Ab Initio Molecular Dynamics Study of Hot Atom Dynamics after Dissociative Adsorption of H_2 on Pd(100)

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The relaxation of hot hydrogen atoms upon the dissociative adsorption of H_2 on Pd(100) was studied by *ab initio* molecular dynamics simulations based on density functional theory, modeling the full dissociative adsorption process in a consistent manner. In spite of the nonlinear dependence of every single trajectory on the run conditions, on the average it is the energy dissipation to the substrate that determines the mean distance of the two H atoms after adsorption which amounts to three to four lattice units and provides an upper bound for heavier species such as oxygen.

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The dissociative adsorption of molecules on surfaces is the first, often crucial step in reactions in heterogeneous catalysis [1]. In a direct dissociative adsorption event, the molecules gain kinetic energy in addition to their initial energy when they enter the attractive adsorption well. It takes some time before this excess kinetic energy is dissipated to the substrate, in particular, when a light molecule such as H_2 is adsorbing on a substrate consisting of heavy metal atoms. The energy gain upon the dissociative adsorption leads 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 propagate along the surface. The mean free path of these hot atoms is relevant for catalytic reactions on surfaces since it determines whether adjacent reactants can react directly after the dissociative adsorption with another species or whether some diffusive motion is required before any further reaction can occur.

Experimentally, the distance of O_2 dissociation fragments was studied on Al(111) [2] and on Pt(111) [3] in scanning tunneling microscopy studies. For $O_2/Al(111)$, a mean distance of 40 Å was found [2], which seems to be much too large to originate from a simple dissociative adsorption mechanism. In contrast, on Pt(111) a mean oxygen distance after O_2 dissociation of two Pt lattice units was observed [3] corresponding to 5.5 Å. These results have motivated some theoretical studies addressing the relaxation dynamics for oxygen atoms on Al(111) [4,5] and of hydrogen atoms on Pd(111) [6] on parameterized potential energy surfaces partially derived from first-principles electronic structure calculations. These simulations did not treat the full dissociation event, but rather studied the relaxation dynamics of isolated adsorbate atoms with initial conditions typical for dissociative adsorption events. They found final mean displacements of about 10–15 Å for oxygen atoms on Al(111) [4,5] and less than 4 Å for hydrogen atoms on Pd(111) [6]. Furthermore, kinetic Monte Carlo simulations addressing the dissociation of O_2 on Pt(111) indicated that the distribution of oxygen atoms after the dissociation cannot be explained by thermal events [7].

These theoretical studies did not consider the mutual interaction of the two dissociation fragments on the surface. Furthermore, the substrate relaxation and its influence on the hot atom dynamics was either entirely neglected [4,5] or treated in an approximate manner [6]. This is due to the fact that the modeling of the dissociative adsorption dynamics including substrate relaxation requires a high-dimensional potential energy surface whose parameterization is not trivial [8,9]. The problem of the parameterization of the potential energy surface can be avoided in *ab initio* molecular dynamics (AIMD) simulations in which the forces necessary to integrate the equations of motion are determined "on the fly". The AIMD simulations require a high computational cost so that typically only a few trajectories could be evaluated [10,11]. However, due to the improvement in computer power and the development of efficient periodic electronic structure algorithms [12] based on density functional theory it has become possible to run a sufficient number of AIMD trajectories in order to obtain statistically significant adsorption probabilities, as has recently been demonstrated [13].

Here I present AIMD simulations addressing the hot atom dynamics after the dissociative adsorption of H_2 on Pd(100) in which the whole dissociation process until the accommodation of the hot atoms is treated in a fully consistent manner. The periodic density functional theory calculations have been performed using the Vienna *ab initio* simulation package (VASP) [12]. The exchange-correlation effects have been described within the generalized gradient approximation using the Perdew-Wang (PW-91) [14] functional. The one-electron valence states were expanded in plane waves with kinetic energies up to the cutoff energy of 200 eV, and the ionic cores were represented by ultrasoft pseudopotentials [15]. In order to minimize the interaction of the hot hydrogen atoms with their periodic images, a large (6×6) surface unit cell was chosen. Because of the large unit cell, it was sufficient to use only the Γ point in the *k*-point sampling. The Pd(100) surface was modeled by a slab of three layers with the uppermost layer free to move while the two bottom layers were kept fixed at the bulk geometry. Additional runs with a five-layer slab and the two uppermost layers allowed to move were performed as well.

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 a kinetic energy of typically 200 meV along the surface normal corresponding to normal incidence. This kinetic energy was chosen in order to avoid dynamical trapping events before dissociation which occur at lower kinetic energy [16–18] and would have made the AIMD simulations computationally prohibitively expensive. On the other hand, the total energy gain of the hydrogen atoms upon entering the adsorption wells amounts to about 1 eV [19] so that the initial kinetic energy in the simulations is only a small fraction of the kinetic energy available to the hydrogen atoms after dissociation.

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 nonrotating and nonvibrating. 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 in this system [16,20] since the sum of all zero-point energies stays approximately constant along the reaction path. Tunneling plays only a minor role since the tunneling paths are exponentially suppressed compared to the classically allowed paths in these systems [21].

A typical AIMD trajectory of the dissociative adsorption of a hydrogen molecule run for 2.5 ps is plotted in Fig. 1. The impact points of the two hydrogen atoms on the surface are indicated by the small filled circles whereas the open circles denote the equilibrium positions of the Pd atoms. The trajectory shows that the single hydrogen atoms visit several surface sites before they come to rest. In this particular trajectory, after the initial separation the atoms approach each other again before eventually separating, indicating that the mutual interaction can be important for the hot atom movement.

The computed mean lateral distance of the two hydrogen atoms as a function of the run time is plotted as the full line in Fig. 2 and denoted by full MD. One hundred trajectories were evaluated for H_2 impinging on the three-layer slab with the uppermost Pd layer allowed to move. Although every single trajectory depends sensitively on the initial conditions, already after 50 trajectories the averaged results are converged within ±1 Å to the results shown in Fig. 2. Performing the AIMD simulations with a 5-layer slab does not alter the results significantly, either, as Fig. 2 demonstrates.

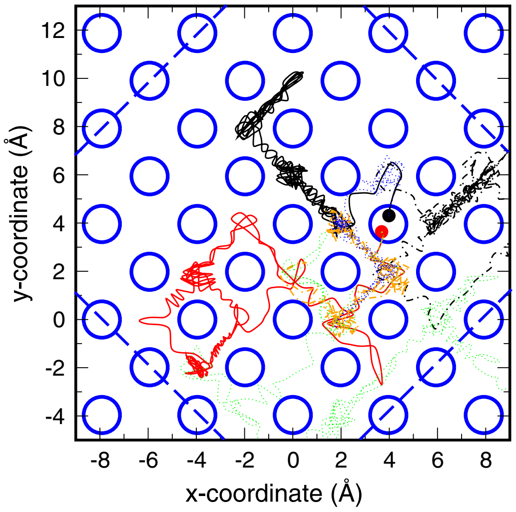

FIG. 1 (color online). Calculated trajectories of hydrogen atoms upon the dissociative adsorption on clean Pd(100) within a (6 × 6) surface unit cell. The initial kinetic energy was 0.2 eV. The total run time was 2.5 ps. Three sets of trajectories with the same initial conditions are shown. The full lines correspond to the joint motion of the two hydrogen atoms while for the lighter dash-dotted lines the trajectories were computed individually after the two hydrogen atoms reached a separation of 2.5 Å. The dotted lines correspond to a trajectory with a fixed substrate but dissipation included via velocity rescaling. The surface unit cell of the simulations is indicated by the dashed blue line.

In Fig. 3, the average total kinetic energy of the Pd substrate atoms and of the hydrogen atoms is plotted as a function of the run time for two initial H_2 kinetic energies of 200 meV and 500 meV. When the H_2 molecule hits the surface after about 100 fs, the molecule quickly dissociates and the hydrogen atoms enter adjacent atomic adsorption

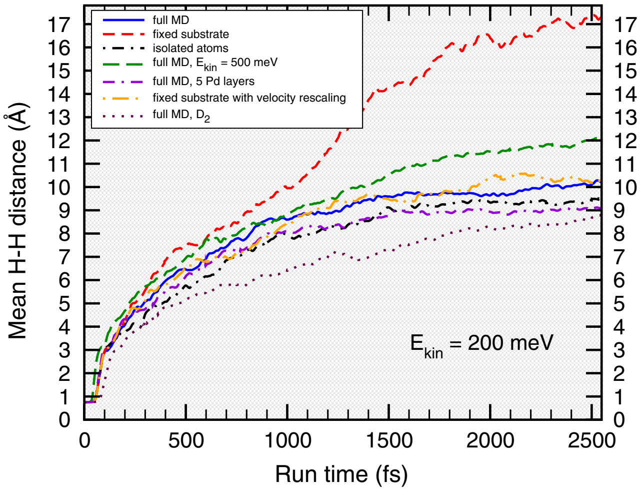

FIG. 2 (color online). Mean lateral distance of the two hydrogen atoms upon the H_2 dissociative adsorption on Pd(100) as a function of the run time determined by averaging over AIMD trajectories for different computational setups (see text). The basic AIMD results denoted by full MD were obtained by averaging over 100 trajectories whereas the other results are based on at least 75 trajectories in each case.

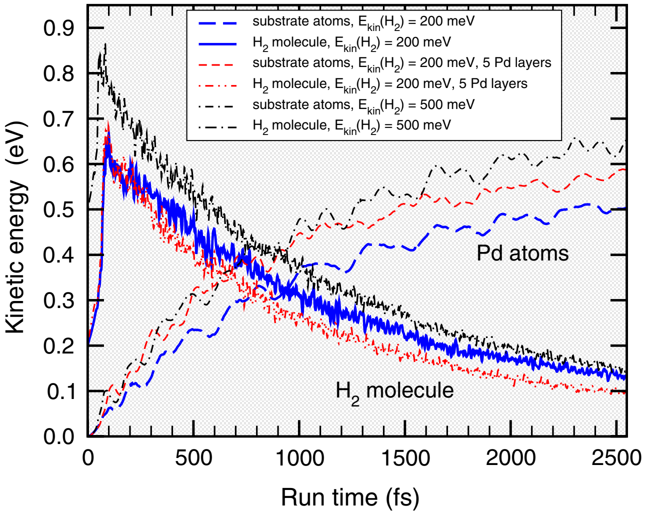

FIG. 3 (color online). Calculated mean total kinetic energy of the Pd substrate atoms and the impinging H_2 molecule as a function of the run time for initial kinetic energies of 200 meV and 500 meV. The substrate was modeled as a three-layer slab with the uppermost Pd layer allowed to move. In addition, results for five-layer slab calculations and $E_{\rm kin}(H_2) = 200$ meV with the two uppermost Pd layer allowed to move are included.

sites where they gain about 500 meV kinetic energy on the average. Because of this high kinetic energy that is much higher than the diffusion barrier of hydrogen on Pd(100), the hot hydrogen atoms can make further jumps. However, when hitting the Pd atoms they constantly transfer energy to the substrate atoms. After about 1 ps, the hydrogen atoms have lost half of their kinetic energy irrespective of their initial kinetic energy, and the mean distance of the two hydrogen atoms starts to level off. After 2 ps, the atoms together have less than 200 meV kinetic energy left, and their mean distance hardly changes any more. There is a weak dependence on the initial kinetic energy resulting in final H-H distances of about 10 Å ($E_{\rm kin} = 200$ meV) and of about 12 Å ($E_{\rm kin} = 500$ meV), respectively, which corresponds to roughly three to four Pd lattice units. Note however, that there is a relatively wide distribution in the H-H distances centered around the mean distance with a variance of $\pm 5 - \pm 6$ Å for the different setups. To be specific, for the full MD simulations about 42% (65%) of all considered trajectories have a final H-H distance that is within ± 2 Å (± 4 Å) around the mean H-H distance.

The relatively weak dependence of the final H-H distance on the initial kinetic energy can be understood by comparing the kinetic energy distributions in Fig. 3 for the initial kinetic energies of 200 meV and 500 meV. First of all, a large portion of the kinetic energy of the hot atoms comes from the energy gain upon entering the adsorption well which is independent of the initial kinetic energy. Second, molecules with a higher kinetic energy bump with a larger impact into the surface so that a higher amount of energy is transferred to the substrate phonons. As Fig. 3 shows, after 500 fs, from the additional 300 meV in kinetic energy only about 100 meV are left, and after 2 ps the kinetic energy left is almost the same for the two different initial energies considered. Furthermore, performing the five-layer AIMD simulations with the two uppermost Pd layers allowed to move increases the energy transfer to the substrate only slightly.

Additional trajectories of H_2 impinging on the surface were run with the substrate atoms kept fixed so that there is no energy transfer to the substrate. In this case, the mean total kinetic energy of the two hydrogen atoms stays constant at a value of about 700 meV which corresponds to half of the sum of the initial kinetic energy of the H_2 molecule and the adsorption energy. As Fig. 2 indicates, for the initial dissociation process for H-H distances up to 4 Å at a run time of about 250 fs, the energy transfer to the substrate does not play a significant role. At later times, the energy dissipation slows down the hydrogen atoms leading to a reduced H-H separation speed compared to the hydrogen atoms not suffering any energy dissipation. These continue to increase their distance roughly linearly dependent on the time before it starts to level off after about 1500 fs. At larger times, one would expect an increase proportional to the square root of time corresponding to the time dependence of the mean displacement of a random walker. The oscillatory structure in the mean distance at longer time is due to the fact that for these large distances there are collisions between a hydrogen atom and the periodic image of the other H atom within the 6×6 periodicity at relatively high kinetic energy because of the missing energy dissipation. In the other runs involving dissipation, the interaction with the periodic images does not influence the dynamics significantly, as was also checked by performing a few runs in 8×8 geometry, because first the distances are smaller so that there are relatively few collisions (only for about 20 per cent of the trajectories) and second, the collisions occur at run times larger than 1 ps when the kinetic energy of the hydrogen atoms is already strongly reduced (see Fig. 3).

The positions and velocities of the hydrogen atoms at the configuration when their distance reached 2.5 Å in the full MD simulations were used as the initial conditions for AIMD runs of isolated hydrogen atoms. Technically, when the distance became larger than 2.5 Å, one of the two hydrogen atoms was omitted from the simulations which were then continued. Afterwards, the distance of the two hydrogen atoms as a function of time between the trajectories of the isolated atoms was determined. In Fig. 1, the trajectories of the two isolated hydrogen atoms are included as dashed lines which differ considerably from the results obtained with both hydrogen atoms included in the run. This emphasizes again the high sensitivity of the trajectories on the conditions of the simulations. The propagation dynamics is nonlinear resulting in chaotic trajectories. However, on the average the mean distance of the isolated atoms (dash-dotted line in Fig. 2) hardly differs from those of the full MD simulations. This means that the effect of the mutual interactions between the hydrogen atoms "averages out," as far as their mean distance is concerned.

Furthermore, AIMD simulations with D_2 at an initial kinetic energy of 200 meV were carried out. The mean distance of the deuterium atoms plotted in Fig. 2 seems to be smaller than the results for H_2. However, if the time axis for the D_2 results is rescaled by a factor of $1/\sqrt{2}$ according to the mass difference between H and D, the results for D_2 are only slightly below the corresponding results for H_2. This can be understood considering the fact that due to the larger mass of deuterium there is a somewhat stronger energy transfer to the substrate, i.e., a stronger dissipation which leads to a slightly reduced D-D distance on the average.

It may well be that the surface rearrangement along the trajectories has a decisive influence on the dynamics of the hot atoms. Therefore, I have run additional trajectories with the substrate kept fixed but in which the velocities of the hydrogen atoms were rescaled every 50 fs in such a way that the mean total kinetic energy of the hydrogen atoms as a function of the run time resembled the one of the full dynamical simulations. This corresponds to including an appropriate friction term while keeping the substrate fixed. The dotted lines in Fig. 1 correspond to such a trajectory with a fixed substrate but dissipation included via velocity rescaling; this leads to an entirely different final configuration. But again, the resulting mean H-H distance is very similar to the full dynamical results (see Fig. 2).

Finally, I have also considered the mean displacement of the single hydrogen atoms and the H_2 center of mass from their impact points on the surface. And again, except for the simulations with the substrate kept fixed and no energy dissipation, all other results look rather similar. The mean displacement of the single hydrogen atoms is about 7 Å (note that there is a difference between the displacement of the single hydrogen atoms and the H-H distance), whereas the H_2 center of mass also does not stay fixed but is replaced by about 5 Å on the average. This confirms the conclusion of this work that the distance of three to four lattice units that hot hydrogen atoms travel on Pd(100) after dissociative adsorption is on the average mainly determined by the energy dissipation to the substrate whereas the mutual interaction or surface relaxation effects play only a minor role. There are other molecule or surface systems in which the energy is dissipated more quickly to either surface phonons because of a larger mass of the impinging molecule or to electron-hole pairs because of electronically nonadiabatic effects (which is, however, rather unlikely for H_2/metal systems [22]). For such systems, the separations determined in this study should present an upper bound for the distance of the fragments after dissociative adsorption provided the corresponding potential energy surface is similar.

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