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Langmuir is still right: Hydrogen dissociation dynamics on precovered Pd surfaces

Axel Groß and Arezoo Dianat*
Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm, Germany

A recent scanning tunneling microscopy study by Mitsui *et al.* (Nature **422**, 705 (2003)) challenged the well-accepted picture based on early studies of Langmuir that an ensemble of at least two empty, catalytically active sites is required for the dissociative adsorption; instead, aggregates of three or more vacancies should be necessary. We have performed the first *ab initio* molecular dynamics study of the adsorption dynamics on a precovered surface providing detailed insights into the coverage dependence of the adsorption probability. The simulations show that there is no need to refine the Langmuirian picture: A dimer vacancy is still sufficient to dissociate hydrogen provided the kinetic energy of the molecules is large enough to overcome the relatively small adsorption barrier. In addition, we elucidate further aspects of the dissociation dynamics at precovered surfaces.

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The dissociative adsorption of molecules is a crucial reaction step in most catalytic processes at surfaces. In particular, the interaction of hydrogen with transition metal surfaces has served as a model system for the study of elementary reaction steps in the dissociation dynamics on surfaces, both experimentally as well as theoretically [1–4]. Although coverage effects are important for a true understanding of the reaction dynamics in realistic catalytic systems, most of the results have been obtained for clean surfaces. Hence the role of the coverage in the adsorption dynamics on surfaces whose understanding is also relevant for establishing fundamental concepts in heterogeneous catalysis is still elusive.

It has been a well-accepted picture based on early studies of Langmuir [5] that an ensemble of at least two empty, catalytically active sites is required for the dissociative adsorption reaction. In a recent STM work, Mitsui *et al.* [6, 7] studied the formation of ordered hydrogen layers on Pd(111). Surprisingly, they found that hydrogen molecules impinging on an almost complete hydrogen overlayer did not adsorb dissociatively in a hydrogen dimer vacancy. Rather, aggregates of three or more vacancies were required to dissociate hydrogen. These findings led to speculations that the accepted notion that two empty sites are required for the dissociative adsorption of diatomic molecules might not be correct [6, 8].

A subsequent study based on density functional theory (DFT) that was entitled “When Langmuir is too simple: H_2 dissociation on Pd(111) at high coverage” [9] showed that the dissociative adsorption of H_2 in a hydrogen dimer vacancy is still exothermic. However, the presence of the hydrogen overlayer has a poisoning effect by leading to a relatively small energetic barrier in the meV range which hinders the dissociative chemisorption of H_2. On the other hand, the adsorption process requires the dissipation of more than 1 eV [9], and it has been speculated that the dissipation to phonons or electron hole-pairs could be suppressed due to surface stiffening or the modification of the electronic band structure, respectively, caused by the hydrogen overlayer [10]. The relevance of these effects, however, could not be assessed so far.

Here we introduce *ab initio* molecular dynamics (AIMD) simulations as a reliable and versatile tool for the quantitative and qualitative determination of the adsorption dynamics and reaction probabilities on complex surface structures. The hydrogen adsorption dynamics has usually been studied by performing quantum [1, 2] or classical [11–13] molecular dynamics studies on parameterized potential energy surfaces (PES) taking into account the six degrees of freedom of the diatomic molecule and keeping the substrate fixed. However, at precovered surfaces, the energy transfer to the adsorbates can not be neglected. Furthermore, the increased complexity because of the additional degrees of freedoms makes any parameterization of the PES quite cumbersome if not impossible. These problems can be circumvented by performing AIMD simulations in which the forces necessary to integrate the classical equations of motion are calculated “on the fly” in each step by first-principles electronic structure calculations. So far, however, such simulations have been restricted to a small number of trajectories [14, 15] due to their high numerical effort.

Because of the increase in computer power and the development of efficient algorithms it has now become possible to run a statistically meaningful number of DFT-based AIMD trajectories for the determination of reaction probabilities. We have addressed the dissociation of H_2 on clean and hydrogen-precovered Pd(111) and Pd(100) by performing DFT calculations and molecular dynamics simulations using the Vienna *ab initio* simulation package (VASP) [16]. Our study which is based in total on the outcome of more than 4,000 AIMD trajectories shows clearly that H_2 dissociation in a hydrogen dimer vacancy on almost hydrogen-covered Pd(111) is still possible provided the energy is sufficient to overcome the activation barrier so that there is no need to refine the traditional Langmurian picture.

The calculations have been performed using density

*New address: Institut für Werkstoffwissenschaft, Technische Universität Dresden, D-01069 Dresden, Germany

functional theory (DFT). The exchange-correlation effects have been described within the generalized gradient approximation (GGA) using the Perdew-Wang (PW-91) [17] and the very similar PBE [18] functionals. The one-electron valence states were expanded in plane waves with kinetic energies up to the cutoff energy of 200 eV. The surface was modeled by a slab of four layers for the (111) surface and five layers for the (100) surface. The surface was modeled with (2×2) and (3×3) unit cells using a Monkhorst-Pack grid of $5{\times}5{\times}1$ and $3{\times}3{\times}1$ **k**-points, respectively. The adsorption energies are converged within 50 meV with respect to the number of layers in the slabs, the k-point sampling and the cutoff energy.

Sticking probabilities were determined as a function of the kinetic energy by averaging over at least 200 trajectories for each kinetic energy leading to a statistical error of $\sqrt{s(1-s)}/\sqrt{200} \leq 0.035$, where s is the adsorption probability. The uppermost two (three) layers of the Pd(111) (Pd(100)) surface were allowed to move. The MD simulations were performed using the Verlet algorithm with a time step of 1 fs within the microcanonical ensemble. The trajectories were started 4 Å above the surface with specified kinetic energies of the center of mass of the H_2 molecule between 0.02 and 1.0 eV along the surface normal corresponding to normal incidence. The initial lateral positions and orientations of the H_2 molecule were chosen randomly. The substrate atoms were initially at rest, and the molecules were initially non-rotating and non-vibrating. This means that no zero-point motion was considered in the initial conditions which leads in fact to a better agreement with quantum dynamical simulations since the sum of all zero-point energies stays approximately constant along the reaction path [2]. Tunneling plays only a minor role since the tunneling paths are exponentially suppressed compared to the classically allowed paths in these systems [19]. A trajectory was considered to correspond to a dissociation event when the interatomic distance of the molecule exceeded 2.5 Å and to a scattering event when the molecule returned to the initial distance of 4 Å from the surface.

In order to validate the AIMD simulations, we have first evaluated the adsorption probability on clean Pd(111) and Pd(100) and compared to experiment (see Fig. 1). For Pd(111), we have also included the results of classical molecular dynamics simulations on an interpolated *ab initio* potential energy surface [12]. Two sets of experimental data are shown, for molecules in the rotational ground state $j = 0$ [20] and for a molecular beam with a thermal distribution of rotational states which leads to a suppression of the adsorption probability [24]. The agreement between the different experimental and theoretical data sets is rather satisfactory.

This situation is quite different for H_2/Pd(100) where large discrepancies between theory and experiment exist (see Fig. 1B). In contrast to the experiment [22, 23], we find, as one would also expect, that the more open Pd(100) surface is more reactive with respect to H_2

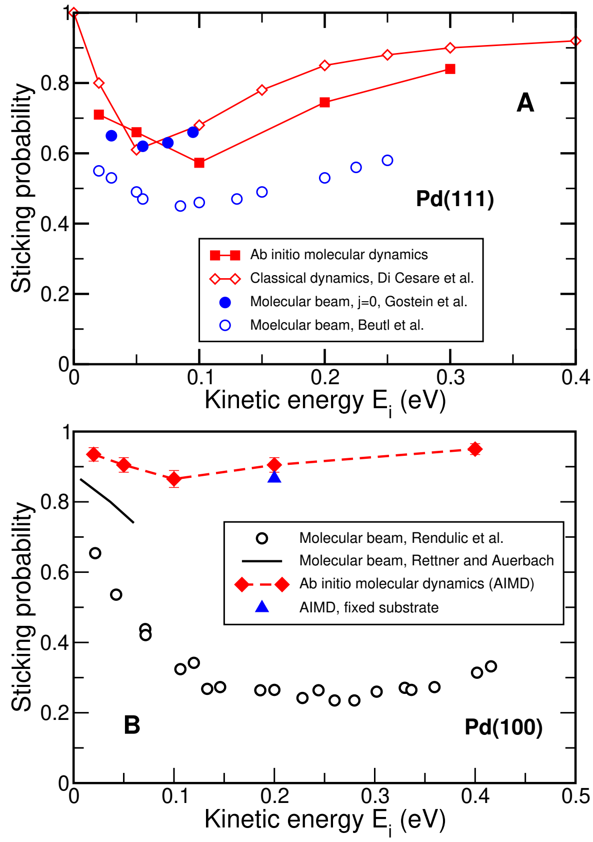

FIG. 1: Dissociative adsorption probability of hydrogen on clean (A) Pd(111) and (B) Pd(100) calculated by *ab initio* molecular dynamics simulations. The results are compared to experimental molecular beam data by Gostein and Sitz [20] for non-rotating molecules (rotational quantum state $j = 0$) and by Beutl *et al.* [21] for molecules with a thermal distribution of rotational states on Pd(111) and by Rendulic *et al.* [22] and by Rettner and Auerbach [23] on Pd(100). For Pd(111), further theoretical *ab initio* results by Di Cesare *et al.* [12] obtained by classical trajectory calculations for a fixed substrate are included.

dissociation than the close-packed Pd(111) surface. It should be noted that the results of the two different experiments also differ significantly. Recently it has been demonstrated that the Pd(100) surface becomes rapidly contaminated by hydrogen after a cleaning process [25]. Such a contamination, in addition to further probable contaminants such as sulfur, would explain the low sticking coefficient in the earlier experiment by Rendulic *et al.* [22] whereas the agreement between the later molecular beam results of Rettner and Auerbach [23] and the AIMD results is again satisfactory considering the uncertainties of both theory and experiment.

With respect to previous theoretical results of the adsorption probability of H_2/Pd(100) obtained within a quantum dynamical framework which were much lower [2] we note that the PES used in these simulations was only based on high-symmetry points of the surface unit cell. Test calculations showed that the interpolated

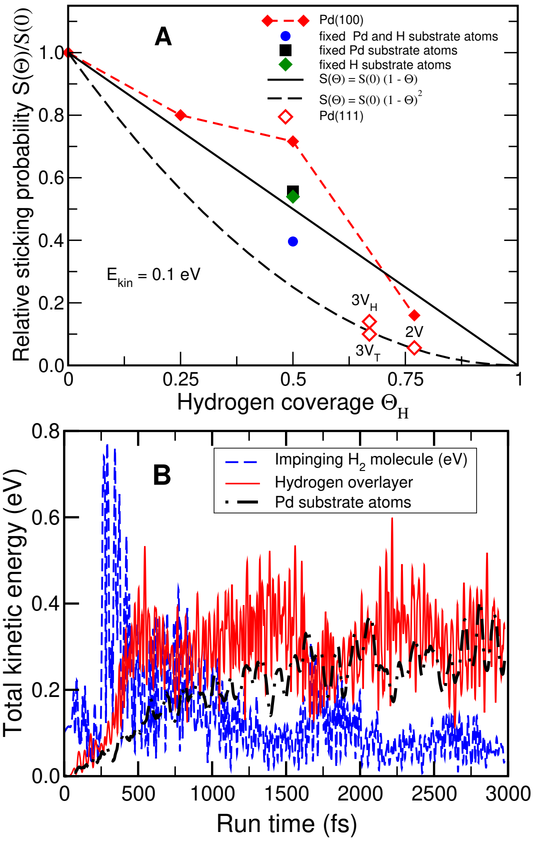

FIG. 2: A) Dissociative adsorption probability of hydrogen on hydrogen-covered Pd(100) and Pd(111) as a function of coverage for an initial kinetic energy of 0.1 eV. 2V, $3V_H$ and $3V_T$ denote the dimer vacancy and the trimer vacancy centered around a Pd hollow and a Pd top site, respectively. B) Energy distribution upon the dissociative adsorption in a hydrogen dimer vacancy on Pd(100) along a typical trajectory.

PES thus contained artificial symmetries that influenced the dissociation dynamics considerably.

The activity of hydrogen vacancy sites has been studied by preparing a hydrogen-covered surface with a dimer vacancy within a (3×3) geometry corresponding to a surface coverage of $\Theta_H = 7/9 \approx 0.78$. For a low initial kinetic energy of 0.02 eV which roughly corresponds to the kinetic energies of the H_2 molecules in the experiment [6] we did not observe any single dissociative adsorption event on the almost hydrogen-covered Pd(111) surface, thus confirming the experimental findings.

In order to check whether the dimer vacancy can accommodate any hydrogen molecules at all, we increased the initial kinetic energy to 0.1 eV so that the small barrier found for H_2/Pd(111) at that coverage [9] can be overcome. The results both for Pd(111) and Pd(100) are plotted in Fig. 2 normalized to the sticking probability at the corresponding clean Pd surfaces for that kinetic energy. For Pd(111), we find a small, but non-vanishing relative adsorption probability of 0.05. This means that indeed the dissociative adsorption probability of H_2 in a

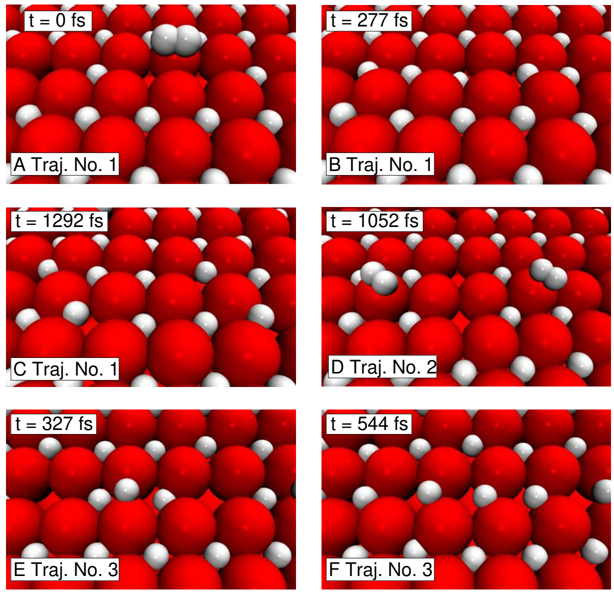

FIG. 3: Snapshots of three trajectories within a (6×6) surface periodicity illustrating details of the adsorption dynamics at a hydrogen-covered Pd(100) surface with a dimer vacancy.

hydrogen dimer vacancy is possible if the kinetic energy is large enough to overcome the barrier. In addition, we have also determined the adsorption probability in trimer vacancies on Pd(111) where the vacancy is either centered around a hollow site ($3V_H$) or a Pd top site ($3V_T$). Although the area of the trimer vacancy is only 50% larger, the adsorption probability is at least two times larger than on the dimer vacancy (2V). This is caused by the fact that the barrier for the approach towards the trimer vacancy are smaller than the corresponding barrier for the dimer vacancy [9]. At the more open Pd(100) surface the adsorption probability in a dimer vacancy is more than two times larger than on Pd(111).

According to our simulations, H_2 molecules entering the dimer vacancy transfer their energy towards substrate vibrations within one to two picoseconds. This is illustrated in Fig. 2b, where the energy redistribution along a typical trajectory upon the adsorption of H_2 in a hydrogen dimer vacancy on Pd(100) is plotted. Snapshots of this trajectory are shown in Fig. 3A-C. The impinging molecule (Fig. 3A) first hits the Pd surface close to a Pd top site and is then steered towards the dimer vacancy. When the H_2 molecule enters the dimer vacancy site after about 250 fs (Fig. 3B), it gains quite a significant amount of kinetic energy due to the conversion of potential energy into kinetic energy. This energy will then be dissipated to the substrate, first mainly to the hydrogen overlayer atoms, visible as the large displacements of the H surface atoms from their equilibrium positions (Fig. 3C), whereas the Pd substrate takes up kinetic energy relatively slowly.

For a kinetic energy of 1.0 eV, the total adsorption probability increases to 0.4 according to our AIMD simulations. This shows that even an energy dissipation of 2 eV is easily possible in the dimer vacancy. Thus there is no reason to assume that the energy transfer due to the presence of the almost complete hydrogen overlayer is compressed, on the contrary, it is rather facilitated due to the small mass mismatch between impinging hydrogen molecules and the hydrogen overlayer.

For Pd(100), we have also determined the adsorption probability at hydrogen coverages of one quarter and one half monolayer in a (2×2) geometry. In Fig. 2A, we have included two curves which are relevant if the adsorption at a precovered surface was determined by pure site-blocking. In that case, if adsorption only requires one empty site, then the sticking probability would be given by $S(\Theta_{\rm H}) = S(0)(1 - \Theta_{\rm H})$, while it would be $S(\Theta_{\rm H}) = S(0)(1 - \Theta_{\rm H})^2$, if two adjacent sites are required.

As Fig. 2a demonstrates, at low and intermediate coverages the sticking probability of hydrogen is significantly larger than predicted from a simple site-blocking picture, in particular for $\Theta_{\rm H} = 0.5$. Experimentally, qualitatively similar curves have been found for the hydrogen adsorption on precovered reactive metal surfaces [26]. When all the substrate Pd atoms and the hydrogen overlayers atoms are kept fixed in the simulations, the sticking probability drops dramatically indicating the crucial role of the surface motion in the adsorption process at hydrogen-precovered Pd surfaces, in contrast to the clean surface (see Fig. 1B). A rather surprising result is, however, that due to the larger corrugation of the hydrogen-covered surface both the motion of the hydrogen atoms and the Pd atoms contribute to the high sticking probability at the precovered surfaces, as the comparison of simulations with only fixed Pd atoms and with only fixed hydrogen overlayer atoms shows.

At the high coverage surfaces, the sticking probabilities are close to the results expected for the site-blocking models although the promoting effects of the substrate motion are still operative. However, at such a high coverage, the minimum energy paths towards the empty adsorption sites become less attractive. This is due to a well-known poisoning effects [27]: the presence of the adlayer influences the electronic structure of the substrate thus reducing the adsorption energies. Hence it is the cancellation of the promoting dynamical effects and the poisoning electronic effects that leads to sticking probabilities close to the pure site-blocking values.

The AIMD simulations not only yield statistically reliable sticking probabilities, they also allow for valuable microscopic insights into the dissociative adsorption dynamics. In Fig. 3D-F, we have collected some snapshots of further trajectories illustrating typical adsorption events at a hydrogen-covered Pd(100) surface with a dimer vacancy. The impinging H_2 molecules do not necessarily either dissociatively adsorb or scatter back into the gas phase. In fact, there exists a molecular precursor state above the top sites, very similar to the one already identified at the hydrogen-covered stepped Pd(210) surface [28, 29] which becomes stabilized due to the poisoning effects of the pre-adsorbed hydrogen atoms. About 5% of the impinging H_2 molecules become trapped in these sites. One of these events is depicted in Fig. 3D. Hence we predict the existence of these molecular precursor states on hydrogen-covered Pd(100) which are bound by 0.1 eV according to our calculations. They should be detectable at low surface temperatures by, e.g., isotope exchange experiments.

Another interesting adsorption geometry that has to the best of our knowledge not been discussed before is shown Fig. 3E. One of the impinging hydrogen atom enters a four-fold hollow site adjacent to an occupied site while the other one remains trapped for some tenths of a picosecond at the bridge site. Finally, the hydrogen atom at the bridge site displaces the preadsorbed hydrogen atom which is pushed to an adjacent empty site (Fig. 3F). If the adjacent site is not empty, the additional atom at the bridge site even stays for several picoseconds.

In conclusion, by performing *ab initio* molecular dynamics simulations we have shown that hydrogen molecules can still dissociatively adsorb in a hydrogen dimer vacancy site on almost fully hydrogen-covered palladium surfaces for kinetic energies larger than the dissociation barrier which is caused by the poisoning effect of the hydrogen adlayer. The adsorption energy gained upon entering the vacancy site is transfered within one to two picoseconds to the substrate. In addition, we have identified further adsorption geometries such as a molecular precursor above the top site and a bridge-bonded hydrogen species adjacent to occupied adsorption sites.

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