

## Potential-energy surface for H<sub>2</sub> dissociation over Pd(100)

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The potential-energy surface (PES) of dissociative adsorption of H<sub>2</sub> on Pd(100) is investigated using density-functional theory and the full-potential linear augmented plane-wave method. Several dissociation pathways are identified which have a vanishing energy barrier. A pronounced dependence of the potential energy on “cartwheel” rotations of the molecular axis is found. The calculated PES shows no indication of the presence of a precursor state in front of the surface. Both results indicate that steering effects determine the observed decrease of the sticking coefficient at low energies of the H<sub>2</sub> molecules. We show that the topology of the PES is related to the dependence of the covalent H(*s*)-Pd(*d*) interactions on the orientation of the H<sub>2</sub> molecule.

### I. INTRODUCTION

Hydrogen dissociation on metal surfaces has become one of the benchmark systems for the understanding of dissociative adsorption processes. The H<sub>2</sub>/Pd system is particularly interesting as an example of nonactivated dissociation over a transition-metal surface. The dissociation process has been studied using molecular-beam adsorption experiments<sup>1</sup> as well as state resolved time-of-flight measurements of desorbing hydrogen molecules.<sup>2-5</sup>

Hydrogen molecules dissociate spontaneously at Pd(100), i.e., molecules with low kinetic energy dissociatively adsorb at Pd(100) surfaces with a large initial sticking coefficient.<sup>1,6</sup> The preference of nonactivated dissociation pathways for low kinetic energies of the H<sub>2</sub> molecules is also consistent with the independence of the initial sticking coefficient on incident angle  $\Theta$  as well as with the measured Maxwell-Boltzmann velocity distribution of desorbing H<sub>2</sub> molecules, which corresponds to the surface temperature of the palladium substrate.<sup>5,7</sup>

There are, however, clear indications that activated pathways exist as well. After a decrease for beam energies below  $\approx 0.15$  eV the initial sticking coefficient continuously increases.<sup>1</sup> At those larger kinetic energies the dependence of the initial sticking coefficient on the incident angle of the molecules changes into a  $\cos^{n-1}(\Theta)$  behavior with  $n$  increasing up to  $n \approx 1.6$  for beam energies of 0.4 eV. State resolved desorption experiments show that the occupancy of the first vibrational excitation is significantly higher than that corresponding to a gas of hydrogen molecules in equilibrium with the surface temperature.<sup>2,4,5</sup> This finding is called vibrational heating. On the other hand, the rotational degrees of freedom are occupied less than what the surface temperature would imply (rotational cooling).<sup>3</sup> In order to explain the vibrational heating and the values for  $n > 1$  in the angular distribution, as well as the increase of the sticking coefficient with the kinetic energy of the H<sub>2</sub> molecules, it has been found necessary in dynamic studies on two-dimensional model potential-energy surfaces (PES's) to assume the presence of a small (about 0.1 eV) barrier in the *exit channel*, i.e., in the region of the reaction pathway where the H-H bond is already significantly stretched.<sup>4,8</sup> Such an energy barrier, how-

ever, yields an additional kinetic energy of thermally desorbing molecules which has not been measured experimentally.<sup>4</sup>

There has been a long debate about the origin of the initial decrease of the initial sticking coefficient with increasing beam energies. Such a decrease and the observed dependence of the initial sticking coefficient on the angle of incidence with a coefficient  $n \leq 1$  have been usually assigned to the presence of a weak, metastable molecular bound state of the H<sub>2</sub> molecule at large distance from the surface (precursor state).<sup>1,10,11,9</sup> The presence of a precursor state has also been assumed in order to explain the slow decrease of the sticking coefficient with hydrogen coverage.<sup>6</sup> An alternative explanation relates the initial decrease to the presence of both activated and nonactivated dissociation pathways on the PES.<sup>12-14</sup> At low kinetic energies molecules with unfavorable orientations may reorientate during the dissociation process and follow a nonactivated pathway but with increasing kinetic energy this steering is more and more hindered and the number of molecules proceeding along activated pathways increases.

The fundamental understanding of the dissociative adsorption of hydrogen rests on the knowledge of the PES, which, as will be stressed here, depends rather crucially on all six coordinates of the two hydrogen atoms of the H<sub>2</sub> molecule. Experimental data have been interpreted in terms of a simple, often two-dimensional model PES as discussed above. Very recently, accurate density-functional theory (DFT) calculation of PES's (Refs. 15-19) and high-dimensional quantum-dynamical simulations<sup>14,20-22</sup> of H<sub>2</sub> dissociation have become available, thus opening the way for complete *ab initio* investigations of dissociative adsorption and associative desorption processes. Previous DFT studies of the H<sub>2</sub> interaction with metal surfaces concentrated mainly on systems where the dissociation is activated. There are a few studies of the interaction of H<sub>2</sub> molecules in front of surfaces of transition metals with partly filled *d* states.<sup>15,18,19</sup> In the recent work of White, Bird, and Payne<sup>19</sup> investigating hydrogen dissociation on W(100) the presence of nonactivated dissociation pathways was confirmed, but independence of the center-of-mass position of the molecule in the surface unit cell even for the most favorable orientation of the molecular axis activated dissociation has been ob-

tained as well. Molecules with their axes perpendicular to the surface have been found to experience no attractive interaction. Summarizing their results, White, Bird, and Payne expect molecular steering to play an important role in the dissociation dynamics at low incident energies.

In this paper we present and discuss detailed calculations of the potential-energy surface for hydrogen dissociation on Pd(100). Here we analyze the physical properties behind the topology of the PES. We note that the results are now sufficiently complete for a six-dimensional quantum-dynamical simulation of the dissociation of H<sub>2</sub> molecules on Pd(100).<sup>22</sup>

## II. CALCULATION METHOD

The calculations have been performed using density-functional theory within the generalized gradient approximation (GGA) (Ref. 23) and the full-potential linear augmented plane-wave method (FP-LAPW).<sup>24,25</sup> The application of the GGA is of crucial importance for the calculation of the PES of hydrogen dissociation,<sup>16,26,27</sup> but some important questions concerning the accuracy of PES's calculated applying the GGA remain.<sup>28</sup> The good agreement of experimental data with the results of high-dimensional quantum-dynamical simulation of H<sub>2</sub> dissociation based on the calculated PES for H<sub>2</sub>/Cu(111) (Ref. 20) and the PES presented in this paper<sup>22</sup> shows that the GGA reproduces the important features of these PES's with sufficient accuracy.

The FP-LAPW wave functions in the interstitial region are represented using a plane-wave expansion up to  $E_{\text{cut}}=11$  Ry, and due to the small radius of the muffin-tin sphere around H atoms ( $r_{\text{MT}}^{\text{H}}=0.37$  Å) it is necessary to take into account plane waves up to  $\tilde{E}_{\text{cut}}=169$  Ry for the potential representation.<sup>25</sup> Inside the muffin-tin spheres the wave functions are expanded in spherical harmonics with  $l_{\text{max}}=10$ , and nonspherical components of the density and potential are included up to  $\tilde{l}_{\text{max}}=3$ . For the  $\mathbf{k}$  integration we used 64 uniformly spaced points in the two-dimensional Brillouin zone corresponding to the  $c(2\times 2)$  surface unit cell. All calculations were performed nonrelativistically.

In the calculations we used a supercell geometry. The metal substrate is modeled by three layers of slabs which are separated by a 10-Å-thick vacuum region. Hydrogen molecules are placed at both sides of the slab. We used a rigid substrate because, due to the large mass ratio between Pd and H, the substrate will not change during the scattering event. The slab thickness of only three layers has been chosen with respect to the large computational demand of the evaluation of the PES. The application of such small layer thickness for the Pd(100) substrate gives an acceptable accuracy of the PES because, due to the large density of states at the Fermi energy, perturbations in the electronic structure induced by the impinging H<sub>2</sub> molecule are screened very effectively. We confirmed this by increasing the layer thickness of the substrate to five layers and comparing the total energy with respect to the separated H<sub>2</sub> and Pd(100) surface at various points of the reaction pathways. We found that in the region of the PES where the H<sub>2</sub> molecule approaches the surface and starts to dissociate the differences of the potential energy are less than 0.05 eV per H<sub>2</sub> molecule. In particular, the character of the dissociation pathway, whether it is activated or nonactivated, is not influenced. This part of the PES de-

termines the dynamics dissociation of the hydrogen molecule.<sup>22</sup> The dependence of the adsorption energy on the layer thickness is more pronounced in the region of the PES corresponding to adsorbed H atoms and strong H-Pd bonds. Here, the energy changes with increasing layer thickness up to 0.12 eV per H<sub>2</sub> molecule. For the PES calculation we employed a supercell with a  $c(2\times 2)$  surface structure. However, in the case of the geometry where the H<sub>2</sub> hits an on-top site and dissociates into two hollow positions, H atoms belonging to H<sub>2</sub> molecules in different surface unit cells within a  $c(2\times 2)$  structure would come too close during the dissociation process and the unit cell has been enlarged to a  $p(2\times 2)$  structure. The convergence of our results was tested using a  $p(2\times 2)$  surface unit cell, a plane-wave cutoff for the wave-function expansion of  $E_{\text{cut}}=13$  Ry, and a larger H muffin-tin radius  $r_{\text{MT}}^{\text{H}}=0.48$  Å in the exit channel region. The resulting changes of the potential energy were again found to be less than 0.08 eV per H<sub>2</sub> molecule.

The potential energy of a hydrogen molecule as it is used throughout the paper is defined as the DFT-GGA total energy. The energy zero is the energy of the geometry difference where the molecule is sufficiently far away from the surface ( $Z=3.7$  Å), such that there is practically no interaction between the molecule and the surface. Zero-point corrections and other vibrations are not included in the PES.

## III. RESULTS

First, we briefly summarize the properties of bulk Pd, the clean Pd(100) surface, and adsorbed hydrogen atoms.<sup>29,30</sup> The calculated lattice constant of Pd calculated by the DFT-GGA is 4.03 Å. This value is 3% larger than the lattice constant obtained within the local-density approximation (LDA), and 3.5% larger than the experimental value.<sup>29</sup> The clean Pd(100) surface shows a slight inward relaxation of the topmost Pd layer of  $-0.9\%$  of the bulk interlayer distance. This value is close to the relaxation of  $-0.6\%$  obtained by DFT-LDA calculation.<sup>29</sup> The equilibrium position of the hydrogen is the surface hollow site with a small adsorption height  $Z_0=0.1$  Å.<sup>29</sup> At the bridge site the adsorption energy is about 0.3 eV less favorable and the adsorption height increases to  $Z_0=1.3$  Å. Adsorption at the on-top position is even unstable against associative desorption.<sup>29</sup> Obviously, this pronounced dependence of the H-Pd bond strength on the geometry of the H adatom affects the potential energy during the dissociation process as will be discussed below.

Assuming that the positions of the substrate metal atoms can be kept fixed the PES of hydrogen dissociation depends on the six coordinates defining the position of the two hydrogen atoms of the H<sub>2</sub> molecule. Figure 1 shows the coordinate system used to describe the position and orientation of the H<sub>2</sub> molecule. The center-of-mass position is given by the three Cartesian coordinates ( $X, Y, Z$ ) for which the origin is at the center of a surface Pd atom. The two rotational degrees of freedom are given by the angle of the molecular axis with the  $Z$ -axis  $\theta$  (cartwheel rotation) and with the  $X$ -direction  $\varphi$  (helicopter rotation). The distance between the hydrogen atoms is denoted by  $d_{\text{H-H}}$ .

In order to investigate possible nonactivated pathways Fig. 2 gives the PES as functions of H-H distance  $d_{\text{H-H}}$ , and the molecular center-of-mass distance from the surface,  $Z$ ,

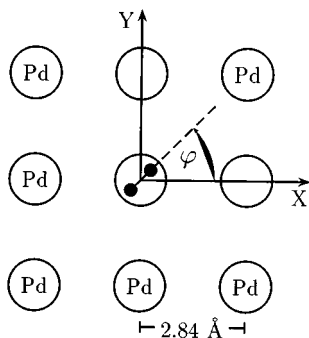


FIG. 1. Coordinate system used to describe the orientation of the  $H_2$  molecule with respect to the surface Pd atoms. The height of the H-H center of mass above the surface is  $Z$ , the H-H distance is  $d_{H-H}$ , and the angle of the molecular axis with the surface normal is  $\theta$ .

for fixed, characteristic positions of the molecule's center of mass in the surface unit cell: the bridge ( $X=0, Y=0.5 d_{Pd-Pd}, \varphi=0^\circ$ ) (a), the hollow ( $X=Y=0.5 d_{Pd-Pd}, \varphi=0^\circ$ ) (b), and the on-top ( $X=Y=0, \varphi=45^\circ$ ) (c) sites. The molecular axis is kept parallel to the surface ( $\theta=90^\circ$ ). For all geometries investigated in Fig. 2 this  $\theta=90^\circ$  orientation is the energetically most favorable one (see also Fig. 3 below). The dissociation over the bridge [Fig. 2(a)] and over the hollow site [Fig. 2(b)] is nonactivated and proceeds with a continuous gain of energy without a hampering energy barrier. The dissociation of a hydrogen molecule over the on-top site with fixed coordinates ( $X=0, Y=0$ ) is activated. The barrier has an energy of about 0.15 eV and is situated in the exit channel region. Figure 2 shows that nonactivated dissociation of  $H_2$  molecules on Pd(100) is possible over several nonactivated pathways including a large region of center-of-mass positions of the hydrogen molecule in the surface unit cell.

The two-dimensional cuts through the PES in Fig. 2 refer

to the situation that the orientation of the molecular axis is *fixed*. In reality the impinging hydrogen molecule rotates. In the following we discuss the dependence of the potential energy on the orientation of the molecular axis, i.e., on the angles  $\theta$  and  $\varphi$ .

The change of the orientations of the molecular axis with respect to the surface normal,  $\theta$ , and away from  $\theta=90^\circ$ , implies a significant increase of the potential energy. Figure 3 displays the change of the potential energy of a  $H_2$  molecule in dependence on the angle  $\theta$  of the molecular axis with the surface normal for two positions in the PES of Fig. 2(a), all other parameters being fixed. For both distances,  $Z=1.6 \text{ \AA}$  and  $Z=1 \text{ \AA}$ , the potential energy increases as  $\cos^2(\theta)$ . Figure 3 shows that with decreasing distance from the surface a minimum in the dependence of the potential energy on angle  $\theta$  with increasing depth develops. The cart-wheel rotations are more and more hindered. There is, however, a large difference between the "entrance" channel region, where the hydrogen molecule approaches the surface and the  $H_2$  bond is still intact, and the "exit" channel region where the H-H bond is stretched and the dissociation of the molecule starts. In the entrance channel, at larger heights  $Z$  (see open circles in Fig. 3), there is no or only a small repulsive interaction of the molecule with the surface even for a configuration with the molecular axis perpendicular to the surface  $\theta=0^\circ$ . Thus, the hydrogen molecules may approach the Pd(100) surface without an appreciable loss in energy and independent of their initial rotational state. In the exit channel where bonds of the hydrogen atoms with the surface form, the potential energy depends sensitively on the orientation  $\theta$  (see filled circles in Fig. 3) and the interaction of the molecule with the surface becomes repulsive already for small deviations from  $\theta=90^\circ$ . These conclusions are confirmed for the extreme case of a hydrogen molecule hitting the surface at the hollow site with its axis fixed perpendicular to the surface. We find that in the entrance channel the downmost hydrogen atom may approach the surface plane without a substantial barrier but

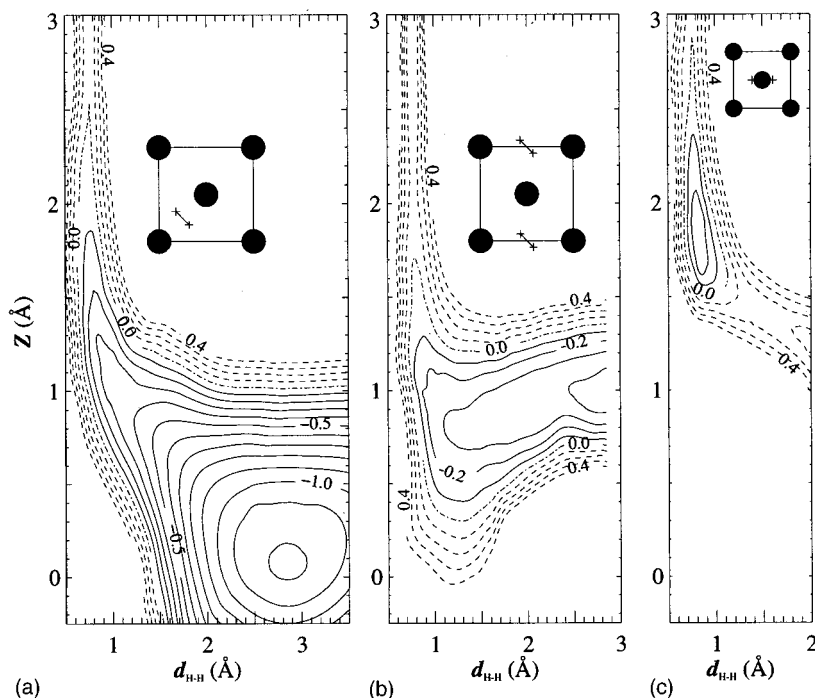


FIG. 2. Cut through the six-dimensional potential-energy surface (PES) of a  $H_2$  molecule in front of Pd(100). We display "elbow plots" where  $Z$  is the height of the  $H_2$  center of mass over the surface, and  $d_{H-H}$  is the distance between the two hydrogen atoms. The cut is defined by keeping the molecule parallel to the surface at an azimuthal orientation shown in the inset. The units of the potential energy are in eV and the interval between adjacent contour lines is 0.1 eV.

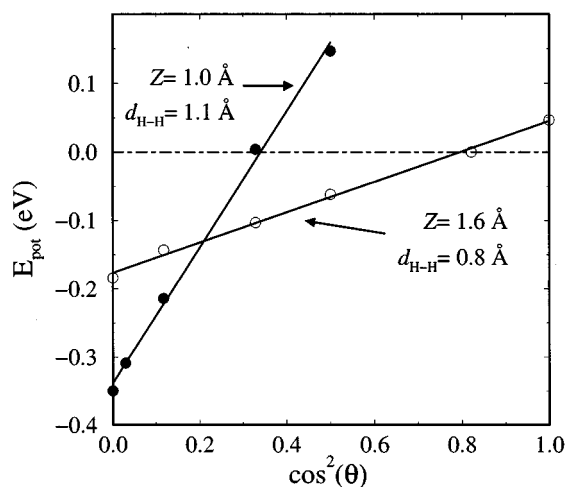


FIG. 3. Dependence of the potential energy of an H<sub>2</sub> molecule on the angle  $\theta$  of its molecular axis with the surface normal. The geometry for  $\theta=90^\circ$  corresponds to Fig. 2(a). The molecule is in the entrance channel at ( $Z=1.6 \text{ \AA}$ ,  $d_{\text{H-H}}=0.8 \text{ \AA}$ ) (open circles) or in the exit channel at ( $Z=1.0 \text{ \AA}$ ,  $d_{\text{H-H}}=1.1 \text{ \AA}$ ) (filled circles).

for *fixed* orientation of the molecular axis at  $\theta=0^\circ$  the potential energy increases drastically if the H-H bond is stretched and a nearly classical hard wall potential blocks the exit channel. Without any steering of the molecular axis during the dissociation, nonactivated dissociation pathways are possible only for molecules entering the exit channel region within a narrow region of orientations  $\theta$  of the molecular axis, and a low initial sticking coefficient would result.

We expect, however, that the steering of the molecular axis toward energetically favorable orientations is rather effective. At low kinetic energies the rotational period of the molecule is comparable to the time the molecule spends at distances  $Z$  corresponding to the end of the entrance channel. A molecule with a kinetic energy of  $E_{\text{kin}}=0.05 \text{ eV}$  travels  $0.6 \text{ \AA}/0.03 \text{ ps}$ , and when it is in the  $j=2$  rotational state it rotates during this time (or pathway) by about  $90^\circ$ . The large increase of the potential energy with angle  $\theta$  in Fig. 3 at the end of the entrance channel corresponds to large forces aligning the molecular axis towards orientations where the dissociation becomes energetically favorable (“steering effect”). With increasing beam energy in the adsorption experiments<sup>1</sup> both the kinetic and rotational energy of the molecules increase. This shortens the time the molecule spends at the end of the entrance channel and it becomes more likely that the molecule is reflected before the axis is aligned. An increase of the rotational energy implies that states with shorter rotational periods are occupied and those molecules turn out of the favorable orientation again more easily. As a consequence of the reduced steering the initial sticking coefficient is reduced.<sup>1,22</sup>

In the high-symmetry configurations shown in Fig. 2 the most favorable orientation of the H<sub>2</sub> molecule is that where the molecular axis is parallel to the surface ( $\theta=90^\circ$ ). For other center-of-mass positions and orientations  $\varphi$  of the molecule the minimum of the potential energy with respect to the angle  $\theta$  deviates from  $\theta=90^\circ$ . As an example, if the center of mass of the molecule is between the hollow and bridge positions ( $X=0.25d_{\text{Pd-Pd}}$ ,  $Y=0.5d_{\text{Pd-Pd}}$ ,  $\varphi=0^\circ$ ) the optimal

angle at a height  $Z=1.1 \text{ \AA}$  is  $\theta=65^\circ$ , i.e., the H atom pointing toward the hollow site is closer to the surface than that pointing toward the bridge site. This tilting of the molecular axis is consistent with the different adsorption heights of hydrogen adatoms at the hollow and bridge adsorption site. The potential energy is  $-0.3 \text{ eV}$ , a value between those found along the reaction pathway for a center-of-mass position over the bridge [Fig. 2(a)] and hollow site [Fig. 2(b)] at this height. Generally, the energetically most favorable orientation of the molecular axis,  $\theta$ , optimizes the H-surface bond strength of both H atoms of the H<sub>2</sub> molecule.

In the case of helicopter rotations, a pronounced decrease of the potential energy is found for geometries where H and Pd atoms get closer than a typical H-Pd bond length ( $1.7 \text{ \AA}$ ). These geometrical constraints affect different positions in the surface unit cell differently. Dissociation over the bridge site is nonactivated in the geometry shown in Fig. 2(a) ( $\varphi=0^\circ$ ). In the case where the hydrogen atoms are oriented towards the Pd atoms ( $\varphi=90^\circ$ ) helicopter rotations are not hindered only at large distances  $Z$ . For this configuration a steep increase of the potential energy is found already at the end of the entrance channel ( $Z=1.2 \text{ \AA}$ ,  $d_{\text{H-H}}=0.9 \text{ \AA}$ ). The H-Pd distance is  $1.54 \text{ \AA}$  and the potential energy for H atoms oriented towards the Pd atoms is  $E_{\text{pot}}=+0.25 \text{ eV}$ , i.e.,  $0.57 \text{ eV}$  higher than in geometry with the H atoms oriented toward the hollow sites [see Fig. 2(a)]. In the case where the center-of-mass position of the impinging molecule is over the hollow site, helicopter rotations are not hindered. A substantial increase of the potential energy for the orientation of the molecule with the H atoms oriented toward the surface Pd atoms ( $\varphi=45^\circ$ ) is found only in the exit channel where the H-H bond is already broken and both H atoms may easily reorient separately. In contrast to the cartwheel rotations the importance of the steering of the impinging hydrogen molecule into favorable orientations  $\varphi$  of the molecular axis will depend on the position of the molecule in the surface unit cell.

Metastable, weakly bound molecular states of H<sub>2</sub>, which may act as precursor states to the dissociation of the molecule, are commonly assumed to arise due to an interplay of the Pauli repulsion between the closed-shell electronic configuration of H<sub>2</sub> and the tails of the metal surface electronic states and the attractive van der Waals interaction.<sup>9</sup> In our calculations there is no indication of local minimum of the potential energy related to such types of precursor states at large distances in front of the Pd(100) surface. Although the long-range tail of the van der Waals interaction related to polarization fluctuations is not described within the GGA, recent calculations of the PES of He atoms in front of Rh(110) have shown<sup>31</sup> that the GGA is capable of adequately reproducing weakly bound states of adsorbates with a closed-shell electronic configuration. The absence of a considerable repulsive interaction of the impinging H<sub>2</sub> molecule with the surface at larger distances  $Z$  even for unfavorable orientations of the molecular axis and the large decrease of the potential energy already at distances  $Z \approx 2 \text{ \AA}$  found in Fig. 2 make this mechanism of the formation of molecular bound states in front of the metal surface rather improbable.

Local minima in a restricted subspace of the high-dimensional PES may arise not only at large distances in front of the surface due to the interplay of the Pauli repulsion

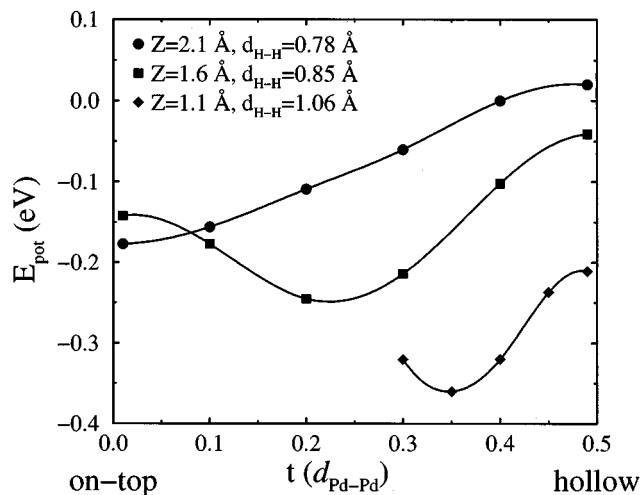


FIG. 4. Dependence of the potential energy of  $H_2$  on its center-of-mass position along a path  $R=(X=-t, Y=t, Z=\text{const})$  for three heights of the molecule. The molecular axis is parallel to the surface ( $\theta=90^\circ$ ) and the angle  $\varphi$  is fixed at  $\varphi=45^\circ$ . The point  $t=0$  corresponds to the geometry in Fig. 2(c).

and attractive van der Waals interaction but also at distances  $Z$  where the direct H-metal interaction dominates. They are a consequence of the pronounced dependence of the H-metal bond strength on the orientation of the molecule and the H-Pd distances. For an example, the dissociation pathway on top of a Pd surface atom [Fig. 2(c)] shows a minimum of  $E_{\text{pot}}$  in the entrance channel for a *fixed* center-of-mass position of the molecule.

A more detailed investigation of the dissociation over the on-top site shows that the minimum of potential energy seen in Fig. 2(c) is *not* a local minimum in the PES. The molecule can follow a purely attractive pathway if its center-of-mass position is able to relax in order to optimize the H-Pd bonding. Figure 4 shows the variation of the potential energy for different heights  $Z$  in the case where the center-of-mass coordinate is changed along a path  $t$ ,  $R=(X=-t, Y=t, Z=\text{const})$ . At large distances  $Z > 1.8 \text{ \AA}$  a position on top of the surface Pd atom ( $t=0$ ) is most favorable. At smaller heights the optimal reaction pathway involves a motion of the center-of-mass position towards the hollow sites. This geometry for lower  $Z$  is similar to the energetically most favorable orientation of a  $H_2$  molecule in front of a Rh(100) surface.<sup>15</sup>

It is interesting to compare the PES of hydrogen dissociation on W(100) (Ref. 19) with that on Pd(100). Both substrates are transition metals but tungsten and palladium crystallize into different lattice types (W is bcc, and Pd is fcc). Furthermore, W is in the middle of the 5d and Pd at the end of the 4d transition-metal series. The PES of hydrogen dissociation on Pd(100) and on W(100),<sup>19</sup> however, is qualitatively similar. Both PES's exhibit several nonactivated dissociation pathways. The pronounced dependence of the potential energy on the orientation of the molecule with respect to the surface metal atoms, especially on cartwheel rotations, is found also on W(100). There are also characteristic differences between both PES's. This is already documented in the different equilibrium adsorption site, which is at the bridge position on W(100) in contrast to the hollow

site on Pd(100). The geometry of the nonactivated dissociation pathways on both surfaces is different. For example, the dissociation with fixed center-of-mass position over the hollow site has an energy barrier of 0.3 eV on W(100) but no barrier on Pd(100). These differences will influence details of the dynamics of the hydrogen molecules on the PES. The calculations confirm, however, that the central features of the PES of hydrogen dissociation, e.g., the presence of nonactivated dissociation pathways, are determined by the presence of a partly filled  $d$  band in the electronic structure of both transition-metal substrates.

#### IV. BREAKING OF THE MOLECULAR BOND AND MAKING OF NEW ADATOM-SURFACE BONDS

The large reactivity of transition metals for hydrogen dissociation given by the presence of dissociation pathways with no or only small energy barriers is actuated by a partly filled  $d$  band.<sup>15,18,32-36</sup> The mechanism by which the  $d$  band may affect the energetics of hydrogen dissociation has been interpreted in different ways. Within the Harris-Andersson model<sup>32</sup> the repulsive interaction and the formation of barriers for  $H_2$  dissociation on surfaces of simple and noble metals is based on the work of Zaremba and Kohn,<sup>37</sup> related to the Pauli repulsion between the closed-shell configuration of the  $H_2$  molecule and the tails of the  $s, p$  waves of the surface electronic structure. At transition-metal surfaces the Pauli repulsion is suppressed by a low-energy occupation redistribution of electrons out of the  $s, p$  tails into the large density of holes in the  $d$  band just above the Fermi energy. Thus there is no direct interaction with the metal  $d$  states and the dissociation barriers are governed by the interaction at large distances to the surface. The analysis of the PES of hydrogen dissociation on various metal surfaces has shown that the top of the energy barriers occurs in the *exit channel*, i.e., at a point where the H-H interaction is significantly weakened and strong H-metal bonds are already being formed.<sup>18,34</sup> Those results, which are not consistent with the Harris-Andersson model,<sup>32</sup> have been consistently explained within a reactivity model<sup>18,34,38</sup> related to the frontier orbital concept.<sup>33,39</sup> Superimposed to the interaction of the hydrogen molecule with the  $s, p$  states of the metal, which gives rise to energy barriers found in simple metals, there is a contribution due to the direct interaction of  $H_2$  with the metal  $d$  states. It is repulsive as long as both the bonding and the antibonding states of the interaction of the  $H_2 \sigma_g$  orbital with the metal  $d$  bands are occupied, but becomes attractive in the case where the antibonding states get depleted. For transition metals with a high density of  $d$  states just at and below the Fermi level the states which are antibonding with respect to the adsorbate surface interaction are pushed above the Fermi level. Thus these antibonding states remain empty already in the case of a weak  $H_2$ -surface interaction and a small or no dissociation barrier results.

Feibelman<sup>15</sup> calculated the dependence of the potential energy of a hydrogen molecule in front of a Rh(100) surface in dependence of the orientation of the molecule with respect to the surface metal atoms for fixed heights  $Z$ . He found that the potential-energy variations are governed by the orientation dependence of the bond strength of the H atoms and the

metal  $d$  state. The most favorable orientation of the H<sub>2</sub> molecule is not that of the highest symmetry but that optimizing the H-surface bond strength.

Our results confirm the conclusion that the topology of the PES is determined by the direct interaction of the hydrogen molecule with the electronic states of the metal surface. The PES reflects the subtle balance between the weakening of the H-H bond in the molecule and the energy gain connected with the rehybridizing into bonds with the metal substrate.<sup>15,38</sup> Therefore, it is not unexpected that a correlation exists between the energy at a given height  $Z$  along the reaction path and the energy and optimal adsorption height of a hydrogen adsorbate at the position of the atoms of the H<sub>2</sub> molecule. The end of the entrance channel regions in Fig. 2 and, hence, the height  $Z$  of a hydrogen molecule at which a significant stretching of the intermolecular H-H distance occurs, correlates with the adsorption height of a single hydrogen adatom at the center-of-mass position ( $X$ ,  $Y$ ).<sup>29</sup> At large distances,  $Z > 1.9$  Å, center-of-mass positions of the hydrogen molecule on top of a Pd atom are energetically most favorable and center-of-mass positions over the hollow site have the lowest gain in potential energy. The direct dissociation with the center of mass of the molecule over the bridge site into two neighboring hollow sites ( $d_{\text{H-H}} = 2.85$  Å) in Fig. 2(a) is connected with a large gain in potential energy and a small curvature in the “elbow” plot, which is consistent with the large difference in adsorption height and energy between the bridge and hollow positions.<sup>29</sup> In the case where the molecule impinges at the hollow site [Fig. 2(b)] the situation is reversed. The molecule first closely approaches the surface but during the dissociation process the hydrogen atoms move upward to the energetically less favorable bridge positions. Consequently, although the dissociation pathway shown in Fig. 1(b) is nonactivated as well, the energy gain during the dissociation process of the hydrogen molecule is smaller and the curvature in the “elbow” plot is larger. The impact position of the molecule over the on-top site of a surface Pd atom [Fig. 2(c)] is energetically most favorable for larger  $Z$ . However, the H-Pd interaction on top of a metal atom is not strong enough to break the H-H bond without the formation of an energy barrier, which is in correspondence with the calculated instability of hydrogen adatoms against associative desorption at on-top sites.<sup>29</sup>

A more detailed picture of the interaction of a hydrogen molecule with the metal surface may be obtained by analyzing the electron density induced by a hydrogen molecule in front of the surface. In Fig. 5 we show the difference of the electron density between a hydrogen molecule in front of Pd(100) at a height  $Z = 1.8$  Å and that of the superposition of the density of the clean surface and of free hydrogen molecules. Two different configurations are considered. In Fig. 5(a) the H<sub>2</sub> molecule is over the on-top site and the potential energy has already a large negative value of  $-0.28$  eV and corresponds to the minimum in Fig. 2(c). In comparison, Fig. 5(b) shows the situation where the H<sub>2</sub> molecule is over the hollow site and the potential energy is close to zero. Figure 5(a) clearly shows that the H<sub>2</sub>-metal surface interaction is connected with a large polarization of both the H<sub>2</sub> molecule and the metal valence electrons. The drop in the potential energy in Fig. 2(c) is caused by a direct interaction between the  $\sigma_g$  state of the H<sub>2</sub> molecule and the  $3z^2-r^2$  orbital of the

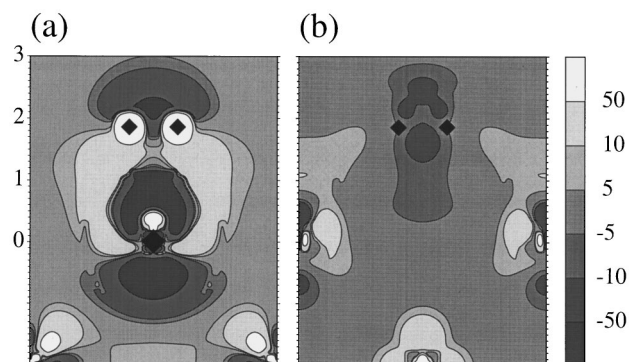


FIG. 5. Difference of the charge density between a hydrogen molecule in front of Pd(100) at a height  $Z = 1.8$  Å and that of the superposition of the charge density of the clean surface and of free hydrogen molecules. The center-of-mass position of the molecule is over the on-top site (a) and the hollow site (b). The cut plane is perpendicular to the surface and contains the H<sub>2</sub> molecule. The units for the charge density are  $10^{-3}$  Å<sup>-3</sup> and Å for the height above the surface.

surface Pd atom, which has a large density of states just below the Fermi level.<sup>35,36</sup> There is an occupation redistribution *inside* the  $d$  shell, which *depletes* the  $3z^2-r^2$  orbital, thus reducing the Pauli repulsion. Furthermore, holes are introduced into the  $\sigma_g$  state, weakening the H-H bond. In addition, an increase of electron density around the center of the H atoms and a more delocalized accumulation of charge density around the Pd atom occurs, corresponding to an interaction of the antibonding  $\sigma_u^*$  orbital of the hydrogen molecule with metal states just above the Fermi level. In the case where the H<sub>2</sub> molecule is shifted from the on-top site towards the hollow site, in Fig. 5(b), the interaction with surface Pd  $d$  states having a large density of states just below the Fermi energy is much weaker. The charge density induced around the hydrogen molecule is now more similar to the orthogonalization hole found for hydrogen dissociation at the  $s,p$  metal surface Al(110).<sup>40</sup> But also in this case there is a considerable depletion of the  $3z^2-r^2$  orbitals of the surface Pd atoms and an internal occupation conversion inside the  $d$  shell. Due to the weaker polarization of the  $d$  orbitals the potential energy is increased in comparison to the position over the on-top site, but also in this case no barrier forms. It is interesting to note that the polarization pattern in Fig. 5 is close to that deduced from the electronic properties of the *noninteracting* Pd(100) surface using the reactivity function introduced in Ref. 36. The induced charge density shown in Fig. 2 is consistent with the reactivity model developed in Refs. 18 and 34.

## V. CONCLUSION

We have calculated the PES of hydrogen dissociation on the clean Pd(100) surface using density-functional theory and treating exchange correlation in the generalized gradient approximation (GGA).<sup>23</sup> The results confirm the presence of several nonactivated dissociation pathways. It is shown that cartwheel rotations of the molecular axis out of the favorable orientation parallel to the surface are connected with a large increase of the potential energy, thus confining nonactivated

dissociation pathways to a small angular region of molecular axis orientations nearly parallel to the surface. Helicopter rotations, on the other hand, are hindered mainly because of steric restrictions if the H-Pd distance becomes shorter than a typical H-Pd bonding length. The calculations gave no evidence of a weak molecular bound state, or precursor state, of the H<sub>2</sub> molecule at large distances in front of the surface. There is nearly no repulsion of H<sub>2</sub> molecules in the entrance channel of the reaction pathways even in the case of the activated adsorption pathways and thus no appreciable energy is required for the hydrogen molecule to come close enough to the surface in order to form hydrogen-metal bonds. The observed pronounced differences in the potential energy in dependence on the geometry of the molecule with

respect to the surface are governed by the orientation and bond-length dependence on the covalent interaction of the hydrogen atoms mainly with the different Pd *d* bands. Summarizing these results it is concluded that the dynamics of the hydrogen molecule in the high-dimensional PES cannot be understood using low-dimensional model surfaces but requires a quantum-dynamic simulation including all degrees of freedom of the hydrogen molecule. Those calculations have been performed using the calculated PES presented in this paper as an input.<sup>22</sup>

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