Manuscript Printed April 30, 1995

Prepared for Submission to
Surface Science

The Sticking and Dissociation of
NH_3 on W(110): a three-state model

D. P. Masson,[a] R. P. Merrill,[b] and P. L. Houston[c]

Materials Science Center
Cornell University
Ithaca, New York 15853

---

[a] Also Field of Applied Physics; current address: Department of Chemistry, University of California San Diego, LaJolla, CA, 92093-0358

[b] Also School of Chemical Engineering.

[c] Also Department of Chemistry

Abstract

The kinetics of the adsorption of NH_3 on W(110) and its subsequent dissociation have been investigated using molecular beam techniques and temperature programmed desorption (TPD) for surface temperatures ranging from 140 to 700 K. NH_3 shows a wide desorption peak around 270 K and a smaller peak at 170 K while H_2 and N_2, produced by dissociation, desorbed at 550 K and 1350 K, respectively, with kinetic parameters similar to those reported for H and N generated by adsorption of H_2 and N_2. At normal incidence and for a surface temperature of 140 K, the NH_3 sticking coefficient was found to decrease from unity at a beam energy of 0.8 kcal/mol to 0.5 for a beam energy of 5.4 kcal/mol. The sticking coefficient generally decreases with surface temperature to a value of 0.05 at 700 K, but, for a 5.4 kcal/mol beam, it exhibits a relative minimum near 300 K. The reflection coefficient of NH_3, for an angle of incidence of 49°, increases with temperature and incident beam energy in agreement with the sticking measurements. The TPD peak positions, sticking and reflection data are all well reproduced by a three-state model based on simple kinetics. The model assumes that NH_3 initially traps in a molecular state and that dissociation occurs by thermal activation into an intermediate state. At no temperature is the sticking probability enhanced by increasing the kinetic energy of the incident molecules and there is no evidence for a direct dissociation channel which has a translational energy barrier less than 5.4 kcal/mol.

I. Introduction

Decomposition of ammonia on several transition metal surfaces has been investigated in order to provide some understanding of the reactions involved in the synthesis of ammonia.[1] On most surfaces at low surface temperature, ammonia binds to the metal via the nitrogen lone pair with the hydrogen atoms pointed away from the surface. The large electron transfer from the molecule to the metal leads to a strong dipole moment of ~2 D for the adsorbates. At higher surface temperature the NH_3 either desorbs or dissociates to leave hydrogen and nitrogen on the surface.

Ammonia readily dissociates on tungsten, and it is generally believed that the formation of stable nitride structures reduces tungsten's catalytic activity when compared to iron. The rate of ammonia decomposition at elevated temperature (~900 K) on the low Miller index planes of tungsten was found to decrease in the order (111) > (100) > (110) indicating that the close-packed (110) surface has the lowest activity.[2] The rate of decomposition is given by the product of the sticking coefficient and the dissociation probability. In these experiments, the surfaces were dosed by leaking ammonia into the vacuum chamber, thus exposing the edges and the back of each crystal with a thermal flux of molecules. The authors acknowledged that using this procedure made it difficult to separate the catalytic activity of the more reactive (111) facets, naturally formed on the edge of the crystal, from the reactivity of the exposed surface. In the work reported here, the kinetic energy of the incident ammonia molecules was controlled by using a seeded molecular beam. The collimation of the beam and the methods used to gather the data insured that only the surface of interest, the least reactive (110) surface, was investigated.

The sticking and reflection probabilities of ammonia on W(110) have been obtained for incident kinetic energies in the range from 0.8 to 5.4 kcal/mol and for surface temperatures from 140 to 700 K. We will show that the dynamics underlying these measurements can be understood by a simple three-state model using first order rate coefficients. The temperature dependence of the relevant surface processes -- trapping, direct-inelastic scattering, thermal desorption and dissociation -- can be derived from the model.

One motivation for the present study was to assess whether the NH_3/W(110) system might be an appropriate one on which to search for an enhancement in the dissociation probability with increasing incident kinetic energy and/or vibrational excitation of the incident molecules.[3] Although only a limited number of studies have been published, it does appear for some systems that the surface reactivity may be enhanced for vibrationally excited molecules. For CH_4 on W(110),[4,5] which exhibits a barrier to dissociation, dissociation can be enhanced by increasing either the translational or vibrational energy of the incoming molecule. Since 10-20% of the ammonia molecules in a molecular beam can be excited to one of two vibrational modes using a commercial F-center laser, we had hoped to find that a similar barrier might exist for NH_3 dissociation on W(110). It was anticipated that the close-packed W(110) surface would be less reactive than the other more open planes and yet not be totally inert to ammonia dissociation, as suggested by the work of McAllister and Hansen.[2] Indeed an XPS study[6] of this system has revealed that ammonia does dissociate on W(110), but the rate parameters for this channel were not investigated. The results of our study of the translational energy dependence for the sticking, trapping-desorption, direct-inelastic scattering and dissociation of ammonia on W(110) demonstrate that, to within our experimental error, ammonia adsorption on W(110) does not have a direct channel for dissociation with a translational energy barrier less than 5.4 kcal/mol. We found instead that the formation of an intermediate state preceeds dissociation.

II. Experimental

A. Apparatus

All experiments were performed in an ultra high vacuum (UHV) chamber equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), three mass spectrometers and a pulsed molecular beam. A pressure of less than 5×10^{-11} Torr was typically obtained after a 48 hour bake-out at 170 °C. One mass spectrometer was mounted on a rotatable platform and could be positioned to intercept the molecular beam at the entry port to the UHV chamber and on the opposite side of the chamber. Time-of-flight measurements of the molecular beam at these two points were used to find its mean velocity. A second mass spectrometer was mounted within a liquid nitrogen shroud isolating the instrument from the main chamber except for an angular aperture positioned so that only the central portion of the crystal was in a direct line-of-sight with the ionizer of the mass spectrometer. The third mass spectrometer was mounted within the main chamber to monitor the time dependent chamber concentration for specific components of the pulsed molecular beam and to obtain temperature programmed desorption (TPD) measurements for H_2.

The tungsten sample (9 mm dia x 2 mm disc) was cut to expose the (110) surface and was polished using standard metallographic techniques. A Berg-Berrett X-ray showed an unstrained surface across the whole crystal. The sample was mounted on tungsten rods (0.5 mm dia.) attached to a manipulator which could be translated along three orthogonal spatial axes and rotated about the axis perpendicular to the principle scattering plane of the molecular beam. A W-5%Re/W-26%Re thermocouple spot welded to the edge of the sample was used to monitor the crystal temperature. For temperatures above 1000 °C, we were able to compare the thermocouple readings with the temperatures measured by an optical pyrometer. The pyrometer gave temperatures slightly lower (by 25°C) than those indicated by the thermocouple. The attenuation of light through the view port window was probably responsible for this small difference. All temperatures reported here were those indicated by the thermocouple. The sample mount was connected to a liquid nitrogen cold finger via a copper braid. Using liquid nitrogen, the crystal could be cooled from 2000 K to 140 K in 15 minutes. The tungsten crystal was heated (up to 2500 K) by electron bombardment with a variable bias of up to 1500 volts. The filament was mounted in an alumina cup positioned behind and very close to the crystal so as to prevent stray electrons from reaching its front face. A gas doser (1.3 cm dia) connected to a leak valve was used to shower the sample with oxygen during the cleaning procedure described below.

A pulsed supersonic beam of ammonia seeded in He, H_2, or Ar was directed at the crystal, and surface coverage was subsequently measured by Temperature Programmed Desorption (TPD). The molecular beam originated from a pulsed nozzle (Newport BV-100, 0.5 mm orifice) and then passed through a skimmer, a beam on/off flag, and two further stages of collimation and differential pumping prior to entering the UHV chamber. The intensity profile of the molecules impinging on the surface had an effective diameter of 2.5 mm. The geometry of the molecular beam did not produce a uniform intensity profile at the crystal but rather an intensity distribution similar to a truncated cone. This profile may be understood by considering the line of sight between the crystal and the nozzle source. For a small region near the center of the crystal, the intensity is uniform since the entire nozzle orifice is in direct sight through the skimmer and collimating aperture. For positions somewhat further from the center of the crystal, the nozzle (and/or skimmer) aperture becomes partially occluded by the collimating aperture, so that the intensity decreases. A mathematical description of the beam profile in our apparatus was derived and used in the analysis below in order to extract the sticking coefficient from the integrated TPD curves at various exposures. A backing pressure of 2 atm and seeding ratios of about 6% NH_3 in helium, argon or hydrogen were used. The frequency of the pulses was 25 Hz and the pulse duration ranged from 100 to 300 μs. For the TPD data, a personal computer was used to ramp the crystal temperature linearly in time (20 K/s) and simultaneously to collect the mass spectrometer signals of the desorbing molecules.

B. Procedures

The crystal was cleaned by repeated cycles of oxidation at 1700 K under an O_2 partial pressure of 10^{-6} Torr, followed by heating to 2500 K. No traces of oxygen or carbon (indicating coverages of less than .0003) were detected in the Auger spectra.

The conventional method of King and Wells[7] to obtain the sticking coefficient is inadequate for ammonia because of its long residence time on the chamber walls. Indeed, no pressure increase in the background at mass 17 could be detected with the beam on and the crystal fully saturated or simply removed from the beam path. Instead, the sticking coefficient and the dissociation probability were found by determining the flux of the molecular beam impinging on the sample and by integrating the time dependent flux of desorbing molecules in the subsequent TPD. Calibration of the flux of the molecular beam is described elsewhere,[8] where it is also shown that the seeded ammonia beams used contain up to 10-15% clusters, most of them dimers. Because of their weak binding energy, dimers are expected to dissociate to monomers when they collide with the surface, and they should not significantly affect the results reported in this paper.

The flux of molecules in the TPD for NH_3 and N_2 was obtained by carefully calibrating the liquid N_2 cooled mass spectrometer. The average velocity of the desorbing molecules was assumed equal to $(2kT_s/m)^{½}$ where T_s is the surface temperature during the TPD, m is the molecule's mass, and k is Boltzmann constant. The flux angular distribution of N_2 and NH_3 has been shown to vary as $\cos\theta$ (see Fig. 4, described below). It is generally agreed that such distributions reflect thermal equilibrium of the desorbing molecules with the surface.

The TPD technique employed here determines the surface coverage of a species as a function of the ammonia dose received by the surface while held at a specific temperature. Some selected TPD spectra for N_2 (mass 28) and NH_3 (mass 17) are shown in Figs. 1 and 2. Possible interference in these TPD profiles from adsorption of background gas was checked by leaving the clean sample with the beam off for periods of time as long as those used while dosing with the ammonia beam. No detectable background signals were observed at H_2O and CO masses. For H_2, however, it was found that the background pressure in the liquid N_2 cooled mass spectrometer remained too high to enable us to observe the H_2 desorbed from the surface by the normal method. Instead, we monitored the H_2 pressure rise with the mass spectrometer located in the main chamber. For typical conditions, about 50% of the signal observed during the TPD was due to background adsorption of H_2, while 50% was due to ammonia decomposition on the surface. In principle, the amount of hydrogen produced by the dissociation of NH_3 could be obtained simply by subtracting the H_2 background profile from the raw TPD profile. The amount of H_2 thus observed agreed within 25% with the amount of N_2 ($3H_2$ for each N_2) detected by the line-of-sight mass spectrometer. Day-to-day variations in the hydrogen partial pressure and pumping speed of the chamber were large enough to account for the differences observed.

The zero coverage reflection coefficients at an angle of incidence of 49° from the normal were also measured by monitoring the intensity of the boxcar-integrated reflected NH_3 flux (49° from the normal) immediately after the molecular beam flag was opened. In order to calibrate the reflection coefficients, the scattered signal from the clean surface was normalized to the signal from a saturated surface or from a hot surface kept well above the desorption temperature. Although this technique resembles the beam reflectivity method of King and Wells, it measures the molecular fraction that is scattered at the specular angle rather than the fraction that actually does not stick to the surface. The scattering event may occur either inelasticly or after a trapping-desorption either of which is fast on the time scale of the boxcar gate. Such measurements can be expected to give good results for the sticking probability only when the angular and speed distributions of the specularly reflected beam are relatively independent of the parameters varied during the experiment, in our case the surface temperature.

III. Results and Discussion

A. Qualitative Aspects of the TPD Data

TPD spectra taken following dosing with ammonia beams at 0° incidence and at low (0.8 kcal/mol) or high (5.4 kcal/mol) kinetic energy showed similar features. Ammonia (near 270 K), H_2 (500 K), and N_2 (1300 K) were all seen to desorb from the surface. Figures 1 and 2 show a series of TPD spectra for NH_3 and N_2 which were obtained using the mass spectrometer in line of sight with the crystal. At a dosing temperature of 140 K, the ratio of NH_3 to N_2 flashed from the surface was found to be about 0.8.

The TPD traces for ammonia revealed the presence of at least three features, located at 160 K, 270 K and 315 K. While the peak at 315 K is not easily seen from Fig. 1a, it appears as the sole peak when the surface is dosed at 260 K, as shown in Fig. 1b. We found that the growth of the 315 K peak saturates at 0.01 monolayer after only 1 L of exposure and that the peak does not decrease when the surface is kept at 260 K for several minutes before the TPD experiment. In view of its low coverage and its stability in time, it seems reasonable to assign the 315 K peak to ammonia adsorbed at surface defects. We note, however, that the model developped later in Section IV, includes an intermediate state with a desorption near 300 K. For this model, the choice of kinetic parameters which best simulate the results suggest that (with a 20 K/s TPD ramp rate) the intermediate's TPD peak would be too small to detect. The major peak of the TPD profiles, at 270 K, is most likely a chemisorbed state on the (110) surface. In the proposed kinetic model, molecules are initially trapped into this chemisorbed state. The early growth of the smaller peak at 160 K suggests that a second chemisorbed state is also being populated at low coverage.

None of the ammonia peaks could be fit using simple first- or second-order kinetics. Nor did the inclusion of a simple linear coverage dependent term for the activation energy improve the fits. The difficulty arises because at these low temperatures (<300 K), the width of a TPD curve should be of the order of 20 K when values compatible with transition state theory are used for the pre-exponential factor (*e.g.*, $A=10^{13}$ to 10^{15} s^{-1}). Although the width of a TPD peak increases with smaller pre-exponential values, the simulations described later indicate that the width cannot be increased significantly even when the pre-exponential factor is lowered by several orders of magnitude. It thus appears that as many as four adsorption sites of different activation energy would be required to fill the wide ammonia peak observed at 270 K if regular simple kinetics and conventional transition state theory applied.

Wide ammonia TPD peaks are not peculiar to tungsten; ammonia desorption from Fe(100), Fe(110) and Fe(111)[9] also produced wide peaks extending from 125 to 350 K. Desorption traces of ammonia from Ir(111)[10] and Pt(100)-hex[8] obtained in this laboratory have also shown similar wide and complex structures below 400 K. In a study of NH_3/Ru(001), Benndorf and Madey[11] proposed a coverage dependent activation energy of the form $E=E_o-W\theta^{3/2}$ to explain their wide TPD data. They also point out that dipole-dipole interactions between the adsorbates are not sufficient to account for their large value of W (160 kcal/mol). Rosenzweig and Asscher proposed that both the activation energy and pre-exponential are coverage dependent for the similar NH_3/Re(0001) system.[12] A rather large variation of 5 orders of magnitude in the pre-exponential factor was suggested. Wu and Kevan[13] have measured the isothermal desorption of NH_3 from Cu(100) and found a value for the pre-exponential factor, smaller than expected from conventional transition state theory. A more careful analysis including the adsorbed ammonia's frustrated modes, was proposed by Wu and Kevan to explain the low pre-exponential values observed over the dynamic range (209-244 K) used in their work. Their analysis also predicts a temperature dependence for both the pre-exponential and the activation energy.

An XPS study of ammonia dosed W(110)[6] has revealed the presence of NH_3 on the surface for temperatures ranging from 80 to 300 K. While dissociation of the first N-H bond to form an NH_2 species occurs at temperatures less than 170 K, NH begins to appear at about 200 K. In agreement with the wide TPD we observe, it is clear from these XPS data that ammonia undergoes a complex dissociation in this temperature range possibly involving more than a single absorption site.

Our TPD for N_2 were remarkably similar to those reported by Lee *et al.*[14] who dosed the same surface with N_2. They observed three features at 1180 K, 1245 K and 1350 K which they labeled β_1, β_2 and β_3, respectively. We have assigned the labels β_2 and β_3 to the two peaks described below based on the fact that their shape and behavior with coverage are similar to those of Lee *et al.* Our N_2 spectra at low coverage were roughly symmetric about the β_3 peak and had full width at half maximum (FWHM) of about 180 K. At higher coverages, we observed the growth of a peak at 1180 K, labeled β_2 in Fig. 2a. No shift in temperature was detected for the β_2 peak, while a slight decrease in temperature was observed for the β_3 feature with increasing coverage, suggesting second-order kinetics. For crystal dosing temperatures in excess of 400 K, the growth of both β_2 and β_3 appeared to be simultaneous, while dosing below 300 K favored the growth of the β_3 peak. Lee *et al.* also observed the β_2 peak near 1220 K when W(110) was dosed at 820 K with a 25 kcal/mol N_2 beam kinetic energy; only the β_3 peak appeared after dosing with a lower N_2 kinetic energy beam at 2.0 kcal/mol.

Second-order kinetic analysis gave good agreement with the experimental β_3 peaks obtained for dosing at or below 300 K. An example of such a fit is shown in Fig. 2b, where the activation energy was 60 kcal/mol and the pre-exponential factor was 2.0×10^{-2} cm^2 s^{-1}. Tamm and Schmidt[15] and Cosser *et al.*[16] have reported a peak desorption temperature for the β_3 nitrogen from W(110) higher than that obtained by Lee *et al.* and by us, ~1500 K vs ~1350 K. The activation energy reported by Tamm and Schmidt, 79 kcal/mol, is consequently higher than ours. It seems likely that the desorption rate parameters change during desorption. Lee *et al.* reported that the isothermal desorption spectra under dosing conditions known to give both the β_2 and β_3 features (and in their case a small shoulder, labeled β_1, near 1180 K) indicated that the desorption rate increased at intermediate coverage.

Our TPD traces for H_2 were similar to those reported for H_2 adsorbed on W(110).[17] An example of a set of such curves is shown in Fig. 3. In both cases there are two desorption peaks which are designated β_1 and β_2 and show second-order desorption kinetics. These two states are populated concurrently during the dosing period. Tamm and Schmidt[17] report binding energies of 27 kcal/mole for the β_1 peak, 32.5 kcal/mole for the β_2 peak, and similar pre-exponential factors for the desorption rate coefficients. There is, however, an important difference between the two sets of data. In Fig. 3 the β_1 state is preferentially populated at low dosing levels. It is nearly saturated before the β_2 feature grows significantly. This means that population of the more stable β_2 state is limited by kinetics. It also means that there is no appreciable mixing between the two states during the thermal desorption process.

When these two states are populated by adsorption of H_2,[17] however, the opposite behavior is found. The β_2 state is populated preferentially, followed by β_1. Such a difference might be expected if our heating rates for the thermal desorption were much larger than those used with the H_2 but, in fact, our rates were a factor of ten *less* than those used by Tamm and Schmidt.[17] Thus, the β_1 state (27 kcal/mole) is more directly coupled to the dissociating NH_3, while the β_2 state (32.5 kcal/mole) is kinetically coupled more directly to gas-phase H_2. This difference has implications in understanding the details of how NH_3 actually dissociates on this surface, but one cannot choose with only this information from among several alternatives which suggest themselves.

The angular distributions of N_2 and NH_3 desorbing from the W(110) surface are plotted in Fig. 4; a cosine distribution (solid line) fits the data reasonably well. These plots were obtained by tilting the crystal normal away from the line-of-sight mass spectrometer axis. Since for our geometry the mass spectrometer views a portion of the crystal larger than the molecular beam spot size, the collected signal is expected to give a direct measure of the angular distribution. Because our main interest was the initial sticking and dissociation coefficients for ammonia, we used a low nitrogen atom coverage (estimated at 0.04 monolayer) for the angular distribution data. A somewhat more peaked angular distribution ($\cos^n\Theta$ with $3 < n < 4$) was obtained by Cosser *et al.*[16] for N_2 adsorbed on W(110). From the detailed data of Lee *et al.*,[14] we estimate that the nitrogen atom coverage used by Cosser *et al.* was near 0.2 and hence substantially larger than the coverage used to obtain our angular distribution. This is an important point for the analysis that follows.

B. Quantitative Analysis of the TPD Data

Figure 5 shows a typical plot of the integrated N_2 TPD spectra for various exposures. The solid line is a "corrected" second-order adsorption kinetic fit described below. For such plots, we observed that while first- or second-order adsorption kinetics could fit the initial rise reasonably well, they did not reproduce the slower increase seen at higher exposures. Although Lee *et al.*[14] (who also used a molecular beam) did not elaborate on this point, their figure for N_2 coverage vs N_2 exposure also seems to exhibit a slow increase at higher coverages.

This phenomenon can be partially attributed to the non-uniform flux profile of our molecular beam, which, as described in Section II.A, resembles a truncated cone. The portion of the crystal hit by the lower flux in the wings of the beam profile will take longer to saturate than that hit by the center. The beam profile can be estimated from the geometry of the collimating apertures, and the sticking coefficient and saturation coverage can then be corrected. The procedure is described in detail elsewhere.[8] The correction, used in conjunction with simple second-order adsorption kinetics, resulted in much improved fit to the amount of N_2 desorbed from the surface at different exposures. The solid line of Fig. 5 shows a typical fit obtained using this analysis. While the beam profile correction might explain the continued production of desorbates observed both in our experiments and in others, it should be noted that other phenomena such as the subsequent growth of a more dense layer or diffusion of molecules beyond the beam diameter may also contribute.

A more serious potential problem is that the coverage-dependent signal detected in a line-of-sight mass spectrometer will be affected by the dependence of the angular and velocity distribution of the desorbing molecules on coverage. For example, an apparent overgrowth would be observed if the angular distribution becomes more peaked at higher coverages. When compared to our low-coverage angular distribution, the angular distribution measured by Cosser *et al.*[16] at higher coverage suggests this possibility. However, a coverage-dependent angular distribution should have little effect on our determination of the initial sticking coefficient, since our measurements are made in the limit of zero coverage.

Both ammonia and nitrogen molecules were seen to desorb from the surface, so that our initial sticking probabilities include both the integrated NH_3 peak (for dosing temperatures lower than 300 K) and (twice) the integrated N_2 peak. A plot of the number of N atoms desorbed from the surface vs NH_3-exposure yields the initial sticking-coefficient as the zero-coverage slope, extracted by a least-squares fit assuming, for convenience, second-order Langmuir kinetics with the appropriate correction for the beam profile (see ref.8, appendix A) The resulting sticking coefficients as a function of surface dosing temperature for two incident kinetic energies are shown in Figs. 6a and 7a. The solid lines in these figures are fits from the three-state model described in Section IV. At a dosing temperature of 140 K, the ratio of nitrogen atoms desorbing as NH_3 to those desorbing as N_2 was roughly the same (~0.4) for the two kinetic energies used, so that at this dosing temperature the branching ratio does not appear to depend strongly on incident translational energy. The contribution to the initial sticking coefficient from desorbing ammonia molecules obviously vanished for dosing temperatures above its desorption temperature of 300 K.

Two interesting features of the data should be noted at this point. First, the low energy beam sticks with higher probability to the surface for low surface temperatures. Second, the sticking probability for the high energy beam does not decrease monotonically but rather exhibits a relative minimum near a surface temperature of 300 K. These observations will be discussed in Section IV.

C. Reflectivity Measurements

Measurements of the low coverage reflection coefficients as a function of surface temperature were performed for an incident ammonia beam at 49° and for detection at the specular angle. The surface was flashed between measurements to remove the small amount ($\theta \leq .04$) of adsorbed material. Figures 6b and 7b show the reflection coefficient for three different beam energies. The solid lines are fits obtained from the three-state model discussed in Section IV. The beams were obtained by seeding the ammonia in argon, helium, and hydrogen, respectively. In these figures the intensity of the reflected ammonia normalized to the intensity at 800 K is plotted as a function of surface temperature. It is assumed that at 800 K nearly all of the molecules are reflected. A boxcar gate width of 1.4 ms was used for detecting the reflected signal. Even though hydrogen sticks to the W(110) surface for temperatures lower than 600 K, the presence of hydrogen in the molecular beam had no effect on the results since only the initial reflected signal (low coverage) was used. Moreover, the fractional flux of H_2 striking the crystal was estimated to be only 10% (this is because the heavier molecules tend to concentrate on the beam center-line during the supersonic expansion).

A similar reflection experiment was performed with deuterated ammonia, ND_3, seeded in helium to yield a kinetic energy roughly equal to that for the NH_3 seeded in helium. No isotope effect was found in the specularly reflected signal of ND_3 and NH_3.

D. Auger and LEED Data

The saturation coverage of our surface was also measured with Auger spectroscopy. For a dosing temperature of 475 K, the ratio of the peak-to-peak KLL transition of nitrogen at 379 eV to the tungsten peak-to-peak signal at 350 eV was 1.8. This corresponds to a surface coverage of 0.23, in good agreement with the N-saturation coverage (0.27) estimated from the second-order growth curve of our integrated TPD data. At this coverage the LEED evolved into a two domain (2x4) pattern. The sharpness of the LEED pattern began to fade after the crystal was flashed to 700 K (about half the desorption temperature of N_2) and disappeared after flashing to 800 K. The Auger signal remained unchanged after such treatments. Further NH_3 dosing did not increase the Auger signal, nor did it reproduce the original LEED pattern. Adsorption of ammonia at T=140 K, on the bare W(110) surface, was found to yield no new spots in the diffraction pattern but gave rise to an increase in the background intensity.

Similar results were obtained by Estrup and Anderson[18] for ammonia on a W(100) surface held at 300 K. They observed extra spots after raising the surface temperature above the desorption temperature of hydrogen, leaving only nitrogen on the surface. Ordered structures of NH_3 on surfaces are believed to be difficult to observe because electrons may damage the overlayer. Weiss *et al.*[9] did, however, report a poor quality LEED structure for ammonia on Fe(110), but none for Fe(100) and Fe(111). It is difficult, therefore, to know whether the lack of extra spots in the LEED patterns of ammonia is caused by electron damage or simply because the adsorption takes place on the surface either at random or in a p(1x1) overlayer.

E. Comparison to Previous Work

The fact that the growth of the β_2 peak in the nitrogen desorption spectra is seen at surface temperatures above 400 K suggests a correlation with the increase of S_o at the same temperature. Pfnür *et al.*,[19] who dosed W(110) with N_2, have observed a p(2x2) and a c(4x2) LEED structure at coverages of 0.25 and 0.5 respectively. The growth of the latter required higher kinetic energy for the incident N_2 and was correlated with the fully developed β_2 peak reported from the same laboratory.[14] The nitrogen structure formed by dosing with ammonia shows a LEED pattern which suggests the growth of a (2x4) overlayer having similarity to the structures reported by Pfnür *et al.* and Somerton and King,[20] who also reported the p(2x2) structure. It is plausible that for complete dissociation, NH_3 needs more empty neighboring sites than N_2 for the release of its three hydrogen atoms, thus reducing the saturation coverage below that of the p(2x2) overlayer.

Somerton and King have proposed that the N atoms do not occupy conventional sites on the surface but are sandwiched between the two top layers of tungsten atoms.[20] Grunze,[6] who dosed W(110) with ammonia, interpreted his XPS data at high surface temperature (>600 K) as evidence for the formation of surface structures reminiscent of nitrides. Pfnür *et al.* have suggested some possible surface structures based on known bulk tungsten nitrides.[19]

IV. Interpretation of results: the three-state model

A. Description of the model

There are three processes likely to take place when an ammonia molecule impinges on a clean tungsten surface. (1) The molecules may be reflected after having exchanged energy with the surface, a process referred to as direct-inelastic scattering. The reflected molecules will typically retain much of their translational energy and will be scattered to solid angles near the specular direction. (2) If the molecules lose enough energy in the translational coordinate perpendicular to the surface, they may become trapped. Such molecules lose memory of their incident energy and direction, and their residence time is determined by the surface temperature and by the depth of the well in which they are trapped. Those that desorb do so with a translational energy characterized typically by a

Boltzmann (or nearly Boltzmann) distribution at the surface temperature and with a cosine angular distribution with respect to the surface normal. (3) A fraction of the incident molecules may "permanently" stick to the surface, in either a molecularly adsorbed or a dissociatively adsorbed state. Those that stick in a molecularly adsorbed or chemisorbed state will typically have lost so much energy that they are unable to escape the surface attractive forces. Those that stick in a dissociative state may have reached that state either directly, that is with trajectories from the gas phase that lead directly to dissociation, or perhaps, indirectly from a molecularly adsorbed state.

Experimentally the distinction between the three processes is partly one of time scales: molecules scattered by the direct-inelastic process come off the surface rapidly at times less than 10^{-13} seconds with only a weak dependence on the surface temperature, those scattered by the trapping-desorption process come off more slowly with temperature-dependent surface residence times that are much larger than 10^{-13} s, and those which stick come off only after heating the surface. For example, the sticking coefficients obtained from the integrated TPD after dosing for a few minutes, refer to dissociated or chemisorbed molecules. The reflection coefficients on the other hand refer to molecules that either scatter quickly in an inelastic process or are emitted thermally when the surface is sufficiently hot.

We have constructed a model which simulates the time and temperature dependence of the various processes described above. The model, based on simple kinetics, can reproduce the important features of the sticking and reflection measurements as well as the two molecular surface states observed in the ammonia TPD. As shown in Fig. 8, it consists of three potential energy minima along a reaction coordinate which leads from the gas phase to a completely dissociated NH_3 molecule. State *p*, in the first minimum, can be assigned to a chemisorbed NH_3, state *a* is the dissociated molecule and state *m* is a reaction intermediate, possibly a partially dehydrogenated ammonia molecule. In the model, *p* molecules may either desorb or react to form *m* species, which can either dissociate to *a* or desorb through state *p* into the gas phase. These processes are indicated by arrows in Fig. 8. We do not propose here that only these states exist on the surface. In fact, the data suggest that at least two different chemisorbed *p* states could be initially populated depending on the incident energy used. The three-state model refers instead to the key steps of the reaction dynamics. The model results in three coupled differential equations:

$$\frac{dN_p}{dt} = -N_p(k_d+k_m) \tag{1}$$

$$\frac{dN_m}{dt} = -N_m(k_a+k_e)+N_p k_m \tag{2}$$

$$\frac{dN_a}{dt} = N_m k_a \tag{3}$$

where N_i are the surface concentration and k_i are the rate coefficients, presumed to be of the form:

$$k_i = \nu_i \exp(-E_i/kT) \tag{4}$$

where ν_i is a pre-exponential factor, E_i is the activation energy, T is the surface temperature, and k is the Boltzmann constant. In Eq. (1) we have neglected population of p from m because it will be shown *a postiori* that the barrier between m and p is significantly higher than the barrier between p and the gas phase, as shown qualitatively in Fig. 8.

In our experiment the dosing time (the duty cycle of the pulsed molecular beam) is small compared to our observation time: 0.2 ms vs 1.4 ms for the reflectivity measurements and 0.2 ms vs minutes for the sticking measurements. This suggests an initial boundary condition where all the molecules, except those which scattered by a direct-inelastic process, are initially trapped in state p. This is clearly an approximation, since the some reaction takes place during the 0.2 ms dosing time, but for most temperatures the approximation is reasonable. At sufficiently long times both wells p and m will be empty, that is, molecules will have either desorbed or dissociated into a. The solution to equations 1-3 with these boundary conditions is:

$$N_p(t) = N_p(0)e^{-t/\gamma} \tag{5}$$

$$N_m(t) = N_p(0)k_m\left(\frac{\epsilon\gamma}{\gamma-\epsilon}\right)\left(e^{-t/\gamma} - e^{-t/\epsilon}\right) \tag{6}$$

$$N_a(t) = N_p(0)k_a k_m\left(\frac{\gamma\epsilon}{\gamma-\epsilon}\right)\left[\epsilon\left(e^{-t/\epsilon}-1\right) - \gamma\left(e^{-t/\gamma}-1\right)\right] \tag{7}$$

where

$$\gamma = (k_d+k_m)^{-1} \tag{8}$$

and

$$\epsilon = (k_e+k_a)^{-1} \tag{9}$$

At large times the solution gives:

$$\frac{N_a(\infty)}{N_p(0)}=\left(\frac{k_m}{k_d+k_m}\right)\left(\frac{k_a}{k_e+k_a}\right) \tag{10}$$

An identical result is obtained by assuming steady state for the intermediate, *m*. At large times then the initial sticking probability is:

$$S_o(\infty)=\xi\frac{N_a(\infty)}{N_p(0)} \tag{11}$$

where ξ is the trapping probability into state *p*. In our model, (1-ξ) is the probability for a direct-inelastic collision since it is assumed that molecules impinging on the surface must otherwise be trapped into *p*. For finite observation times the reactions on the surface need not be complete and the sticking coefficient is:

$$S_o(t)=\xi\frac{N_p(t)+N_m(t)+N_a(t)}{N_p(0)} \tag{12}$$

Equation (12) has been used to model the sticking measurements, Figs. 6(a) and 7(a), obtained from the analysis of the integrated TPD spectra. In this case, t was the time it took to dose the surface for low coverage values, typically 100 s. However, the calculation is insensitive to times between 30 s and 5 min.

In order to model the reflection measurements shown in Figs. 6b and 7b we define the reflection coefficient as:

$$R(t)=1-S_o(t) \tag{13}$$

Here the time *t* is set equal to the open time of the gate used during the acquisition of the reflected signal. The time gate used in the reflection measurements (1.4 ms) was much smaller than the average time used to extract the sticking data from the integrated TPD's. The difference in the time scales used to obtain the sticking and reflection data is critical only for a certain range of intermediate temperatures where the time for desorption is much faster than a few minutes but slower than a few ms.

The model was also used to simulate the TPD of ammonia dosed at low surface temperature (140 K). In the TPD, the surface temperature increases linearly with time and the temperature dependent reaction rates, k_i's, will change accordingly. This time dependence can be obtained by setting $T = mt$, where m is the linear temperature ramp rate, into the form used for the rate coefficients (equation 4). It is assumed that prior to the TPD (surface kept at 140 K) all molecules are initially trapped in the p well. As the surface temperature begins to increase, molecules either desorb from the p well or enter the m state from which they may desorb or dissociate to the a state. The simulation of the ammonia TPD must, according to the proposed model, include the desorption from both the p and m states. This is best accomplished by seeking the time dependent solution of the number of molecules in the three states of the model. These are respectively for the p, m and a states:

$$N_p(t)=N_p(0)\exp(-\int^{t}[k_d(t')+k_m(t')]dt') \tag{14}$$

$$N_m(t)=\frac{\int_0^t[\exp(\int_0^{t'}(k_a(t'')+k_e(t''))dt'')][N_p(t')k_m(t')]dt'}{\exp(\int_0^t(k_a(t''')+k_e(t'''))dt'''} \tag{15}$$

$$N_a(t)=\int_0^t N_m(t')k_a(t')dt' \tag{16}$$

The flux of ammonia molecules from the p and m wells is then given by:

$$F_{OUT}(t)=N_m(t)k_e(t)+N_p(t)k_d(t) \tag{17}$$

As it turned out, our choice of parameters for the three wells indicates that for the 20 K/s ramp rate used, the vast majority of the molecules observed in the TPD desorb from the *p* state. Molecules which do come from the *m* state reside in the *p* state a time small compared to desorption times. A condition which further restricted the choice of parameters in our model is the ratio of dissociated (state *a*) to desorbed ammonia molecules at the end of the TPD. This ratio can be found by integrating equations 14 through 16. The set of parameters used to fit the high energy data reproduce the dissociation/desorption ratio found from experiments, but the parameters used to fit the low energy data do not as explained below.

B. Comparison with experiment

The "best fit" parameters are listed in Table I. These include the pre-exponentials and activation energies of the reaction rates used in our model. Values for the trapping probabilities are taken from the low temperature limits of the reflection coefficients in Figs. 6b and 7b. It is apparent from the values listed in Table I that a single set of parameters could not be found to fit simultaneously the fast and slow incident beam data. In the case of both the fast and slow beams, $E_e >> E_d$, which justifies our neglect of the population of *p* from *m* in Eq (1). We first describe the fits obtained from the fast beams; 9.3 and 5.4 kcal/mol.

Fast beams

The results of the fast beam best fit activation energies are shown on Fig. 8. The pre-exponential factor for k_e is 10^{13} sec^{-1}. Those for k_d, k_m, and k_a are between 10^8 and 10^9 sec^{-1}. While these latter values are lower than the normal expectation of about 10^{13} sec^{-1}, they are certainly not unreasonable. The solid line in Fig. 6a is the model fit for $S_o(T)$ for an incident kinetic energy of 5.4 kcal/mol. The local minimum (250 K), the subsequent maximum (450 K) and the final decrease at high temperatures are all well represented by the model. The decrease in $S_o(T)$ between 200 K and 250 K is caused by the temperature dependence of the desorption rate from state p. Above 250 K the rate of transfer to the intermediate state m, which has a larger activation energy than the desorption rate, causes an increase in $S_o(T)$. Above 450 K $S_o(T)$ is dominated by direct desorption from the the intermediate state, m, instead of dissociation into the state a. The trapping probability for this fit is 0.52 which is closer to the value estimated from the 9.3 kcal/mol reflection data (0.55) than it is to the value estimated from the 5.4 kcal/mol reflection data (0.72). Recall, however, that the data in Fig. 6a was taken with the beam perpendicular to the surface but the reflection data in Fig. 6b was taken with an incident angle of 49^o, which would result in a normal energy component of 6 kcal/mol for the 9.3 kcal/mol but only 3.5 kcal/mol for the 5.4 kcal/mol beam.

The model also gives good agreement with the reflection coefficients for incident energies of 5.4 kcal/mol and 9.3 kcal/mol (see the solid lines in Fig. 6b, which pass through these points for the resepctive energies). In this case equations 12 and 13 were used with an integration time of 1.4 ms, the box-car gate used to obtain the experimental data. For temperatures below 300 K all the adsorbed species have surface residence times greater than 1.4 ms and the reflection coefficient is constant at a value of $(1-\xi)$. Above 300 K desorption from the p state becomes faster than 1.4 ms and the reflection coefficient increases rapidly. In this temperature range, a fraction of the molecules also transfer to the intermediate m

state and enter the dissociation path. At about 470 K there is a "kink" in the reflection coefficient which represents the transition between desorption from the *p* well and desorption from the *m* state.

The "kink" in the model calculation at 470 K is a direct result of the presence of the intermediate in our three step model. It is present in the experimental reflection coefficient for all kinetic energies. This "kink", along with the maximum in S_o, for high kinetic energy in Fig. 6a are compelling evidence for the three step model.

As explained above (see equations 14-17) , the position of the TPD peaks may also be modeled by including the time/temperature dependence of the rate coefficients during the TPD. The prediction of the model, using the fast beam parameters in Table I, is shown by the dotted line centered at 270 K in Fig. 9. The solid line in Fig. 9 is a measured TPD. The position of the main peak at 270 K is reproduced within a few degrees K by the model but the predicted width is too small. As pointed out in section III.A., however, this is not a specific defect of the model but rather a characteristic of NH_3 desorption from most metals. The model indicates that, for a temperature ramp rate of 20 K/s, the peak at 270 K is due to NH_3 desorbing from the *p* well with very little desorption from the intermediate *m* state. The model also predicts, in agreement with experiments, that a significant fraction of NH_3 transfer to the *m* state during the TPD but quickly dissociate (state *a*) rather than desorb. The fast beam parameters were chosen such that the ratio of desorbed NH_3 to dissociated NH_3 (detected as N_2) agreed with the value determined from the integrated TPD of ammonia and nitrogen molecules ($[NH_3]/[N_2]=0.8$).

Slow beam

The low kinetic energy sticking coefficients and reflection coefficients (Fig. 7a & b) show three important differences when compared with the high kinetic energy data. At low energy the trapping probability, ξ, is near 100% indicating that no molecules scatter inelastically. The reflection coefficients for the 0.8 kcal/mol data begin increasing at temperatures near 170 K as compared to 300 K for the high kinetic energy coefficients. Finally, only a few values of S_o were measured at low kinetic energies and it is not clear from them whether or not a local minimum exists. The data suggests that there may be an alternate pathway for adsorption and dissociation at low kinetic energies. In particular, the rapid rise of the reflection coefficient at low surface temperature indicates that initial trapping and desorption might occur in a shallower well when compared to the high energy data.

The low kinetic energy reflection data can in fact be reproduced by our three-step model if we reduce the depth of the *p* well where incident molecules are assumed to trap initially from 10.9 to 3.4 kcal/mole. Concomittantly, E_m is reduced from 12.2 to 3.6 kcal/mole and the pre-exponentials to the unreasonably low values of 4×10^4 sec^{-1}. The result is shown by the solid line in Fig. 7b, and the slow beam parameters used were those listed in Table I. This choice of parameters also predicts a minimum in S_o, as shown by the solid line in Fig. 7a, but there are too few experimental points to confirm this behavior. As discussed below, the apparent lack of a minimum in S_o when the low incident energy beam is used could be caused by a slow transfer of molecules from the shallower *p* well to the deeper *p* well used to model the high energy beam data. It is conceivable that for the fast beams, molecules do not lose enough incident kinetic energy to remain trapped in the shallower well.

The existence of a shallower *p* well, accessed at low incident energy, is confirmed by the smaller peak observed in the TPD near 150 K. Using the slow beam parameters in Table I, we have modeled the TPD from this shallower well. The result is shown in Fig. 9 and correlates well with the position of the smaller peak observed experimentally near 160 K.

We note however that both TPD peaks, at 160 K and 270 K, were present independent of the incident kinetic energy used to dose the surface. There are at least two possible explanations for this apparent contradiction. At low incident energies, initial trapping could occur in both the deep and the shallow *p* states. Attempts to fit the data of Fig.7 using this hypothesis gave poorer fits as the fraction of molecules interacting with the deeper *p* state was increased. Another plausible explanation is that molecules initially trapped in the shallower *p* state can, after some time (or during the TPD) transfer along an activated path to the deeper *p* well and hence desorp at 270 K in the TPD. Within this hypothesis, the rapid rise of the low energy reflection coefficient at low temperature, would suggest that the rate of transfer to the deeper *p* well is long compared to the reflection measurement time (1.4 ms). On the other hand, the rate of transfer would have to be comparable to the time scale used for the TPD (a few minutes) since the TPD curves always show more ammonia desorbing from the deeper *p* well (270 K) than from the shallower *p* well (150 K). The similarity of the ammonia TPDs dosed at different incident energies could mean that an equilibrium is established between the deep and shallow *p* wells. The interaction suggested between the two *p* wells might also explain the apparent lack of a minimum in S_o for the low incident energy data and the failure of the model to reproduce the ratio of nitrogen to ammonia desorption when the slow beam parameters are used.

A more elaborate model then, should probably include a second chemisorbed *p* state with bridging paths to allow transfer to the other *p* state as well as to the intermediate *m* state. If this is indeed true, then the rate coefficients k_d and k_m may not be elementary rate coeficients, and thus it is not surprising that the pre-exponentials could be so low. The more elaaborate model, however, leads to a set of coupled differential equations which is not easily solved. In our opinion, the simplicity of our three-state model provides sufficient insights into the kinetics and dynamics of NH_3 dissociation.

In summary, the simple three-state model is consistent with our results namely, the sticking measurements, the reflection coefficients and the TPD peaks positions. In the three-state model, ammonia is first trapped in a molecular state and may subsequently desorb or enter an intermediate state from which dissociation or desorption may occur. The presence of the intermediate state is evidenced by a minimum in the sticking coefficient data (Fig. 6a) and a kink in the reflection coefficient data (Fig. 6b and 7b). One feature of the model, the initial trapping probability, decreases with incident kinetic energy. Both the NH_3 TPD curves and the reflection data indicate that two molecular states are available for initial trapping. At high kinetic energy, trapping occurs only in the deeper well and a significant fraction of the incident molecules scatter inelastically from the surface. At low incident energy, molecules are initially trapped by the shallower molecular well. Although not included in our simple three state model, some of the data suggests that a transfer path exists between the deep and shallow molecular states.

V. Conclusions

TPD spectra of ammonia dosed W(110) have revealed that ammonia, hydrogen and nitrogen molecules all desorb from the surface. The ammonia TPD profiles are very wide, suggesting complex kinetics and/or multiple adsorption sites, while the nitrogen TPD behavior resembles that observed for dosing the same surface with N_2 molecules that is, second order recombination kinetics. The hydrogen TPD's also show second order recombination kinetics in both β_1 and β_2 states. Further, the β_1 state is more strongly coupled kinetically with NH_3 decomposition than the β_2 state. Just the reverse is true for gas-phase hydrogen molecules.

A combination of reflectivity and integrated TPD measurements was used to determine the fraction of molecules interacting with the surface by direct-inelastic scattering, by trapping-desorption, and by sticking. At low surface temperatures only molecular NH_3 is present in the adsorbed phase. Above 300 K all the adsorbed ammonia dissociates or desorbs from the surface.

We have developed a simple three-state model based on simple first order kinetics which reproduces all of the important features of the sticking, reflection and TPD data. In this model the ammonia molecules are initially trapped in a molecular state. At higher surface temperature the ammonia can be activated into an intermediate state from which dissociation may proceed. Thermal desorption of the ammonia molecules occurs from the molecular state at low temperatures and from the intermediate state at higher temperatures.

To within experimental error, there is no surface temperature in the range from 100 K to 800 K for which the high energy (5.4 kcal/mole) molecular beam has a higher sticking coefficient than the low energy (0.8 kcal/mole) beam. Dissociative adsorption of ammonia on W(110) therefore appears not to have a direct channel with a (normal) translational energy barrier less than 5.4 kcal/mol.

Acknowledgements

This work was supported in part by the Cornell Materials Science Center under grant DMR-8818558 and in part by the Exxon Education Foundation. DPM is grateful to the Canadian NSERC for a graduate fellowship.

References

1. M. Grunze in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, D. A. King and D. P. Woodruff, eds., (Elsevier, Amsterdam, 1982).
2. J. McAllister and R. S. Hansen, J. Chem. Phys. **59**, 414 (1973).
3. P. L. Houston and R. P. Merrill, Chem. Rev. **88**, 657-671 (1988).
4. C. T. Rettner, H. E. Pfnür and D. J. Auerbach, Phys. Rev. Lett., **54**, 2716 (1985).
5. C. T. Rettner, H. E. Pfnür and D. J. Auerbach, J. Chem. Phys. **84**, 4163 (1986).
6. M. Grunze, C. R. Brundle and D. Tomanek, Surf. Sci. **119**, 133 (1982).
7. D. A. King and M. G. Wells, Surf. Sci. **29**, 454 (1971).
8. D. P. Masson, Ph D Dissertation, Cornell University 1991.
9. M. Weiss, G. Ertl and F. Nitschké, Appl. Surf. Sci. **2**, 614 (1979).
10. R. J. Purtell, Ph.D. Thesis, Cornell University, Ithaca, N.Y. (1981).
11. C. Benndorf and T. E. Madey, Surf. Sci. **135**, 164 (1983).
12. Z. Rosenzweig and M. Asscher, Surf. Sci. **225**, 249 (1990).
13. K. J. Wu and S. D. Kevan, J. Chem. Phys. **94**, 7494 (1991). See also K. J. Wu and S. D. Kevan, J. Chem. Phys. **95**, 5355 (1991).
14. J. Lee, R. J. Madix, J. E. Schlaegel and D. J. Auerbach, Surf. Sci. **143**, 626 (1984).
15. P. W. Tamm and L. D. Schmidt, Surf. Sci. **26**, 286 (1971).
16. R. C. Cosser, S. R. Bare, S. M. Francis and D. A. King, Vacuum **31**, 503 (1981).
17. P. W. Tamm and L. D. Schmidt, J. Chem. Phys. **54**, 4775 (1971).
18. P. J. Estrup and J. Anderson, J. Chem. Phys. **49**, 523 (1968).

19. H. E. Pfnür, C. T. Rettner, J. Lee, R. J. Madix and D. J. Auerbach, J. Chem. Phys. **85**, 7452 (1986).

20. C. Somerton and D. A. King, Surf. Sci. **89**, 391 (1979).

	Fast beams 9.3 & 5.4 kcal/mol	**Slow beam** 0.8 kcal/mol
ν_d (s^{-1})	1×10^8	4×10^4
E_d (kcal/mol)	10.9	3.4
ν_m	5.1×10^8	4×10^4
E_m	12.2	3.57
ν_e	1×10^{13}	1×10^{13}
E_e	20.3	20.3
ν_a	1×10^9	1×10^9
E_a	9.56	9.56

Figure Captions

1. *a*. TPD of NH_3/W(110), dosing temperature 140 K, Temperature ramp rate 20 K/s. *b*. TPD of NH_3/W(110) dosed at different surface temperatures. The exposure was 1.2 L, while the beam energy was 5.4 kcal/mol.
2. *a*. TPD of N_2/W(110) after dosing with ammonia at a surface temperature of 475 K. *b*. TPD of N_2/W(110) following NH_3 dosing at 300 K. The dashed lines are a second-order desorption fit using E_a=60.2 kcal/mol and a pre-exponential factor of $2x10^{-2}$.
3. TPD of H_2 after dosing with ammonia. The temperature ramp rate was 20 K/s.
4. Angular distribution of the desorbing species. The estimated NH_3 coverage was 0.02, while the estimated N coverage desorbed as N_2 was .04.
5. Growth of total nitrogen desorbed as a function of ammonia exposure using second-order adsorption kinetics with S_o=0.28 and a saturation coverage of 0.27. The surface temperature during dosing was 475 K, and the beam energy was 5.4 kcal/mol.
6. Sticking and reflection coefficients for the fast incident beams. *a*. Initial Sticking coefficient of NH_3/W(110) for the normal incident 5.4 kcal/mol beam. The line is the result of the three-state model described in the text. *b*. Reflection coefficients of ammonia measured at 49° from the normal for the fast 49° incident beams.
7. Sticking and reflection coefficients for the slow incident beam. *a*. Initial Sticking coefficient of NH_3/W(110) for the normal incident 0.8 kcal/mol beam. The line is the result of the three-state model described in the text. *b*. Reflection coefficients of ammonia measured at 49° from the normal for the slow 49° incident beam.
8. One-dimensional representation of the three states (*a*, *m* and *p*) model. NH_3 initially traps in a chemisorbed state (p). Dissociation into the *a* state proceeds via an

intermediate state (m). Desorption can occur from the *p* and *m* state. The model assumes that all processes, indicated by the arrows, are activated and can be represented by simple first order kinetics. The model, described in section IV, is used to fit the data in Figs. 6, 7 and 9. Barrier energies relative to gas-phase ammonia are given in kcal/mole based on a fit for the fast beam.

9. TPD of ammonia. The solid line is a typical TPD observed with a ramp rate of 20 K/s. The dashed line centered at 270 K is a fit obtained from the three states model using the fast beam parameters (deeper *p* well). The dashed line centered at 150 K was obtained using the slow beam parameters (shallower *p* well). The parameters are listed in Table I.