Nitrogen interactions at metal surfaces

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Abstract
Molecular beam experiments with specially prepared beams allow the study of the interaction of very reactive species with surfaces. In the present case the interaction of N-atoms with Ag(111) is studied. The energy of the atoms is around 5 eV, precisely between the classical energy regimes of seeded molecular beams and low energy ion scattering. We will show evidence that the electronic state of the incident atoms is very important in the interaction. The systems studied experimentally have also been investigated by theoretical modeling. The comparison between theory and experiment will be discussed. We will consider if N-atoms can lead to a passive adlayer that is not reactive to subsequent N-atoms. It appears unlikely, which may be a consequence of incident N-atoms removing adsorbed N-atoms in an Eley-Rideal reaction.

Keywords: hyperthermal, molecular beam, translational energy, Eley-Rideal reaction, surface scattering, potential (surfaces), corrugation, Ag, DFT, electronic (state), energy transfer, passivation.

Introduction

The interactions between atoms or molecules and solid matter are determined by the relative energy of the colliding species. A diagram showing the various processes that can occur as a function of energy is shown in Figure 1. At the highest practical energies in the mega-electronvolt (MeV) regime the interaction is determined by the coulomb repulsion and Rutherford scattering at an ordered array of point charges. Nuclear reactions can even be initiated, as utilized in the technique of nuclear reaction analysis (NRA). At the other extreme, in the milli-eV range, the interaction is dominated by Pauli repulsion between the atoms outermost electrons, and diffraction and elastic scattering from a closed solid surface occur. In the middle of Figure 1 the regime of inelastic ion surface collisions is found. Besides the dynamical processes mentioned, this regime is used for extracting structural information from ion scattering and ion energy loss data [1, 2]. A scattering mechanism that can be found over quite a broad range of interaction

energies is rainbow scattering [3-6]. Rainbows are caused by focusing in (at least) double collisions at surfaces. The low energy analogue of rainbow scattering is diffraction that currently can also be studied with grazing-incidence fast ion beams [7-9]. When using molecular projectiles dissociation can occur. At low energies this may lead to dissociative chemisorption. In this case the energy gained by binding the molecular fragments to the surface is enough to break the molecular bond [10-12]. At higher energies dissociation can be directly caused by the kinetic energy available in the collision [13, 14].

Although figure 1 suggests continuity in the physics as a function of energy, in experimental practice this is not so much the case, as different installations are required. Ion beams can be easily made with energies from tens to hundreds of eV up to many MeV. At the low energy end effusive and supersonic molecular beams can be made with typical energies up to 2 eV, but not above. The regime of 3-100 eV is a relative no-man's land where few experiments can be found. Our group has in the past done many experiments with very low energy ion beams, for instance in [15, 16] and references given earlier in this report. Very recently, we have started to make fast molecular beams using arc plasma sources, which will be the topic of the present report. We will focus on experimental studies involving reactive nitrogen atoms and Ag(111). These results will be compared to similar studies with inert noble gas atoms for calibration. A comparison with theory will also be made.
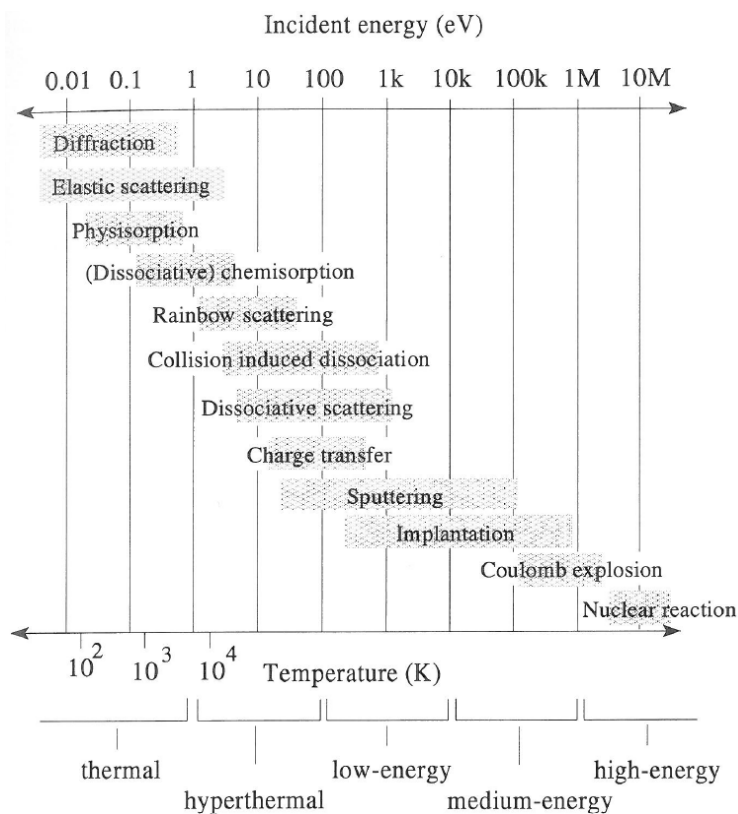

Figure 1: Diagram showing the physical processes occurring in atom or molecule surface interactions as a function of the relative energies. Inelastic ion surface collisions occur in the middle of the figure.

The importance of surface scattering experiments was already realized in the 1970th [17, 18]. From the early work two regimes are identified and the corresponding terms '*thermal scattering*' and '*structure scattering*' were coined. In the first case the processes are dominated by an energy constraint and the thermal energy of the surface is an important parameter. In addition, parallel momentum conservation applies. In the second case the dynamics at the surface is determined by the potential hypersurfaces and the surface structure. Often rainbow scattering is seen. Collisions are not constrained by a lack of energy and can be seen as one or more binary collisions that are approximately independent. In this case parallel momentum conservation does not apply. The transition between the two regimes was at a few eV of translational energy.

Most of the studies in this field have been performed using scattering of noble gas atoms. When studying reactive particles the interaction becomes more complex because there is a strong attractive force between projectile and surface [11]. Most studies with reactive atoms have been carried out with alkali, O- or F-atoms or ions, and mostly at energies well above 10 eV [8, 19-22].

Studies with fast N-atoms are rare due to the difficulty in making fast beams of these atoms. In this work we use an atmospheric plasma arc to produce a nitrogen beam that contains a mixture of N-atoms and N_2 molecules. Other methods to make fast beams are laser detonation or charge exchange [23-25]. N-atoms have low-lying excited states that can be populated in molecular beams [26-28]. Excitation or de-excitation of these states makes it possible to study electronically non-adiabatic processes at surfaces. Such processes have been studied extensively at energies of tens of eV's for charge transfer processes at surfaces such as neutralization of protons, noble gas ions, alkali atoms and several molecular ions [20, 29]. The connection of those studies to the lower energy work has been underestimated, see e.g. [9].

The ground state interaction of N-atoms and N_2-molecules with metal surfaces is currently being studied by density functional Theory (DFT) methods by a number of groups; see e.g. [30-33]. Such studies yield potential energy hypersurfaces describing the interaction. The actual interaction dynamics can be studied separately if the processes are electronically adiabatic and the Born-Oppenheimer approximation is valid. Interactions with excited state particles still pose a formidable challenge for theoretical analysis.

The structure of the N-containing surfaces is not known in all cases. For Ag(111) the knowledge is summarized in [34] and is limited. For Cu and Ru more is known [35-40]. In general, the N-atoms reside in three fold hollow sites and are almost inside the metal lattice. Their presence can give rise to restructuring and loss of long-range order of the surface.

The control of reactant energy and internal state needed for the experiments discussed can be achieved by molecular beam techniques. The approach itself is very well established [11]. Using these techniques we have recently studied the interactions of fast argon atoms, and atomic nitrogen radicals and molecules with metal surfaces. Energies in the 3-6 eV range have been achieved. Notably their adsorption and scattering from Ag and Ru surfaces, and their interaction with pre-adsorbed nitrogen atoms has been studied [41-44].

Experimental

The measurements relating to the interaction of argon and nitrogen with mainly silver surfaces that are discussed in this text were collected in a plasma beam scattering apparatus [44-46]. It consists of a triply-differentially-pumped beam line connected to a UHV scattering chamber. The cascaded arc beam line in its current configuration produces a high-temperature effusive beam. The particles have average energies $\langle E_i \rangle$ typically in the range of 4-6 eV, with a very broad energy distribution (full-width at half-maximum values (E_{FWHM}) greater than $\langle E_i \rangle$). The beam is a high-temperature effusive beam.

The beam line contains a chopper to allow measurements in time-of-flight (TOF) mode. The sample is mounted in the center of the scattering chamber on a three-axis goniometer. The main diagnostic tool is a differentially-pumped quadrupole mass spectrometer (QMS) that can be rotated around the sample to detect particles leaving from the surface along in-plane scattering directions. For the presentation of data in this paper, the incident angle (Θ_i) and outgoing angle (Θ_f) are defined with respect to the surface normal, while the total scattering angle (Θ_t) is defined as ($180°-(\Theta_i + \Theta_f)$). For details of the sample cleaning, characterization, and preparation methods, the reader is referred to the relevant published work for Ag(111) [43, 44].

N-atom scattering at bare Ag(111)

Scattering at surfaces gives information on the nature of the gas-surface interaction. For the case at hand, it is illustrative to compare N-atom scattering to that of Ar from the same surface. A comparison of the angular intensity distributions for beams of fast Ar and N with $\langle E_i \rangle$ of around 5 eV scattered from a bare Ag(111) surface for $\Theta_i=60^o$ is shown in figure 2(a). The surface temperature (T_s) was maintained at 600 K by radiative heating during the measurements. It is known that at temperatures $\geq$500 K the nitrogen does not chemisorb at the surface [34]. The incident N atoms can adsorb at the surface but, due to the high surface temperature, they will quickly recombine and desorb. A theoretical study has indicated that at the present beam energy even temporary trapping in the chemisorption well is unlikely (Martin-Gondre, private communication). Note that both the N intensities (left-hand ordinate) and Ar intensities (right-hand ordinate) are normalized relative to their respective intensities in the direct beam. Since the Ar-atoms are confined to a comparatively narrow scattered angle range, their relative intensities are significantly higher than those of the scattered N-atoms.
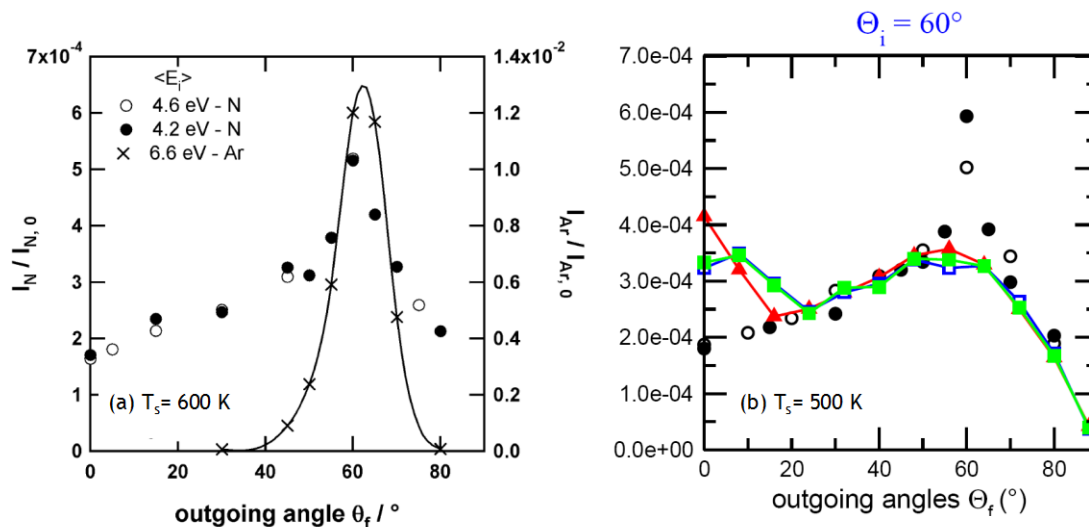
Figure 2: (a) Angular intensity distributions of Ar and N atoms scattered from a bare Ag(111) surface at Θ_i=60° and T_s = 600 K . (b) Comparison of the experimentally measured angular distribution of N atoms scattered from a bare Ag(111) surface at Θ_i=60° and T_s = 500 K with classical trajectory modeling for a rigid surface (red trace), a thermally moving surface (blue trace) and a thermally moving surface with electronic friction (green trace).

The angular distribution of Ar is typical for scattering in a system dominated by van der Waals forces. It is in the transition between thermal scattering and structure scattering. Specular reflection occurs with a peak relative reflection intensity of about 0.012 with respect to the primary beam intensity. It is not unreasonable to assume that all Ar from the primary beam is scattered into the specular peak observed, and that no significant out-of-plane scattering occurs.

The angular distribution of the N-atoms shown in figure 2(a) is distinctly different from that of Ar. A very broad distribution is observed with a peak at the specular angle. This pattern is more connected to structure scattering. The relative reflection intensity at the specular peak is about 0.0005 with respect to the primary beam intensity, a decrease of a factor of 25 with respect to Ar. A full integration of all scattered signal is not possible in our apparatus, but it is very reasonable that the dramatic increase of the width of the in-plane distribution leads to the observed decrease of the relative reflection probability in the specular peak. In fact, in the case of N scattering there is only a small preference for specular scattering. Decreasing Θ_i to 40° (results shown in [44]) leads to a broadening of the specular peak for Ar, as expected. For N-atoms the peak at the specular angle almost disappears.

As noted by Ueta *et al.* [44], the angular distributions of N-atoms shown in figure 2 appears to be the result of two distinct distributions: an 'Ar-like' specular peak and an additional very broad distribution. No consistent argumentation could be found for attempts to attribute the two distributions to different physical processes in scattering of ground state N-atoms. In addition, as shown in figure 2(b), recent theoretical calculations

by Martin-Gondre *et al.* [47] show a very good reproduction of the broad component of the spectrum, but the specular peak is absent. The angular distribution is shown to be dominated by structure scattering from the corrugation of the potential energy surface, which is evident from contour plots of the potential.

The absence of a specular peak in the calculations for N-atom scattering from Ag(111) is to be expected. The potential energy surface shows a very deep chemisorption well and consequently a very corrugated potential. This gives rise to structure scattering in many directions because parallel momentum is not conserved in collisions involving such a potential. It is parallel momentum conservation that gives rise to the strong specular peak for Ar scattering. Unless we assume that the DFT potential surface is quite incorrect, for which there are no indications, we must conclude from the comparison between experiments and theoretical results in figure 2(b) that there is an ingredient in the physics that is absent in the above approach.

Ueta *et al.* suggest that this missing component might be the presence of excited N-atoms (^{2}P and ^{2}D) in the beam. It is well known that atom sources can deliver such excited atoms, which have long lifetimes [26-28]. Indeed, excited state atoms have been detected during analysis of the primary N-atom beam using Threshold Electron Appearance Potential measurements with the mass spectrometer detector of the system. The amount of excited atoms has been estimated as a few percent of the total intensity, although a detailed quantification has not been performed. In this case, and in light of the results of the DFT calculations for ground-state N, we have to consider that the specular peak in the N-atom signal is due to scattering of excited atoms.

N-atom scattering at N-covered Ag(111)

Lowering the surface temperature to T_s=300 K while exposing a bare Ag(111) sample to the nitrogen plasma beam results in the surface becoming covered by N-atoms. Even though the N-atom beam energy is rather high, post-irradiation TPD measurements confirm increasing N-atom adsorption with exposure time, leading to an eventual saturation. The N_2 desorption peak occurs at 430K, in agreement with earlier measurements by Carter *et al.* [34]. The structure of the N-covered Ag(111) surface is not very well known. By analogy to other systems and following the calculations by Martin-Gondre *et al.* we assume that the N-atoms reside in the hollow sites. Most likely, every other hollow site will be empty. The bonding distance between the N-atoms and the plane through the outermost Ag nuclei is 0.1 nm, meaning that the N-atoms are almost absorbed into the Ag lattice.

Scattering N-atoms from such an N-covered Ag(111) surface at Θ_i=60° yields an angular intensity distribution such as is shown in figure 3. The corresponding angular distribution from the "bare" surface at T_s=500 K is also shown. The result is quite remarkable because there is very little change between scattering from the bare surface and from the N-atom covered surface. The energy transfer in scattering from the N-covered surface (not shown) is also essentially undistinguishable from that for scattering

from the bare surface. It is important to note that the relative reflection intensity also
remains unchanged, excluding the possibility of loss of a significant amount of the
incident N flux, for instance by sticking. Recent scattering calculations by Blanco-Rey et
al. demonstrate that the scattering mechanism from bare and N-covered Ag(111) is in fact
very different, but that the final results are none-the-less very similar [33]. It appears that
the adsorbed N-atom exhibits a strong attraction towards incident N-atoms leading to a
very corrugated potential. The shape of this potential is different from that of the bare
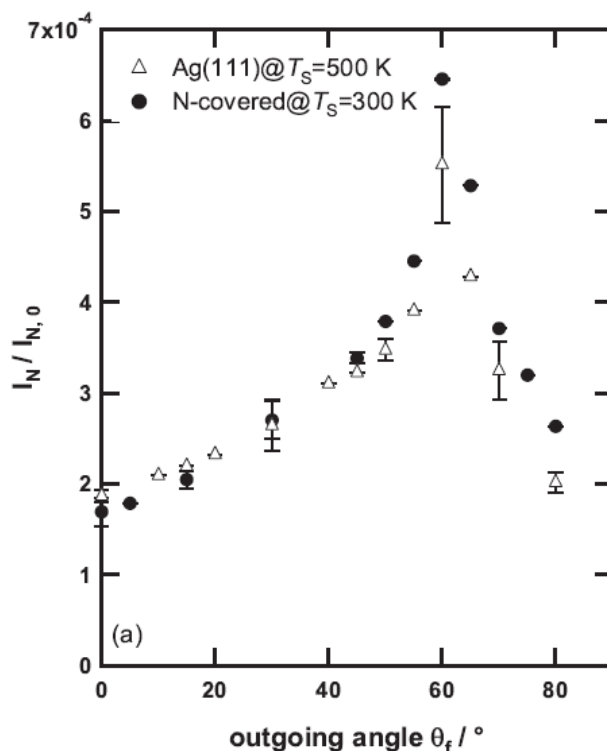surface but the resultant scattering pattern is very similar.

*Figure 3: Comparison of the N-atom angular distributions for N atoms
scattering from bare and N-covered Ag(111). The incidence angle is 60°.*

We note that the onset of repulsive forces between Ar atoms and Ag(111) at the
threefold hollow site occurs at about 0.2 nm [48]. For incident N-atoms interacting with
this hollow site the value is more like 0.1 nm. This very close approach is due to the
strong attraction. If adsorbing an N-atom were to make the local interaction for incident
N atoms "Ar/Ag-like", then half of the unit cell would become "uncorrugated" resulting
in a dramatically increased specular intensity. This is clearly inconsistent with the
measurements, since the specular intensity is very similar to that from the bare surface.
From the close correspondence between N-atom scattering patterns we infer that the deep
chemisorption well is not passivated by the adsorbed N-atom. As confirmed by Blanco-
Rey et al. [33], the reason for this is that the strong Ag-N attraction is replaced by a
strong N-N attraction. It seems likely that thanks to this N-N attraction the overall

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interaction between N-atoms and the (N-)Ag(111) surface does not change much. This conjecture could be tested by measurements of Ar scattering from N-Ag(111).

N$_2$ scattering and formation at N-Ag(111)

The relative angular intensity distribution for scattering of N$_2$ at Θ_i=60° from bare Ag(111) (T$_s$=500 K) and N-covered Ag(111) (T$_s$=300 K) are plotted in figure 4 [43]. A very sharp specular peak is observed with a relative angular intensity ($\approx$0.02) that is significantly higher than that observed for Ar ($\approx$0.012; see figure 3(a)).
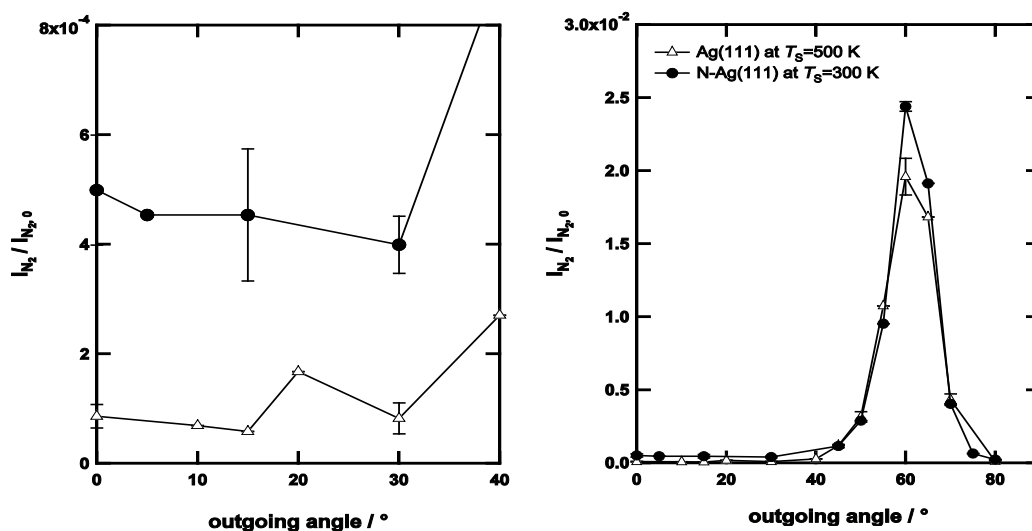

Figure 4: Angular intensity distributions of N$_2$ scattered from bare and N-covered Ag(111). The left-hand-side panel is a blow-up of the small outgoing angle region of the right-hand-side panel.

Clearly the surface is completely inert and lacks corrugation toward N$_2$. The adsorbed N-atoms do not appear to play a major role. Presumably, this is because it is positioned at a depth of only 0.1 nm above the surface plane of Ag atoms where is it is largely invisible for the incident N$_2$. However, a careful inspection shows that there is additional N$_2$ signal at the surface normal in the case of the N-covered surface, which is absent for the bare surface. There can be various explanations for this signal. One is that it is due to the increased roughness of the surface. If this is the case Ueta *et al.* [43] argue that it should also result in a broadening of the specular peak at both sides. This is not evident, in particular at Θ_f=80° where measurements for corrugated systems, for instance N-atom scattering, do show significant signal. By contrast, the signal for N$_2$ at Θ_f=0° has a higher relative angular intensity ($\approx$0.0005) than that for N-atoms at the same angle ($\approx$0.0002). This analysis suggests that this signal is not due to scattering of N$_2$ from the beam.

An alternative explanation for the N$_2$ signal is that it is due to a pick-up reaction of a surface N-atom by a fast N-atom. This would be an Eley-Rideal reaction or a hot

atom reaction [49, 50]. A detailed analysis of the energies of the N_2 formed could shed more light on this. It was found that a consistent fit of all N_2 time-of-flight data could not be obtained on the basis of a single shifted Maxwell Boltzmann distribution, although a reasonable fit for a subset of the angular data could be obtained in this way. However, good fits to all angular time-of-flight data could only be obtained using a combination of a slow and a fast N_2 component. Note that the slow component was faster than the Maxwell distribution representing thermalization at the surface.

If indeed an Eley-Rideal like process is being observed it would be the first observation of such a reaction for a non-hydrogenic system. Eley-Rideal reactions have been observed for the pick-up of hydrogen by fast projectiles such as the DABCO molecule, Cl atoms, hydrogen atoms and O atoms [51-54]. Although the evidence seems to point to such a process a definitive experimental proof has not been given and this remains a topic for future research in our laboratory. Independently, theoretical analysis of the present data could lead to a convincing proof of the mechanism.

Conclusions

Molecular beam scattering of fast radical atoms from surfaces is a unique tool to investigate the dynamics of the interaction and for the study of the onset of chemical reactions at surfaces. From the material presented we conclude that the interaction of radical atoms is dominated by deep attractive potentials, leading to large corrugation and very broad angular distributions from structure scattering. We note that adsorbed N-atoms do not significantly change the angular distributions of scattered N atoms. We have demonstrated strong evidence for an important role of electronic excitation of the N-atoms, although further work on the composition of the beam is clearly needed. Finally, we note that Eley-Rideal reactions between incident and adsorbed N-atoms on Ag(111) may occur.

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