text{ eV}^{-1}$, the observed photodesorption yield is also low [33].) 3) If one assumes that the DOS close to the Fermi level ($\sim 1/2 \text{ eV}$) is much smaller than further away, we find that the repulsive Pt-NO first excited state has the longest lifetime of any excitation, and *may be produced by both types of hot carriers*. We see no reason why this state could be omitted from future more realistic dynamical studies. Pending such calculations, we believe our results are not inconsistent with the experimental observations [33].

6. SUMMARY

We have explored several aspects of ground- and excited-state potential energy surfaces relevant to photochemical processes on surfaces involving chemisorbed molecules. We have argued for the importance of *multi*-dimensional ground-state PESs. We have found the consideration of multi-dimensionality essential for understanding data obtained from quantum-state resolved experiments [9,16,34]. For the $\text{NH}_3:\text{Pt}(111)$ system, we have concluded that the portion of the hard wall which is important to the desorption dynamics is accessed by internal molecular motion. The speed of this hydrogen motion assists this path in dominating the desorption probability. We have shown that without a fairly detailed knowledge of excited state forces or quantum-state

resolved experimental data, one cannot determine which of the several very different dynamical pictures, made possible by even a two-dimensional ground-state surface, dominates in nature.

The above observations stress the need for accurate excited-state PESs. We have shown that two commonly accepted assumptions fail for chemisorbed molecules: First, if the chemisorption bond has appreciable covalent character, hot carrier attachment does **not** simply produce an ion such as in the gas phase. If attachment is to a molecular orbital not involved in the chemisorption bond, repolarization of the bond occurs on the timescale of the bond-strength. This screens the charge, and must be considered in estimating the effect of attachment. If attachment occurs into the orbital which *is* involved in the covalency, excitations of the molecule-surface bond are made and a *multiply*-charged ion is possible in some cases. Since the longest-lived excitations are those which are local-stationary states of the system, these PESs need to be considered. Second, even if negligible covalent character exists in the chemisorption bond, or a multiply-charged ion is made, at typical chemisorption distances above the surface (~ 2.0 - 2.5 Å), the $-q^2/4z^2$ image-charge model of the forces fails **totally**. Only when we reach > 3 Å do we recover validity for this model.

Thus we find that photo-induced processes involving chemisorbed molecules are much more complex but also much more interesting than "conventional wisdom" might dictate. Fortunately, the advent of ever more powerful and accurate *ab initio* electronic-structure codes, such as DMol, coupled with ever more detailed experimental methods, such as quantum-state resolved REMPI, allows us to extract at least some of the basic principles.

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