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The interaction of hyperthermal nitrogen with N-covered Ag(111)

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A mixed beam of hyperthermal N atoms and N₂ molecules was scattered from the N-covered Ag(111) surface held at 300 K. The angular distribution of scattered N atoms is very broad. In contrast, N₂ molecules exhibit a sharp angular distribution. Taking into account the relative mass ratio, N loses more energy at the surface than N₂. In terms of energy loss, the atoms approximately follow the binary collision model while the molecules do not. Instead, the energy curves of scattered N₂ are more comparable to the parallel momentum conservation model for near specular outgoing angles (40°–65°). For both atoms and molecules the angle-resolved intensity and final energy curves are very similar to those from the bare surface. However, the N-covered surface yields non-negligible N₂ intensity for a broad range of outgoing angles, including along the surface normal. This was not the case from the clean surface, where the measured intensity distribution was confined to the narrower angular range indicated above. Backscattering and direct abstraction reactions are evaluated as possible origins of this additional N₂ signal. Of these, an abstraction mechanism appears to be the most consistent with the measured data. © 2011 American Institute of Physics. [doi:10.1063/1.3615520]

INTRODUCTION

In general, due to the strength of the triple bond, N₂ is an inert molecule except when adsorbed at the most reactive of surfaces.¹ Hence, it is very unreactive toward the Ag(111) surface.^{2,3} However, when the molecular bond is broken the resulting N atoms interact strongly with a large range of surfaces including Ag. Hyperthermal N atom scattering from the bare Ag(111) surface has been studied recently.⁴ The scattered atoms have a very large angular spread containing both a broad distribution and a sharp specular peak. The results were interpreted in terms of probing different potential energy surfaces by the N atoms. The interaction was either attractive or primarily repulsive depending on the electronic state of the atom.

When an adsorbate is already present on a surface, the nature of the surface as seen by incident particles is changed. The extent to which the covered surface differs from the bare surface is dependent on the precise details of the adsorption location and the potential probed by the incident species. In addition to sticking and scattering, impinging reactive atoms also have the possibility of reacting with the adsorbate. Previously, a number of instances of reactions involving reactive gas with chemisorbed reagents on metal surfaces have been reported. In particular, H atom related reactions have been extensively studied.^{5–7} Two principal mechanisms are involved: the Eley-Rideal (ER) mechanism in which an adsorbate is abstracted from the surface in a direct collision

with an incident atom,⁸ and the hot atom (HA) mechanism in which incident atoms do not fully accommodate on the surface before they react with an adsorbate and the resulting product desorbs.⁹ These mechanisms are non-thermal processes, in contrast to the thermal reaction process—the so-called Langmuir-Hinshelwood mechanism—in which the reagents chemisorb and equilibrate at the surface prior to the reaction.¹⁰ Even in the absence of a reaction, desorption of adsorbates may occur if the incoming particle transfers sufficient energy to the adsorbate/lattice (i.e., collision induced processes)¹¹ or if it chemisorbs—the so-called dynamic displacement process.¹²

Recombinative desorption of N₂ from the N-covered Ag(111) surface has been studied.³ It was reported that the angular distribution of the desorbing N₂ had an extremely sharp peak along the surface normal, which could be fitted with a $\cos^7\theta_d$ function. Vibrationally and rotationally excited N₂ desorption was inferred from the absence of N₂ ($v = 0, 1, J$) states in state-resolved experiments. N adsorption on Ag(111) has been characterized by Wang *et al.* on the basis of density functional theory (DFT) calculations.¹³ Their calculations of the N adsorption energy as a function of adsorption site indicate that the fcc hollow site is the most stable point for adsorption and that the N atoms sit ~ 1.1 – 1.4 Å above the Ag atomic plane. Kokh *et al.* computed potential energy curves of ground and excited state N atoms with Ag₉₁ clusters using the embedded cluster and multi-reference single- and double-excitation configuration interaction methods.¹⁴ They show a large difference between the potential of ground state N(⁴S) + Ag₉₁ and excited state N(²D) + Ag₉₁. The N(²D) + Ag₉₁ potential has a more attractive well than the N(⁴S) + Ag₉₁ potential. Wang *et al.* have also calculated the activation energy for the N₂ dissociation on Cu(111) and Au(111). The barrier heights for N₂ dissociation on Au(111) and Cu(111) are ~ 6.5 and ~ 3.75 eV,

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respectively. There have been no equivalent reports for Ag(111). However, based on the similarity to Au(111) in terms of N atom binding energy, N₂ dissociation on Ag(111) can also be expected to have a high activation barrier.

N₂ scattering from the Ag(111) surface has been extensively studied in the incident energy (E_i) range from thermal up to ~ 1.5 eV.^{15,16} For the lower incident energies N₂ molecules interact with a flat potential energy surface, resulting in an energy distribution of the scattered particles as a function of outgoing angle that follows the parallel momentum conservation model. At the higher incident energies the energy loss is essentially constant as a function of outgoing angles, in contrast to the physisorption system of Ar which qualitatively resembles the binary collision model. The N₂ angular distribution has a single sharp peak with the maximum at around the specular angle. The full width at half-maximum (FWHM) of this peak decreases with the increasing E_i .¹⁶ Those studies indicate that the effective N₂-Ag interaction potential remains relatively flat even at incident energies exceeding 1 eV. Separately, the internal state distribution of scattered N₂ has been investigated in detail.^{2,17}

In this paper, hyperthermal N and N₂ interacting with the N-covered Ag(111) surface are described. The results are very similar to comparable measurements from clean Ag(111), indicating that the surface seen by the incident species is not dramatically altered by the presence of N atoms. However, there is a subtle addition to the scattered N₂ intensity. The results appear to be consistent with the introduction of an abstraction mechanism as a minor component in the measured signal.

EXPERIMENTAL

The experiments were carried out in a plasma beam scattering apparatus,^{4,18,19} consisting of a triply differentially pumped beamline connected to a UHV scattering chamber. The first stage of the beamline contained a cascaded arc source,²⁰ which produced a high-density linear plasma. N₂ (purity 99.999%) plasma was generated by discharge at three symmetrically mounted cathode tips and transported through a $\varnothing = 2.5$ mm channel in a stack of 5 floating, mutually isolated copper plates before expanding into the first vacuum stage. The second stage contained a chopper in order to produce a pulsed beam, a beam flag to block the beam, and a pair of deflection plates in order to eliminate charged particles. For time-of-flight (TOF) measurements, a double slit 0.5% duty cycle chopper was employed. The third stage functioned as a buffer chamber.

The sample was mounted in the center of the scattering chamber on a three-axis goniometer.²¹ A differentially pumped quadrupole mass spectrometer (QMS) could be rotated around the sample to detect particles leaving from the surface along in-plane scattering directions. In combination with the motion of the manipulator, it was possible to directly measure the incident beam and scattered particles for a large range of incidence angles. By changing the electron impact energy of the QMS ionizer, N was detected in the direct beam at ionization energies below the threshold of the ground state. This confirmed that the beam contained electronically excited

N atoms [N(²D) and/or N(²P)]. In contrast, no excited state N₂ was detected.

The Ag single crystal was oriented to within 0.1° of the (111) face. The surface was cleaned by repeated cycles of Ar⁺ sputtering followed by annealing to 800 K for several minutes. The sample temperature (T_S) was monitored with a K-type thermocouple inserted into a hole in the side of the crystal. The surface structure was checked by low-energy electron diffraction (LEED). N₂ temperature programmed desorption spectra from N-covered Ag(111) were in agreement with those reported previously.³ The N-covered surfaces were prepared by continuous (unchopped) beam irradiation at an incidence angle (θ_i) of 60° and $T_S = 300$ K.

For the TOF experiments, the flight time of the N and N₂ was measured from the chopper to the rotatable QMS in the scattering chamber. All data points shown in this paper were derived from TOF measurements after applying corrections for instrumental time delays, flight time of ions through the QMS and, in the case of N atoms, the N₂ cracking factor to the raw data.⁴ The cracking contribution to the measured N signal was determined on the basis of matching the tail of the incident (scattered) N TOF distribution to the slower incident (scattered) N₂ TOF distribution. This method represents an upper-limit of the cracking factor, potentially overestimating the contribution from N₂. The incident particle energy, final energies as a function of scattering angle, and angular intensity distributions were all derived from TOF measurements after fitting with shifted Maxwell-Boltzmann (MB) distributions convoluted over the finite chopper opening time and over the spread of arrival times of particles at the surface.^{18,22} In this study, the N and N₂ in the incident beam had average energies ($\langle E_i \rangle$) of ~ 4.3 eV and ~ 5.6 eV, respectively. The beam had a broad energy distribution ($E_{FWHM}/\langle E_i \rangle \sim 1.14$ for N and ~ 1.13 for N₂). In all cases, θ_i was 60° with respect to the surface normal.

RESULTS

N Scattering

Figure 1(a) shows the angular distribution of N atoms scattered from the N-covered Ag(111) surface at $T_S = 300$ K. Results for scattering from the bare Ag(111) surface at $T_S = 500$ K are also shown on this panel for comparison. Since adsorbed N atoms undergo recombinative desorption at < 500 K,^{3,23} the latter data represents scattering from a quasi-clean surface. Note that our N₂ cracking correction procedure is chosen to ensure that the analyzed signal in both cases is unequivocally due to N scattering (see Experimental section). Qualitatively, the measurements from the two surfaces are very similar. Both distributions exhibit a sharp peak superimposed on a broad background. The peak is located around the specular angle and its angular position is not influenced by the presence of N on the surface. In both cases, allowing for out-of-plane scattering with a similar distribution to that of in-plane scattering, the broad background represents the major fraction of scattered N. This implies that the majority of scattered N atoms experiences an attractive potential energy surface (PES) during their interaction with the surface.

FIG. 1. (a) Angular-resolved density distributions of N atoms ($\langle E_i \rangle \sim 4.3$ eV; $\theta_i = 60^\circ$) scattered from bare and N-covered Ag(111) at $T_S = 500$ K and 300 K, respectively. The scattered intensities have been normalized to the intensity of the corresponding direct beam. (b) Angle-resolved ratios of final-to-initial energy ($\langle E_f \rangle / \langle E_i \rangle$) for N atoms scattered from the bare and N-covered surfaces. The solid line represents the model of single-collision hard-sphere scattering of the incident atoms from an isolated “silver” atom (mass ratio of $m_N/M_{Ag} = 14/108$).

Quantitatively, there are some subtle differences between the two distributions shown in Fig. 1(a). For the N-covered surface: (1) more N atoms are scattered to large outgoing angles (θ_f); (2) there is more intensity along the specular direction; and (3) there appears to be slightly less N scattered to small θ_f . The first two points are more evident, whereas the difference at small θ_f is less pronounced and should be treated with caution.

The corresponding comparison of the angle-resolved N energy ratio (ratio of the average energy after the collision to the average initial energy; $\langle E_f \rangle / \langle E_i \rangle$) is shown in Fig. 1(b). In contrast to the scattered intensity, there is no significant change to the energy ratio as a result of N addition to the surface. Any changes that do occur are within the error margins of the determination. The solid line on this panel is the model of a binary (hard sphere) collision of mass 14 (N) with mass 108 (Ag). The data points generally follow or are slightly lower than this model, except at the very grazing angle where the average energy of the scattered particles becomes significantly higher than that of the incident beam (see Ref. 4 for details). Note that since the $\langle E_f \rangle$ of the scattered atoms has energies much larger than thermal energy of the surface (300 K), there is no indication of any appreciable thermal trapping at the surface.

N₂ scattering

Turning our attention to the N₂ scattering, the angular distribution measured from the N-covered surface ($T_S = 300$ K) is displayed in Fig. 2. As before, the N₂ angular distribution from clean Ag(111) at $T_S = 500$ K is also shown. Both distributions have a sharp peak around the

specular angle. The peak intensity from the N-covered surface is $\sim 25\%$ larger than that from the clean surface. The FWHM of the N₂ distributions from the clean and N-covered surfaces are $\sim 13^\circ$ and $\sim 11^\circ$, respectively. These FWHM

FIG. 2. N₂ ($\langle E_i \rangle \sim 5.6$ eV; $\theta_i = 60^\circ$) angular intensity distribution from the bare and N-covered surfaces. These distributions were obtained by integrating the TOF distribution recorded at each outgoing angle. The data have been normalized to the intensity of the corresponding direct beam distribution.

FIG. 3. A series of N_2 TOF spectra (thin black lines) collected from the N-covered surface at $T_S = 300$ K at various θ_f ($\theta_i = 60^\circ$). The fitted curves (thick black lines) are based on the assumption of a single shifted MB distribution arising from scattering of N_2 . Corresponding spectra collected from the bare surface at $T_S = 500$ K are also shown as red lines in the panels for $\theta_f =$ (a) 0° , (b) 15° , (c) 30° , and (f) 60° . The chopper frequency was 400 Hz.

values are similar to the previous result ($\sim 14^\circ$) obtained for $E_i = 1.5$ eV under comparable experimental conditions ($T_S = 600$ K and $\theta_i = 60^\circ$).¹⁶ The main difference between the two distributions is that N_2 signal was detectable in the TOF spectra at *all* outgoing angles measured from the N-covered surface, including along the surface normal. This results in the low intensity broad component that is evident in Fig. 2. In contrast, negligible N_2 was detectable in the measurements at small outgoing angle ($\theta_f < 40^\circ$) from the clean surface.

Figure 3 shows a series of N_2 TOF spectra collected from the N-covered surface. TOF data collected from the clean surface for $\theta_f = 0^\circ$ – 30° is also shown on the relevant panels, illustrating the new signal that appears as a result of the addition of N to the surface. A single shifted MB distribution has been fitted to the TOF data under the assumption that the signal is solely the result of N_2 scattering. It is evident that the measured spectra are not well-described by such a distribution. This is particularly the case for outgoing angles between 55° and 70° , where the fits are very poor. Note that the poor description of the TOF spectra in this angular region by a single shifted MB distribution is equally the case

for measurements from the clean surface and, hence, is not related to the presence of N on the surface. This is illustrated by the TOF spectrum collected from the clean surface at $\theta_f = 60^\circ$, which is shown on the relevant panel in Fig. 3. The quality of the fits to the TOF spectra measured for $\theta_f = 0^\circ$ – 30° is better, although still not entirely satisfactory.

The angle-resolved $\langle E_f \rangle / \langle E_i \rangle$ curve derived from the fittings shown in Fig. 3 is plotted in Fig. 4. The corresponding angle-resolved $\langle E_f \rangle / \langle E_i \rangle$ curve derived from the clean surface data at $T_S = 500$ K is also shown. As can be seen, the datasets do not differ significantly in the angular region where they overlap ($\theta_f = 45^\circ$ – 70°). In this region the data qualitatively follows the parallel momentum conservation model. Outside of this region the trend in the data points (from only the N-covered surface) represents a clear break with that exhibited by the near-specular data. These points qualitatively follow the binary collision model.

The result of an alternative, two-component fitting (based on two independent shifted MB distributions, both assumed to originate from incident N_2) is shown in Fig. 5. This fitting involves six parameters as described in Ref. 24, making it very easy to obtain a good description of the overall shape of the

FIG. 4. Angle-resolved $\langle E_f \rangle / \langle E_i \rangle$ ratios as a function of θ_f for N_2 scattering from the N-covered surface (filled circles). The values were derived from the single shifted MB distribution fittings that are illustrated in Fig. 3. The solid line represents the model of single-collision hard-sphere scattering of the incident atoms from an isolated “silver” atom (mass ratio of $m_{N_2}/M_{Ag} = 28/108$). The broken line corresponds to parallel momentum conservation. The open triangles are the corresponding $\langle E_f \rangle / \langle E_i \rangle$ values derived from TOF spectra acquired from the clean surface.

TOF distribution at all outgoing angles. The resultant angle-resolved $\langle E_f \rangle / \langle E_i \rangle$ ratios for the individual components and for the overall distribution are shown in Fig. 6. The energy of the slow component is relatively constant as a function of outgoing angle within the accuracy of the determination. In contrast, the energy of the fast component undergoes large variations, and there is a net energy gain at small outgoing angles. The final energy determined is remarkably high at those angles. The value of the overall average energy follows the trend set by the fast component. It should be noted that since our detector is density sensitive, the apparent contribution from the fast component in a TOF spectrum (see Fig. 7) appears smaller than it actually is in flux-corrected terms. Thus, the fastest particles—which are less well described by the single shifted MB fitting—have a significant contribution to the value of average energy. Similar to Fig. 4, the trends and absolute values of $\langle E_f \rangle / \langle E_i \rangle$ determined from the two-component fitting of TOF spectra measured from the bare Ag(111) surface at $T_s = 500$ K (not shown) were indistinguishable from those of the N-covered surface in the $\theta_f = 45^\circ$ – 70° region.

DISCUSSION

N scattering

As outlined in Results section, some minor changes are observed in the scattered N angular distribution upon pre-adsorption of N on the surface, whereas the N energy distribu-

tion appears unchanged within the margin of error. The angular changes may be due to the presence of N in the threefold hollow sites but, since the surface temperature is lower, they can also be related to the relative differences in the thermal motion of the surface atoms or to a combination of both effects. In any case, the very broad angular distribution strongly suggests that the surface potential “seen” by the majority of incident N atoms remains a deep attractive well. Subtle effects that may be induced by adsorbed N, such as, for instance, an enhanced repulsive corrugation, are not obvious.

The NO + Ru(0001) system also exhibits a deep potential well. Pre-adsorption of H on that surface leads to a very sharp angular distribution of scattered NO as a result of passivation.²⁵ However, in spite of this the sticking coefficient for NO remains high, indicating that an attractive potential persists on the surface. The effect was attributed to a very local change of the surface potential induced by H in the region of unit cell (fcc-threefold hollow site) in which it resides. Another part of the unit cell (hcp-threefold hollow site) remained attractive for the incident NO. In the case of hyperthermal N scattering from clean Ag(111), the results were interpreted in terms of the probing of different potentials by incident N atoms with differing electronic state.⁴ The minor changes that result from pre-adsorption of N demonstrate that these adatoms do not significantly alter the potential seen by the subsequent N atoms that impinge on the surface.

N_2 scattering

The presence of N adatoms also does not dramatically modify the effective surface probed by the incident N_2 . The N_2 angular distributions from the clean and N-covered surfaces are very sharp, indicative of an interaction with an uncorrugated repulsive potential and a structurally smooth surface. The near-specular peak is slightly sharper and more intense in the case of the N-covered surface. The angle-resolved $\langle E_f \rangle / \langle E_i \rangle$ curves for $\theta_f = 45^\circ$ – 70° are almost identical. Both the clean and N-covered surface show a very small energy loss for N_2 scattered around the specular direction. Neither show an increasing $\langle E_f \rangle / \langle E_i \rangle$ with increasing θ_f as was observed for Ar scattering from Ag(111) at $\theta_f = 30^\circ$ – 80° .^{4,24}

Adsorbed N might not be visible to the incident N_2 , since the threefold hollow adsorption site allows it to sit relatively deep in the surface layer (binding position is ~ 1.1 – 1.4 Å above the Ag atomic plane¹³). By way of comparison, Ar with $E_i = 3$ eV could only approach to within about 2 Å of the surface atom cores of the Ag(111) surface.²⁶ If the N atoms are too deeply adsorbed, the potential seen by the incident N_2 will be largely unchanged by their presence. Only the incident particles with the highest initial energy would probe sufficiently deep into the surface to directly interact with these atoms.

In the case of scattering from the N-covered surface, a non-negligible N_2 signal is present at small outgoing angles, as shown in Figs. 2 and 3. Figure 7 shows a N_2 TOF spectrum acquired at $\theta_f = 0^\circ$ compared with a simulated 300 K MB distribution, which assumes incident N_2 trapping on the surface followed by thermal desorption. It is obvious that the

FIG. 5. N_2 TOF spectra collected from the N-covered surface at $T_S = 300$ K (same spectra as shown in Fig. 3). These have been fitted with two shifted MB distributions under the assumption that both originate from scattering of incident N_2 .

measured intensity cannot be attributed to a thermally desorbing component. In addition, since the experiments on the N-covered surface were performed at $T_S = 300$ K, thermal recombinative desorption should not occur. One possible explanation for the additional N_2 signal is related to surface roughness. As already discussed, the N atoms reside in three-fold hollow sites of the surface. In the case of Ru it is known that this leads to small local displacements of the surface atoms. Such local relaxations could give rise to a loss of long range order. Adsorption of N atoms on the Ag(111) surface has been reported to result in a disordered structure at 300 K on the basis of LEED.³ Hence, the surface might consist of patches of well-ordered (and atom reflecting) domains separated by steps. In such a case the resulting scattering pattern would be the sum of the scattering from the ordered, flat domains and from the highly corrugated stepped regions. Stepped and corrugated surface features will be reflected in the distribution of scattered particles. For example, thermal energy N_2 scattering from the corrugated Cu(110) surface exhibits a broad feature around the specular in-plane direction, while diffraction-like features were observed out-of-plane.²⁷

The strong surface corrugation results in an in-plane distribution that is more-or-less symmetrically broad.

If the additional broad feature in the scattered N_2 distribution from N-covered Ag(111) is due to steps, then they can represent only a small fraction of the total surface. It is evident from the sharp and intense N_2 specular peak that scattering from well-ordered domains dominates on both the clean and N-covered surfaces. Indeed, the N-covered surface produces a more intense specular peak than the clean surface, which is contrary to what would be expected from an adsorbate-induced, defected surface. Furthermore, scattering at steps would be expected to produce a uniform broadening of the angular distribution on either side of the specular peak. This is not observed in the current study. There is indeed some additional N_2 intensity at $\theta_f = 80^\circ$ from the N-covered surface, but the intensity gain is much lower than that at small θ_f . Furthermore, a different behavior is observed for the N-atom distribution (Fig. 1(a)). In this case there is an appreciable increase in the intensity at large θ_f , but the intensity at small θ_f is unchanged or even slightly reduced as compared with scattering from the clean surface. This difference

FIG. 6. Angle-resolved $\langle E_f \rangle / \langle E_i \rangle$ ratios as a function of θ_f for N_2 scattering from the N-covered surface at $T_S = 300$ K. These values were derived from the fitting with two shifted MB distributions illustrated in Fig. 5. The solid line represents the model of single-collision hard-sphere scattering of the incident N_2 from an isolated “silver” atom (mass ratio of $m_{\text{N}_2}/M_{\text{Ag}} = 28/108$). The broken line corresponds to parallel momentum conservation.

is also inconsistent with scattering from randomly oriented steps.

An alternative to a scattering process is that direct ER or HA abstraction reactions create an additional N_2 signal across a broad range of outgoing angles. In this case, the molecules detected would be associated with the incident N atoms rather than the incident N_2 , altering the basis on which intensity and energy values are derived from the TOF distributions. This also raises the question as to whether or not the N_2 TOF distributions at small θ_f consist of more than one component. If they are due to N_2 scattering, then the presence of two components at these angles can be rationalized by extension from the TOF profiles measured at large θ_f . In contrast, there is no *a priori* reason to assume two distributions in the case of an abstraction mechanism. None-the-less, the distributions measured at small θ_f consistently exhibited what appears to be a double structure. This was particularly true for measurements along the surface normal (compare the TOF spectrum shown in Fig. 7 with that shown in panel (a) of Figs. 3 and 5). The result of fitting a $\theta_f = 0^\circ$ N_2 TOF spectrum with two shifted MB distributions under the assumption of N atoms as the incident particles (two direct pick-up reactions) is shown in Fig. 7.

As illustrated by Figs. 5 and 7, a two-component shifted MB fitting invariably produces a better match to the overall TOF spectra than a single-component fitting, irrespective of the parent particle that is considered. However, Fig. 3 shows that a single-component N_2 scattering scenario fits the spectra for $\theta_f = 0^\circ$ – 45° reasonably well. Similarly, these spectra can

FIG. 7. N_2 TOF spectrum measured for $\theta_f = 0^\circ$ ($T_S = 300$ K; $\theta_i = 60^\circ$) compared with a simulated 300 K MB distribution (dashed line), which assumes incident N_2 trapping on the surface followed by thermal desorption. In addition, the results of fitting the spectrum with two shifted MB distributions under the assumption that the measured N_2 is the result of a direct recombination reaction involving incident N atoms are shown. The chopper frequency was 200 Hz.

also be well-described by a single shifted MB distribution under the assumption of N-to- N_2 recombination. The quality of such fits is comparable to that shown in Fig. 3 and the trend in E_f derived is similar to that shown in Fig. 4, although the absolute values are lower. This is a general feature: fitting analysis based on using the spread of arrival times of N_2 always results in a higher E_f than one based on the arrival times of N, since the incident N_2 are slower than the incident N. We will first evaluate the data on the basis of two-component fitting. Further consideration will be given to a single component analysis later in the text.

Figure 8 shows a comparison of the final energies and beam-normalized intensities derived from the TOF distributions measured for $\theta_f = 0^\circ$ – 45° on the basis of the two different two-component fitting scenarios outlined above. The first set (Figs. 8(a) and 8(b)) assumes the presence of two N_2 components along these outgoing angles, both arising from recombination reactions involving incident N atoms. The second set (Figs. 8(c) and 8(d)) assumes that both arise from scattering of incident N_2 molecules. The data in the latter case is the same as that shown in Fig. 6, except that $\langle E_f \rangle$ is plotted instead of $\langle E_f \rangle / \langle E_i \rangle$. Note that there is no indication of any significant contribution from ER/HA type reactions to the N_2 measured for $\theta_f = 45^\circ$ – 70° . The TOF distributions at these angles are directly comparable to those from the clean surface, where no reaction pathway is available. Given the low N_2 intensity measured for $\theta_f = 0^\circ$ – 40° , any contribution from a recombinative process at larger θ_f would likely be negligible compared to the directly scattered N_2 signal.

There are various reasons why recombination reactions might produce two components, including:

- The presence of more than one electronic state of N in the incident beam as confirmed by the appearance potential measurements; the different states will react differently and with different energy release.
- The possibility that independent reaction pathways (ER and HA) may be simultaneously operative and produce significantly different N_2 energy distributions.⁶

FIG. 8. Intensity and energy distributions determined from two-component fittings of the N₂ TOF distributions measured for $\theta_f = 0-45^\circ$. (a) and (b) show angle-resolved N₂ intensity and energy distributions, respectively, that were derived based on the assumption of two N₂ components at these outgoing angles, both originating from recombination reactions involving incident N atoms ($\langle E_i \rangle \sim 4.3$ eV). (c) and (d) show the corresponding distributions derived on the assumption of two N₂ components, both originating from scattering of incident N₂ molecules ($\langle E_i \rangle \sim 5.6$ eV).

Comparing the two fitting scenarios shown in Fig. 8, the trends in the angular intensities (panels (a) and (c)) of the individual components are not significantly affected by the choice of originating particle, although the relative contributions do change slightly. The trends in the angular dependence of the energies are also independent of the chosen parent. However, the absolute final energies do differ dramatically. It is difficult to account for the high energy of the fast component derived under the assumption of N₂ scattering. In contrast, it is relatively easy to account for the energy that is predicted if re-

combination between an incident N and an adsorbed N gives rise to fast N₂. The N≡N bond energy is ~ 9.8 eV. The adsorption energy of a N atom on Ag(111) is about 4 eV, which is the upper limit of reported values based on DFT calculations, with the N atoms binding in hollow sites.¹³ In the extreme case, recombination of a gas phase N atom and a N atom adsorbed on Ag(111) by direct ER is exothermic by ~ 5.8 eV. Additionally, scattered N atoms can retain a substantial fraction of their original energy even at small outgoing angles, as shown in Fig. 1(b). Hence, N₂ produced

as a result of ER can be expected to carry a significant amount of excess energy, not only in translation but also in ro-vibrationally excitation.

In light of the reasonable quality of the fits at small θ_f shown in Figs. 3(a)–3(c), more detailed consideration will now be given to the single component possibility. As illustrated by Fig. 4, the final energy at these angles cannot be used to discount N_2 scattering. In this case, the $\langle E_f \rangle / \langle E_i \rangle$ values and trend at small θ_f are reasonable from a mechanical scattering perspective. Two possibilities can be proposed as to why the scattered N_2 might exhibit only one component at small θ_f . The first is that only one of the two components evident at large θ_f is broadened over a larger angular range. In this case, the data points for the single component fit at small θ_f connect best with those of the fast component at large θ_f . The second possibility is that a third, broad component is present when scattering from the N-covered surface. This would imply that the adsorbed N induces an attractive interaction between a minority fraction of the incident N_2 and a localized region of the surface.

The main weakness with the scattering processes suggested above is that they require that a fraction of the N_2 that was originally scattered at large θ_f be re-directed to small θ_f . There is no evidence in Fig. 2 that such a redistribution is occurring. On the contrary, the N_2 intensity around the specular angle increases when N is added to the surface. In contrast, there is an indication of a reduction in the number of N atoms scattered along the surface normal (Fig. 1(a)). While it cannot be ruled out that this is solely the result of redistribution of the scattered intensity to larger θ_f (particularly since we have no out-of-plane information) it is none-the-less consistent with an abstraction reaction. Scattering from steps—the alternative explanation for normally exiting N_2 —is not indicated by the angular distributions of scattered N_2 as discussed earlier.

If a N atom related ER recombinative desorption does occur, one can envisage that the reaction cross-section will be small since the adsorbed N atoms are relatively close to the surface. Steering effects will not be strong due to the hyperthermal energy of the incident atoms, unlike in previous reported instances of pick-up reactions on H + H/metal and H + Cl/metal surfaces.⁷ Hence, for a recombinative reaction to be effective, the trajectory of the incident N should pass very close to the adsorbed atom. As such, the mechanism might be restricted to the high energy fraction of the incident beam, since only these atoms can approach sufficiently close to the adsorbed atoms. However, as evident from the very broad N angular distribution (see Fig. 1(a)), the majority of N atoms experiences an attractive interaction with the surface, while retaining relatively high translational energy. Hence, multiple collisions at a relatively corrugated PES can be anticipated, making recombinative desorption as a result of a HA reaction mechanism feasible.

At present, it is not possible to definitively conclude whether the N_2 signal at small θ_f is due to (in)elastically scattered N_2 or to abstraction reaction processes involving incident N. However, an explanation based on the ER/HA reaction appears to be more consistent with the measured TOF

data. Additional experiments (for example, using isotopically labelled N_2) and theoretical analysis will be required for a definitive confirmation.

CONCLUSIONS

Hyperthermal N atoms and N_2 molecules were scattered from the N-covered Ag(111) surface held at 300 K. The resultant angular and energy distributions of both atoms and molecules are similar to those from the clean surface at 500 K, indicating that the adsorbed N does not dramatically alter the surface potential seen by the incident species. Both N and N_2 show some enhanced intensity around the specular direction from the N-covered surface at 300 K, which suggests that the surface structure appears somewhat smoother than that of the clean surface at 500 K. The main difference between the two surfaces is the appearance of additional N_2 intensity at small outgoing angles and along the surface normal when N is adsorbed. This may be the result of recombination of incident N atoms with adsorbed N leading to N_2 desorption.

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