Collision-induced desorption of ammonia chemisorbed on Pt\{111\}: From direct measurement of the threshold energy to determination of the surface–adsorbate bond strength

Gregory Szulczewski and Robert J. Levis  
The Department of Chemistry, Wayne State University, Detroit, Michigan 48202

(Received 27 June 1995; accepted 14 September 1995)

We report the desorption of a chemisorbed polyatomic adsorbate from a transition metal surface by a beam of neutral, energetic Ar atoms. From direct measurement of the threshold energy for collision-induced desorption we calculate the surface–adsorbate bond energy. The absolute cross sections for NH$_3$ desorption at one-quarter of a monolayer coverage were measured for Ar beam energies up to ~3 eV at incident angles of 0°, 30°, 45°, and 60°. For the NH$_3$/Pt\{111\} adsorbate–surface system, the threshold desorption energy is found to be 1.95±0.17 eV. Using a classical energy transfer mechanism this threshold energy corresponds to a bond energy of 1.1±0.1 eV using an effective mass of 1 Pt atom. The threshold desorption energy scales with the total energy of the noble gas atoms for each angle of incidence. This result is consistent with a strong lateral corrugation in the NH$_3$/Pt\{111\} potential energy surface and a similar ejection mechanism at each angle. © 1995 American Institute of Physics.

I. INTRODUCTION

Molecular beam scattering is a powerful technique to probe intermolecular potentials for gas phase and condensed phase systems.\(^1\) In principle it is possible to “invert” low energy, elastic scattering data and recover the interaction potential. For gas–surface interactions this method is limited to the diffraction of H, He, and H$_2$ particles from a periodic lattice or adlayer of adsorbates.\(^2\) By measuring bound state resonances\(^3\) in the diffraction event it is possible to determine the well depth of the interaction potential. Unfortunately, the potential energy surface well depth for polyatomic chemisorption systems cannot be determined by this method because the scattering process is highly inelastic and diffraction cannot be observed. We have previously demonstrated that collision-induced desorption (CID) experiments\(^4a\) can be used to calculate the potential energy surface well depth (i.e., surface–adsorbate bond dissociation energy) for both physisorption\(^5\) and chemisorption systems.\(^6\) The collision-induced desorption experiment involves an impulsive collision of a hyperthermal (1–10 eV) neutral, noble gas atom with an adsorbate to induce impulsive ejection from the surface. The key to determining the potential energy surface well depth from a collision-induced desorption experiment is measurement of the threshold energy, or minimum energy, of the noble gas atom required to eject the adsorbate from the surface. Our hypothesis is that the potential energy surface well depth can then be calculated by accounting for the energy transferred in the noble gas atom–adsorbate and adsorbate–surface collisions, respectively.

The concept of collision-induced desorption of molecular adsorbates by a neutral, energetic atom from a surface without damage to the outermost layer of substrate atoms was first investigated theoretically by Zeiri, Low, and Goddard.\(^7\) These researchers suggested that measurement of the kinetic energy and angular distribution of the desorbing particles could be used to determine the surface–adsorbate binding energy and deduce the symmetry of the adsorption site. In this work, classical stochastic trajectory calculations were used to model the desorption of Xe atoms from a Si cluster by incident Xe atoms. Only direct collisions between the noble gas atom and adsorbate were found to induce desorption. Subsequent simulations of N$_2$ desorption from a W\{100\} surface by neutral Ar atoms\(^8a,b\) suggested that the mechanism of desorption was the result of direct collisions. In this example, the binding energy of the N$_2$ was 0.45 eV. Also, just above the threshold energy for desorption, 1 eV, the internal energy content in N$_2$ was negligible. Additional simulations\(^8b\) demonstrated that desorption was not the result of local heating. Subsequent calculations by Yang et al.\(^9\) support the elastic collision mechanism.

Experimentally, Beckerle et al. studied the collision-induced desorption\(^10a\) and dissociation\(^10b\) of methane molecules physisorbed on Ni\{111\} by neutral Ar, Kr, and Xe atoms. These investigations demonstrated the ability to cleave and form chemical bonds at a surface with hyperthermal collisions. The desorption of methane with 1–2 eV Ar atoms was facile because the interaction between the adsorbate and nickel surface is rather weak (\(-125 \text{ meV}\)). In the case of dissociation, high resolution electron energy loss measurements showed that the physisorbed methane was converted to an adsorbed methyl group and hydrogen atom (presumably in a concerted process) after impact with an inert atom. In addition to desorption of adsorbates, hyperthermal collisions can cause the ejection of substrate and impurity ions from surfaces.\(^10\) These experimental results and other theoretical calculations\(^11\) indicate that neutral, hyperthermal atom sputtering results in less damage to the surface as compared to high energy (\(-1000 \text{ eV}\)) ion beam bombardment.\(^12\) Hyperthermal particle–solid collisions have also been observed to promote dissociative ionization of the incident particle,\(^13\) eject substrate atoms\(^14\) (both ions and neutrals), and create electron/hole pairs in semiconductor solids.\(^15\)

The interaction of ammonia with Pt\{111\} has been pre-
viously studied by ultraviolet photoelectron spectroscopy (UPS), high resolution electron-energy loss spectroscopy (HREELS), thermal programmed desorption (TPD), work function experiments, and x-ray photoelectron spectroscopy (XPS). These studies indicate that below one-quarter of a monolayer (ML) NH₃ bonds molecularly in a threefold hollow site via the lone pair of electrons in the 3a₁ molecular orbital. In this bonding configuration the C₃₃v symmetry axis lies along the surface normal. A very large change in the Pt[111] work function (about −2 eV) at 0.25 ML has been reported in the UPS measurements. At this coverage the NH₃ dipole moment is measured to be 2.0 D and an activation energy of 0.9 eV is reported for NH₃ desorption from the Pt[111] surface. The remainder of the paper is organized in the following manner. Section II describes the experimental apparatus and procedures used to perform the collision-induced experiments. It includes a description of the molecular beam source, pumping system, and ultrahigh vacuum chamber. In Sec. III we summarize the results for collision-induced desorption of low coverage NH₃. The discussion and interpretation of the results is given in Sec. IV and the conclusions are summarized in Sec. V.

II. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Description of molecular beam source

The molecular beam source used in these experiments was based on the free-jet design. A schematic drawing of the molecular beam source, differential pumping chambers, and ultrahigh vacuum (UHV) chamber is shown in Fig. 1. The molecular beam source was an 8 in. × 0.25 in. molybdenum (Mo) tube sealed at one end by a Mo disk (EMI Corp.). The disk has a 50 μm laser drilled conical aperture and was electron beam welded to the tube. The other end of the tube was connected to a bakeable mixing cell/gas reservoir. The mixing cell was evacuated by a mechanical oil pump to 1 × 10⁻³ Torr and could be pressurized to 100 psi. A ballast was used to set the pressure of the gas mixture with absolute precision of ±0.5 psi.

To obtain the high kinetic energies for the collision-induced desorption experiments the molar ratio of Ar to carrier gas (He or H₂) was fixed and the nozzle temperature was varied. Typically ~175 W were required to heat the nozzle and the last 5 cm of the Mo tube. Radiant heat was generated by passing 10–15 A of current at 10–15 Vac through a 10 in. long × 0.25 mm diam tungsten wire wound into a coil around the last 5 cm of the Mo tube. The temperature was measured with a Chromel–Alumel thermocouple (K-type, Omega) positioned near the nozzle. To reduce heat transfer to the chamber walls the nozzle was enclosed by a water cooled radiation shield. A molecular beam skimmer (1 mm diam) was mounted on a tube away from the inside wall of the source chamber. This helped minimize the loss of beam intensity due to gas molecules scattering from the chamber wall. The nozzle aperture/skimmer distance was fixed at ~1 cm. The source chamber was evacuated by a water baffled 5000 l/s diffusion pump (CVC Corp.) and a 171 cubic foot per minute rotary piston pump (Leybold, model E250). The base pressure in this chamber was ~1 × 10⁻⁷ Torr and rose to ~5 × 10⁻⁴ Torr under operating conditions.

The skinned portion of the molecular beam entered the first stage of differential pumping where the continuous flow from the free-jet was chopped by a slotted Al disk mounted to a 400 Hz ac synchronous motor (Globe, model 75A1004-2). The motor had vacuum compatible bearings to reduce outgassing and was driven by an asynchronous power supply. The 10 cm diam Al disk had three slots (2 mm wide × 15 mm long) cut into the outer periphery and was dynamically balanced to reduce the load on the bearings. When a continuous beam was passed across the rotating disk, a 1200 Hz chopped beam was produced (~3% duty cycle). This technique was used to record a time-of-flight (TOF) spectrum. The timing for the TOF analysis was triggered by a LED/photodiode pair straddled across the disk to coincide with the opening and closing of the slot. The chamber was evacuated by a water baffled 2400 l/s diffusion pump (Varian, VHS-6)
and a 500 /min mechanical pump (Welch, Model 1397) to yield a base pressure of $\sim 4 \times 10^{-8}$ Torr.

The second differential pumping chamber had a base pressure of $\sim 2 \times 10^{-8}$ Torr and was evacuated by a 1500 /s liquid nitrogen trapped diffusion pump (Varian, VHS-4) and a 160 /min mechanical pump (Welch, Model 1402). A mechanical shutter (beam block) was attached to a rotary motion feedthrough on a 2-3/4 in. flange on top of the chamber. Using the shutter the continuous flow from the supersonic beam was manually interrupted and the effects of background and direct gas flow were measured with the quadrupole mass spectrometer (QMS). Using this method the intensity of the directed flow was measured to be more than 100 times greater than the effusive portion. Between the chambers in the beam line were a set of collimating apertures used to define and maintain differential pumping. Two circular apertures were used; one 4 mm in diameter and the other 6 mm. The former was located in the first stage of pumping and the latter in the second stage. The 4 mm aperture was $\sim 56$ cm from the crystal while the 6 mm aperture was $\sim 30$ cm away from the crystal.

The chopper to sample distance was measured to be 78 cm. This was compared with the value calculated from the TOF analysis to calibrate the timing circuit for the slotted chopper. The terminal velocity, $V_\infty$, of a monatomic gas in a supersonic expansion is given by the equation

$$V_\infty = \left(\frac{5RT}{MW}\right)^{1/2},$$

where $R$ is the ideal gas law constant, $T$ is the nozzle temperature, and $MW$ is the molecular weight. The velocity predicted by Eq. (1) was used to calculate the flight distance from the measured time-of-flight spectrum for He and Ar beams as a function of temperature. Using this procedure, the calculated distance agreed with a physical measurement of the length to within 2%. Therefore, we concluded that any error in the photodiode trigger pulse or timing electronics was negligible and the thermocouple provided an accurate measurement of the nozzle temperature. In addition, the measured time-of-flight spectrum has a contribution due to the Ar ion flight time from the ionization region to the QMS electron multiplier. This time must be subtracted from the measured TOF distribution since the kinetic energies of the neutral species were (~1–3 eV) comparable to the energy with which the ions were extracted ($E_{\text{ion}} \sim 20$ eV). The following iterative procedure was used to determine the TOF for the neutral Ar atoms. The ion flight time, $t_{\text{ion}}$, was computed without regard of the initial energy of the neutral atoms from the following relationship:

$$t_{\text{ion}} = \frac{l}{(2E_{\text{ion}} \text{MW}_{\text{ion}})^{1/2}},$$

where $l$ is the distance from the QMS ionizer to electron multiplier and $\text{MW}_{\text{ion}}$ is the ion molecular weight. This time was subtracted from the TOF spectrum and the energy of the neutral beam was determined. Next the ion flight time was recalculated to include the energy of the neutral species. This procedure was repeated until the calculated neutral energy converged to a constant value.

B. Time-of-flight analysis of atomic beam

For the time-of-flight measurements the QMS was operated in an analog mode. The low level current pulses from the QMS electron multiplier were first amplified (Pacific Instruments, 150 MHz bandwidth, gain of 100). The amplified pulses were filtered at 100 kHz and finally digitized by a 150 MHz oscilloscope (LeCroy, 9410). The oscilloscope collected the individual TOF waveforms and simultaneously averaged up to 10 000 chopped beams to produce the TOF distribution. The final digitized waveform was sent to a computer for storage and data analysis. The TOF distribution was converted to a flux weighted velocity distribution using the appropriate Jacobian transformation from time to velocity space. It has been previously shown that such a velocity distribution can be modeled by the equation

$$f(v) \sim v^3 \exp\left[-(v-v_0)^2\alpha^2\right],$$

where $v_0$ is the stream velocity and $\alpha$ is the width parameter. The width parameter is related to the parallel temperature of the beam by the equation below

$$\alpha^2 = \frac{2RT_{\text{parallel}}}{m}.$$

To obtain the flux-weighted velocity distribution a TOF spectrum was fit to Eq. (3) by a nonlinear least squares algorithm. The algorithm was based on a three parameter fit. The program began with an initial estimate for $v_0$, $\alpha$, and peak height and compared the numerically calculated velocity distribution to the experimentally measured distributions. The three parameters were then varied to minimize the sum of the squares of the deviations between the calculated and observed velocity distributions. A typical Ar TOF spectra is shown in Fig. 2. The total backing pressure behind the nozzle was 20 psi with 1% Ar seeded in He and the nozzle at 1000 K. It has been corrected for Ar ion flight time from the ionization region to the QMS electron multiplier. Figure 3 shows the corresponding velocity distribution and the best fit obtained from the analysis described above.

To determine the absolute Ar beam flux we calibrated the QMS ionization efficiency over various background pressures of Ar. Since the QMS is a density sensitive detector (i.e., inversely proportional to velocity) the Ar flux was determined from the QMS signal and measured velocity. Typically the flux was measured to be $\sim 1 \times 10^{15}$ Ar cm$^{-2}$ s$^{-1}$. All of the gases used in generation of the hyperthermal beam were research grade purity (i.e., $\geq 99.995\%$). Using the QMS we measured no detectable N$_2$, O$_2$, H$_2$O, and CO$_2$ in the beam relative to the Ar signal.

C. UHV chamber

The UHV chamber has been specifically designed for these experiments and was fabricated commercially. The UHV chamber was evacuated by a 470 /s turbopump (Varian, V-450) and after bakeout at 150 °C for 24 h a base pressure of $1 \times 10^{-10}$ Torr was measured by a Bayard–Alpert nude-type ionization gauge (Granville Phillips, series 274). This chamber utilized an ion gun (Perkin Elmer, model 04-191) for sputtering, quadrupole mass spectrometer (UTI,
model 100C) for residual gas analysis and TOF measurements, two variable leak valves (Varian, model 951-5106) for gas dosing, and an x-ray photoelectron spectrometer (Fisons, Clam2) for surface analysis.

In the UHV chamber a Pt\{111\} single crystal\(^{20}\) oriented to within 0.5° of the (111) plane was mounted on a precision X, Y, Z, Θ manipulator (Thermionics, Series EM200). The crystal mounting stage of the manipulator consisted of a molybdenum plate to which the crystal was fixed by spotwelding with a few small Ta tabs. A tungsten filament was used to perform electron beam heating of the sample. With the filament biased at \(-800\) VDC and passing 1 mA of current about 60 mA of emission current was generated which was capable of heating the crystal to \(\sim 1300\) K in approximately 30 s. The sample temperature was measured by a Chromel–Alumel thermocouple wire located between the side of the crystal and one of the Ta tabs. The crystal was cooled by flowing liquid nitrogen through the hollowed body of the manipulator head. Using this method the crystal can be cooled to 100 K in less than 10 min after flashing to 1300 K.

The Pt\{111\} crystal was initially cleaned by cycles of 2 keV Ar\(^\text{+}\) sputtering, oxidation at 800 K with \(1\times10^{-7}\) Torr O\(_2\) and annealing at 1100 K. After several weeks of this procedure the crystal was determined to be clean when the impurities (especially C and O) were below the detection limit of x-ray photoelectron spectrometer (<1% ML). On a more regular basis the crystal was cleaned by sputtering for 10–15 min with a 500–1000 eV Ar\(^\text{+}\) beam followed by annealing for 2 min at 1300 K. Once the crystal was free of bulk impurities we no longer used oxygen in the cleaning procedure. Since ammonia is readily oxidized on platinum\(^\text{30}\) great care was taken to maintain an oxygen free UHV chamber.

III. EXPERIMENTAL RESULTS

A. Characterization of molecular and fragment species of ammonia on Pt\{111\} by XPS

X-ray photoelectron spectroscopy was used to measure the N(1s) intensity as a function of NH\(_3\) exposure with the Pt crystal maintained at 110 K. Most of the XP spectra reported here were taken with Mg \(K_\alpha\) radiation (1253.6 eV) operating at 280 W and the analyzer set at a constant pass energy of 20 eV. Acquisition of each spectra usually took 30 mins. The individual peaks in an XP spectra were fit to a Gaussian peak with a fixed full-width at half-maximum (FWHM) of 1.8 eV after subtracting the spectra of the clean background and the inelastic tail due to scattered photoelectrons. Figure 4 shows a plot of the integrated N(1s) intensity vs exposure in Langmuirs (where 1 L = \(10^{-6}\) Torr s). The insert shows an expanded view of the low exposure limit. The N(1s) binding energy decreased from 400.4 to 400.0 eV and the FWHM of the peak increased from 1.7 to 2.2 eV as the surface coverage was increased from 0.1 to 1.0 ML. The shift in the binding energy and change in peak FWHM suggests the presence of two forms of ammonia on the surface. In fact, for exposures above 0.4 L, the envelope was a convolution of two N(1s) states. The low coverage peak was centered at 400.4 eV and the high coverage peak was centered at 399.8 eV. The result was broadened peak at 400.0 eV. A difference spectra illustrating the presence of the second feature at high coverage is shown in Fig. 5.

Ammonia is known to readily dissociate under the influence of electron beam bombardment,\(^{31}\) especially from the
filaments in the QMS ionizer and ionization gauge. To measure the extent of ammonia fragmentation a series of control experiments were conducted using the QMS ionization filament as an electron beam source. First a clean Pt\{111\} surface was saturated with ammonia at 110 K [see Fig. 6(a)] and the N(1s) XP spectra was recorded. The crystal was moved directly in line-of-sight of the QMS ionizer and irradiated with an excess of 70 eV electrons escaping from the ionization region. Figures 6(b) and 6(c) show the XP spectra taken after 20 and 40 min of electron irradiation, respectively. After the first 20 min most of the initial ammonia desorbed while a smaller fraction dissociated to a fragment at 399.0 eV. Based on previous ESDIAD experiments,\textsuperscript{21} it is likely that the incident electrons cause N–H bond rupture to form the NH\textsubscript{2} species. An additional 20 min of electron bombardment caused a further decrease of molecular NH\textsubscript{3} peak at 400.4 eV and a new N(1s) peak centered at 398.5 eV appeared. Presumably this species resulted from the dissociation of the 399.0 eV fragment. After recording the XP spectra in Fig. 6(c) the crystal temperature was briefly increased to 500 K and cooled back to 110 K. The XP spectra was taken again and no nitrogen containing species were observed. This suggests that one or two events occurred as the surface temperature was increased; (i) the NH\textsubscript{x} species dehydrogenated to form atomic nitrogen and hydrogen which recombinatively desorb as N\textsubscript{2} and H\textsubscript{2} and/or (ii) the NH\textsubscript{x} fragments hydrogenated during heating to form NH\textsubscript{3} which subsequently desorbed.

**B. Collision-induced desorption experimental procedure**

The collision-induced desorption experiments were performed with the crystal maintained at 110 K. For these experiments, the crystal was dosed to prepare 0.25 ML of ammonia and a N(1s) XP spectra was taken. While the XP spectra were recorded, the temperature of the nozzle was increased to the desired value and the gas mixture (~1\% Ar
in He or \( \text{H}_2 \) was passed through the heated Mo tube to achieve thermal equilibrium before passage through the nozzle. The atomic beam was prevented from entering the UHV chamber by closing a gate valve between the UHV chamber and the second stage of differential pumping. Once the XP spectrum in the \( N(1s) \) region was recorded the crystal was removed from the beam path, the Ar beam was admitted to the UHV chamber and a TOF spectrum was acquired. XPS analysis indicated that no change in the integrity of the ammonia surface layer occurred during the TOF measurement. After this procedure the Pt crystal was set to the desired incident angle and the hyperthermal Ar atoms were allowed to bombard the \( \text{NH}_3 \) covered Pt\([111]\) surface for a given period of time (usually 300–600 s). Subsequently the crystal was positioned back toward the x-ray photoelectron spectrometer. The \( N(1s) \) region was reinvestigated by XPS and a scan of the \( O(1s) \) and \( C(1s) \) was performed to check for the presence of any impurities. No evidence was found for any surface species containing a \( C(1s) \) signature. The \( O(1s) \) XP spectra typically revealed \( \sim 1\% \) of a monolayer of water. Note that this quantity of water was also observed when a clean Pt surface was exposed to the effusive gas load from the molecular beam source and had no discernible effect on the CID results.

C. Results of collision-induced desorption

Using the experimental procedure outlined above the energy of the Ar beam was continually increased until post-collision-induced desorption surface analysis with XPS indicated that the 400.4 eV \( N(1s) \) peak decreased. The XPS measurements from a typical experiment is shown in Figs. 7(a) and 7(b). The spectrum shown in Fig. 7(a) corresponds to 0.25 ML ammonia. This saturates the available threefold hollow sites with \( \sim 2.5 \times 10^{13} \text{ \text{NH}_3 \text{ cm}^{-2}} \) (relative to \( 1.5 \times 10^{13} \text{ Pt cm}^{-2} \)). The spectrum shown in Fig. 7(b) was the result of directing \( \sim 6 \times 10^{17} \) Ar atoms at the surface in Fig. 7(a) with a kinetic energy of 2 eV. Clearly the intensity of the peak centered at 400.4 eV decreased and a second feature appeared at 399.0 eV. This was very strong evidence both ammonia desorption and dissociation occurred upon impact of the Ar beam. A number of control experiments were performed to ensure that the carrier gas (\( \text{H}_2 \) or He) or possible impurities had no effect in the CID experiment. Indeed, XPS analysis indicated that neither desorption or dissociation occurred in the null experiments.

To verify the presence of collision-induced desorption the quadrupole mass spectrometer was used to monitor the gas phase evolution of ammonia upon Ar atom impact. These experiments were performed by preparing a 0.25 ML ammonia overlayer and analyzing the partial pressure rise in the UHV chamber as the Ar beam bombarded the surface. Figure 8 shows that as the Ar beam bombarded the surface the ammonia partial pressure increased and returned to the background level when the Ar beam was blocked. The limited signal to noise ratio was a result of collision-induced desorption just above threshold kinetic energy required to induce desorption. The QMS signal in Fig. 8 was corrected for the electron stimulated desorption of \( \text{NH}_3 \) from the crystal by stray electrons escaping from the ionizer of the quadrupole mass spectrometer by a background subtraction method. The stray electrons also induce fragmentation of \( \text{NH}_3 \), hence the
This species was assigned as NH$_2$. It is important to note that above revealed the growth of an N(1$s$) desorption signal. For instance, the species was not due to water desorption from the sample or chamber walls which would result in the detection of the daughter ion at 17 amu from desorption from the sample or chamber walls which would result in the detection of the daughter ion at 17 amu as a monolayer of ammonia was bombarded with 2.4 eV Ar beam at at 30° and 45°. The result from a low coverage experiment is also shown for comparison in (c).

A second set of control experiments were designed to determine the outcome of a collision between the Ar and the NH$_2$ species. The electron irradiation method was used to prepare the NH$_2$ fragment. The XPS measurement of the product of this experiment is shown in Fig. 9(a). The XP spectrum clearly shows the NH$_2$ species at 399.0 eV with a small amount of intact NH$_3$ left on the surface (as indicated by the shoulder at 400.4 eV). The computer generated fit to the data is shown as a solid line. To this mixed overlayer of ammonia and NH$_2$ a 2.5 eV Ar beam was generated and allowed to bombard the surface for 600 s ($\sim 6 \times 10^{17}$ Ar cm$^{-2}$) at 45°. The XP spectra was recorded immediately after this experiment and is shown in Fig. 9(b) with the same computer fit used in Fig. 9(a). A further fraction of the molecular ammonia has desorbed and the intensity of the 399.0 eV peak has slightly increased. This experiment suggests that over the range of Ar energies employed in the collision-induced desorption experiments (1–3 eV) NH$_2$ does not desorb from the surface or dissociate to NH.

A few collision-induced desorption experiments were also conducted at higher initial ammonia coverages. Figure 10 shows the quadrupole mass spectrometer signal at mass 17 amu as a monolayer of ammonia was bombarded with 2.4 eV Ar atoms at $\theta = 30°$ [Fig. 10(a)] and $\theta = 45°$ [Fig. 10(b)]. A comparison of the collision-induced desorption result at 0.25 ML (Fig. 8) is shown in Fig. 10(c) for comparison. Note that the relative increase in the signal intensity for the two angles at high coverage has been corrected for the total number of Ar atoms striking the surface. Also, x-ray photoelectron spectra taken after Ar bombardment at both 399.0 eV peak is NH$_2$ and not a surface nitride species since the latter species has been shown to desorb near $\sim 950$ K.$^{19}$

A few isotopic exchange experiments with ammonia (by pre- or postdosing the Pt[111] surface with deuterium) indicated only a slight amount of H/D scrambling in TPD.$^{18}$ No deleterious results were expected at 110 K when hydrogen was used as the carrier gas. When the surface containing the two forms of ammonia shown in Fig. 7(b) was warmed from 110 K to 500 K (i.e., above the desorption temperature for molecular NH$_3$), and immediately cooled to 110 K, the XPS measurements revealed no N(1$s$) species remaining on the surface. This further suggests that the assignment of the 400.4 eV peak and small increase in the 399.0 eV feature. The solid line is the identical fit to the spectra in (a) to illustrate the loss of intensity in the 400.4 eV peak and small increase in the 399.0 eV feature. Both data sets are normalized to the same scale to make an absolute comparison of the peak areas.
polar angles indicated the appearance of the 399.0 eV and 398.5 eV fragment peaks. Due to the second dissociation channel and the likelihood of desorption of multiple adsorbates at these high collision energies no intensive study was performed at high surface coverages.

IV. DISCUSSION

A. Definition of absolute cross sections for collision-induced desorption

One of the central points of this paper is the determination of the probability for collision-induced desorption as a function of collision energy. A measure of the probability of a chemical or physical event occurring is expressed in terms of a cross section. By analogy to the gas phase reaction cross-sections the following expression for the collision-induced desorption rate is given:

\[ -d(\Theta_{\text{NH}_3}) dt = \sigma_{\text{CID}}(\Theta_{\text{NH}_3}^t, E_i, \theta_i) F_{\text{Ar}}(\Theta_{\text{NH}_3}^t), \]  

(5)

where \( \sigma_{\text{CID}} \) is the absolute desorption cross section, \( \theta_i \) is the incident angle of the Ar beam, \( F_{\text{Ar}} \) is the absolute flux of the Ar beam measured along the surface normal, \( E_i \) is the average energy of the Ar beam, and \( \Theta_{\text{NH}_3} \) is the ammonia surface coverage. Rearranging Eq. (5) and integrating from time \( t=0 \) to \( t=t \) we arrive at the equation for the collision-induced desorption cross section,

\[ \sigma_{\text{CID}}(E_i, \theta_i) = \frac{\ln \left( \frac{\Theta_{\text{NH}_3}^{t=0}}{\Theta_{\text{NH}_3}^t} \right)}{F_{\text{Ar}} \cos(\theta_i)}, \]  

(6)

where the \( \cos(\theta_i) \) term is included to convert the incident flux to the number of incident Ar atoms per unit surface area (thus \( \sigma_{\text{CID}} \) has the dimensions of surface area). Note that in addition to collision-induced desorption the XPS results indicated that collision-induced dissociation\(^{40}\) was a competing reaction channel. Thus a second rate equation must be included to correctly calculate \( \sigma_{\text{CID}} \) under such conditions. The relevant equations which describe both product channels are

\[ \text{Ar}(E_i) + \text{NH}_3(\text{ads}) \rightarrow \text{NH}_3(\text{gas}) + \text{Ar}(E_f), \]  

(7)

\[ \text{Ar}(E_i) + \text{NH}_3(\text{ads}) \rightarrow \text{H}_2(\text{ads}) + \text{NH}_2(\text{ads}) + \text{Ar}(E_f), \]  

(8)

assuming first order kinetics for both events. After solving the coupled equations for \( \sigma_{\text{CID}} \) the corrected expression becomes

\[ \sigma_{\text{CID}}(E_i, \theta_i) = \frac{\ln \left( 1 - \frac{\Theta_{\text{NH}_3}^{\text{des}}}{\Theta_{\text{NH}_3}^t} \right)}{\frac{\Theta_{\text{NH}_3}^t}{\Theta_{\text{NH}_3}^{\text{des}}}} \frac{F_{\text{Ar}} \cos(\theta_i)}{1 + \frac{\Theta_{\text{NH}_3}^t}{\Theta_{\text{NH}_3}^{\text{des}}}}, \]  

(9)

where \( \Theta_{\text{NH}_3}^{\text{des}} \) is the amount of ammonia desorbed from the surface and \( \Theta_{\text{NH}_3}^t \) is the amount of NH\(_3\) formed on the surface at time \( t \). All of the quantities in Eq. (9) can be experimentally measured allowing \( \sigma_{\text{CID}} \) to be calculated. The results for \( \sigma_{\text{CID}} \) as a function incident Ar energy and angle are plotted in Fig. 11. The desorption cross sections increase rapidly as the Ar energy was increased above the threshold energy for each angle of incidence. Note that Fig. 11 provides a direct measurement of the desorption threshold.

B. Determination of the threshold desorption energy

In this experiment sufficient translational energy must be transferred from the incident Ar atom to dissociate the NH\(_3\)/Pt[111] bond. A similar type of bond dissociation experiment has been conducted in the gas phase. Armentrout and co-workers have systematically studied the collision-induced dissociation of transition metal ion clusters by neutral noble gas atoms.\(^{35}\) By accelerating a size selected, monoenergetic cluster into a thermalized bath of neutral, noble gas atoms enough energy can be transferred in a collision to cause dissociation of a metal–metal bond in the cluster. In this process, the collision is impulsive and the cluster decomposes in a RRKM fashion.\(^{36}\) From measurement of the dissociation threshold of a given cluster a particular metal–metal bond dissociation energy can be calculated. To accurately determine the dissociation threshold the following equation\(^{37}\) was used:

\[ \sigma_{\text{CID}}(E) = S \left( \frac{E - E_{\text{thrs}}}{N} \right)^N, \]  

(10)

where \( S \) and \( N \) are fitting parameters, \( E \) is the relative kinetic energy in the center-of-mass reference frame, and \( E_{\text{thrs}} \) is the threshold energy. The general form of Eq. (10) has been derived from statistical theories\(^{38–42}\) for the simplest example of gas-phase collision-induced dissociation, \( A + BC \rightarrow A + B + C \). For the case when \( A, B, \) and \( C \) are neutral species, Levine and Bernstein\(^{43}\) have used an optical model to generate a parameterized form of Eq. (10) in which the value of \( N \) equals 2.5. Maier\(^{44}\) derived a form of Eq. (10) with \( N = 1–2 \) for collision-induced dissociation of ions. Parks, Wagner, and Wexler\(^{45}\) have experimentally measured \( N \) to range from 1.4 to 2.3 for collision-induced dissociation of TIX (where X=Cl, Br, and I) into TI\(^{+}\) and X\(^{-}\) ions from collisions with Kr and Xe atoms. Finally, note the line-of-centers collision model\(^{46}\) explicitly determines \( N \) to equal 1.

In each of the examples cited above it is assumed that only translational energy was available to activate the endothermic reaction. Consider the following interpretation of Eq. (10) proposed by Park, Wagner, and Wexler\(^{45}\) to describe gas phase collision-induced dissociation. For two colliding particles in the gas phase the relative energy, \( E_{\text{rel}} \), can be written as

\[ E_{\text{rel}} = E_{\text{rad}} + \left( \frac{L^2}{2\mu r^2} \right) + V(r), \]  

(11)

where \( E_{\text{rad}} \) is the radial kinetic energy, \( L \) is the angular momentum, \( \mu \) is the reduced mass, and \( V(r) \) is the interaction potential. By definition \( E_{\text{rel}} \) is zero at threshold (assuming the reaction is barrierless). Since \( V(r) \) decreases more rapidly than \( 1/r^2 \) (as is the case of neutral–neutral interactions) then
fit to the data using the method outlined by Rebick and
deviation of the two data sets reached a minimum. Using this

\[ 1.95 \]

The average value of the true threshold was calculated to be
desorption of ammonia

C. Model used to describe the collision-induced
Figure 11 is independent of the Ar incident angle. This indi-
cates a common collision mechanism at each angle of inci-
dence. Based on intuitive arguments this behavior is quite
reasonable. Ammonia chemisorbs to Pt(111) by donating
electrons from the lone pair on the nitrogen atom to the
surface adsorption site (i.e., threefold hollow). This results in
a highly corrugated potential between the adsorbate and sur-
face. Such corrugation will convert parallel kinetic energy
into normal energy and total energy scaling is expected. Con-
versely, for a closed shell molecule physisorbed to a surface
the interaction potential is dominated by van der Waals type
forces with no lateral corrugation. Since no mechanism ex-
ists to convert parallel energy into normal energy, normal
ergy scaling is expected. This view is supported by the
normal energy scaling observed for the threshold energy of
CH$_4$ collision-induced desorption from Ni(111).\(^5\)

The first step in the collision-induced desorption event is
a bimolecular collision between the argon atom and ammo-
nia molecule. The interaction time, \( t \), of the collision can be
estimated from the equation \( v = d/t \). For an Ar atom travel-
ning with the typical velocity, \( v \), used in these experiments
(3000–4000 m/s) and an estimated interaction distance,
\( d = 1 \text{ Å} \), the calculated interaction time is \( \sim 30 \text{ fs} \). This is on
the same time scale of vibrational motion and suggests that
an impulsive collision model can describe the scattering
physics because insufficient time is present to transfer energy
to the internal modes. As a result, ammonia will be treated as
a hard sphere. Furthermore, the attractive potential between
ammonia and Ar will be neglected since the collision ener-
gies (>1 eV) were much greater than the Ar–NH$_3$ well depth
of 167 meV. From energy and momentum conservation in a
head-on collision the amount of energy transferred from Ar
to ammonia is given by the equation

\[ E_{\text{NH}_3}^i = E_{\text{Ar}}^i \left( \frac{4m_{\text{NH}_3}m_{\text{Ar}}}{m_{\text{Ar}} + m_{\text{NH}_3}} \right)^{1/2}, \]

where \( E_{\text{Ar}}^i \) is the incident kinetic energy of the Ar atom, \( m_{\text{Ar}} \)
is the mass of the Ar atom and \( m_{\text{NH}_3} \) is the mass of ammonia.
As a result, an incident Ar atom can deliver no more than
84% of its translational energy to an ammonia adsorbate.

Once the ammonia adsorbate has received this quantity of
kinetic energy, \( E_{\text{NH}_3}^i \), it will move closer the surface plane
until it reaches some critical distance along the potential
energy surface. At some critical distance the ammonia encoun-
ters the repulsive wall of the potential and reflects from the
surface (assuming a second collision with Ar does not oc-
cur). This process essentially mimics the repulsive portion of
the scattering physics of a gas phase ammonia molecule with
a clean surface. To determine how much energy the ammonia
loses to the surface in this collision a hard cube model\(^48\) is
used. In this model the Pt atoms in the collision region are
treated as an effective mass to account for the collective
effects present at a given scattering energy (see below). The
energy retained by the ammonia molecule, \( E_{\text{NH}_3}^f \), after col-
liding with the surface is given by the equation

\[ E_{\text{NH}_3}^f = E_{\text{NH}_3}^i \left( 1 - \frac{4m_{\text{NH}_3}m_{\text{eff}}}{m_{\text{NH}_3} + m_{\text{eff}}} \right)^{1/2}, \]

where \( m_{\text{eff}} \) is the effective surface mass. The effective mass is
an approximation to account for the collective interaction of
Pt atoms during the collision event.

\[ L \]
The third step in this mechanism determines whether the NH$_3$/Pt(111) bond is broken. If the NH$_3$ scatters from the Pt surface with enough energy directed away from the surface, $E_{\text{NH}_3}^{\text{eff}}$, then it can escape the exit barrier of the one-dimensional square well. The NH$_3$ will travel into the gas phase with a final kinetic energy determined by the equation

$$E_{\text{NH}_3}^{\text{gas}} = E_{\text{NH}_3}^{\text{eff}} - E_b,$$

where $E_b$ is the surface–adsorbate binding energy. Note, if the NH$_3$ has the same amount of kinetic energy as the well depth of the potential energy surface then the desorbed leaves the surface with essentially zero kinetic energy. This fact illustrates the threshold nature of the collision-induced desorption since the NH$_3$ cannot desorb if $E_{\text{NH}_3}^{\text{eff}}$ is less than $E_b$. By combining Eqs. (12), (13), and (14) the following equation accounts for the various energy transfer events and can be used to calculate the surface–adsorbate binding energy, $E_b$, from the threshold for desorption:

$$E_b = E_{\text{thres}}\left(\frac{4m_{\text{NH}_3}m_{\text{Ar}}}{(m_{\text{NH}_3} + m_{\text{Ar}})^2}\right)\left(1 - \frac{4m_{\text{NH}_3}m_{\text{eff}}}{(m_{\text{NH}_3} + m_{\text{eff}})^2}\right).$$

(15)

Substituting the values of $m_{\text{NH}_3} = 17$ amu, $m_{\text{Ar}} = 40$ amu, $m_{\text{eff}} = 1 \times 195$ amu and $E_{\text{thres}} = 1.95 \pm 0.17$ eV into Eq. (15) the upper limit to the NH$_3$/Pt(111) binding energy is calculated to be $1.1 \pm 0.1$ eV. Note, this value represents an upper limit of the bond dissociation energy for three reasons: (1) the model assumes zero impact parameter collisions to induce desorption at the threshold; (2) the model neglects the internal degrees of freedom in the molecule (see Sec. IV D); and (3) the model neglects any attractive interaction between the incident Ar and NH$_3$. Using an effective mass of 3 Pt atoms, an upper limit to the binding energy of $1.45 \pm 0.13$ eV is calculated.

The only adjustable parameter in Eq. (15) is the effective mass of the Pt atom in the collision region. Our estimate for the effective mass of 1 Pt atom at the 1.95 eV threshold is based on an empirical model that is based on the speed of sound in the Pt lattice and the velocity and the size of the incident particle. In essence we propose that the effective sound in the Pt lattice and the velocity and the size of the based on an empirical model that is based on the speed of sound. The only adjustable parameter in Eq. (15) is the effective mass of the Pt atom at the threshold for CID. From the previous Ar/Pt scattering experiments we calculate an effective mass of 1 Pt atom at similar incident velocities. Note that in our previous communication we estimated the effective mass of the Pt surface to be 3 Pt atoms using a model wherein the total energy of the collision system was used for calibration with Ar scattering experiments.

Even though the effective mass may vary over the range of energies used in this experiment, the determination of $E_b$ is rather insensitive to this choice. For instance, as $m_{\text{eff}}$ increases from 1 to 5 Pt atoms $E_b$ increases by less than 25%. A plot of the calculated binding energy from Eq. (15) vs the selection of $m_{\text{eff}}$ is shown in Fig. 12. Note the large mass of the Pt atoms causes $E_b$ to reach a limiting value of $\sim 1.55$ eV.

Experimental studies gas–surface scattering have calculated the effective surface mass within the hard cube model and given the crudeness of a hard cube model many experimental results can be reproduced reasonably well. The effective surface mass depends strongly on the incident energy of the particle. At very low energies (less than $\sim 0.1$ eV) the turning point of a given trajectory is far from the surface and the incident particle will interact with several surface atoms. When the incident energy nearly $\sim 1$ eV the particle will penetrate closer to the surface and interact with fewer atoms. As the energy is increased the particle will eventually collide with a single surface atom. This trend has been experimentally verified in several studies. In the case of 0.03–1.7 eV Ar atoms scattering from a Pt(111) single crystal Hurst, Wharton, Janda, and Auerbach calculated an effective surface mass of 1.7 and 2.5 Pt atoms with and without including an attractive well, respectively. Winters, Coufal, Rettner, and Bethune also fit their Ar/Pt(111) scattering data with a hard cube model to determine a Pt effective mass of $\sim 5$ atoms for Ar atoms below 1 eV of kinetic energy and an effective mass of 1.5 Pt atoms when the Ar energy was increased to 7 eV. More recently classical trajectory calculations have been used to compute the final translational energy for 0.1–30 eV Ar atoms inelastically scattering from a Pt(111) surface. For 1–10 eV Ar atoms these calculations determined the ratio of the final energy to initial Ar kinetic energy to be 0.5–0.6.

Other calculations have shown that this type of cooperative response in the surface region is quite reasonable. At low initial velocities (i.e., 300 m/s) a typical gas–surface collision time is about 300 fs and will generate an impulse in the crystal that will propagate at the speed of sound and travel about 10 Å (i.e., ~3 lattice spacings). At higher collision energies, or alternatively shorter interaction times, the motion of the surface atoms becomes less collective and more independent. Thus, the effective mass can be viewed as a measure of the impulsiveness of the collision. The change in the effective surface mass with increasing kinetic energy
of the incident particle closely parallels the transition from thermal to structure gas–surface scattering. For incident energies above a few eV, the distance of closest approach for an incident particle decreases and the interactions are stronger with fewer surface atoms. That is, the incident particle reacts to the corrugation of the potential energy surface (PES) and exchanges both parallel and normal components of energy. The few gas–surface experiments conducted at high incident energy clearly illustrate the deviation from normal energy scaling predicted by hard cube models.

D. Collision dynamics

Central to this investigation is an understanding of the energy transfer steps and molecular dynamics underlying the collision-induced processes. Based on the experimental data in this work and previous theoretical calculations, collision-induced desorption can be modeled by classical molecular dynamics. This is reasonable since the energies used in this experiment (i.e., 1–3 eV) should not involve any electronic transitions in ammonia or the Pt lattice. Moreover, internal excitation of the adsorbate should be minimal. In contrast, above the threshold for desorption, energy may partition into rotational, vibrational, translational, and electronic degrees of freedom in the desorbate. The hypothesis of this paper is that ammonia has just enough kinetic energy to escape the attractive force to the Pt surface at the threshold for collision-induced desorption.

The angular dependence of cross sections in the post-threshold region of Fig. 11 provides some insight into the collision dynamics at the threshold. Notice that at 0° a slightly higher threshold was measured compared to the other angles and the cross sections increase less rapidly above the threshold. This is probably due to a multiple collision sequence enhanced by the adsorbate binding in a three-fold hollow. Zeiri, Low, and Goddard have shown that multiple collisions “quench” the desorption of Xe atoms from a Si cluster. This quenching occurs because the distance for ammonia recoil from the surface is small [i.e., ~2.1 Å (Ref. 24)]. As a result, the ammonia may collide with the noble gas atom a second time as it tries to scatter away from the surface. In addition, note that at 60° the cross sections just above the threshold parallel the behavior observed at 0°. At this angle of incidence large impact parameters may be blocked (i.e., “shadowed”) by neighboring adsorbates since the separation between adjacent molecules is ~5 Å at 0.25 ML. However, for intermediate angles of incidence (30°–45°) a noble gas atom can approach the adsorbate with a trajectory which favors a single encounter. Thus, quenching is less likely to occur at these angles and a large range of impact parameters are available for the collision. The result is a more pronounced increase of the cross sections in the post threshold region for 30° and 45°. These intuitive arguments can only qualitatively describe the collision processes above threshold. The collision dynamics above threshold may be very complex, and as a result, further experimental measurements (i.e., velocity, angular, and internal state distributions of the desorbate) and molecular dynamics simulations are required to fully understand the microscopic details of the molecular collision dynamics.

Experiments focusing on the role of translational energy in elementary gas–surface interactions shed some insight on the total energy scaling observed in this work. For example, several investigations report a “normal energy” scaling law for the initial dissociative sticking probability of CH₄ on Pt(111), CH₃ on Ni(111), and CO₂ on Ni(100). Also, the trapping probability of methane, ethane, propane, and Xe on Pt(111) exhibit normal energy scaling. Such observations were associated with weakly interacting systems and suggest very little (if any) energy exchange parallel to the surface, which is no lateral corruga-

tion in the interaction potential. However, if strong chemical forces exist between the adsorbate and surface then the interaction potential should reflect a strong lateral corrugation. Total energy scaling has been observed in scattering experiments involving chemisorption systems such as CO and NO on Pt(111), CO on Ni(111), and N₂ on W(110). Thus, the total energy scaling of the threshold energy for NH₃ collision-induced desorption from Pt(111) implies that parallel and perpendicular components of energy in ammonia are strongly coupled. For example, a mechanism based on normal energy scaling is unreasonable for collision induced desorption of a chemisorbed molecule because an Ar atom incident at 60° has 25% of the normal energy as compared to an Ar atom at 0°, yet both angles of incidence have the same probability of desorbing NH₃ from the surface. A plausible explanation for total energy scaling at threshold is maximum energy transfer between noble gas atom and adsorbate (i.e., head-on collisions) followed by rapid exchange of parallel to perpendicular energy. This conversion of parallel energy, or momentum, is a consequence of the highly corrugated adsorbate–surface interaction potential. The assumption that zero impact parameters, or head-on collisions, facilitate desorption at the threshold is supported by calculations done by Zeiri. The calculations modeled the desorption of N₂ desorption from W(100). At 0° and 45° the simulations clearly indicate the desorption probability was highest for small impact parameters and declined rapidly as the collision becomes more glancing. Thus, the assumption of head-on collisions in the derivation of Eq. (12) is reasonable.

One outstanding question is whether internal energy excitation occurs at the desorption threshold. To address this possibility simulations of collision-induced desorption of N₂ from W(100) have been performed. In this study several quantities were computed, including the average translational energy of the scattered Ar and N₂, the average scattering angle of Ar and N₂, the N₂ internal energy content, and desorption probability as a function of Ar incident angle and energy. In general, the results were sensitive to the initial conditions of the simulation. The results indicated N₂ rotational excitation, <170 meV, but very little vibrational, <12 meV, excitation after a collision with a 5 eV Ar atom. Note that this energy is well above the 1 eV desorption threshold. At this energy, the average rotational energy in the N₂ molecule decreased from ~170 to ~32 meV as the angle of incidence increased from 0° to 60°. However, near threshold the total vibrational and rotational energy in the desorbing N₂ molecule was less than 20 meV. The fact that the total internal energy in a desorbing N₂ molecule was small at threshold...
dissociation is considerably lower than the threshold for de-
energy transfer model. This suggests that the threshold for
dissociation remains constant as a function of incident energy for a
specifically collision-induced dissociation, is indicated in
Fig. 7. The probability for collision-induced dissociation as a
function of Ar kinetic energy and angle as measured from the surface
normal. Legend key, squares (0°), filled diamonds (30°), unfilled triangle
45°, and filled circles (60°). Note that the lines are drawn as a guide to the
eye.

suggests our NH₃ hard sphere approximation is not severe. The
small degree of internal excitation approximation suggests that kinetic
energy transfer from the noble gas atom to the adsorbate
center-of-mass controls collision-induced desorption from the surface. The small amount of vibrational excitation in N₂
also confirms the well known observation in gas phase stud-
ies of translational to vibrational energy transfer. This
suggests the impulsive collision model outlined in Sec. IV C can
adequately describe the essential energy transfer steps of
collision-induced desorption.

While we do not anticipate considerable excitation of
desorbrates near the threshold for desorption, other surface
reaction channels must be accounted for in the near threshold
region. For instance, the presence of a second reaction chan-
el during the interaction of the Ar atom with the adsorbate,
specifically collision-induced dissociation, is indicated in
Fig. 7. The probability for collision-induced dissociation as a
function of incident energy and angle can be generated from the
same files used to generate the curves shown in Fig. 11.
The cross sections for collision-induced dissociation are
shown in Fig. 13. The trends observed in the collision-
induced dissociation plot are clearly different from the CID
plot. The first difference concerns the fact that the cross sec-
tions of translational to vibrational energy transfer.64 This sug-
gests our NH₃ hard sphere approximation is not severe.

E. Effect of surface coverage

So far this discussion has assumed the limit of isolated
adsorbates on the surface. However, adsorbate–adsorbate in-
teractions will alter the surface–adsorbate bond energy as
compared to the isolated molecule limit. In the case of ther-
al desorption, ammonia molecules experience strong repul-
sive forces while laterally diffusing on the surface before
desorbing.22 This is a consequence of the large permanent
dipole moment in ammonia. Also, the large dipole moment
induces an image charge in the metal. Thus, the total poten-
tial energy, ω, due to the “static” dipole–dipole and dipole–
image dipole interactions can be estimated from the simple
equation21

\[ \omega \approx 2 \pi \frac{\mu^2}{r^3}, \]

where \( \mu \) is the permanent dipole moment and \( r \) is the dis-
tance separating the two permanent dipoles. Using the dipole
moment, \( \mu = 2 \), obtained from work function
measurements16 and the expected separation distance of 5.4 Å at
0.25 ML, the calculated interaction energy (averaged
over the six ammonia nearest neighbors) is 0.2 eV. This in-
teraction energy should result in a small effect in a collision-
induced desorption experiment because, unlike thermal de-
sorption, lateral diffusion is minimal in the ejection event.
Moreover, in a second set of experiments the initial NH₃
coverage was decreased to 0.13 ML and the threshold re-
mained 1.9 eV ± 0.2 eV for each angle. These findings indi-
cate that NH₃–NH₃ interactions do not affect measurement
of the NH₃–Pt bond strength in the collision-induced desor-
p tion experiment.

The coverage dependence of the thermal activation en-
ergy and pre-exponential factor for NH₃ desorption from
Re[0001] has been extensively studied by Rosenzweig and
Asscher.22 Temperature programmed desorption and optical
second harmonic generation were used to measure the ki-
etic parameters of adsorption and desorption under isother-
mal and isobaric equilibrium conditions. At coverages below
\( \Theta_{NH_3} = 0.4 \) ML and above \( \Theta_{NH_3} = 0.8 \) ML the activation
energy for desorption and pre-exponential factor were highly
coverage dependent, yet in the intermediate coverage regime
both parameters were independent of coverage. In order to
compare this behavior to the case of NH₃ chemisorption on
Pt[111] the monolayer state must be carefully defined be-
cause two different conventions have been employed. Rosen-
zweig and Asscher defined the monolayer state as the point

![FIG. 13. Absolute collision-induced dissociation cross section of α-NH₃ as
a function of Ar kinetic energy and angle as measured from the surface
normal. Legend key, squares (0°), filled diamonds (30°), unfilled triangle
45°, and filled circles (60°). Note that the lines are drawn as a guide to the
eye.](image-url)
just before formation of the second layer. In contrast, the coverages reported in this work use the definition used by Fisher. Where the monolayer is defined as just before onset of the multilayers (i.e., saturation of the \( \alpha \) and \( \beta \) states). After normalizing the two coverage regimes, it is expected that collision-induced desorption of \( \text{NH}_3 \) from \( \text{Pt}[111] \) at 0.25 ML should not dramatically effect the binding energy of the remaining adsorbates (assuming similar behavior on both metals). Note that no more than \(~\sim\)25% of the initial coverage was depleted in the collision-induced desorption experiment so the surface–adsorbate bond energy should not change by the end of the experiment.

At high initial ammonia coverages the model proposed in Sec. IV C will not adequately describe the collision dynamics. A comparison of the collision-induced desorption signal at 45° for 0.25 and 1.0 ML revealed that the desorption yield was only slightly higher at the higher coverage (see Fig. 10). Since the second layer of ammonia is more weakly bound than the layer directly in contact with the surface one might anticipate that the desorption yield per incident Ar atom would be greater. However, at high coverage, the network of hydrogen bonding between the ammonia molecules acts as an energy sink. When an Ar atom collides with an adsorbate in the overlayer, the adsorbate scatters into a first layer molecule(s) which will absorb considerably more energy than the case of scattering into a Pt atom. Thus, the collision sequence becomes more inelastic. Furthermore, it is possible with the proper impact parameter that a single Ar atom can desorb more than one ammonia from the second layer. As a result, it is not reasonable to assume first order desorption kinetics. This conclusion is supported by the results of collision-induced desorption of \( \text{CH}_4 \) from \( \text{Ni}[111] \). At high coverages, the methane desorption signal showed non-first-order kinetics. Also, the ejection of multiple adsorbates in collision-induced desorption was observed in a molecular dynamics simulation by Zeiri and Luchesse. When a beam of hyperthermal Xe atoms collided with a monolayer of Ar atoms physisorbed to \( \text{W}[100] \) more than one adsorbate could be ejected from the surface. This was a direct result of the large fraction of energy retained in the Xe after its first collision with the overlayer.

V. CONCLUSIONS

The minimum energy required to desorb a chemisorbed \( \text{NH}_3 \) molecule from a \( \text{Pt}[111] \) surface by a beam of neutral Ar atoms was measured to be 1.95 ± 0.17 eV. Using a classical energy transfer model the threshold energy for desorption is used to calculate the \( \text{NH}_3 /\text{Pt}[111] \) bond energy of 1.1 ± 0.1 eV for an effective mass of one Pt atom. The threshold scales with the total translational energy of the Ar atoms for incident angles between 0° and 60°. The total energy scaling for the threshold suggests a common ejection mechanism of the adsorbates from the surface. The cross sections above threshold display a complex angular dependence which requires further experimental measurements and molecular dynamics simulation to understand the microscopic details of the desorption event.

The results presented here extend the particle based desorption methods to an energy regime relatively unexplored. To our knowledge this is the first report of collision-induced desorption of a chemisorbed polyatomic molecule from a metal surface by a neutral, noble gas atom. In contrast to the traditional thermal methods of energy deposition in a solid system (i.e., bulk heating), the collision-induced process delivers energy to the near surface region of the system. This mode of energy deposition circumvents the possibility of surface reconstruction. Also, lattice sputtering is unlikely in the collision-induced desorption experiment since the beam energies are quite low (<3 eV).

ACKNOWLEDGMENTS

We are thankful for Argonne National Laboratory for electron beam welding the Mo disk in our supersonic beam source. We are grateful to Leo Wiseman (custom electronics) and Alex Dubrish (welding) for technical help during construction of our apparatus. Finally R.J.L. would like to acknowledge the National Science Foundation for financial support through a Young Investigator Award, CHE 9248193.

2 H. Hoinkes, Rev. Mod. Phys. 52, 933 (1980).
19 R. C. West, CRC Handbook of Chemistry and Physics, 72nd ed. (Chemical Rubber, Boca Raton, 1992).
26 The electron beam welding was done at Argonne National Laboratory.
28 Nor-Call Products Inc., Yreka, California.
29 The crystal was cut from a boule at the Cornell Materials Laboratory, oriented by Laue diffraction and polished by standard crystallographic techniques.