Intramolecular Motion during Stimulated Surface Processes

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Ammonia and deuterated ammonia exhibit an anomalously large isotope effect in their relative yields and rotational spinning energy for electron-stimulated desorption from Pt(111). Quantum-resolved desorption measurements and *ab initio*, two-dimensional, potential energy calculations suggest that the desorbate undergoes a geometry change (molecular inversion) induced by the excited state. Inverted molecules deexcite to a repulsive hard wall potential and desorb. In general, *multidimensional* potential energy surfaces determine the dynamics of stimulated surface processes.

Electron- and photon-stimulated desorption and dissociation of adsorbates are the basis of important nonthermal processing technologies for metal and semiconductor surfaces [1]. Stimulated surface processes are also of great fundamental interest in surface science because they involve the conversion of electronic excitation energy into internal and translational energy [1,2]. Thus, in principle, molecule-substrate potential energy surfaces can be determined by detailed observations of quantum-resolved product internal energies and state-selective translational energies, combined with *ab initio* theoretical analysis [2-4].

The 6.3 eV photon stimulated desorption of NH_3 from GaAs(100) was found by Zhu and co-workers [5] to exhibit an isotope effect in its yield ($NH_3/Nd_3 \cong 4$) that is anomalously large relative to the Menzel-Gomer-Redhead (MGR) prediction for motion along a *one*-dimensional molecule-substrate potential energy surface [6]. However, NH_3 has several internal degrees of freedom, and isotopic substitution has a relatively large influence on the time scale for molecular vibrational motion. Zhu and co-workers thus concluded that the large isotope effect is due to differences in internal molecular vibrational excitation (caused by the short-lived electronic excitation), which induced desorption either by vibrational energy transfer to the molecule-surface mode or by vibrational "predesorption" [5].

This Letter reports our experiments and theoretical analysis of the electron stimulated desorption (ESD) of NH_3 and ND_3 from Pt(111). As did Zhu and co-workers [5], we observe an anomalously large isotope effect for the ESD yields ($NH_3/ND_3 \cong 3$). With the full quantum specificity of resonance-enhanced multiphoton ionization (REMPI), we find that translational energy distributions are virtually independent of the amount of adsorbate rovibrational energy. These observations argue strongly against a vibrational mode coupling or predesorption mechanism. Instead, the observations suggest that the desorbate undergoes an internal geometry change induced by the excited state potential and then leaves the surface

from a region of the ground-state potential energy surface that is far from equilibrium.

The desorption dynamics of the ammonia-surface system therefore must necessarily be viewed *only* on multidimensional potential energy surfaces. Similar conclusions were found in previous studies [3,4]. Since mode-to-mode energy transfer is unlikely, the desorbate at the point of deexcitation must have enough energy specifically in the reaction coordinate (molecule-surface bond) in order to escape. We have computed a multidimensional, *ab initio* ground-state potential for chemisorbed NH_3 that, together with our experimental observations, suggests that *full inversion* of the adsorbate is required to promote desorption.

It is generally believed that NH_3 molecularly adsorbs N-end down on all substrates, partially through the $3a_1$ lone pair electrons on the N atom. Thermal desorption data reveal a minimum of two distinct binding energies. At low coverages (≤ 0.25 ML, ML = monolayer), the adsorbate is in the "high" binding energy "α" state. Coverage-dependent thermal desorption behavior on Ru(001) suggests an α binding energy of ~ 1 eV [7]. At higher coverages (> 0.25 ML), "β" states are present. The Pt(111) β adsorbates have been described as a distinct "second layer," with 0.4 eV binding energy [8,9].

Exposures of the Pt(111) substrate to $NH_3(ND_3)$ were performed at $T = 120$ K, allowing saturation of the α and β states but no multilayer growth. The dosed sample was then cooled to 90 K prior to data acquisition. Particular care was taken to prevent H-D exchange before adsorption of Nd_3; exchange on Pt(111) itself has not been detected [9]. The "$\alpha+\beta$" saturated surface is converted to an "α-only" surface by thermally desorbing the β adsorbates at 200 K [10,11], followed by recooling to 90 K. The β layer coverage is roughly 1.5 times that of the α-only surface [8,11].

The ESD of NH_3 and ND_3 from Pt(111) is detected 0.5 cm above the surface by (2+1) REMPI via the two-photon transition $\tilde{C}' \leftarrow \tilde{X}$ [12]. Sharply focused (20 cm focal length) laser pulses (5 ns, 4.5 mJ) were used at

varying delay times after excitation by short electron pulses [4]. For time-of-flight translational energy (E_{trans}) distributions as shown in Fig. 1, the electron beam had a fixed energy of 350 eV and a pulse width of 0.4 μs. The E_{trans} distributions are independent of beam energy and were acquired at 350 eV to maximize signal (with secondary electrons). The small focal region of the laser precludes angle integration [4]; thus the flux-weighted E_{trans} distributions correspond to desorbates that leave the surface nearly normal ($< \pm 10°$).

From the E_{trans} data, three important observations can be noted: (1) For $\alpha+\beta$ coverage, the NH_3 and ND_3 E_{trans} distributions are identical (Fig. 1); (2) the distributions do not change for α-only coverage (Fig. 1, ND_3 not shown); and (3) the E_{trans} distributions show little or no variation with desorbate internal energies [11].

For rotational/vibrational spectra and threshold measurements, the electron beam width was increased to 3 μs to span the peak translational energies (0.06–0.2 eV), while the energy was reduced to < 100 eV to insure negligible monolayer erosion during scans. There are several important observations. First, *only v_2 ($\sim$950 cm^{-1} for NH_3 and $\sim$750 cm^{-1} for ND_3) symmetric bending vibrations, called "inversion" or "umbrella" modes, were detected.* No excited N-H(D) stretching vibrations (v_1 or v_3, $\sim$3400 cm^{-1}), or asymmetric bending vibrations (v_4, $\sim$1630 cm^{-1}), were seen in any $\tilde{C}'$ $\leftarrow \tilde{X}$ transitions [13]. Second, the NH_3 and ND_3 v_2 population distributions are quite similar: approximately (1.0):(0.26):(0.09) for v_2=0,1,2, respectively, for NH_3 and (1.0):(0.30):(0.14) for ND_3 [11]. These distributions are based on calculated Franck-Condon factors [14], and roughly correspond to vibrational "temperatures" of 974 $\pm$ 40 K for NH_3 and 938 $\pm$ 50 K for ND_3. No significant change in vibrational excitation is observed for the α-only coverage.

The $\tilde{C}'(v_2'=0) \leftarrow \tilde{X}(v_2''=1)$ rotational spectrum for desorbed NH_3 in the first excited level of the v_2 mode is shown at the top of Fig. 2. The data clearly indicate considerable intensity for the $K=J$ lines ("spinning" motion
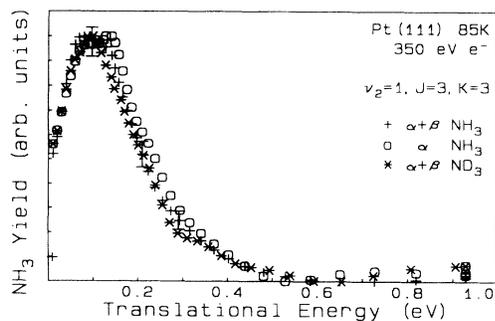
about C_{3v} axis), below 62920 cm^{-1}, whereas the $K \ll J$ lines ("tumbling" motion) above 62950 cm^{-1} are less intense. Also shown in Fig. 2 are calculated spectra that were derived from published rotational constants [12]. Although details concerning the spectral simulations will be published elsewhere [11], we show in the middle spectrum that a poor fit for the $K \ll J$ region results if the rotational energy is evenly distributed between "spinning" and "tumbling" at a temperature of 650 K. We obtained through computer iteration a much better fit for $K \ll J$, as shown in the bottom spectrum, for tumbling and spinning temperatures ($\pm$ 50 K) of T_t =350 K and T_s =650 K, respectively. (Laser-induced predissociation is unlikely to be the origin of the decreased intensity of the $K \ll J$ lines, as this has been observed only for $v_2 > 3$ in the $\tilde{C}'$ state [12].)

Roughly the same rotational energy distribution is seen for all the electronic ground-state NH_3 v_2 levels, as well as for NH_3 desorbed from the α-only surface. *The ND_3 spectra, however, are rotationally much "colder" (T_s $\approx$ 200 $\pm$ 50 K, T_t $\approx$ 200 $\pm$ 50 K for v_2=0,1,2), for both $\alpha+\beta$ and α-only coverages.*

The specific NH_3 desorption cross section from *both* the $\alpha+\beta$ saturated surface *and* the α-only coverage is $\sim$6×10^{-19} cm^2 for 100 eV excitation [11]. The corresponding ND_3 desorption cross section is a factor of 3 lower, $\sim$2×10^{-19} cm^2, for both coverages. This anomalously large isotope effect is consistent with that observed for NH_3 desorption from GaAs [5].

The threshold for $NH_3(ND_3)$ ESD for both $\alpha+\beta$ and α-only coverages is approximately 7 eV [11]. Ultraviolet photoemission spectra [8] of NH_3 on Pt(111) have distinct α and β peaks derived from the highest occupied $3a_1$ (nonbonding) orbital at 8 $\pm$ 0.5 eV and 6 $\pm$ 0.5 eV, respectively. No enhancement in the yield was seen above the 1e (N-H bonding) threshold [8] at 12 eV. Thus we assign the initial NH_3 (ND_3) excitation which leads to
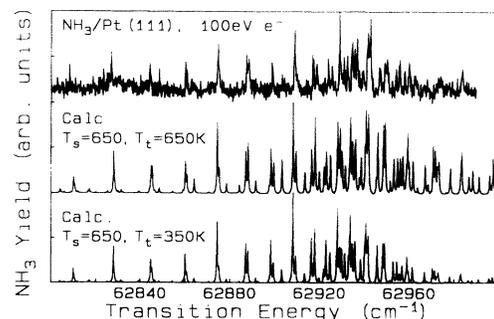

FIG. 1. TOF E_{trans} distributions as a function of site occupation (α-only vs $\alpha+\beta$) and isotopic substitution. The data were acquired for (J=3, K=3) v_2=1.

FIG. 2. (Top): Desorbed NH_3 v_2=1 rotational spectrum of the $\tilde{C}'(v_2'=0) \leftarrow \tilde{X}(v_2=1)$ band, for E_{trans}=0.06–0.2 eV, 0.5 ML coverage. (Middle): Calculated spectrum using constants from Ref. [11] and T_s =650 K for "spinning" and T_t =650 K for "tumbling." (Bottom): Calculated spectrum for T_s =650 K for "spinning" and T_t =350 K for "tumbling."

desorption to the promotion or ionization of the $3a_1$ electron. This assignment is consistent with the observation of exclusively v_2 vibrational excitation, since it is well known that the electronic states derived from the removal or promotion of a $3a_1$ electron have a planar equilibrium configuration [12], with only a very small change in the N-H bond length relative to the ground state [12,13].

The ESD of ammonia from Pt(111) may be briefly summarized as follows. Two isotope effects are observed: the overall yield $(NH_3/ND_3 \approx 3)$, and the much greater rotational (spinning) energy for NH_3. The TOF E_{trans} distributions do not vary with isotope, surface coverage, or internal energy. Vibrational excitation is restricted to the v_2 symmetric deformation mode and appears to be nearly equal for NH_3 and ND_3. The absence of enhanced desorption above the $1e$ bonding threshold and the absence of stretching excitations in the desorbates clearly indicate that N-H stretching excitation is not involved in NH_3 desorption. It thus appears unlikely that desorption results from vibrational energy transfer or vibrational predesorption [5]. Below we propose an alternate mechanism.

The observation of v_2 excitation and the large isotope effects indicate that symmetric bending of the molecule is somehow required for desorption to occur. The invariant E_{trans} distributions further indicate that there must be a repulsive hard wall, for motion away from the surface, encountered by those molecules that have experienced some minimum amount of symmetric bending. In order to see if this conjecture is reasonable, we calculated the chemisorption potential energy surface for NH_3 with at least two degrees of freedom, namely the Pt-NH_3 bond distance and the Pt-N-H bond angle.

All calculations were done with the DMol local-density-functional code [15], which uses the von Barth-Hedin exchange and correlation potential [16]. Because of the uncertainty in the binding site, atop, bridge, and threefold hollow potential energy surfaces were simulated with an 18-atom Pd cluster, having 12 atoms in the first layer and 6 atoms in the second. (Pd was used because DMol does not currently include relativistic effects in Pt). These all-electron calculations used the frozen-core approximation (through Xe), and were converged to 10^{-6} Hy (1 Hy$=27.21$ eV).

Consistent with earlier calculations [17], we find that the binding energy at the atop site (1.1 eV) is greater than in the threefold hollows or bridge sites (both ~ 0.8 eV). Nevertheless, the topological features shown in Fig. 3 of the potential energy surface are the same for all three sites. In Fig. 3, the distance x of the hydrogen plane relative to the N atom is directly related to the bond Pt-N-H angle ϕ through $x = -r_0 \cos\phi$, where r_0 is the N-H bond length (1.9 a.u., a.u.$=0.529$ Å). The zero of energy is arbitrarily the lowest point on the surface. At large distance z of the N atom from the surface (Pd-NH_3), the double-well potential in x is evident, reflecting the equivalent noninverted $(x = -0.7$ a.u.) and inverted
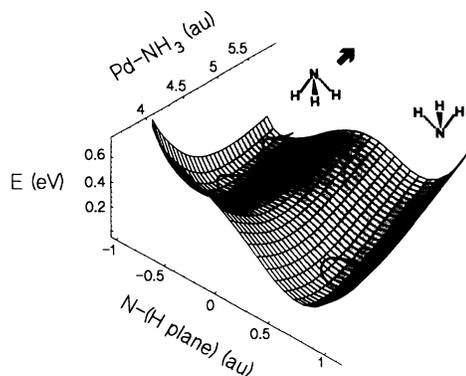

FIG. 3. Calculated two-dimensional potential energy surface for chemisorbed NH_3. The initial noninverted wave packet is the circle at right. Upon electronic excitation, the molecule moves towards inversion and encounters the repulsive hard wall (dark area at left). The inverted molecule then follows a direct desorption trajectory out of the inverted well, with little translational-vibrational coupling.

$(x = +0.7$ a.u.) configurations. The calculated inversion barrier is 0.28 eV, which is close to the gas-phase value of 0.25 eV [12]. At smaller z, the potential is asymmetric due to the inequivalent interaction of the hydrogens, and the $3a_1$ orbital, with the surface.

We propose the following desorption scenario shown schematically in Fig. 3 as a calculated trajectory. The initial noninverted wave packet, shown centered at $(x,z) = (0.7$ a.u., 4.4 a.u.), is electronically excited to the $3a_1^{-1}$ state. The molecule evolves towards the equilibrium planar configuration. Given enough time in the excited state, the molecule passes through planar and reaches the inverted configuration. The initial noninverted minimum in z is 4.4 a.u., while the inverted minimum is $z = 5.1$ a.u. substantially further from the surface. Thus deexcitation at this time places the inverted wave packet on a sufficiently repulsive hard wall with respect to the surface to allow desorption. Since the inversion motion actually moves the N atom *away* from the surface to maintain the center-of-mass (c.m.) distance, some compensating inward z motion while in the excited state may be necessary to give the molecule enough energy to break the surface bond. An image charge model would predict substantial inward motion. However, it should be noted that calculations [11] used to estimate the excited-state forces in z reveal that the net force is substantially less than predicted by an image charge model.

There are two critical consequences of this mechanism. The first is that substitution of D for H increases the time for the excited molecule to reach the inverted geometry prior to decay. *Thus ND_3 has a much lower probability of being excited long enough to reach the hard wall,* and hence will have a lower desorption yield. One can estimate the time required for inversion by $t = \pi/\omega$, where ω is the frequency of the inversion mode. For NH_3, $t \approx 1.7 \times 10^{-14}$ s; whereas for ND_3, $t \approx 2.2 \times 10^{-14}$ s.

Since the desorption yield is roughly proportional to the exponentially decaying probability of staying in the excited state, this difference in time scales can easily account for a factor of 3 difference in yield. A reasonable excitation lifetime of 5×10^{-15} s explains the experimental yield ratio $NH_3/ND_3 = 3$ [11].

The rotational spinning of NH_3 desorbates is a second consequence of the increased molecule-substrate interaction in the inverted state. Since adsorbed NH_3 is essentially a free rotor [7] with little or no zero-point energy, "spinning" energy must be derived from the desorption dynamics, whereas "tumbling" energy can be accounted for in large measure by the kinetic part of the zero-point rocking energy (260 K for NH_3), and 205 K for ND_3 [10]). Since we see the same rotational energy at low (α-only) coverages, spinning is not likely due to adsorbate-adsorbate interactions. The cause of the spinning motion is thus a dynamical effect due to the *increased corrugation of the surface potential seen by the inverted molecule*. The H (D) atoms feel a force which depends on the slope of the rotational potential. Since the moment of inertia for NH_3 is half that of ND_3, only half as much rotational energy is expected for ND_3 relative to NH_3. Experimentally, we see that ND_3 has about one-third the spinning rotational temperature T_s as NH_3. Thus inverted ND_3 must be seeing less corrugation which is consistent with little or no c.m. motion in the excited state. In the DMol calculations, the inverted molecule sees sufficient corrugation (~ 0.35 eV) at the *noninverted* molecule equilibrium distance from the hollow and bridge sites to explain the > 650 K NH_3 rotational energy; however, the corresponding corrugation at the atop site is too small (0.018 eV).

An important experimental result that remains to be explained is the apparent insensitivity in both yield and dynamics to the surface coverage and hence the initial ground-state binding energy (α vs β). Unfortunately, we need to know more about the α and β adsorption geometries and potential energy surfaces, especially in high and low coverage regimes, before we can further address this issue.

In summary, we have shown that the translational and internal energies of NH_3 and ND_3 are the consequence of multidimensional dynamics of polyatomic stimulated desorption. Since intramolecular motion is of the same time scale as the excited-state lifetime, molecular geometry changes play a crucial role in the desorption mechanism. We have shown that the inversion in excited NH_3 can explain both significant isotope effects (yield and ro-

tational energy). Potential energy calculations support the desorption model; however, the energetically favored atop adsorption site does not provide sufficient corrugation to explain desorbate rotational energies. The relative difference in NH_3 binding energies at the various sites does decrease with Pd cluster size, and may decrease further for Pt clusters.

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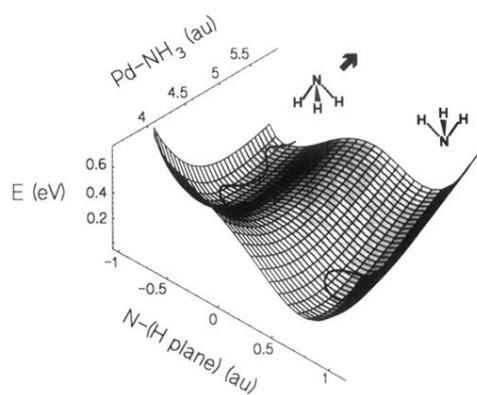FIG. 3. Calculated two-dimensional potential energy surface for chemisorbed NH₃. The initial noninverted wave packet is the circle at right. Upon electronic excitation, the molecule moves towards inversion and encounters the repulsive hard wall (dark area at left). The inverted molecule then follows a direct desorption trajectory out of the inverted well, with little translational-vibrational coupling.