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Photoinduced Electron Attachment to N_2 Adsorbed on Platinum

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Theoretical calculations on ground and excited electronic states of N_2 adsorbed on Pt(100) are carried out to investigate the properties of photoinduced electron attachment states. The metal−adsorbate system is described by an embedded cluster method, and configuration interaction theory is used to resolve the electronic states. The N_2 molecule is found to adsorb at an atop Pt atom site with an adsorption energy of 0.18 eV and with a vibrational frequency 70 cm^{-1} lower than in the gas phase. Only the perpendicular orientation is stable. An electron attachment state corresponding to excitation of an electron from the Fermi level of the metal to a π^* orbital of N_2 is found to occur at a vertical excitation energy of 4.2 eV (triplet state) and 4.3 eV (singlet state). The NN internuclear distance increases in the excited state and this leads to a range of excitation energies, from 3.6 eV to the minimum of the excited triplet state potential surface to 4.2 eV for the vertical excitation. The corresponding range for singlet states is 3.8 to 4.3 eV. The equilibrium distance of nitrogen from the surface is 2.09 Å for the ground state and 1.96 Å for the electron attachment state. Deexcitation from the excited state to the repulsive region of the ground-state potential can lead to desorption from the surface. Nitrogen does not desorb or dissociate in the excited electronic state.

I. Introduction

Photochemistry at solid surfaces is strongly influenced by the short lifetimes of excited electronic states of adsorbed species. These states often have considerable overlap with metal states and in such cases appear as broadened resonances.[1−4] Nonetheless, excited states can have a clear molecular identity which in turn can be used to describe the behavior of the adsorbate when the excited state is populated. An example is excitation to an antibonding level of an adsorbate by optical or electron impact excitation and the consequent weakening of internal bonds of the adsorbate or bonds between the adsorbate and the surface. Many such processes have been studied experimentally.[1−12] Because the cross section for direct electronic excitation of an adsorbate on a metal surface is small, most experiments have been explained in terms of a transient electron attachment process, whereby photons are first absorbed by the metal and photoemitted electrons become transiently attached to the adsorbate. Electron attachment to polar adsorbates and adsorbates with low lying valence excited states such as π^* states have been reported.[3−5,12] Excited states corresponding to atomic or molecular Rydberg states can also attach electrons and be stabilized by localized positive holes in the metal.[13−15] In all of these cases, there is a distinctly molecular aspect to the excited electronic state even in the presence of strong mixing with metal electronic states.

First-principles studies of excited electronic states or resonances of complex adsorbates on metals are only now becoming available, and for most systems studied experimentally theoretical information on the behavior of transient species is lacking. Although it is often qualitatively correct to interpret experiments based on the electronic structure of gas phase molecules or ions, it is the projection of the wave function primarily associated with the adsorbate out of the total wave function of the system that determines the bonding properties of the adsorbate, and this wave function is dependent on the image charge and other interactions with the metal. For a quantitative understanding, high quality potential energy surfaces for excited states will be required. Configuration interaction theory provides a good way to resolve excited electronic states provided the adsorbate−surface problem can be recast to permit accurate calculations on a system that is large enough to capture metal delocalization effects.

In this paper, we consider a theoretical description of electron attachment to N_2 adsorbed on Pt(100). Experiments on N_2 adsorbed on Pt(111) by Harrison and co-workers have shown definitively that photodesorption occurs over a 308−193 nm range.[10,12] The nitrogen molecule is reported as being only weakly bonded to the surface, at 0.15 eV, and the desorption process is attributed to the formation of an electron attachment state 3.5 to 4 eV above the Fermi level of the metal.[12] The most likely candidate, suggested by the authors, is attachment to a π^* level of adsorbed nitrogen. A 2266 cm^{-1} N−N stretch frequency was assigned to nitrogen vertically bonded atop Pt(111) on terrace sites. Experiments by Yates and co-workers have shown that nitrogen adsorbs most strongly at step defect sites on Pt(111) with a 2234 cm^{-1} vibrational signature.[16] Because nitrogen adsorbs near the physisorption regime, the behavior on Pt(100) studied in the present work should be very similar to that on Pt(111). A key question concerning the dynamics of photodesorption is whether the molecule desorbs from the excited state or desorbs after deexcitation to the ground state. Because nitrogen is weakly bound, electron attachment to a π^* orbital could disrupt bonding to the surface and lead to a repulsive potential in the excited state. In such a case, a Menzel-Gomer-Redhead analysis of the dynamics should be appropriate.[17] Alternatively, if the molecule in the electronic attachment state is sufficiently attracted toward the surface by the image charge in the metal, then on return to the ground state, it can rebound from the surface as described by Antoniewicz.[18] Gadzuk has analyzed the electron induced desorption process to determine desorption probabilities and translational energy distributions.[19] In the work reported in this

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paper, the description of N_2 allows for the formation of either a π^* or Rydberg attachment state or a mixing of these two types of electronic states.

II. Theory

Embedded Cluster Description of the Metal−Adsorbate System. The metal−adsorbate system is described using an embedded cluster method that has been applied previously to many ground-state processes; details of the method and references to previous applications are reported in refs 20 and 21. The main objective of the embedding approach is to set up the electronic structure problem in a way that allows an accurate many-electron treatment of the adsorbate/surface portion of the system while coupling this region to an extended lattice. Localized orbitals extracted from a treatment of the clean surface are used to define the coupling matrix elements.

Calculations are carried out for the full electrostatic Hamiltonian of the system (except for core electron potentials), and wave functions are constructed by self-consistent-field (SCF) and multireference configuration interaction (CI) expansions

$$\Psi = \Sigma_{\mathrm{k}} \lambda_{\mathrm{k}}\, det\, (\chi_1^{\ \mathrm{k}}\, \chi_2^{\ \mathrm{k}} \ldots \chi_n^{\ \mathrm{k}})$$

The embedding procedure expresses the coupling of the local electronic subspace and adsorbate to the bulk lattice electrons, $\{\phi_{\mathrm{j}},\ j = 1,\ \mathrm{m}\}$, by the modified Hamiltonian

$$H = \Sigma_i^{N}(-1/2\nabla_i^{\,2} + \Sigma_k^{\,Q} - Z_k/r_{ik}) + \Sigma^{N}_{\ i<j}\, 1/r_{ij} + \Sigma_i^{\,N}\, V_i^{\mathrm{emb}}$$

where

$$< a(1) \mid V_1^{\mathrm{emb}} \mid b(1) > \; = \; < a(1)\, b(1) \mid 1/r_{12} \mid \rho(2)>$$

$$- < a(1)\, b(2) \mid 1/r_{12} \mid \gamma(1,2)> + \Sigma_m\, \lambda_m < a|Q_m><Q_m|b>$$

and ρ, γ, and Q_m denote densities, exchange functions and atomic orbitals derived from $\{\phi_{\mathrm{j}},\ j = 1,\ m\}$, respectively. Relativistic effects are important for platinum and are included as described in ref 20, where the Pt core potential is described. For nitrogen, the split basis of ref 22 is used along with additional Gaussian functions with exponents equal one-half the value of the most diffuse s and p components in the valence basis. Figure 1 depicts the embedded cluster and defines those atoms that are described by an extended basis.

Configuration Interaction Description of Electronic States. Ground and excited electronic states of the Pt−N_2 system are calculated by configuration interaction, where wave functions are expanded as

$$\Psi = \Sigma_k \lambda_k\, \mathrm{det}\, (\chi_1^{\ k}\, \chi_2^{\ k} \ldots \chi_n^{\ k}) = \Sigma_k \lambda_k \Phi_k$$

An electronic configuration, Φ_r, corresponding to the Pt−N_2 excited state of interest is formed and single and double excitations from this single determinant wave function are then generated

$$\Psi_r = \Phi_r + \Sigma_{ik}\, \lambda_{ik}\, \Gamma_{i\to k}\, \Phi_r + \Sigma_{ijkl}\, \lambda_{ijkl}\, \Gamma_{ij\to kl}\, \Phi_r$$

All configurations, Φ_{k}, that interact with Φ_{r} such that

$$|< \Phi_k \mid H \mid \Phi_r >|^{\,2}/|E_k - E_r \mid\, > 10^{-4}\ \mathrm{a.u.}$$

are retained explicitly in the CI expansion.[23,24] This procedure ensures that the representation of the excited state, Ψ_r, is orthogonal to and noninteracting with intervening excited states, at least within the CI space considered. When $< \Psi_k \mid H \mid \Psi_r > \; = 0$ and $< \Psi_k \mid \Psi_r > \; = 0$ for all lower energy states, Ψ_k, then the calculated energy of Ψ_r is an upper bound to the exact energy. Separate CI calculations are carried out on the ground state to ensure an accurate description of the bonding and equilibrium distance from the surface.

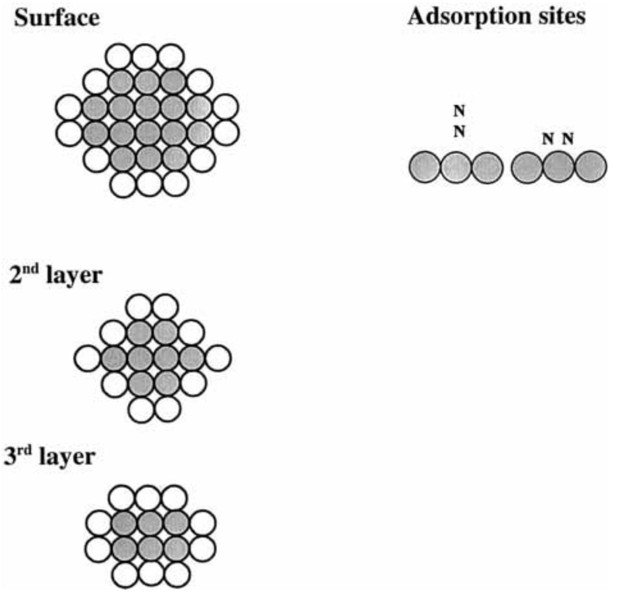

Figure 1. Embedded cluster model of Pt(100). Shaded atoms have valence basis orbitals; other atoms are described by neutral atom embedding potentials. The six central Pt atoms of the surface layer are described by a 5s, 5p, 5d, 6s, 6p basis. Calculations are performed for adsorption of N_2 at an atop Pt site and at a bridge site for perpendicular and parallel orientations of the NN axis.

In our previous work involving electron attachment to Rydberg orbitals of methane physisorbed on platinum, a SCF calculation on the positive ion adsorbate−surface system was used to define the initial description of the excited state of interest.[15] Virtual levels of the positive ion corresponding to Rydberg levels could easily be identified and from this initial configuration a refined description was generated by the excitation procedure described above.

In the present system, at distances comparable to the ground-state equilibrium distance of N_2 from the surface, it turns out that electron attachment to a π^* level is favored over a Rydberg state, and, for the π^* state, a positive ion starting point provides a poor description. This is primarily due to interactions that tend to localize the electron hole in the metal near the adsorbate and to interactions of the π^* electron with the other nitrogen electrons. We proceed instead by solving directly at the SCF level for the lowest triplet state in which the N_2 π^* orbital is occupied. To perform such a calculation, virtual orbitals that produced intervening metal−metal excitation states were temporarily removed from the SCF calculation. The triplet state occupied and virtual orbitals and the previously removed virtual orbitals were then used in a configuration interaction calculation of the type described above for both triplet and singlet excited states. Because hole localization is an important factor in stabilizing the excited state, optimization of the electron−hole pair excited state prior to the CI calculation leads to more rapid convergence of the transition energy than a calculation based on positive ion orbitals.

III. Results

Adsorption Sites and Ground State. Ground-state potential curves for N_2 approaching the surface atop a Pt atom are shown

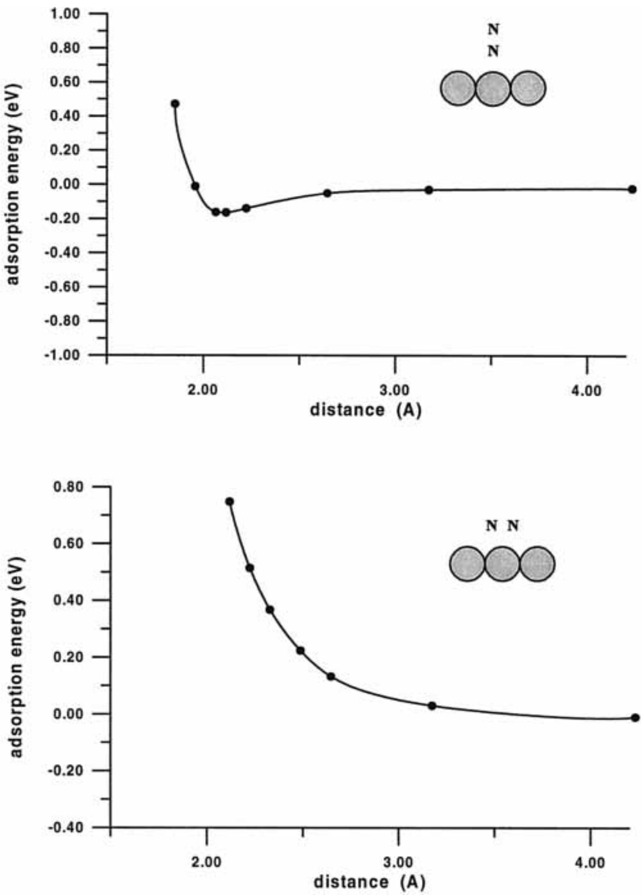

Figure 2. Ground-state potential curves for perpendicular and parallel adsorption of N_2 on Pt(100). The shallow minimum at $R = 2.09$ Å for the perpendicular orientation corresponds to an adsorption energy of 0.18 eV.

in Figure 2 for perpendicular and parallel orientations of the molecule. At each distance, the energy plotted is for the optimum N−N internuclear distance with basis set superposition corrections included. For the perpendicular approach, there is a shallow minimum of 0.18 eV at 2.09 Å. The N−N equilibrium distance is calculated to be only 0.004 Å longer than that of the 1.098 Å value for the molecule in the gas phase. In contrast, the parallel orientation is found to be unbound at all distances except for a very small <1 kcal minimum around $R = 4.23$ Å. Calculation of the ground state at the bridge adsorption site for the NN axis perpendicular to the surface showed no bonding. For the perpendicular orientation, analysis of the wave function shows d-π^* back-bonding reminiscent of CO bonding to Pt. A measure of the importance of back-bonding can be obtained by performing a constrained SCF calculation in which the π^* orbitals of N_2 are removed from the basis. If this is done, then nitrogen is no longer bound to the surface at any distance. Because bonding occurs at the SCF level, it follows that more than physisorption electron correlation interactions are involved.

However, compared to CO, which has π^* orbitals polarized toward C, back-bonding into the symmetric π^* orbitals of N_2 is much less pronounced and the energy stabilization dramatically weaker. In addition, electron donation to the metal is less stabilizing because the relevant σ orbital is lower in energy in N_2 than in CO. Although possible in principle, side on bonding is found to be insufficient to produce a local minimum other than the <1 kcal stabilization noted above. Although corrected for basis superposition effects, this shallow minimum may still be an artifact of the calculations. The calculated adsorption energy at the atop site of 0.18 eV (4.2 kcal/mol) is comparable to the 0.15 eV value cited by Harrison and co-workers for adsorption on Pt(111).[12] Although bonding to the Pt(100) surface may in fact be slightly stronger than to Pt(111), a discrepancy of this magnitude is at the limit of accuracy of the theoretical treatment. A 70 cm^{-1} reduction in the NN stretch frequency was calculated for N_2 on the surface. This value is in excellent agreement with 65 cm^{-1} shift reported by Harrison and co-workers.[12]

DFT calculations carried out in conjunction with the experimental study of nitrogen on Pt(111) reported in ref 16 showed strongest bonding of N_2 at a step defect site and a corresponding 2244 cm^{-1} vibration which compares favorably with the 2231−2234 cm^{-1} range observed experimentally. The adsorption energy was sensitive to the choice of functional. Using a PW91 functional, which gave a good account of bonding of CO to metals, an adsorption energy of 0.67 eV was found for N_2 adsorbed (perpendicular) atop Pt(111) terrace sites. However, using an improved RPBE functional, which generally gave more reliable chemisorption energies for other systems, adsorption at the terrace sites became unbound, whereas at the step defect site, N_2 was bound by 0.16 eV. Assignment of the 2234 cm^{-1} vibration to N_2 at a defect site has been definitively established by annealing experiments by Harrison and co-workers.[10,12]

Although there may be some question about the exact value of the ground-state adsorption energy, the experimental and theoretical studies are all in agreement that N_2 is at most weakly adsorbed on the platinum surface.

Concerning the present study, the description of the Pt−N_2 system shows a nearly degenerate ground state at all distances, as should be the case for a metal. The embedded cluster is large enough to produce closely spaced s-type single particle levels and the gap that exists at the Hartree−Fock level is nearly eliminated when the level is populated and a SCF calculation is carried out on the excited state. For example, at a perpendicular distance of $R = 2.11$ Å, a value close to the equilibrium distance in the ground state, the lowest triplet state formed by a metal−metal excitation lies only 0.05 eV above the singlet ground state.

Electron Attachment Excited States. We now consider an electron attachment excited state formed by excitation from one of the metal levels near the Fermi level to an unoccupied level associated with the N_2 adsorbate. Two questions occur at the outset concerning this electron−hole pair excited state: the nitrogen orbitals involved and the extent of localization of the electron hole in the metal. The initial SCF calculation on the excited state shows that attachment to the antibonding π^* orbital is favored over a Rydberg state if the metal hole is allowed to relax. Without hole relaxation, the π^* electron attachment state formed by occupation of the positive ion orbital is high in energy, slightly above the work function of the metal. When the N−Pt distance is comparable to that of the ground-state equilibrium distance, allowing the Pt metal hole to relax and the N_2 π^* orbital to optimize lowers the energy of the electron attachment state by about 1.5 eV from the positive ion starting point. On optimization, the Rydberg mixing with the π^* orbital is reduced and the metal hole acquires more d character from the Pt atom directly below the nitrogen.

Results for a typical excited-state calculation are reported in Table 1. Excited states with appreciable π^* character are listed in the table; at the ground-state equilibrium distance, these states are found to be distributed about a central component at 3.98 eV above the ground state. For a stretched N−N distance, a similar but less broad distribution is shown in the table. This distribution of states is typical of that found for other distances

TABLE 1: Dispersion of the π^* Electron Attachment State of N_2 on Pt(100) Due to near Resonant Interactions with Pt−Pt Excitations[a]

	N−N distance 1.098 Å		N−N distance 1.145 Å	
state[b]	ΔE	coeff	ΔE	coeff
a	3.773	0.16		
b	3.947	0.38	3.286	0.12
c	3.977	0.48	3.710	0.74
d	4.154	0.60	4.077	0.17

[a] The mixing coefficient of the metal hole − π^* electronic configuration corresponding to the electron attachment state with configurations corresponding to Pt−Pt excitations is shown for two N−N distances at a nitrogen-surface distance of 2.06 Å, a value close to the ground-state equilibrium distance for a perpendicular orientation. The ΔE is the excitation energy from the ground-state equilibrium geometry. [b] Excitation energies are for triplet states. The singlet state mixing coefficients are approximately the same as shown in the table but the energies are higher by 0.18 eV for state d at 1.098 Å and by 0.17 eV for state c at 1.145 Å.

and illustrates the resonant mixing expected when there are degeneracies or near degeneracies with metal levels. The singlet−triplet splittings are 0.14 and 0.18 eV for the shorter and longer N−N distances, respectively. The splitting is due to the exchange interaction between the singly occupied orbital of the metal hole and the π^* level, an interaction that decreases rapidly with increasing spatial separation. The spatially larger Rydberg states are stabilized less than the π^* state by localization of the metal hole and at larger distances from the surface (greater than ~ 3 Å), the lowest energy electron attachment state becomes predominately Rydberg in character.

The full set of excited-state calculations for N_2 on Pt(100) is shown in Figure 3. These results are for N_2 adsorbed atop Pt with the N−N axis perpendicular to the surface; both the N−Pt and the N−N distances are varied. The figure illustrates three important points: first, the vertical excitation energy from the ground state to the triplet state is 4.2 eV; second, the N−N internuclear distance increases in the π^* electron attachment state; and third, nitrogen moves toward the surface in the excited state. Because of the change in internuclear distance in the excited state, the transition energy from the ground-state ranges from 3.6 eV for excitation to the energy minimum of the triplet excited state (N−N distance, 1.145 Å) to 4.2 eV for a vertical excitation (N−N distance, 1.098 Å). For the singlet state, the range is from 3.8 to 4.3 eV. The calculated range in excitation energies for N_2 on Pt(100) is in quite good agreement with the 3.5 eV to 4.0 eV range of values reported by Harrison for N_2 on Pt(111).[12] The fact that the Pt−N distance decreases in the electron attachment state resolves the question about the desorption mechanism. Nitrogen does not desorb on the excited state surface. Instead, after deexcitation, the molecule will most likely end up on a repulsive portion of the ground-state potential and desorb from the surface via Antoniewicz dynamics. The variation in energy of the excited state with distance of nitrogen from the surface for a perpendicular orientation of N_2 is shown in Figure 4.

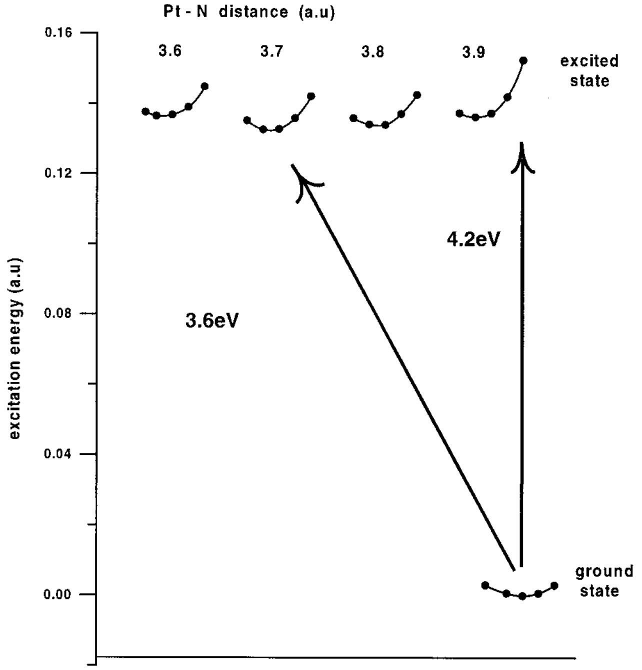

Figure 3. Energies of the ground state and triplet electron attachment π^* excited state of N_2 adsorbed on Pt(100). The curves correspond to the energy of the excited state with the largest π^* character. Energies are given for several Pt−N distances and 0.03 au incremental increases in N−N internuclear distance, from right to left, from the ground-state equilibrium geometry of 2.074 au (1.098 Å). In the ground state, 0.03 au incremental changes are centered about the equilibrium geometry.

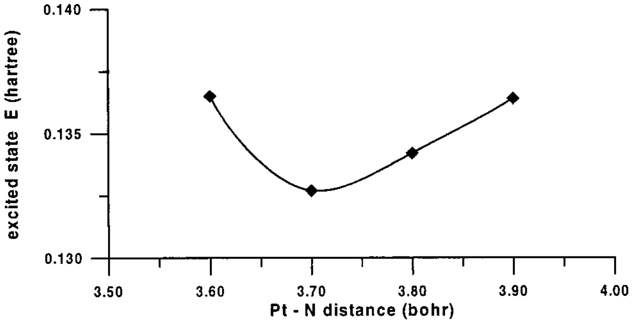

Figure 4. Variation in energy of the electron attached excited state with distance from the surface for a perpendicular orientation of N_2. The Pt−N distance is to the N closest to the surface. Energies are in hartree atomic units, 27.21 eV, and distances are in bohr atomic units, 0.5292 Å. The initial slope on vertical excitation from the ground-state equilibrium geometry is $dE/dR = 0.022$ hartree/bohr = 1.13 eV/Å.

To rule out the possibility of a local minimum in N−N stretch, a few longer distances were examined. The energy of the excited state as well as the ground state was found to increase sharply. For example, at a Pt−N distance of 1.96 Å, corresponding to the minimum for the excited state, a 0.16 Å increase in N−N distance caused the energy to increase by more than 1 eV. It follows that perpendicular N_2 cannot dissociate on the excited-state surface. Another possibility for dissociation is to rotate N_2 in the excited state until the N−N axis is parallel to the surface. Although unfavorable for the ground state, this would in principle allow formation of N-surface bonds as the molecule is stretched in the excited state. Calculations for this orientation of N_2 were also carried out and showed a considerable lengthening of the N−N internuclear distance in the excited state. At a distance of 2.49 Å from the surface for the parallel orientation, measured from the Pt nucleus to the N−N axis, the N−N equilibrium distance increases 0.05 Å beyond the already stretched value for the perpendicular orientation. In this stretched geometry, the energy is lowered further by moving the molecule closer to the surface. The minimum energy of the excited state occurs at a Pt−N−N axis distance of 2.33 Å. However, even at this minimum, the total energy of the parallel, stretched N−N, configuration remained 0.8 eV higher than that of the excited state in a perpendicular orientation. Thus, it is also possible to rule out dissociation on the excited-state surface in a parallel orientation.

We conclude therefore that the ultimate fate of the electron attachment excited state is only to undergo deexcitation back to the ground state. When this happens, the ∼4 eV energy of the excited state would likely induce desorption because the molecule is so weakly bound to the surface. Although the experiments by Harrison and co-workers did not resolve the detailed desorption dynamics, the authors pointed out that NO on Pt(111) which followed Antoniewicz type dynamics[1] should be somewhat analogous to N_2/Pt(111). Our work is fully in accord with the conclusion that desorption occurs after deexcitation to the ground state and further agrees with the fact that the N_2 electron attachment state does not dissociate. Our work also suggests that some of the desorbing N_2 should be vibrationally excited because of the increased equilibrium bond length in the electron attachment state.

IV. Summary

1. The N_2 molecule is found to adsorb weakly at an atop site on Pt(100). The orientation is perpendicular to the surface.
2. Electron attachment states corresponding to excitation of an electron from the Fermi level of the metal to a π^* orbital of N_2 are found to occur at 4.2 eV for a vertical excitation from the ground state to a triplet state.
3. In the electron attachment state, N_2 is attracted toward the surface by a localized image charge in the metal.
4. The N−N internuclear distance increases in the electron attachment state, and this leads to a range in excitation energies for triplet states from 3.6 eV to the potential minimum of the excited state to 4.2 eV for the vertical excitation. Singlet states lie 0.1 to 0.2 eV higher than the corresponding triplet states. The calculated range in excitation energies is in good agreement with the range observed experimentally.
5. Dissociation of N_2 does not occur in the excited electronic state in either a perpendicular or a parallel orientation.
6. The only outcome for the excited state is to undergo deexcitation back to the ground electronic state. Some of the molecules will land on the repulsive part of the ground state potential and desorb from the surface. Some of the desorbing molecules should be vibrationally excited because of the larger internuclear distance in the excited state.

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