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Scattering of fast N₂ from Pd(111): A classical trajectory study

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Molecular nitrogen is well known for its chemical inactivity. Experimental results for grazing incidence N₂ scattering from Pd(111) surfaces in the keV range also reveal negligible influences of electronical processes on molecular fragmentation. Therefore, we carry out an appropriate classical treatment of this system. The N₂-Pd(111) interaction is mediated by an analytical six-dimensional potential energy surface, based on *ab initio* density-functional-theory calculations and empirical data. The molecule-surface interaction seems to be strongly influenced by the azimuthal direction of incidence as well as the molecular axis orientation. Particularly, the fragmentation is found to be mainly due to vibrational excitation for highly indexed azimuthal directions, whereas for incidence along lowly indexed directions rotational excitation is more important. © 1997 American Institute of Physics. [S0021-9606(97)00611-9]

I. INTRODUCTION

The importance of the different dissociation mechanisms involved in the interaction of fast molecules and molecular ions with metal surfaces has been discussed with great interest in recent years.¹ For inert molecules as N₂, electronical interactions with the surface are of minor importance for adsorption as well as for scattering and dissociation. Therefore, a description of the scattering process in terms of elastic collisions of the molecule with surface atoms seems reasonable.^{2,3} It has to be noted, that some authors however found a sizeable influence of electronical excitation of the N₂⁺ due to violent collisions, leading to dissociation.⁴ Furthermore, dissociation due to “hot” electrons, created by the projectile travelling through the surface electron gas and captured into excited molecular states, is proposed.⁵ Recent results of collision induced electron emission indicate dissociation involving the N₂⁺(³Σ_g⁺) state, leading to the appearance of metastable N⁻*(¹D).⁶

In a recent publication,⁷ we showed that glancing N₂ scattering from Pd(111) seems to be dominated by elastical interactions and may be well described in terms of classical trajectory calculations. Simulations of fast molecule scattering from metal surfaces are often based on rather simple interaction potentials, such as sums of screened Coulomb potentials or *ab initio* dimer potentials from Hartree-Fock-Slater (HFS) calculations describing the interaction between projectile atom and surface atom and Morse potentials mediating the intramolecular interaction.⁸ In contrast, for modelling adsorption systems, realistic potential energy surfaces depending on all six degrees of freedom of the diatomic are used.⁹ Recently, several authors found strong influences of

the surface geometry on adsorption and dissociation dynamics.¹⁰⁻¹² Naturally, potential energy surfaces (PES) from adsorption studies are suitable only for rather low translational energies. It is of particular interest to extend results from simulations of adsorption¹³ and hyperthermal molecule scattering¹⁴ to higher translational energies.

In the following, we present the first classical-trajectory study of the scattering system N₂-Pd(111) based on a realistic six-dimensional PES. This analytical PES is based on *ab initio* calculations and empirical data for the low energy regime but also gives the correct asymptotic behavior for close collisions.

II. SIMULATIONAL DETAILS

A. Classical trajectories

The code used to simulate the N₂-Pd(111) interaction has been successfully applied to the H₂-Pd(110) system.¹⁵ Basically, Newton's equations of motion are solved numerically along the trajectory of the molecule. For each launched molecule, the single-crystal-surface is initialized, i.e., within a cell of laterally 50×50 first-layer atoms, each atom is thermally displaced perpendicular to the surface in terms of the Debye model. Within this model,¹⁶ uncorrelated Gaussian distributions of the atomic displacements are assumed and the mean square atomic displacement is proportional to $T/\Theta_{\perp}$, where T is the surface temperature and $\Theta_{\perp}$ is the surface Debye temperature perpendicular to the surface ($\Theta_{\perp}=198$ K for Pd(111)).¹⁷ Thus, for each first layer atom, a random number is chosen and weighted by this mean square value to get the thermal displacement. The parallel displacements are neglected because of the grazing angle of incidence (85° with respect to the surface normal), they have no influence on collision impact parameters.

The surface atoms are kept fixed during the interaction

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period, since the vibrational timescale is large compared to the interaction time with projectiles of translational energies in the keV range. The infinity of the surface is achieved by periodic boundary conditions. Interactions with up to 8 layers of surface atoms are taken into account. A relaxation between the topmost layers is allowed, i.e., the distance between these layers can be changed with respect to the bulk value. Furthermore, the surface may be supplied with point defects and steps.

Initially, each molecule is located randomly within the surface unit cell. The orientation of the molecular axis is chosen randomly, also. A rotational (rigid rotor) and vibrational (harmonical oscillator) temperature is attributed to the molecule. The velocity components of the constituents are calculated from the Gaussian-distributed primary energy.

Each integration step now requires the calculation of the forces acting on the molecules constituents. To this end, the interaction-potential gradient of the constituent and the remaining system is computed; the interaction with surface atoms whose distance exceeds a given cut off is neglected. The set of coupled differential equations is then integrated by means of a 3rd order predictor-corrector method,^{18–20} which has been successfully applied to similar problems.²¹

Using the position r_i , the velocity v_i , and the acceleration a_i at given times t and $t - \Delta t$, the position at time $t + \Delta t$ is given by:

$$r_i(t + \Delta t) = r_i(t) + \Delta v_i(t) + \frac{\Delta t^2}{6} [4a_i(t) - a_i(t - \Delta t)]. \quad (1)$$

With the $r_i(t + \Delta t)$, the accelerations $a_i(t + \Delta t)$ are computed and the new velocities can be calculated as follows:

$$v_i(t + \Delta t) = v_i(t) + \frac{\Delta t}{6} [2a_i(t + \Delta t) + 5a_i(t) - a_i(t - \Delta t)]. \quad (2)$$

The magnitude of Δt determines the conservation of the total energy of the system. Usually, Δt is of the order of some 10^{-17} s and the total energy fluctuations do not exceed 2×10^{-3} a.u.

Optionally, after an integration step, electronical processes such as an inelastic energy loss of the projectile due to electron-hole pair creation and electron transfers between projectile and surface can be included. The inelastic energy loss can be accounted for by discrete changes of the projectile energy. The electron transfer processes may be included by switching to a different PES, describing a different electronic state. In the following, both options are switched off, because of the lack of information regarding these electronical processes.

The important physics enter with the choice of the PES describing the interaction.

B. Analytical form of the potential energy surface (PES)

The interaction of a N₂ molecule and a metal surface can be described by a PES

$$\mathbf{V} = \begin{pmatrix} V_1 & V_{12} \\ V_{21} & V_2 \end{pmatrix} \quad (3)$$

consisting of the diabatic N–Pd(111) PES V_1 , the diabatic N₂–Pd(111) PES V_2 , and the coupling terms V_{ij} .^{22,23} Diagonalization of $\mathbf{V}$ yields the adiabatic PES describing the ground state and an excited state of the N₂–Pd(111) system. In the following, we are interested only in the former:

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2} [V_1(\mathbf{r}_1, \mathbf{r}_2) + V_2(\mathbf{r}_1, \mathbf{r}_2)] - \sqrt{[V_1(\mathbf{r}_1, \mathbf{r}_2) - V_2(\mathbf{r}_1, \mathbf{r}_2)]^2 + 4V_{12}(\mathbf{r}_1, \mathbf{r}_2)^2}. \quad (4)$$

The $\mathbf{r}_i$ are the positions of the N₂ constituents. In the next step, V_1 , V_2 , and V_{12} have to be determined. The diabatic interaction potential of two nitrogen atoms with the Pd(111) surface is assumed to be the sum of a repulsive N–N potential and bonding N–Pd potentials:

$$V_1(\mathbf{r}_1, \mathbf{r}_2) = V_{\text{N-N}}^{\text{ZBL}}(r) + \sum_{i=1}^2 \sum_{j=1}^n V_{\text{N-Pd}}(R_{ij}), \quad (5)$$

where r is the N–N distance, R_{ij} is the distance between i th N atom and j th Pd atom and, n is the number of surface atoms interacting with the molecule. Since the N–N interaction is repulsive in this state, $V_{\text{N-N}}^{\text{ZBL}}$ is taken to be a screened Coulomb potential as proposed by Ziegler *et al.* [Ziegler–Biersack–Littmark (ZBL) potential].²⁴ The Pd–N potential has to comply with three criteria. First of all, it has to give the correct adsorption properties of atomic nitrogen on Pd(111), second the asymptotical behavior for $R_{ij} \rightarrow 0$ has to be correct, and the transition between both regions has to be smooth. In a recent publication,⁷ we showed that this can be achieved by using the expression:

$$V_{\text{N-Pd}}(R_{ij}) = \frac{1 - \tanh(R_{ij} - R_0)a_0}{2} V_{\text{N-Pd}}^{\text{ZBL}}(R_{ij}) + \frac{1 + \tanh(R_{ij} - R_0)a_0}{2} V_{\text{N-Pd}}^{\text{Morse}}(R_{ij}). \quad (6)$$

The high-energy part $V_{\text{N-Pd}}^{\text{ZBL}}$ is assumed to be well described by the ZBL potential. As the low-energy part, a Morse potential is used:

$$V_{\text{N-Pd}}^{\text{Morse}}(R_{ij}) = D_{0,\text{N-Pd}} (1 - e^{-\alpha_{\text{N-Pd}}(R_{ij} - r_{0,\text{N-Pd}})})^2. \quad (7)$$

The parameters in Eq. (7) as well as R_0 are obtained by fitting V_1 to results from density functional theory (DFT)-cluster calculations and experimental data, as described in Sec. II C.

In the same way, the diabatic N₂–Pd(111) potential is defined as:

$$V_2(\mathbf{r}_1, \mathbf{r}_2) = V_{\text{N-N}}^{\text{Morse}}(r) + \sum_{i=1}^2 \sum_{j=1}^n V_{\text{N-Pd}}'(R_{ij}) \quad (8)$$

with

$$V'_{\text{N-Pd}}(R_{ij}) = \frac{1 - \tanh(R_{ij} - R_0)}{2} V_{\text{N-Pd}}^{\text{ZBI}}(R_{ij}) + \frac{1 + \tanh(R_{ij} - R_0)a_0}{2} V'_{\text{N-Pd}}^{\text{Morse}}(R_{ij}). \quad (9)$$

The N–N interaction is now attractive and can be described by a Morse potential:

$$V_{\text{N-N}}^{\text{Morse}}(r) = D'_{0,\text{N-N}}(1 - e^{-\alpha_{\text{N-N}}(r - r'_{0,\text{N-N}})})^2. \quad (10)$$

It is a requirement to the final PES, that it gives the correct experimental dissociation energy, equilibrium distance, and vibrational constant of gas-phase N₂ for an infinite molecule-surface distance. Therefore, the parameters of $V_{\text{N-N}}^{\text{Morse}}$ have to be chosen in agreement with this condition. In particular, the parameters may depend on the coupling term V_{12} .

As for V_1 , the high-energy part of $V'_{\text{N-Pd}}$ is taken to be the ZBL potential. For the low-energy part, again a Morse potential is used

$$V_{\text{N-Pd}}^{\text{Morse}}(R) = D'_{0,\text{N-Pd}}(1 - e^{-\alpha_{\text{N-Pd}}(R - r'_{0,\text{N-Pd}})})^2. \quad (11)$$

Again, the parameters are taken from DFT calculations and experimental data and can be found in Sec. II C.

Henriksen *et al.* use a similar PES to describe the adsorption dynamics of N₂ on a Re(0001) surface, which also takes into account the softening of the N–N bond due to the interaction with the surface. They include an explicit dependence of $D'_{0,\text{N-Pd}}$ on the R_{ij} .⁹ Because of the lack of experimental and theoretical data for the N₂–Pd(111) system, this effect is neglected in the following.

The last step is the definition of the coupling term V_{12} , which mainly influences the dissociation barrier. To our knowledge, for the barrier height of the system under investigation, there is no experimental or theoretical data available. Thus, we just assume a mixing parameter as in²⁵

$$V_{12} = \chi \quad (12)$$

C. Density functional theory (DFT) cluster calculations

In Ref. 7, we simply used a pair potential approach based on *ab initio* DFT results for the Pd–N dimer and experimental results for the N–N interaction, to describe the Pd–N₂ system, i.e., the complete PES was supposed to be the sum of the interaction potentials between both molecule constituents with each surface atom respectively and the intramolecular potential. Not many body effects were included. Obviously, a better agreement with experimental data has to be expected by taking into account the influence of a larger part of the surface. This leads directly to the description of the surface by finite clusters. The present computer resources and quantum chemistry software allows to calculate properties of clusters with sizes of up to 100 atoms and more depending on the theory used. Furthermore, it has to be taken into account that working with a cluster model means of course dealing with effects that are due to the finite size of the system. On the other hand, treating a system of the target used in the classical trajectory calculations would be com-

pletely impossible. Nevertheless, it was shown by, e.g., Kirchner *et al.*²⁶ for the Ar/Ag(111) system, that even relatively small clusters ($n=10,19$) agree quite well with the results from slab calculations. It has to be noted, that for other systems this agreement can be smaller.²⁷

We studied the convergence of the results in dependence of the cluster size, to choose systems of sufficient size. It is well known that for physisorption systems even small clusters ($N < 20$) give a good description of adsorption phenomena whereas on the other hand chemisorption on metals shows slow convergence with cluster size. The N₂–Pd(111) system is known to be an example for physisorption,²⁸ whereas atomic nitrogen chemisorbs on Pd(111).²⁹ However, a reasonable convergence of the calculations was found for cluster sizes of about 20 atoms which is a good compromise between accuracy and computing time.

Our calculations are performed using the commercial DFT software DMol.³⁰ DFT has proved over the past years to be an ideal choice for a rigorous quantum mechanical treatment of large systems. DMol calculates variational self-consistent solutions to the DFT equations, expressed in the molecular orbital (MO). Exchange and correlation energies are included within a local density approximation (LDA). The MO themselves are treated in a linear combination of atomic orbitals (LCAO) approach:

$$\psi_i(\mathbf{r}) = \sum_j C_{ij} \phi_j(\mathbf{r}) \quad (13)$$

$$\phi_j(\mathbf{r}) = F(r) Y_{lm}(\nu, \varphi), \quad (14)$$

where the ϕ_j are the atomic orbitals. The angular part of each function is given by the spherical harmonics $Y_{lm}(\nu, \varphi)$. The radial part $F(r)$ is obtained by solving the atomic DFT equations numerically. ν , φ , and r are the polar coordinates of the atomic system. Closed shells are treated in a frozen-core approximation.

The use of the exact DFT spherical atomic orbitals has the advantage of being able to dissociate the molecule exactly to its constituent atoms. This on the one hand gives the possibility of calculating the potential even far away from the equilibrium distance and on the other hand gives an excellent description of weak bonds which is important for the treatment of physisorption systems.

We use double numeric basis-sets and basis functions one higher in angular momentum than the highest occupied orbital in the free atom, which are referred to as polarization functions. This double numeric polarized (DNP) basis set ensures a good description of the electron distribution near the atoms and therefore improves the bonding itself.

The calculations for atomic nitrogen are done in the following way: First of all, an initial geometry for the substrate clusters containing the Pd-atoms is chosen. With this, geometries of different adsorption sites are simulated. The position of the atoms is given by the bulk fcc structure and the (111) surface. No relaxation effects of the surface are taken into account. The nitrogen atom is then placed in the center of the structure with a given distance to the first layer. In order to determine the Pd_n–N potential, we calculate the total energy of the system for different distances of the adatom to the

FIG. 1. Geometries of the substrate clusters for computation of the binding energies of adsorbed atomic nitrogen in top (a), hcp-hollow (b) and fcc-hollow (c) geometry.

surface. In particular, calculations for the top site as well as the fcc- and hcp-hollow sites are performed. The cluster geometries can be found in Fig. 1. It has to be noted, that different cluster sizes are chosen in order to have the same number of nearest and next nearest neighbor atoms for the nitrogen in each geometry. The obtained binding energies in dependence of the N–Pd_n distance (which is referred to as z) are plotted in Fig. 2 for all three geometries.

The strikingly high binding energy of the nitrogen atom is due to the involvement of two π - and one σ orbital in the bonding. Particularly the latter includes bonding to 2nd layer atoms, with the consequence of a reasonably lowered energy for $z \rightarrow 0$.

The *ab initio* results are now fitted by the PES from Eq. (5) [including Eqs. (6) and (7)] in view of the fact that just one N atom is considered. The fitting procedure leads to the well known problem of overestimating the binding energies for hollow-site adsorption by summation of spherical pair potentials.²⁶ The reason is the nonadditivity of the Pauli repulsion, which leads to an extra repulsion for this geometry, in addition to the overestimation due the DFT calculation

FIG. 2. Binding energies for atomic nitrogen on Pd clusters. Circles: results from DFT calculations; solid lines: hollow-site fit of V_1 ; dotted lines: hollow-site fit of V_1 with adjusted binding energy. The results are calculated for top (a), hcp-hollow (b), and fcc-hollow geometry (c).

itself. Since it is impossible to have a good agreement for both, top and hollow sites, we fit Eq. (5) to the hollow-site data, accepting a poor agreement for the top site (Fig. 2). Equation (7) then results to

$$V_{\text{N-Pd}}^{\text{Morse}}(R) = 0.092(1 - e^{-1.05(R-3.535)})^2, \quad (15)$$

i.e., $D_{0,\text{N-Pd}}^{\text{Morse}} = 0.92$, $\alpha_{\text{N-Pd}} = 1.05$, and $r_{0,\text{N-Pd}} = 3.535$, all in atomic units. The distance R_0 in Eq. (6), which determines the switching between Morse and ZBL potential is set here

FIG. 3. Binding energy of a N₂ molecule in a top site on a Pd₂₂ cluster. The N–N distance is fixed at the gas-phase value; the molecular axis is oriented perpendicular to the surface; z is the distance between surface and lowest N atom. (Note the logarithmic scale of the ordinate as well as the change of the scale at $z = 1.8$ a.u.)

FIG. 4. Contour plots of the N₂-Pd(111) PES for the indicated geometry. Intramolecular distance r and molecule surface distance z are varied, the former symmetrically. All other coordinates are kept fixed.

and in the following to 1.25 a.u. The simulation results depend only weakly on this parameter. The binding energy obtained by the *ab initio* calculations amounts to more than 0.3 a.u., whereas the experimental value is 0.206 a.u.²⁹ This is not surprising, since cluster calculations systematically give to high binding energies. For the same system, Sellers³¹ finds a similar geometry (Pd_n-N distance: 3.76 a.u.), but a binding energy which is about twice as high as the experimental value. To correct the binding energy, we reduce only $D_{0,N-Pd}$ from 0.092 to 0.061 a.u. The parameter α is kept constant, since there is no data on vibration frequencies of N and Pd(111) available. The resulting potential energy curves are also plotted in Fig. 2.

For the nitrogen molecule, a different strategy is used because the number of degrees of freedom makes it impossible to calculate a complete PES by means of DFT within a reasonable timescale. We therefore use the same DFT-cluster method to optimize the equilibrium geometry of the system by using a steepest descent algorithm starting from a bridge

position. Again the positions of the Pd atoms are fixed to bulk distances and only the coordinates of the two nitrogen atoms in the mirror plane of the Pd cluster (point group C_s) are optimized. This gives a total of four degrees of freedom.

The preferred binding geometry seems to be a perpendicularly oriented N₂ molecule, sitting on top of a surface atom. The distance between the lower N atom and the surface is 3.78 a.u. and the N-N equilibrium distance increases to 2.27 a.u.

Based on the resulting equilibrium geometry, the binding

TABLE I. Parameters for Eq. (10) for different mixing-parameters χ (atomic units).

χ	$D'_{0,N-N}$	α'_{N-N}	$r'_{0,N-N}$
0.025	0.388	1.353	2.073
0.05	0.4101	1.35	2.073
0.1	0.4495	1.28	2.07

FIG. 5. Simulated molecular survival probabilities of N₂ scattered off Pd(111) for different mixing parameters χ . All system temperatures are set to zero and a perfect surface is assumed.

TABLE II. Parameters of the N₂-Pd(111) PES (atomic units).

R_0	$D_{0,N-Pd}$	α_{N-Pd}	$r_{0,N-Pd}$	$D'_{0,N-Pd}$	α'_{N-Pd}	$r'_{0,N-Pd}$	χ	$D'_{0,N-N}$	α'_{N-N}	$r'_{0,N-N}$
1.25	0.061	1.05	3.535	0.018	1.3	3.8	0.05	0.4101	1.35	2.073

energy is calculated for different distances between lower N atom and the surface. For this calculation, we use the exact top-site and a nontilted molecule. The intramolecular distance is kept frozen at the gas-phase equilibrium distance. Resulting energies, depending on the distance of the lower N atom to the surface, can be found in Fig. 3. The computed binding energy is 0.013 a.u. and probably overestimated again. Angle-resolved photoelectron spectroscopy studies indicate gas phase character of the physisorbed N₂ and a random orientation of the molecular axis.²⁸ On the other hand, based on sums of spherical pair potentials, it is impossible to give an exact description of an adsorption system which energetically prefers the top site. Therefore, the best we can do is to fit Eq. (8) to the uncorrected *ab initio* data (Fig. 3). Equation (11) now reads

$$V_{N-Pd}^{Morse}(R) = 0.018(1 - e^{-1.3(R-3.8)})^2 \quad (16)$$

with $D_{0,N-Pd}^{Morse} = 0.018$, $\alpha'_{N-Pd} = 1.3$ and $r'_{0,N-Pd} = 3.8$, all in atomic units.

D. Final PES

Up to now, the parameters were determined by fitting to theoretical and experimental data, i.e., no free parameters

were used, yet. As pointed out before, there is no data available regarding the dissociation barrier of N₂ on Pd(111). Therefore, the PES contains the free parameter χ which determines the magnitude of coupling between the two diabatic potentials V_1 and V_2 . Figure 4 shows contour plots of the final PES for three different mixing parameters $\chi = 0.025$, 0.05, and 0.1 a.u. In particular, χ influences the parameters of Eq. (10). For all three values of χ , the parameters are given in Table I. The geometry of the system is shown in the inset of Fig. 4. The N₂ molecule is placed with the molecular axis parallel to the surface. Four degrees of freedom are fixed, and just the molecule-surface distance z as well as the intramolecular distance r are varied, the latter symmetrically with regard to the geometry in Fig. 4.

For all three values of χ , a similar PES is found, which shows the usual elbow structure. There is a flat physisorption well at $z \approx 3.5$ and $r \approx 1.1$ a.u., a chemisorption well starting at $z \approx 2$ and $r > 2$ a.u. and a barrier in between. The choice of χ influences the barrier height (the values for the barrier height are 4.9, 3.5, and 5.5 eV for this geometry, which do not necessarily give the dissociation path, i.e., the dissociation barrier is probably much lower). In Ref. 7, we compared the probability of molecular survival after the interaction with the Pd(111) surface (Y_{N_2}), obtained from experiment and simulation. Figure 5 shows the results for the three values of χ , always for azimuthal incidence along the $[1\bar{1}0]$ direction and a highly indexed direction rotated by 35° against the $[1\bar{1}0]$ direction. For one azimuthal direction, there are just very slight differences, i.e., χ seems to be of minor importance. In the following, we will arbitrarily use

FIG. 6. Simulated molecular survival probabilities of N₂ scattered off Pd(111). The legend always gives the vibrational, rotational, and surface temperature. Full symbols: incidence along $[1\bar{1}0]$ direction; open symbols: incidence 35° with regard to $[1\bar{1}0]$. For comparison, the experimental results from Ref. 7 are plotted, also.

FIG. 7. Simulated molecular survival probabilities of N₂ scattered off Pd(111). The legend always gives the vibrational, rotational, and surface temperature. Full symbols: incidence along $[1\bar{1}0]$ direction; open symbols: incidence 35° with regard to $[1\bar{1}0]$. Additionally, also data for a stepped surface is plotted. For comparison, the experimental results from Ref. 7 are shown, also.

FIG. 8. Experimental and simulated kinetic energy distributions of N₂⁺ (experiment) and N₂ (simulation) scattered off Pd(111). The energies are normalized to the maximum.

$\chi=0.05$ a.u. All the PES parameters are shown summarized in Table II.

III. RESULTS

For a detailed comparison between simulation and experiment, it is useful to leave the zero-temperature N₂-Pd(111) system with a perfect surface structure and simulate a more realistic system with finite vibrational, rotational, and surface temperatures. Figure 6 shows the resulting molecular survival probabilities Y_{N_2} for different combinations of these temperatures. As a reference, the results for the cold system are plotted. It turns out, that only the surface temperature has a noticeable influence on the interaction dynamics and lowers Y_{N_2} in the mid-energy range by 5%–10%.

On the other hand, the experimental data from Ref. 7 deals with ions produced in a plasma source, i.e., by electron impact ionization. Therefore, the vibrational excitation of the N₂ approaching the surface is much higher than the thermal value. Furthermore, the rotational temperature is probably given by the plasma temperature of about 600 K. In addition, a real surface is always stepped. The simulated molecular-survival probabilities for these cases can be found in Fig. 7; for the stepped surface, monoatomic steps and terrace sizes of 50×50 atoms are assumed, i.e., the surface is built up chessboardlike, with identical 50×50 cells, shifted by monoatomic steps with respect to the neighboring cells. Again, it is obvious that the main influence is due to the surface structure, i.e., the surface steps. Rotational and vibrational excitation are again negligible.

Unfortunately, the exact azimuthal angle of incidence for the experimental data is not known. The simulation results for the [1 $\bar{1}$ 0] direction and 35° with respect to [1 $\bar{1}$ 0] represent extreme cases. The experimental value may be assumed to be in between. It is obvious from Figs. 6 and 7, that the molecular survival probability is about twice as high in the simulation, compared to the experiment. Hence, about 50% of the dissociation may be directly due to elastic processes. Additional dissociation mechanism conceivable are the mentioned PES-hopping model, as well as enhancement of the collisional dissociation by inelastic energy losses.

The neglect of the surface inelastic processes aggravates the comparability of the kinetic-energy distributions of the scattered particles, obtained from experiment and simulation. That is why we normalize the experimental time-of-flight (TOF) spectra, on which the molecular survival probabilities from Ref. 7 are based, to the energy maximum, i.e., the TOF spectra are transferred to energy spectra and plotted relative to the energy, where the intensity peaks. Using this scaling, experimental and simulated spectra have the maximum at the same relative energy and are therefore comparable. A description of the experimental technique is given in Ref. 7, also. Figures 8(a)–(c) show the results for different primary energies. We note that different from the simulation, in the experiment, N₂⁺ was used as the primary particle but in Ref. 7 it was shown, that the influence of the initial charge state on the scattering dynamics is negligible.

The (dotted) experimental curves always consist of a broad distribution, which we attribute to the dissociated particles, and a sharp maximum on top due to the surviving

FIG. 9. Phase spaces of squared angular momentum and relative energy in the center of mass system of N₂ scattered off Pd(111). Left column: incidence along a highly indexed direction. Right column: incidence along the [110] direction. Note that dissociative as well as nondissociative events are plotted.

molecules. The energy distribution of the latter is given by the energy distribution of the primary particles modified only by inelastic energy losses due to the interaction with the surface. In the simulations presented in this work, we neglect the inelastic energy losses of the projectiles. An agreement between the kinetic energy distributions of the surviving molecules obtained from experiment and simulations therefore cannot be expected.

The energy distribution of the dissociation fragments is much broader and partly exceeds the primary energy. This distribution is dominated by the kinetic energy release in the molecules center of mass system that is linked to the energy in the laboratory frame by a Galilei transformation. Since the energy distributions of the dissociation fragments seem to be dominated by such elastical processes, a comparison of this distributions with the simulated data for the dissociative events is useful. The histograms represent the corresponding results from the simulation, assuming a stepped surface (ter-

FIG. 10. Lambert projection of the hemisphere of azimuthal (longitude) and polar (latitude) orientation of the molecular axis of surviving molecules for the same events as in Fig. 9. The azimuthal angle of incidence corresponds to 180°, the events at the pole correspond to molecular axis orientations parallel to the surface normal. Left column: incidence along a highly indexed direction. Right column: incidence along the [110] direction.

race size of 50×50 atoms) with $T=300$ K, rotational and vibrational temperatures of 600 K, and azimuthal incidence along a highly indexed direction. As explained above, only the distributions of the dissociated particles are shown.

For lower primary energies [Figs. 8(a) and 8(b)], the simulation fits very well to the part of the experimental spectrum, which is due to dissociated particles. For higher energies [Fig. 8(c)], slight differences are visible. On the other hand, the experimental distribution lost its symmetry which is probably due to channeling effects, i.e., the azimuthal direction in the experiment is not “perfectly” highly indexed. Therefore, the simulation (which is based on a highly indexed direction) cannot be in complete agreement with the experiment. The azimuthal angle of incidence influences the scattering dynamics more for higher primary energies, since the distances of closest approach to the surface is getting

FIG. 11. Mean distances of closest approach between molecule constituent and surface atom (full symbols) as well as mean distances of closest approach between molecule constituent and surface (open symbols) for scattering along the $[1\bar{1}0]$ direction (circles) and along a highly indexed direction (squares). The solid line indicates the distance of closest approach for N–Pd collisions of the corresponding perpendicular energy.

smaller, i.e., the surface becomes more corrugated. This is also in agreement with the simulated results for the molecular survival probabilities, where a sizeable difference appears for energies higher than 2.5 keV. To complete the picture, Fig. 8(d) shows the energy distribution of the surviving molecules for $E_0 = 2$ keV. As expected, the energetic width is

FIG. 12. Randomly chosen trajectories for N₂ scattering from Pd(111) in top (upper plot) and side perspective (lower plot). (a) for azimuthal incidence along the $[1\bar{1}0]$ direction; (b) for azimuthal incidence along a highly indexed direction. Note the different scaling of the axes.

rather small. In fact, the width corresponds to the dissociation energy of N₂ (0.3638 a.u.) and reflects the excitation spectrum of the molecule due to the interactions, with the surface.

In conclusion, the energetic distribution of the dissociated scattered particles at energies between 400 eV up to 5 keV can be fully explained in terms of elastic processes. The influence of inelastic processes is negligible. The kinetic energy distribution of the surviving molecules is much narrower and dominated by the transfer of translational energy to rovibrational excitation. Here, agreement with the experiment can be found also in so far that the energy distributions of the scattered particles consist of a broad structure due to the dissociation fragments and a narrow peak due to the surviving molecules.

IV. DISCUSSION

In Sec. III, we showed that elastic interactions are an important dissociation channel for the interaction of fast N₂ scattered off Pd(111). Therefore, it is worthwhile to investigate these interactions in more detail. To do so, we go back to the Pd(111)–N₂ system where all temperatures are set to zero and surface step defects are neglected.

The simulation results showed a strong dependence on the azimuthal angle of incidence hitherto. Figure 9 shows the phase spaces of squared angular momentum and relative energy in the center-of-mass system of the molecule for different primary energies and incidence along the $[1\bar{1}0]$ direction and a highly indexed direction.

Clearly, the interaction is dominated by different processes; the shape of the density of events depends on the azimuthal angle of incidence. For a given relative energy, the importance of the rotational excitation is much higher for incidence along the $[1\bar{1}0]$ direction. This effect is getting more pronounced with increasing primary energy. That is, elastically induced dissociation is mainly due to vibrational excitation for incidence along a highly indexed direction, whereas for low index directions, the rotational excitation is more important. With increasing primary energy, the distance of closest approach between N and Pd atoms is getting shorter. In other words, the surface atoms are getting smaller and the differences between azimuthal directions are increasing.

More insight into the excitation of the molecules is obtained from the analysis of the molecular axis orientation at time of impact. A (equal area) Lambert projection of the hemisphere of azimuthal (longitude) and polar (latitude) orientation of the molecular axis of surviving molecules for the same events as in Fig. 9 is shown in Fig. 10.

For azimuthal incidence along a highly indexed direction (left column), dissociation occurs only for rather small angles between molecular axis and surface normal. For parallel configurations, the molecule survives. No influence of the azimuthal orientation of the molecular axis is found.

For azimuthal incidence along the $[1\bar{1}0]$ direction (right column), the density of events changes dramatically. In contrast to the former data, a strong dependence on the azi-

FIG. 13. Angular distributions of N₂ scattered off Pd(111) (primary energies 2 and 5 keV) Left: for azimuthal incidence along the $[1\bar{1}0]$ direction; right: for azimuthal incidence along a highly indexed direction.

muthal orientation of the molecular axis is found. Only if molecules are oriented parallel to the surface and along the $[1\bar{1}0]$ channel, i.e., the beam direction, survival is probable. For all other configurations, dissociation is dominant. However, it has to be noted that the separation between the regimes is not very distinct.

The data from Figs. 9 and 10 indicates, that for incidence along highly indexed azimuthal directions, the molecule surface interaction is well described by the approximation of a planar surface which has been used previously (see e.g., Ref. 32).

Figure 11 shows the mean distances of closest approach between one N atom and a surface atom, as well as the mean distances of closest approach between molecule constituent and surface (negative values represent penetration through the plane determined by the first layer atoms). For the whole

energy range under investigation, both values are nearly identical for scattering along highly indexed azimuthal directions. This is in qualitative agreement with the model of a planar surface. Furthermore, the values are almost identical with the ones obtained from single collisions of Pd and N atoms of the respective perpendicular energy. Just for rather small primary energies there are differences, which are due to the many-body character of the PES used in the simulations. In conclusion, the interaction of the N₂ with the Pd(111) surface can be reduced to one collision of each molecule constituent with a surface atom, i.e., short interaction times can be assumed.

The results for the scattering along the $[1\bar{1}0]$ direction are more surprising. The strong rotational excitation (Fig. 9) as well as the dependence of the dissociation on the azimuthal orientation of the molecular axis (Fig. 10) implies a

more complicated interaction mechanism. Furthermore, the distances of closest approach to a surface atom and to the surface respectively are completely different (Fig. 11). The molecule constituents penetrate deep into the surface, but they stay far away from the single surface atoms. To reverse the perpendicular component of the projectile momentum, more than one collision is needed and the interaction times are longer. At the end of the collision sequence, a strong rotational excitation is found. In conclusion, the results indicate a channeling effect. The molecule constituents are scattered from the potential walls of the surface semichannels independently. The occurrence of such “zig-zag” trajectories fits to recent experimental data regarding H₂⁺ scattering from Pd(110).³³

Two randomly taken trajectories for the different azimuthal directions can be found in Fig. 12. The characteristics described above are obvious.

To complete the presented data, in Fig. 13 the angular distributions off all scattered particles are shown for azimuthal incidence along $[1\bar{1}0]$ and a highly indexed direction, respectively, both for an incident energy of 2 and 5 keV. For the $[110]$ direction, the characteristic channeling patterns are observed, for the highly indexed direction, an almost spherical distribution is found. Furthermore, the appearance of surface penetration can be seen. It has to be noted, that the angular distributions for scattering angles exceeding 90° is unphysical, since the trajectories are tracked for a finite time only, i.e., the simulated detector is placed very near to the scattering center.

V. SUMMARY

The scattering of N₂ molecules at energies between 400 eV and 5 keV from Pd(111) surfaces under grazing incidence is strongly influenced by elastical processes. For incidence along highly indexed directions, the most important elastical mechanism is the vibrational excitation. In that case, the surface acts like a plane one. For low indexed azimuthal directions, the elastical interaction dynamics are completely different. The projectiles penetrate deep into the surface, guided by the surface semi channels. Mainly rotational excitation occurs.

Nevertheless, it has to be noted that whereas some characteristics of the experimental data (kinetic energy distributions, slope of the molecular survival probabilities as a function of the primary energy) can be explained in terms of elastical projectile-surface interactions, others (quantity of molecular survival for a given primary energy) cannot. Electronical processes are probably of importance, also. But even for the electronical processes, a detailed knowledge of the elastical interaction is useful, e.g., the mean trajectory length, or the interaction time, is much larger for the $[1\bar{1}0]$ direction than for the highly indexed case. This indicates higher inelastic energy losses which may explain some differences between the presented simulational results and experiment data and is a motivation for further studies.

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