Research Report
Interaction of molecules with surfaces from first principles

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I. OVERVIEW

In September 1998, I moved from the Fritz-Haber-Institut, Berlin, to the Technical University of Munich and started to build up a new research group. While my research in Berlin together with Matthias Scheffler had been mainly focused on the interaction dynamics of hydrogen with metal and semiconductor surfaces (see the research report in the *Gas-Surface News* No. 22, August 1998), the scope of my research interests has since then broadened. Still the theoretical description of gas-surface dynamics represents an important aspect of my work. In addition, we are performing density functional theory studies of the interaction of molecules with complex structured surfaces. These studies are meant to overcome the materials and structure gap between surface science and, e.g., heterogeneous catalysis. The team doing basically the research work consists of six Ph.D. students at the moment. Applications to join our reearch group are always welcome, however, the acceptance might also depend on the positions available.

II. GAS-SURFACE DYNAMICS

The adsorption and desorption dynamics of hydrogen molecules at frozen metal substrates can nowadays be routinely treated within six-dimensional quantum dynamical studies that take all hydrogen degrees of freedom into account [1–3]. We have continued these studies by addressing the dissociation of H_2 on the $(2{\times}2)$ sulfur-covered Pd(100) surface [4–6]. These studies have confirmed the importance of taking the multidimensionality of the adsorption process fully into account. Furthermore, we have addressed the quantum effects in the H_2 dissciation dynamics by comparing classical and quantum dynamics on exactly the same potential energy surfaces [5, 7]. We find that tunneling does not significantly influence the dynamics in the classically allowed energy regime, however, zero-point and quantization effects are often non-negligible.

In a recent five-dimensional quantum study, we have investigated the rotational effects in the adsorption/desorption dynamics of H_2 and D_2 on Pd(100) [8]. In particular, we have focused on the experimentally observed non-monotonous behavior of the rotational alignment in desorption as a function of the rotational quantum number [9, 10]. The experimental results are well-
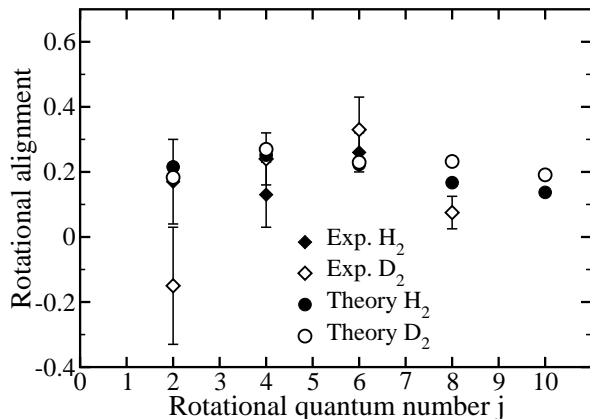

FIG. 1: Comparison of the rotational alignment of H_2 and D_2 molecules desorbing from Pd(100) at a surface temperature $T = 700K$ derived from five-dimensional quantum calculations (circles) with the experimental results [9, 10] (diamonds). Filled symbols: H_2, open symbols: D_2 (from [8]).

reproduced in our calculations (see Fig 1). We have additionally performed quantum dynamical studies with the hydrogen bond length artificially kept fixed at its gas-phase value. Thus we were able to show that the non-monotonous behavior is caused by the change of the hydrogen bond length upon adsorption and desorption. For low rotational quantum numbers, rotational hindering suppresses adsorption and desorption probabilities. For higher rotational quantum numbers, the change in bond length along the reaction path leads to a decrease in the adiabatic rotational quantum energy which causes an effective energy transfer from rotation to translation. This effect which had already been described earlier [11] increases the reaction probabilities and decreases the difference between the reaction probabilities of so-called helicopter and cartwheel molecules leading to a smaller rotational alignment.

If the interaction of molecules heavier than H_2 or D_2 with metal surfaces should be addressed, then the energy transfer to the substrate has to be taken into account in any realistic description. Even more importantly, the energy transfer to the substrate is a necessary ingredient in the modeling of the trapping into molecular adsorption states since no molecule would become permanently trapped without any energy dissipation. Recently, we have been studying the adsorption of $O_2/Pt(111)$. O_2 can in fact adsorb both molecularly and dissociatively
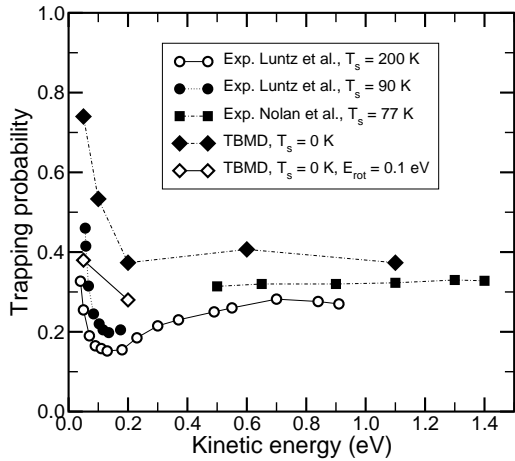
FIG. 2: Trapping probability of O_2/Pt(111) as a function of the kinetic energy for normal incidence. Results of molecular beam experiments for surface temperatures of 90 K and 200 K (Luntz *et al.* [13]) and 77 K (Nolan *et al.* [14]) are compared to tight-binding molecular dynamics simulations for the surface initially at rest (surface temperature $T_s = 0$ K).

on Pt(111). This system is of great technological relevance since it represents, e.g., one of the fundamental microscopic reaction steps occuring in the car-exhaust catalyst. However, although this system is well-studied, the microscopic reaction steps occuring in the adsorption process had not been identified in detail yet.

The realistic modeling of the adsorption of O_2/Pt(111) represents a great challenge. First, an accurate potential energy surface is needed that reliably describes both the molecular as well as the dissociative adsorption channels. Secondly, energy transfer to the substrate has to be treated properly by including recoil processes in the first layers of the substrate in order to simulate molecular trapping processes. Since a high-dimensional quantum treatment of O_2 trapping is not possible at the moment, a classical molecular dynamics scheme has to be employed. From our experience with hydrogen systems we conclude that quantum effects should anyway not play a big role in the oxygen adsorption. However, while direct *ab initio* molecular dynamics simulations are too time consuming to calculate a sufficient number of trajectories [12], empirical classical potentials are in general not flexible and accurate enough to describe the bond-making and breaking process on moving substrates.

As a compromise, we have performed tight-binding molecular dynamics (TBMD) simulations [15] of the adsorption of O_2/Pt(111) using the NRL tight binding (TB) method [16, 17] with all TB parameters derived from ab initio electronic structure calculations [16, 18]. The calculated sticking probabilities of O_2/Pt(111) as a function of the kinetic energy for normal incidence are compared to molecular beam experiments [13, 14] in Fig. 2. The calculated sticking probabilities are systematically larger than the measured ones which we mainly attribute to the overbinding present in the used DFT-GGA func-

tional [18]. Still, the decrease of the sticking probability at lower kinetic energies and its subsequent saturation are well-reproduced by the TBMD calculations.

The strong initial decrease of the O_2/Pt(111) sticking probability has been attributed to the trapping of O_2 into a physisorption state [19] while at higher energies the molecules were assumed to directly access the chemisorbed molecular states [13, 14, 19]. In contrast, our study establishes that the sticking probability over the whole energy range can be understood in terms of trapping into chemisorption states. An analysis of the trajectories reveals that at kinetic energies below 0.2 eV all molecules reaching the molecular precursor well get trapped. Thus it is *not* the energy transfer to the substrate *per se* that determines the sticking probability at low kinetic energies but rather the probability to enter the attractive adsorption channels. Although the majority of adsorption pathways is blocked by barriers, at low kinetic energies most of the incoming molecules with unfavorable initial conditions are redirected towards attractive adsorption paths. Thus it is *steering mechanism* as in the system H_2/Pd(100) that is responsible for the high sticking probability at low kinetic energies.

This is confirmed by the observed rotational effects on the adsorption dynamics. The steering mechanism is not only strongly suppressed at higher kinetic energies but also by additional rotational motion. Indeed, we obtain a significant rotational hindering [11], i.e., a strong reduction in the sticking probability, at $E_i = 0.05$ eV for molecules initially rotating with a rotational energy of $E_{rot} = 0.1$ eV, as Fig. 2 shows. A rotational energy of $E_{rot} = 0.1$ eV also causes rotational hindering at $E_i = 0.2$ eV. The assumption of such an initial rotational population of the O_2 molecules in the molecular beam experiments at this kinetic energy is reasonable. Thus the discrepancy between theory and experiment can partially be accounted for.

At higher energies, the leveling off of the measured sticking probability at higher energy is reproduced by the calculations. To the best of our knowledge, such a behavior has not been obtained before in molecular dynamics simulation which usually yield a monotonously decreasing sticking probability for molecular trapping processes. The underlying mechanism is intimately related to the corrugation and anisotropy of the PES. At such high energies, even molecules with unfavorable initial conditions can get close to the surface. Still there is a negligible probability that in the first collision the high energy particles will transfer enough energy to the surface to remain trapped. However, it is important to note that the impinging molecules also transfer energy into internal molecular degrees of freedom such as rotation and vibration and into lateral motion along the surface. This energy is then not available for a direct escape from the adsorption well. If enough of the initial perpendicular kinetic energy is transferred in the first collision into these other degrees of freedom, the molecule becomes dynamically trapped for a while [20, 21]. While being trapped,
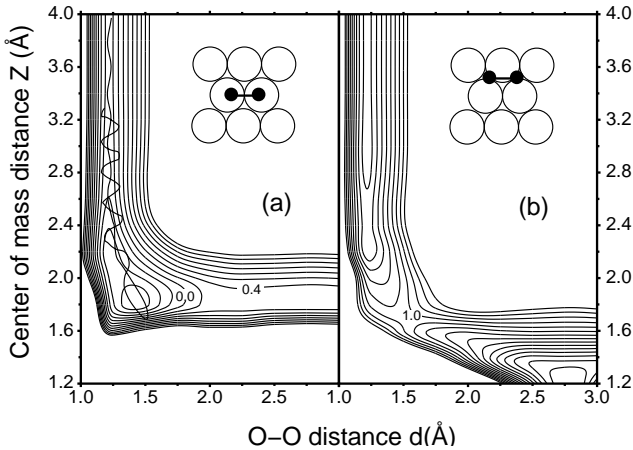
FIG. 3: Potential energy surface of the dissociation of O_2/Pt(111) determined by the *ab initio* derived tight-binding Hamiltonian. The coordinates in the figure are the O_2 center-of-mass distance from the surface Z and the O-O interatomic distance d. The configurations of the remaining O_2 degrees of freedom are illustrated in the insets. The contour spacing is 0.2 eV per O_2 molecule. In (a) a trajectory of an O_2 molecule with an initial kinetic energy of 0.6 eV scattered at Pt(111) is also plotted.

the molecule hits the surface several times and transfers successively more and more energy to the substrate until it equilibrates.

Finally, the TBMD simulations have also given an explanation of the surprising experimental result that at surface temperatures below 100 K O_2 molecules impinging on Pt(111) do not dissociate, even at kinetic energies up to 1.4 eV which are much greater than the dissociation barrier [14, 19]. In fact, no single dissociation event was observed in the molecular dynamics simulations, irrespective of the initial energy. There is a rather simple explanation in terms of the topology of the underlying PES.

Two cuts through the TB potential energy surface of O_2/Pt(111), so-called elbow plots, are plotted in Fig. 3. They show the PES as a function of the distance Z of the O_2 center of mass from the surface and the O-O distance d while the lateral center of mass degrees of freedom, the molecular orientation and the substrate atoms are kept fixed. While panel (a) corresponds to the superoxo molecular precursor state located above the bridge site which can be accessed along a non-activated path from the gas phase, panel (b) demonstrates the large corrugation of the O_2/Pt(111) PES. Although the molecule is only shifted by about 1 Å in lateral direction compared to panel (a), the nature of the interaction is changed from attraction towards the molecular precursor to strong repulsion with a barrier towards dissociation of almost 1 eV.

Dissociation corresponds to an event in which the molecules enter the exit channel towards the lower right

corner of the figures. However, there is a rather narrow curve connecting the entrance and exit channels through the molecular chemisorption states in panel (a). The molecules that enter the chemisorption well become accelerated towards the surface. This makes the molecules so fast that they "do not make it around the corner" into the dissociation channel. This is illustrated by the projection of a trajectory with $E_{\mathrm{kin}} = 0.6$ eV onto the Zd plane in Fig. 3a. The kinetic energy is much larger than the dissociation barrier. Still the molecule does not dissociate. Due to the acceleration by the attractive potential it hits the repulsive wall of the potential almost straight ahead and is reflected back. This means that direct dissociation of O_2 is sterically hindered at the Pt(111) surface; dissociative adsorption of O_2/Pt(111) is rather a two-step process. First the molecule is trapped molecularly in the chemisorption well where it equilibrates. At sufficiently high surface temperatures dissociation will then be induced by thermal fluctuations which make the O_2 molecules enter the dissociation channel.

Concluding the section about the O_2/Pt(111) adsorption, I would like to stress that the presented results can only be obtained and understood if the multidimensionality of the adsorption process is appropriately taken into account. However, in all dynamical simulations presented so far it has been assumed that the electrons stay in their ground state throughout the whole process, i.e., the simulations have been based on the Born-Oppenheimer approximation. Still, at metal surfaces with their continuous spectrum of electronic states at the Fermi energy electron-hole (e-h) pair excitations with arbitrarily small energies are possible. Just recently, experiments determining the so-called chemicurrent [22] have provided some information on the importance of electron-hole pair excitation in adsorption processes. Unfortunately, the incorporation of electronically adiabatic effects in the dynamical simulation of the interaction dynamics of molecules with surfaces is rather difficult. There have been first successful attempts to model the chemicurrent upon adsorption [23], though.

We have been trying to contribute to the understanding of electronically noanadiabatic effects in the interaction of molecules with surfaces. Based on the notion that quantum effects in the dynamics of the nuclei are usually small, we have implemented a mixed quantum-classical surface-hopping scheme based on Tully's fewest switches algorithm. In this approach, the dynamics of the electrons are treated quantum mechanically while the nuclear motion is treated classically [24, 25]. Still, the feedback between quantum and classical degrees of freedom is taken into account self-consistently.

Using this surface hopping scheme, we have addressed the ionization probability in I_2/diamond scattering [24, 25]. The interaction of I_2 with the diamond surface had been modeled by a potential energy surface that has been adjusted to the few experimental data known for this system. In addition to the molecular center of mass we have included one surface oscillator coordinate, the molecu-

lar rotation and vibration. Taking these degrees of freedom into account, we were able to reproduce the observed trend of the ionization probability as a function of the incident kinetic energy of the molecules as well as the measured dissociation probability. According to our model calculations the dependence of the ionization probability on the kinetic energy is not determined by the electronic coupling *per se*, but by the energy transfer to other degrees of freedom during the scattering process. This suppresses the ionization probability because less molecules have sufficient energy to overcome the ionization threshold, in particular at energies close to this threshold. We are currently applying the mixed quantum-classical scheme to the description of the laser-induced desorption of NO.

III. INTERACTION OF MOLECULES WITH STRUCTURED SURFACES

In recent years, DFT calculations have become an indespensable tool in order to study the interaction of molecules with surfaces [26]. Although there are still limitations in the reliablity of DFT results for certain systems, in general DFT studies are very valuable for the elucidation of microscopic details and for establishing chemical trends. Because of more efficient algorithms and the ever-increasing computer power, first-principles electronic structure calculations are no longer limited to the study of simple molecules at low-index surfaces; instead, more and more complex systems can be addressed. For example, the so-called pressure, structure and materials gaps between surface science and heterogeneous catalysis are not only attacked by experimentalists, but also by theorists using electronic structure theory.

In spite of the fact that DFT codes are nowadays routinely applied to surface science problems by many groups, there is still are growing demand for *good* DFT studies. Based on a very fruitful collaboration with G. Kresse and J. Hafner from the University of Vienna, we are employing the VASP code in order to understand the interaction of molecules with structured surfaces such as stepped, precovered or bimetallic surfaces. In a collaboration with the group of Klaus Christmann at the FU Berlin we have studied the adsorption of hydrogen on Pd(210) [27, 28]. Usually hydrogen adsorbs dissociatively on metal surfaces. On Pd(210), the experimentalists had found the coexistence of adsorbed atomic and molecular hydrogen species but had no clue about the microscopic nature of the adsorption states. Our DFT calculations established that on the clean Pd(210) surface H_2 still dissociates spontaneously. Up to three hydrogen atoms can be adsorbed per (210) surface unit cell corresponding to a coverage of $\theta = 3$. However, for a coverage of $\theta = 1$, the dissociative adsorption of further H_2 molecules becomes activated. Still the attractive interaction of the H_2 molecule with the Pd atoms at the kinked steps of the (210) surface is hardly influenced by the presence of the

hydrogen atoms on the surfaces. Thus molecular adsorption wells for the H_2 molecules are created. This means that the molecular adsorption state (see Fig. 4) becomes stabilized by the presence of hydrogen atoms.

As the first part of an ongoing research project about the methanol oxidation on Cu/ZnO catalysts we have studied the dissociative adsorption of H_2 on strained copper surface [29]. This study was motivated by the observation that the methanol oxidation rate could be related to the strain present in small catalytically active Cu crystallites. On all studied Cu surfaces we have found an upshift of the surface d-band center upon lattice expansion. According to the d band model [30] this upshift should be associated with a higher reactivity. Still there is no general trend in the hydrogen adsorption energies at the high-symmetry sites and the dissociation barrier heights as a function of lattice strain. It turns out that the d-band model is no longer fully appropriate in the case of a strong coupling between adsorbate and substrate; in that case the adsorbate-induced change of the Cu local d-band density of states has to be taken into account in order to rationalize the results.

We have found similar results for the strain effects in hydrogen adsorption on compressed Pd surfaces [31]. These calculations were part of the investigation of atomic hydrogen and CO adsorption energies on bimetallic Pd_n/Au overlayer systems with the number n of overlayers ranging from 1 to 3. Bimetallic surfaces are of strong current interest since they offer the possibility to tailor the surface reactivity by preparing specific surface compositions and structures. The system Pd/Au is of particular interest in the field of electrocatalysis because of its catalytic activities in the oxidation reactions of methanol, formic acid and carbon monoxide. At the same time, it is a prototype system for the study of the reactivity of strained overlayers.

In Fig. 5, the calculated hydrogen and CO adsorption energies as a function of the Pd/Au(111) overlayers are
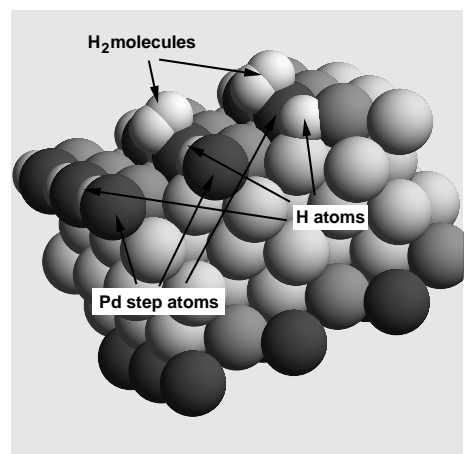

FIG. 4: Side view of the Pd(210) surface with a monolayer H precoverage and the molecular H_2 adsorption state [27].
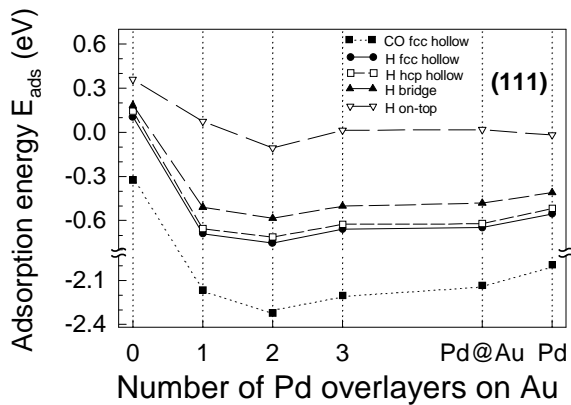
FIG. 5: CO and hydrogen adsorption energies as a function of the number of Pd overlayers on Au for different adsorption sites on the (111) at a coverage of $\theta = 0.25$. The pure Pd substrates with the lateral lattice constant of Au ($a = 4.18$ Å) and Pd ($a = 3.96$ Å) are labeled by Pd@Au and Pd, respectively.

plotted. In addition, the results for a pure Pd(111) substrate with the Pd and the Au lattice constant, respectively, are included in order to disentangle substrate interaction from strain effects for the pseudomorphic overlayers. In general, we find that both the lattice expansion of the pseudomorphic Pd films by 5% as well as the interaction of the Pd films with the Au substrate lead to a

higher reactivity of the overlayers. This can be rationalized within the d-band model. Still, the indirect interaction of the adsorbates with the inert Au substrate on one Pd overlayer reduces the binding energies and leads to a maximum in the binding energies for two Pd overlayers on Au on all adsorption sites that we considered.

On the basis of our findings we thus propose that depositing a reactive metal on an inert metal with a larger lattice constant should in general lead to a higher reactivity of the overlayer since both substrate interaction and strain effects increase the reactivity. Exactly the opposite trend we expect for an overlayer of a less reactive metal deposited on a more reactive metal with a smaller lattice constant, such as, e.g., Pt on Ru. This has in fact been verified in both experiment and theory [32]. We are now extending these studies to the investigation of the reactivity of small Pd clusters supported by Au(111).

Further research projects in our group deal with such diverse topics as the adsorbate-induced work function change of tungsten in order to build better cathode discharge lamps or the adsorption of small amino acids on graphite surfaces. However, all projects can be regarded as being part of a joint research effort for the reliable description and analysis of the energetics, kinetics and dynamics of the interaction of molecules with complex surfaces. The knowledge gained so far in theoretical surface science on the route to this ambitious goal has been summarized in a recent text book [33].

[1] A. Groß, Surf. Sci. Rep. **32**, 291 (1998).
[2] A. Eichler, J. Hafner, A. Groß, and M. Scheffler, Phys. Rev. B **59**, 13297 (1999).
[3] A. Eichler, J. Hafner, A. Groß, and M. Scheffler, Chem. Phys. Lett. **311**, 1 (1999).
[4] M. Rutkowski, D. Wetzig, H. Zacharias, and A. Groß, Phys. Rev. B **66**, 115405 (2002).
[5] A. Groß and M. Scheffler, Phys. Rev. B **61**, 8425 (2000).
[6] A. Groß, C.-M. Wei, and M. Scheffler, Surf. Sci. **416**, L1095 (1998).
[7] A. Groß, J. Chem. Phys. **110**, 8696 (1999).
[8] A. Dianat and A. Groß, Phys. Chem. Chem. Phys. **4**, 4126 (2002).
[9] D. Wetzig, R. Dopheide, M. Rutkowski, R. David, and H. Zacharias, Phys. Rev. Lett. **76**, 463 (1996).
[10] D. Wetzig, M. Rutkowski, R. Etterich, W. David, and H. Zacharias, Surf. Sci. **402**, 232 (1998).
[11] G. R. Darling and S. Holloway, J. Chem. Phys. **101**, 3268 (1994).
[12] A. Groß, M. Bockstedte, and M. Scheffler, Phys. Rev. Lett. **79**, 701 (1997).
[13] A. C. Luntz, M. D. Williams, and D. S. Bethune, J. Chem. Phys. **89**, 4381 (1988).
[14] P. D. Nolan, B. R. Lutz, P. L. Tanaka, J. E. Davis, and C. B. Mullins, J. Chem. Phys. **111**, 3696 (1999).
[15] A. Groß, A. Eichler, J. Hafner, M. J. Mehl, and D. A. Papaconstantopoulos, submitted.
[16] M. J. Mehl and D. A. Papaconstantopoulos, Phys. Rev. B **54**, 4519 (1996).

[17] A. Groß, M. Scheffler, M. J. Mehl, and D. A. Papaconstantopoulos, Phys. Rev. Lett. **82**, 1209 (1999).
[18] A. Eichler and J. Hafner, Phys. Rev. Lett. **79**, 4481 (1997).
[19] C. T. Rettner and C. B. Mullins, J. Chem. Phys. **94**, 1626 (1991).
[20] A. Groß and M. Scheffler, J. Vac. Sci. Technol. A **15**, 1624 (1997).
[21] C. Crespos, H. F. Busnengo, W. Dong, and A. Salin, J. Chem. Phys. **114**, 10954 (2001).
[22] H. Nienhaus, Surf. Sci. Rep. **45**, 1 (2002).
[23] J. R. Trail, M. C. Graham, D. M. Bird, M. Persson, and S. Holloway, Phys. Rev. Lett. **88**, 166802 (2002).
[24] C. Bach and A. Groß, J. Chem. Phys. **114**, 6396 (2001).
[25] C. Bach and A. Groß, Faraday Diss. **117**, 99 (2000).
[26] A. Groß, Surf. Sci. **500**, 347 (2002).
[27] M. Lischka and A. Groß, Phys. Rev. B **65**, 075420 (2002).
[28] P. K. Schmidt, K. Christmann, G. Kresse, J. Hafner, M. Lischka, and A. Groß, Phys. Rev. Lett. **87**, 096103 (2001).
[29] S. Sakong and A. Groß, Surf. Sci. **525**, 107 (2003).
[30] B. Hammer and J. K. Nørskov, Surf. Sci. **343**, 211 (1995).
[31] A. Roudgar and A. Groß, Phys. Rev. B **67**, 033409 (2003).
[32] A. Schlapka, M. Lischka, A. Groß, and P. Jakob, submitted.
[33] A. Groß, *Theoretical surface science – A microscopic perspective* (Springer, Berlin, 2002).