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Nitrogen Scattering at Ru(0001) Surfaces

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Results on the scattering of hyperthermal N₂ molecules from bare and N-covered Ru(0001) surfaces are presented. These are compared with Ar scattering from the same surfaces as a reference non-reactive system. In the case of bare Ru(0001) the measured angular distributions are consistent with scattering from an atomically smooth surface after interaction with a repulsive potential energy surface. Broadening of the N₂ angular intensity distribution at high incident energy, which was observed in molecular beam studies, is not apparent in our measurements. This is attributed to the broadening effect being the result of a transient trapping process that is confined to a relatively narrow incident energy range. The presence of N-adatoms on the surface results in atomic-scale surface roughening and blocking of dissociation pathways. Formation of N₂ molecules as a result of abstraction of N-adatoms by incident N-atoms in an Eley–Rideal-type reaction is considered. Support for such a process is derived from comparison of the trends in the angular energy distributions of N₂ and Ar.

1. Introduction

Breaking of the very strong triple bond of the nitrogen molecule is a major challenge in catalysis. For more than a century the energy-intensive Haber–Bosch process utilizing Fe catalysts has been used for this purpose. Elucidating the mechanism of this reaction contributed to the awarding of the Nobel prize in chemistry to Gerhard Ertl in 2007 [1]. The dissociative chemisorption of N₂ is the rate limiting step of the process. Details of this step have been investigated by a number of methods both experimentally (notably by molecular beam techniques) [2–4] and theoretically, by density functional theory [4–6]. In addition to direct adsorption, desorption has been studied with the intention of linking the two methods by invoking the principle of detailed balance.

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In the specific case of N_2 interaction with Ru(0001), broadly speaking it has been demonstrated that there is a strong activation barrier of about 2 eV toward dissociative chemisorption [6–9]. The barrier is rather late in the dissociation process, implying that there is significant stretching of the N_2 bond before the transition state is reached and it strongly depends on the specific surface site where the dissociation occurs. Dissociation proceeds much more facile at steps on the surface than at terrace sites [4]. The barrier in the dissociation process also depends on the coverage of the surface by nitrogen atoms [10]. It increases with coverage, while the binding energy of the adsorbed N-atoms decreases. As a consequence, N-atoms in a near-monolayer coverage are metastable and will desorb easily upon heating of the surface [11].

Focusing on molecular beam experiments in general, several processes can be observed in such studies [12,13]. Apart from dissociative chemisorption, trapping in a weakly bound state followed by desorption can be seen in the angular distribution of reactants leaving the surface. In addition, direct scattering can be observed. If a state-selective detector is used, rotational and vibrational excitation of molecules due to the collision with the surface can be detected. Energy transfer to the lattice can be monitored using time-of-flight techniques [14–17]. In some cases reaction products resulting from a direct or Eley–Rideal type reaction [18] may be detected.

Scattering experiments are fully complementary to adsorption studies: in the case of weak adsorption, strong reflection is observed. When the translational energy of the incident N_2 beam approaches that of the barrier to chemisorption, one can expect changes in the angular distributions and energy transfer of the scattered molecules. Such experiments have been carried out by several groups [14–17]. Both the total molecular intensity and state-resolved intensities have been measured. A brief summary of these studies is that for beam energies up to ~ 2.0 eV the scattering patterns observed resemble those of completely inert surfaces. At the highest energies Papageorgopoulos *et al.* [15] show a broadening of the angular distribution that was attributed to the approach of the region of the potential energy surface where the barrier to dissociation becomes effective. This broadening of the angular intensity distribution was also found by Díaz *et al.* [7,19] in trajectory studies using a potential that includes the barrier to dissociation. These suggest that the intensity of the scattered N_2 will significantly change with increasing the energy due to changes in the repulsive potential.

In recent work on the scattering of N-atoms from Ag(111) surfaces it was demonstrated that a deep chemisorption well in the potential leads to a distinct broadening of the angular distributions [20–25]. However, broadening of angular distributions can also be observed even in scattering of inert species such as Ar (or N_2) when increasing the collision energy, simply because the corrugation increases with energy. Furthermore, such broadening is also observed when a surface is made more corrugated, *e.g.* by adsorbates, or by destroying the long range order of the crystal *via*, for instance, the introduction of steps. To reduce complexity in interpretation, noble gas scattering is studied because in this case deep adsorption wells do not occur.

The scattering of Ar by Ru(0001) has been extensively investigated. For energies up to 1.5 eV near-specular reflection was observed by Berenbak *et al.* [26]. Splitting of the specular peak due to rainbow scattering was observed at an energy of 0.56 eV. In these experiments a supersonic beam was used, having a fairly narrow velocity spread. Ueta *et al.* observed no big effect of increasing the beam energy to 6.3 eV [27]. Specular scat-

tering was still observed. In all cases the energy transfer to the lattice is complex and not fully understood. The velocity spread in this beam is much broader, blurring structures. Most likely 6 eV Ar starts to manifest surface rainbow scattering in the energy transfer. The Ar–Ru system at these energies resembles the scattering from Ag(111) at 0 K as seen in scattering calculations by Lahaye *et al.* [28], which clearly show surface rainbow scattering.

For the present system – N₂ scattering from clean and nitrogen covered Ru(0001) – we would anticipate rainbow-like scattering for N₂ at low energies but perhaps also significant further broadening due to the opening of a chemisorption well behind a high barrier [15]. Changes can be expected when the surface is covered with N-atoms. For the scattering of N₂ molecules there may be two counteracting effects. Firstly, N adatoms should increase the barrier to dissociative chemisorption leaving the angular distribution unchanged, while the absolute number of scattered molecules will increase. Secondly, the adatoms may change the surface corrugation due to their mutual repulsion and may modify or roughen the surface structure. It is known that N-atoms chemisorb in three fold hollow sites on Ru(0001) [29,30] and reside about 0.1 nm above the plane of the Ru-atoms. The LEED structure of N–Ru(0001) changes from sharp at low coverage to very diffuse at higher coverage [10,11,31]. Thus, the Ru surface loses long-range order when a near-monolayer of N-atoms is adsorbed. If the surface becomes atomically rough, it is likely to scatter N₂ molecules rather diffusely, even if a chemisorption potential is absent. Atomic-scale structural roughening can be distinguished by comparison with Ar atom scattering experiments, which do not experience chemisorption wells but are sensitive to structural roughening. To shed more light on this complex system we have carried out scattering experiments with Ar and N₂ at bare and N-covered Ru(0001). Since the nitrogen beam contains both N₂ molecules and N atoms, the possible formation of N₂ at N-covered Ru(0001) is considered.

2. Experimental

Experiments were performed in a beam scattering apparatus [24,32,33] comprised of an UHV chamber with a triply differentially pumped cascaded arc plasma beamline (see Fig. 1). The beamline consisted of an expanding thermal plasma (ETP) source, a set of skimmers to collimate the plasma expansion into a beam and separate the vacuum stages, and a mechanical chopper to pulse the beam for time-of-flight (TOF) measurements. In more detail, plasma was generated at sub-atmospheric pressures (245–260 mbar) in flowing N₂ or Ar gas (purity 99.999%; flow = 1 slm) at 3 symmetrically-positioned cathode tips by a DC discharge (input powers of 7.8 kW for N₂ and 4.4 kW for Ar, corresponding to an arc current of 60 A). It was transported through a narrow ($\varnothing = 2.5$ mm) channel drilled in the centre of a stack of 4 floating, mutually-isolated, water-cooled copper plates, and finally expanded through a grounded nozzle ($\varnothing = 2.5$ mm) into the first vacuum stage (typical working pressure $\sim 6 \times 10^{-2}$ mbar). At the end of this stage the plasma expansion was collimated through a homemade conical skimmer ($\varnothing = 0.5$ mm) into a beam that entered the second vacuum stage (typical working pressure $\sim 4 \times 10^{-5}$ mbar). This stage contained a double slit (0.5% duty cycle) mechanical chopper wheel. The (pulsed) beam entered the third

Fig. 1. Schematic top-view of the configuration of the scattering apparatus.

stage, which acts as a buffer chamber (typical working pressure $\sim 5 \times 10^{-8}$ mbar), via a second skimmer (Beam Dynamics Inc., $\varnothing = 1.0$ mm).

The sample assembly was mounted in the centre of the scattering chamber (typical working pressure $\sim 4 \times 10^{-10}$ mbar) on a three-axis goniometer that could be moved aside to allow direct measurement of the incident beam. The angular full-width at half maximum (FWHM) of the direct beam was $\sim 1.6^\circ$. This chamber contained an ion sputter gun for sample cleaning, a differentially-pumped fixed quadrupole mass spectrometer (QMS) for gas monitoring and temperature programmed desorption (TPD) measurements (Balzers, model QMG/H 422) and a differentially-pumped rotatable QMS (Extrel, type MEXM060 2.9C/4P8) for scattering studies.

The sample was a Ru single crystal with the surface oriented to within 0.1° of the (0001) face (Surface Preparation Laboratory). It was cleaned by repeated cycles of sputtering with Ar ions (typical pressure 2×10^{-5} mbar) followed by annealing in vacuum at 1500 K for 2 min. Occasionally, annealing was performed in an O_2 atmosphere (1×10^{-8} mbar) for several minutes followed by flashing to 1530 K. The surface temperature of the crystal (T_s) was monitored with a K-type thermocouple spot-welded to the side of the crystal. Regular checks were performed with the Ar beam, scattered in a fixed configuration, to ensure that the state of the Ru crystal surface remained constant over time.

The main diagnostic tool was the rotatable QMS that could be moved around the sample to detect particles leaving the surface. The sample was aligned such that particles were detected in a plane defined by the incident beam and the surface normal. For presentation of data in this paper, the incidence angle (θ_i) and outgoing angle (θ_f) are defined with respect to the surface normal. For TOF experiments, the flight times of the N_2 molecules and Ar atoms were measured from the chopper in the second vacuum stage to the detector of the QMS in the scattering chamber. Corrections for a trigger delay and for the energy dependent flight time of the ionized particles through the QMS

Fig. 2. Measured ETP particle energy distributions of the incident nitrogen and argon plasma beams used in the current study.

were applied to the raw data. The incident particle energies, final energies as a function of the scattering angle and angular intensity distributions presented in this paper were all derived from TOF measurements, after converting from time to energy domain and correcting the intensities from densities to fluxes (multiplication by v) [32]. The scattered intensities were derived from the TOF peak integrated area and were normalized to the incident beam intensity. Error bars represent the reproducibility of measurements at various times and on different days. The average energies ($\langle E \rangle$) are the mean (weighed average) values obtained from integration of these distributions (not the peak energies).

The cascaded arc beamline produces high-temperature effusive beams. The incident beam on the sample was neutral ($I_{\text{beam}} < 0.1$ nA). When nitrogen was used as the feed gas, the direct beam contained both N and N_2 particles in a measured ratio of $\sim 1 : 1$. In its current configuration, particles with average incident energies ($\langle E_i \rangle$) in the range of 4–9 eV were generated. The beams had very broad energy distributions, with full-width at half-maximum values (E_{FWHM}) greater than $\langle E_i \rangle$. The measured energy distributions from the nitrogen and argon plasmas used in the current study are presented in Fig. 2. In the case of the nitrogen plasma the energy distributions for the current and earlier measurements are quite similar; only the N to N_2 ratio in the incident beam has changed (see [34]). In contrast, the current Ar beam energy distribution shows a higher average energy and a broader energy width compared to the previous studies. These changes are attributed to the altered configuration of the cascaded arc (reduced stack size) and different gas flow rates used in the current study.

3. Results and discussion

Figure 3 shows the in-plane angular intensity distributions for N_2 and Ar scattered from the Ru (0001) sample held at 900 K for $\theta_i = 40^\circ$ and 60° . At this temperature, recom-

Fig. 3. Angular resolved intensity distributions of N_2 molecules ($\langle E_i \rangle = 5.6$ eV) and Ar atoms ($\langle E_i \rangle = 8.8$ eV) scattered from a Ru(0001) surface held at $T_s = 900$ K. The scattered intensities (I_{scat}) are normalized to the corresponding direct beam intensity (I_0). The lines connecting the data points are a guide to the eye. The vertical dashed lines indicate the specular scattering direction of 40° and 60° respectively.

binative thermal desorption ensures that the standing coverage of N on the surface remains low (< 0.05 monolayers) [11,31]. No post-exposure desorption of N_2 could be detected by TPD. The sharp angle-resolved distributions and the super-specular peak intensities seen in Fig. 3 are characteristic of a predominantly repulsive interaction. The Ar angular distributions have slightly broader FWHMs and lower normalized peak intensities than those measured for scattering at $T_s = 600$ K by Ueta *et al.* [27]. Thus, this data continues the previously observed trend of decreasing peak intensity and increasing FWHM with increasing sample temperature [27].

The individual data points on Fig. 3 are normalized to the intensity of the corresponding direct beam. This allows for direct comparison of different scattered species. Provided there are no loss or gain processes, full hemi-spherical integration of the normalized scattered intensity would yield a value of 1. Potential loss processes are sticking/trapping or molecular dissociation at the surface, while gain processes are displacement or abstraction/recombinative desorption from the surface. Under the current experimental conditions the inert Ar atoms will not be affected by either loss or gain processes. Thus, the total scattered intensity will match the total incident intensity. A difference in the normalized intensity of another species (in our case N_2) along a given outgoing direction must either be compensated for by matching differences along other trajectories or it signifies the presence of loss/gain processes.

Full integration is not possible in the current apparatus since out-of-plane trajectories are inaccessible. Due to the 3-dimensional nature of the scattering, integrated areas of in-plane distributions from two different species cannot necessarily be expected to match. However, if the species being compared have similar in-plane profiles then, under the assumption that they will also exhibit similar out-of-plane profiles, the integrated areas of the in-plane distributions can be regarded as representative of the overall distributions.

For the data shown in Fig. 3 the Ar and N₂ distributions have similar profiles. However, the integrated areas of the N₂ distributions are significantly less than those of the corresponding Ar distributions (factors of 0.67 and 0.71 for $\theta_i = 40^\circ$ and 60° , respectively). We attribute this to dissociative interactions at the surface. Considering the range of energies in our incident beam, appreciable dissociation can be expected [7,19].

The FWHMs of the N₂ distributions are similar to the *minimum* widths obtained during molecular beam measurements for N₂ on bare Ru(0001) in the same scattering geometry [15]. This previous study reported a significant broadening of the angular FWHM at $\theta_i = 40^\circ$ for $E_i > 1.2$ eV, which was attributed to probing of a metastable precursor state to dissociation with a *normal* energy threshold of ~ 0.65 eV. In contrast, the current data contains no indication of a similar broadening, despite the overwhelming majority of N₂ molecules having energies that exceed the threshold value ($E_i > 1.11$ eV and 2.6 eV for $\theta_i = 40^\circ$ and 60° , respectively).

There are a number of obvious disparities between the two sets of measurements. The earlier study involved a supersonic N₂ beam with a narrow energy distribution, while the current study has a mixed N and N₂ beam with a very broad range of energies. It is remarkable that the less “well-defined” beam, dominated by higher energy particles, is capable of producing a narrower angular distribution. The broadening effect must be “washed out” by the wide energy range. This can be explained by it being the result of transient trapping in the chemisorption well at the surface rather than due to structural scattering at a corrugated potential energy surface. In this case, some molecules experience an energy-dependent increased resident time at the surface, but do not fully equilibrate. Direct evidence for transient trapping was not seen in the TOF data by Papageorgopolous *et al.* [15]. However, the effect was directly observed in the case of O₂ interaction with Ag(111) [35,36]. In that case the trapping probability exhibited a strong energy dependence, passing through a maximum and decreasing again with increasing (normal) energy. Such a variation in trapping probability as a function of incident energy can reconcile the current angular widths with those of Papageorgopolous *et al.* Figure 3 illustrates that for the range of energies present in our beam the majority of scattered N₂ molecules experience a structurally and chemically flat surface.

N-covered Ru was prepared by exposure to a continuous (unchopped) nitrogen beam at an incident angle $\theta_i = 60^\circ$ and a constant T_s of 400 K for 180 s. The uptake as a function of time, based on post-exposure TPD measurements, is shown in Fig. 4. There is an initial increase of the N-coverage as a function of exposure times, followed by a relative stabilization. The inset illustrates a TPD trace acquired directly after exposure of bare Ru(0001) to the continuous nitrogen beam in the stabilized regime. The current experimental configuration is not ideally suited to TPD studies because of the large distance between the sample and the acceptance aperture of the analyzer. Hence an absolute coverage cannot be definitively identified. However, with reference to the nitrogen coverage dependent TPD series reported by Diekhöner *et al.* [11], the onset of desorption signal at $T_s < 500$ K signifies a coverage ≥ 0.54 monolayers (ML).

Desorption features at $T_s \leq 600$ K have been attributed to metastable species that are prone to associative desorption and, consequently, not stable in time [10,11]. If the N-covered sample was allowed to rest in vacuum at $T_s = 400$ K for several hours the desorption intensity from the metastables region (< 600 K) decreased. Diekhöner *et al.* reported these states to be stable for ≥ 30 min [11], which is longer than our

Fig. 4. N uptake curve based on TPD measurements from N-Ru(0001) ($T_s = 400$ K during dosing); the vertical dashed line indicates the surface exposure time used for the scattering experiments. *Inset:* TPD (4 K/s) of nitrogen ($m/e = 28$) from the N-Ru(0001) surface immediately after dosing with the continuous nitrogen beam for 180 seconds.

typical measurement time per data point (~ 10 – 12 min). No significant difference in the integrated areas of TPD spectra taken directly after dosing and following TOF measurements was observed. However, given the relatively poor sensitivity of our TPD configuration, small changes to the N-coverage during TOF measurements cannot be ruled out.

Considering the interactions of Ar and N_2 with N-covered Ru(0001), Fig. 5 shows the resultant normalized angular intensity distributions after scattering from this surface at $T_s = 400$ K. The effect of adding N atoms is a reduction in the peak angular intensity by more than a factor of 10 in both cases, accompanied by a significant broadening in the FWHM of the distributions. The broadening of the inert Ar distribution signifies atomic-scale structural roughening of the surface upon N-atom adsorption.

A LEED study on N-Ru for coverages up to 0.38 ML did not report a substantial loss of long-range order [31], higher coverages resulted in only very diffuse LEED patterns [10,11]. This indicates that the surface roughening is primarily associated with population of the metastable adsorption states. Thus, the Ar angular distribution in Fig. 5 supports the conclusion based on TPD measurement that these states are (partially) populated. Interestingly, while N-atom adsorption on Ag(111) is also reported to produce a very diffuse LEED pattern [37], in that case it had a negligible effect on the scattered N_2 angular distributions [25].

Compared to the data from the bare surface, the shapes of the N_2 and Ar angular profiles from the N-Ru are in less good agreement with each other. The normalized intensities of N_2 exceed those of Ar at small outgoing angles. The near-specular normalized N_2 intensity from N-Ru is lower than that of Ar (factor of ~ 0.83), but the difference is less than was the case for the bare surface (~ 0.53). Furthermore, the total integrated areas of the two distributions are now almost identical; the higher N_2 signal

Fig. 5. Angular resolved intensity distributions of N_2 molecules ($\langle E_i \rangle = 5.5$ eV) and Ar ($\langle E_i \rangle = 8.8$ eV) scattered from the N–Ru(0001) surface held at $T_s = 400$ K. The scattered intensities (I_{scat}) are normalized to the corresponding direct beam intensity (I_0). The lines connecting the data points are a guide to the eye.

at small outgoing angles compensates for the reduced intensity along near-specular directions. With wider *in-plane* integration the N_2 area would exceed that of Ar since the former clearly has intensity at negative outgoing angles whereas the latter does not. If this effect is not counterbalanced by a corresponding narrowing of the out-of-plane N_2 distribution, the total normalized intensity of “scattered” N_2 will exceed 1.

The relative increase in the scattered N_2 intensity from N–Ru can be, in part, attributed to blocking of surface dissociation channels, but this cannot result in the scattered flux exceeding the incident flux. The incident flux can be exceeded if formation of N_2 in a fast pick-up reaction between incident and adsorbed N-atoms also contributes to the measured signal. Slow recombinative desorption processes cannot contribute because the data points are derived from TOF spectra and such processes are lost in the background signal of these measurements. For nitrogen scattering from N-covered Ag(111) the appearance of additional N_2 intensity at small outgoing angles was suggested as a signature of N-atom abstraction *via* an Eley–Rideal or hot atom mechanism [25]. In that case the possibility of scattering of N_2 to small θ_f was inconsistent with the narrow angular width of the dominant near-specular N_2 peak.

As was the case for Ag(111), support for an abstraction contribution to the measured N_2 angular distribution can be derived from the angular energy distributions. Figure 6 shows $\langle E_f \rangle / \langle E_i \rangle$ distributions of Ar and N_2 from N-covered Ru(0001) for $\theta_i = 60^\circ$. From bare Ru(0001) the angular energy distributions of Ar and N_2 (*not shown*) are confined to the 50° – 80° θ_f range and the $\langle E_f \rangle / \langle E_i \rangle$ values are similar to those from N–Ru. The most striking aspect of Fig. 6 is that, while there is good agreement in the near-specular region (50° – 80°), the two datasets deviate from each other at small outgoing angles. The N_2 $\langle E_f \rangle / \langle E_i \rangle$ is significantly higher than that of Ar for $\theta_f \leq 40^\circ$. The N_2 energies can be approximated reasonably well by a binary collision model that assumes scattering from an effective surface mass of 2.3 Ru atoms. This effective mass has been

Fig. 6. Angular resolved final-to-initial energy ratio ($\langle E_f \rangle / \langle E_i \rangle$) distributions for N_2 molecules ($\langle E_i \rangle = 5.7$ eV) and Ar atoms ($\langle E_i \rangle = 8.6$ eV) scattered from N-Ru(0001) surface held at $T_s = 400$ K. For reference, binary collision models for Ar with a single Ru (continuous line) and with 2.3 Ru (dash line) and for N_2 with 2.3 Ru (dash-dot-dash line) are plotted.

observed in various studies on Ru(0001) [38–40]. The Ar scattered to small outgoing angles experience more energy loss. In this case the trend in the final energies is more akin to that expected from a simple binary collision with a single Ru atom. The energy loss by Ar as a function of outgoing angle indicates that scattering to small outgoing angles is dominated by single, hard-collision events. The latter are essentially absent for the atomically smooth surfaces (Fig. 4) but become significant from the N-covered surface due to the induced roughening.

The comparison of N_2 and Ar energy distributions in Fig. 6 shows a break-point at $\theta_f \sim 40^\circ$ – 50° , which coincided with the transition in the normalized intensity distributions from a higher Ar signal ($\theta_f \geq 50^\circ$) to a higher N_2 signal ($\theta_f \leq 40^\circ$). In the absence of a significant decrease in the N_2 $\langle E_f \rangle / \langle E_i \rangle$ at small outgoing angles despite all indications pointing to an atomically-rough surface (increasing hard-collision probabilities and thus promoting energy loss), we conclude that a mechanism other than direct scattering is operative: an Eley–Rideal type reaction process. In this case, the final trajectory and translational energy of molecules formed is determined both by translational energy retained from the incident N-atom and any energy lost or gained during bond breaking/formation at the surface. In the case of Ru(0001) surfaces N adatoms can sit close to the atomic plane of the outermost layer. Hence, any N_2 molecules formed find themselves high up on a repulsive potential wall and will receive an impulse directed primarily along the (local) surface normal. In our case the metastable adsorption states on the surface are partially occupied. Thus, the binding energy of adatoms to the surface can be significantly reduced relative to the most stable adsorption states. The reduced energy penalty in breaking these bonds will result in a higher translational energy gain as a result of N_2 formation relative to abstraction from the more strongly bonded states.

4. Conclusions

The scattering of N_2 and Ar from clean Ru(0001) is dominated by a repulsive interaction. Broadening of the angular distribution to the extent reported by Papageorgopoulos *et al.* is not observed. This is attributed to an energy-dependent transient trapping of N_2 at the surface, with the difference in beam energy range between the two studies accounting for the effect. There is appreciable dissociation of N_2 at the bare surface.

Scattering from the N-covered surface is dominated by N-induced structural roughening. As a consequence the angular intensity distributions of both Ar and N_2 are very broad with substantially reduced peak intensity. This complicates separation of physical scattering effects from those due to altered surface reactivity. None-the-less, relative to the corresponding scattered Ar intensities, there is an overall increase in the N_2 intensity scattered from N-Ru compared with that from the bare surface. This is the result of blocking of dissociative pathways by N-adatoms. The increased scattered N_2 integrated area, the presence of significant N_2 intensity at near-normal angles relative to Ar, and a disparity in the angular energy distribution of the two species, point to a fast abstraction reaction between incident and adsorbed N-atoms at the Ru surface.

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