Ab initio molecular dynamics simulations of the adsorption of H_2 on palladium surfaces

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The interaction of hydrogen molecules with clean and hydrogen-precovered surfaces has been studied using ab initio molecular dynamics simulations based on density functional theory. In particular, the dependence of the dissociative adsorption probability on the hydrogen coverage and the relaxation of hot hydrogen atoms after dissociation have been addressed. The simulations unravel the crucial role of the substrate degrees of freedom in the dissociative adsorption process.

1 Introduction

The interaction of hydrogen with metal surfaces has been one of the benchmark system for the understanding of gas-surface dynamics[1,2]. This is due to the fact that this system is well-suited for both experimental as well as theoretical studies. Furthermore, the hydrogen adsorption on metal surfaces is also relevant from a technological point of view, in particular in the context of hydrogen storage, but also with respect to hydrogenation reaction in heterogeneous catalysis.

Because of the light mass of hydrogen, the dynamics of H_2 adsorption on low-index metal surfaces has mainly been studied using a quantum mechanical treatment on parameterized potential energy surfaces derived from density functional theory (DFT) calculations[3,4]. In these calculations, all six degrees of freedom of the H_2 molecule were explicitly considered, the substrate degrees of freedom, however, were kept frozen since otherwise the calculations would have been computationally much too expensive. This was justified by the large mass mismatch between hydrogen and metal atoms. In addition, comparisons between six-dimensional quantum and classical calculations showed that the role of quantum effects in the hydrogen adsorption dynamics on surfaces is limited[5,6].

If more than six degrees of freedom are involved, quantum dynamical calculations are computationally prohibitive. Furthermore, the parameterization of such high-dimensional potential energy surfaces becomes quite cumbersome. *Ab initio* molecular dynamics (AIMD) simulations of the adsorption dynamics represent an alternative approach. In these simulations, the forces necessary to integrate the equations of motion are determined "on the fly" by first-principles calculations. This does not require any parameterization of the potential energy surfaces. However, up to recently AIMD simulations were restricted to a small number of trajectories because of their high computational effort[7,8].

Previously, we had studied the adsorption and scattering of O_2/Pt(111) using *ab initio* derived tight-binding molecular dynamics (TBMD) simulations[9–11]. This method is about three orders of magnitude faster than AIMD simulations, and it needs relatively little input from *ab initio* total-energy calculations since the tight-binding Hamiltonian already takes the quantum nature of bonding into account[9]. However, the TBMD method still involves a fitting procedure which introduces a source of possible errors; this is in particular true if more than two different elements are included in the simulations.

Fortunately, due to the increase in computer power and the development of more efficient algorithms it has now become possible to determine a statistically meaningful number of AIMD trajectories[12]. In this contribution, this will be demonstrated using the H_2 adsorption on precovered Pd surfaces and the relaxation of the hydrogen atoms after the dissociation on clean surfaces as examples.

2 Theoretical Methods

Periodic DFT calculations were performed within the generalized gradient approximation (GGA)[13,14] for the exchange-correlation functional using the VASP code[15]. The atomic cores were represented by ultrasoft pseudopotentials[16] allowing a small cutoff energy of 200 eV in the expansion of the one-electron valence states in plane waves. The surface was modeled by slabs of three to five layers for the (100) surface and five layers for the (111) surface. The uppermost layers were allowed to move in the simulations in order to enable recoil and energy transfer processes at the surface.

Adsorption probabilities were determined by averaging over at least 200 trajectories with random initial lateral configurations and molecular orientations for one particular kinetic energy. This leads to a statistical error of $\sqrt{s(1-s)}/\sqrt{200} \leq 0.035$, where s is the adsorption probability. All the substrate atoms were initially at rest, i.e., the initial surface temperature corresponded to 0 K. The MD simulations were performed using the Verlet algorithm with a time step of 1 fs within the microcanonical ensemble. The parallel version of the VASP code was written using a message-passing programming model relying on the MPI library to deal with communications.

3 Hydrogen Dissociation on Hydrogen-Precovered Pd Surfaces

In a recent STM study addressing the formation of ordered hydrogen layers on Pd(111), it was found that hydrogen molecules impinging on an almost complete hydrogen overlayer did not adsorb dissociatively in hydrogen dimer vacancies[17,18]. Instead, aggregates of three or more vacancies were required for the dissociation of H_2. As a consequence, it was speculated that the accepted notion that two empty sites are needed for the dissociative adsorption of diatomic molecules might not be correct[17,19]. However, a subsequent DFT study demonstrated that the dissociative adsorption of H_2 in a hydrogen dimer vacancy is still exothermic[20]. Nevertheless, because of repulsive interactions the presence of the hydrogen overlayer leads to the formation of small energetic barriers. Thus the dissociative adsorption of H_2 on hydrogen-precovered Pd(111) is no longer spontaneous but becomes an activated process by the so-called poisoning effect of the hydrogen overlayer.

Still, the H_2 adsorption process requires the dissipation of more than 1 eV[20]. It has been proposed that the energy transfer to substrate phonons or electron hole-pair excitations could be suppressed due to surface stiffening or the modification of the electronic band structure, respectively, caused by the hydrogen overlayer[21]. The magnitude of these effects, however, could not be assessed so far. Therefore we have addressed the dynamics of the H_2 dissociative adsorption on hydrogen-precovered Pd surfaces by performing AIMD simulations.

In a first step, we used a small initial kinetic energy of 0.02 eV as in the STM experiments. And indeed, we did not find any single adsorption event in a hydrogen dimer

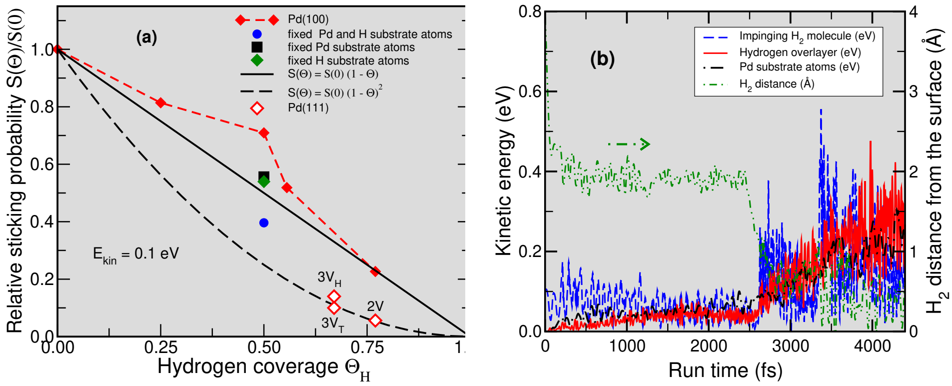

Figure 1. Dissociative adsorption of hydrogen on hydrogen-covered Pd(100) and Pd(111). a) Calculated sticking probability as a function of hydrogen coverage θ_{H} for an initial kinetic energy of 0.1 eV. 2V, $3\mathrm{V}_{\mathrm{H}}$ and $3\mathrm{V}_{\mathrm{T}}$ denote the dimer vacancy and the trimer vacancy centered around a Pd hollow and a Pd top site, respectively. b) Energy redistribution and H_2 center of mass distance from the surface along a particular trajectory for $\theta_{\mathrm{H}} = 5/9$.

vacancy (2V) on Pd(111) within a (3×3) surface geometry, thus confirming the experiment[17] and providing an explanation for the experimental findings: At the low temperatures of 70 K used in the experiment[17] the impinging H_2 molecules had too little kinetic energy to cross the dissociation barrier.

At higher kinetic energies, however, H_2 molecules can adsorb dissociatively in a dimer vacancy on hydrogen-covered Pd(111). This is shown in Fig. 1a where the sticking probabilities for both Pd(111) and Pd(100) are plotted as a function of the hydrogen coverage normalized to the value at the corresponding clean Pd surfaces for an kinetic energy of 0.1 eV. On Pd(111), a small, but non-vanishing relative adsorption probability of 0.05 is found in the dimer vacancy (2V). At the trimer vacancies on Pd(111) centered either around a hollow site ($3\mathrm{V}_{\mathrm{H}}$) or a Pd top site ($3\mathrm{V}_{\mathrm{T}}$), the adsorption probability is at least twice as large as on the dimer vacancy (2V). Since the area of the trimer vacancy is only larger by 50% compared to the dimer vacancy, this indicates that it is not only the area of the vacancies that determines the adsorption probability.

In Fig. 1a, two curves corresponding to $S(\Theta_{\mathrm{H}}) = S(0)(1 - \Theta_{\mathrm{H}})$ and $S(\Theta_{\mathrm{H}}) = S(0)(1 - \Theta_{\mathrm{H}})^2$ are included which would correspond to the sticking probability if it was determined by pure site-blocking requiring one or two empty sites, respectively. At low and intermediate coverages, the sticking probability of H_2 at Pd(100) is significantly larger than predicted from a simple site-blocking picture, in particular for $\Theta_{\mathrm{H}} = 0.5$. Running additional AIMD trajectories with the substrate kept fixed reveals that it is the energy transfer from the impinging H_2 molecule to the substrate and the rearrangement of the substrate atoms that lead to this enhanced sticking probability compared to pure site blocking[12]. These effects overcompensate the poisoning of the H_2 dissociation caused by the presence of the hydrogen overlayer atoms.

A rather surprising result is, however, that both the motion of the hydrogen atoms and the Pd atoms contribute to the high sticking probability at the precovered surfaces, as the simulations with only fixed Pd atoms and with only fixed hydrogen overlayer atoms show (see the results in Fig. 1a for $\theta_{\mathrm{H}} = 1/2$). Not only energy transfer processes alone but also

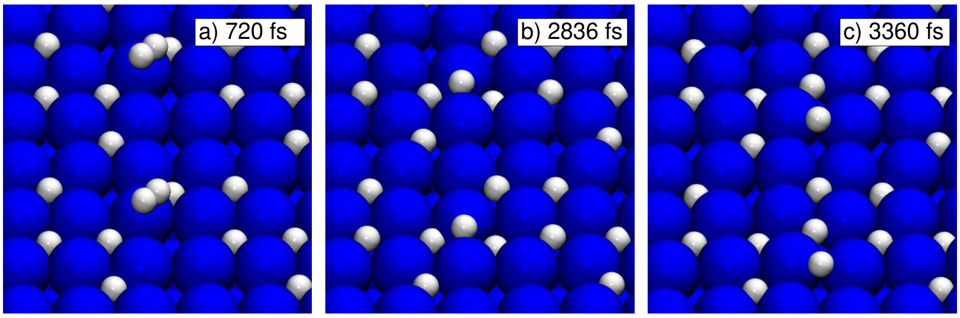

Figure 2. Snapshots of the AIMD trajectory of H_2 impinging on hydrogen-precovered Pd(100) whose energy distribution is plotted in Fig. 1b. The initial hydrogen coverage is $\theta_{\rm H} = 5/9$ within a (3×3) surface periodicity, i.e., there are four hydrogen vacancies in the surface unit cell.

substrate recoil and relaxation effects in the highly corrugated potential energy surface enhance the sticking probability of H_2 molecules, as a detailed analysis of the adsorption dynamics indicates.

Details of the energy transfer along a particular trajectory for an initial hydrogen coverage of $\theta_{\rm H} = 5/9$ are presented in Fig. 1b, and three snapshots along this trajectory within the (3×3) periodicity are presented in Fig. 2. This specific example furthermore demonstrates that AIMD simulations do not only yield statistically reliable reaction probabilities, but also allow for valuable microscopic insights into the dissociative adsorption dynamics. At the hydrogen-covered Pd(100) surface, the impinging H_2 molecules do not necessarily either immediately dissociate or scatter back into the gas phase. In fact, there exists a weakly bound molecular precursor state above the top sites which becomes stabilized due to the poisoning effects of the pre-adsorbed hydrogen atoms, very similar to the one already identified at the hydrogen-covered stepped Pd(210) surface[22, 23]. This state has not been identified experimentally yet, however, it should be detectable at low surface temperatures by, e.g., isotope exchange experiments since it is bound by 0.1 eV. In the case of the particular trajectory considered in Fig. 1b, after impinging on the surface the H_2 molecule becomes first trapped for more than 2 ps in the molecular precursor state about 2 Å above a Pd atom (Fig. 2a).

At about 2.5 ps, one of the two hydrogen atoms enters the four-fold atomic adsorption site which is associated with an energy gain of about 0.5 eV. This energy is first taken up by the corresponding hydrogen atom but is then rapidly transfered to both the hydrogen overlayer *and* the Pd substrate atoms. The other hydrogen atom remains at a bridge site configuration where is stays for about 0.8 ps (Fig. 2b). The additional bridge-site hydrogen atom can actually move in an exchange mechanism[24] which is what happens after 3.3 ps: the bridge-site hydrogen atom replaces one of the adsorbed hydrogen atoms at an adjacent four-fold hollow sites which is then pushed up to an adjacent empty four-fold hollow site so that eventually all hydrogen atoms end up in the most favorable adsorption sites. However, the replaced hydrogen atom can also end up in another bridge-site configuration which corresponds to an exchange-diffusion of this hydrogen species.

Recently, there has been a renewed interest in the hydrogen absorption in metals[25] in the context of the hydrogen technology. It is important to realize that hydrogen storage

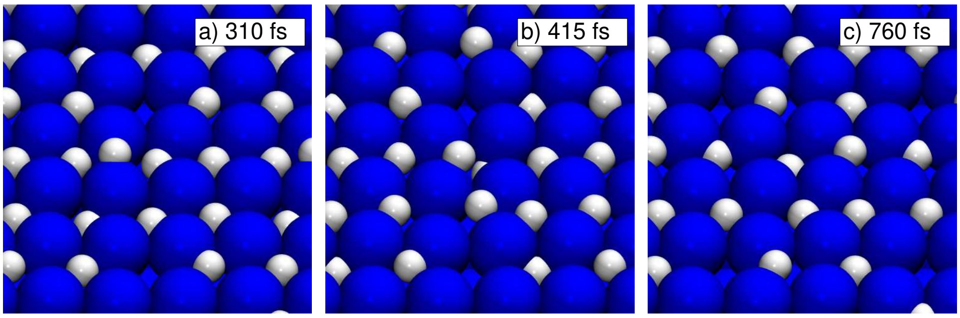

Figure 3. Snapshots of a AIMD trajectory of H_2 impinging on hydrogen-precovered Pd(100) with a kinetic energy of 1.0 eV. Initially, there is a hydrogen dimer vacancy, i.e., the coverage is $\theta_{\rm H} = 7/9$ within the (3×3) surface periodicity.

still remains a problem[26]. Experiments showed that on Pd hydrogen first adsorbs *on* the surface before bulk absorption starts[27]. DFT calculations have confirmed this picture by showing that hydrogen subsurface absorption is energetically less favorable than adsorption on the surface[23]; furthermore, the penetration into the Pd bulk is hindered by a barrier of considerable height[25].

In the AIMD simulations of the hydrogen interaction with hydrogen-precovered Pd surfaces with an initial kinetic energies of 0.1 eV, we did not find any subsurface adsorption events. This is due to the fact that the subsurface penetration corresponds to a rare event because of its activated nature. In order to obtain hydrogen penetration events, we ran trajectories with the unrealistically high initial kinetic energy of 1.0 eV so that the chance is higher that the hydrogen atoms have enough energy to overcome the barrier towards subsurface adsorption. And indeed, thus we observed several hydrogen subsurface adsorption events. Interestingly, most of these events involved a concerted motion of hydrogen atoms which is illustrated in Fig. 3.

Initially, one of the two atoms of the impinging H_2 molecule enters a four-fold hollow site while the other one is again trapped in a bridge configuration (Fig. 3a), as already depicted in Fig. 2b. Note that because of the high initial kinetic energy of 1.0 eV there is a large amount of excess energy available which is mainly transfered to the hydrogen overlayer atoms. After about 400 fs, there is a concerted motion of the hydrogen bridge-site atom and the H atom to its right in Fig. 3b at the adjacent four-fold hollow site. The bridge-site atom replaces the other hydrogen atom, but this time the other atom does not pop up to the surface but is rather pushed into the subsurface layer. Thus it seems that the subsurface penetration is facilitated when more than one hydrogen atom are involved in this process. The elucidation of the mechanism of the hydrogen subsurface adsorption certainly requires further studies.

After the one hydrogen atom has gone subsurface, the remaining hydrogen atoms on the surface are still energetically hot which is reflected in the large amplitudes of the vibrational motion of the hydrogen atoms with respect to their equilibrium positions that are visible in Figs. 3b and c. Through interatomic collisions, one of the hydrogen overlayer atoms in fact gains enough kinetic energy to cross the diffusion barrier and hops into the neighboring vacancy site (Fig. 3c).

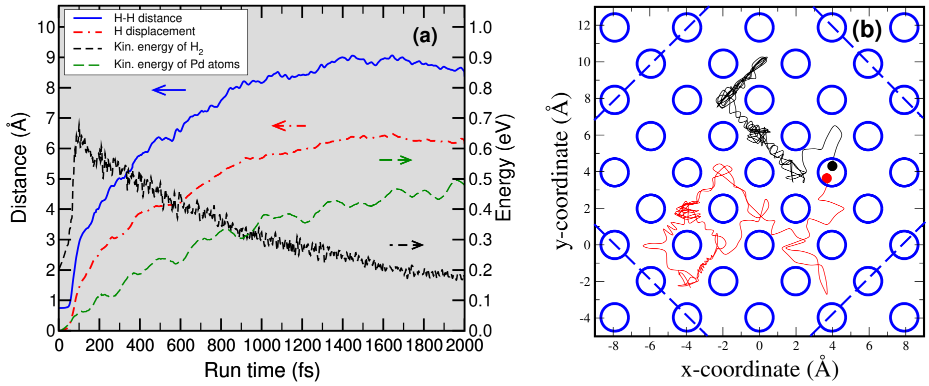

Figure 4. Calculated relaxation of dissociated H_2 molecules on clean Pd(100) within a (6×6) surface unit cell. a) H-H distance, the displacement of the single H atoms from their initial lateral position, the kinetic energy of the H_2 molecules and of the Pd substrate as a function of the run time averaged over 80 AIMD trajectories with an initial H_2 kinetic energy of 200 meV. b) Illustration of a trajectory of the hydrogen atoms after dissociation. The total run time was 2 ps. The surface unit cell of the simulations is indicated by the dashed blue line.

4 Relaxation dynamics of dissociated H_2 molecules

So far we have focused on the dissociation of H_2 on hydrogen-covered Pd surfaces. We were only interested in the question whether H_2 dissociates on Pd or not, but we did not consider the fate of the hydrogen atoms after the dissociation. However, directly after the dissociation when the atoms enter the atomic adsorption wells, they gain a significant amount of energy. For H_2/Pd, this amounts to about 1 eV for the two H atoms together and thus gives rise to the formation of "hot" atoms, i.e., atoms with energies much larger than thermal energies. These atoms can use their kinetic energy in order to travel along the surface. The mean free path of these hot atoms is for example relevant for catalytic reactions on surfaces since it determines whether adjacent reactants can react directly after the dissociative adsorption of one of the species or whether some diffusive motion is required before any further reaction can occur. So far, simulations addressing the relaxation of hot atoms after dissociation have only modeled the motion of single atoms with initial velocities considered to be typical for dissociation fragments directly after the bond-breaking process[28,29]. We have decided to model the full relaxation process including the interaction of the two fragments after the dissociation. We have therefore run AIMD trajectories of the dissociation of H_2 on clean Pd(100). In order to minimize the interaction of the hot hydrogen atoms with their periodic images, we have chosen a large (6×6) surface unit cell. To reduce the computational cost, only three Pd layers were considered but test calculations with five Pd layers yield hardly modified results.

Figure 4a shows the mean H-H distance and the mean displacement of the single H atoms as a function of time averaged over 80 AIMD trajectories whereas in Fig. 4b one specific trajectory is displayed that was run for 2 ps. The trajectory shows that the single hydrogen atoms visit several surface sites. In this particular trajectory, the hydrogen atoms approach each other again after an initial increase in the interatomic distance. At a certain time, they are moving towards adjacent adsorption sites before they separate again. This shows that the mutual interaction can be important for the hot atom movement.

As for the mean distance between the two H atoms, after about 1.5 ps it reaches a value of about 8.5 Å and does not increase any further. This corresponds to about three Pd lattice units. It should be noted that the root mean square deviation in the H-H distance saturates at about ± 4 Å, however, single trajectories show a maximum H-H distance of more than 20 Å. In Fig. 4a, also the kinetic energies of the hydrogen and the Pd atoms, respectively, are plotted. At about 100 fs, the hydrogen atoms gain on the average about 700 meV when they enter the atomic adsorption well. This energy is then transfered from the hydrogen atoms to the Pd substrate atoms. When the mean H-H distance does not change any more, i.e., after 1.5 ps, the hydrogen atoms have only about 250 meV of kinetic energy left which corresponds rather closely to the diffusion barrier for H atoms on Pd(100).

These results demonstrate that AIMD simulations are well-suited in order unravel details of reaction dynamics at surfaces that are not accessible by experiment.

Acknowledgments

These calculations were made possible through a grant of computer time at the John von Neumann Institute for Computing in Jülich.

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