Direct subsurface absorption of hydrogen on Pd(111).

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(March 21, 2022)

Abstract

We summarize and discuss some of the available experimental and theoretical data important for understanding the role played by subsurface sites in dissociative chemisorption calculations for the H₂/Pd(111) system. Then we use a semi-empirical potential energy surface (PES) to model the interaction of a H₂ molecule impinging on a Pd(111) surface. The London-Eyring-Polanyi-Sato (LEPS) construction has been extended to make direct subsurface absorption possible. A 2-dimensional wave packet calculation is used to find qualitative trends in the direct subsurface absorption and to reveal the time scales involved. We suggest that a partial in-plane relaxation occurs for the slowest incoming particles, thus resulting in a higher direct subsurface absorption probability for low energies.

68.35.Ja,82.20.Wt,82.20.Kh,82.65.Pa

Typeset using REVTEX

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I. INTRODUCTION

Hydrogen adsorption on Pd surfaces has during the last two decades been extensively studied for a number of reasons. Palladium has the ability to absorb large amounts of hydrogen in the bulk, and is thus interesting as a model system for understanding a good hydrogen storage [1,2]. The surface reactivity is also important for layered systems, where a thin Pd surface may be used to enhance hydrogen adsorption at low temperatures [3]. The interaction between hydrogen and transition metal surfaces has further importance for the understanding of various catalytic reactions and for metal embrittlement. Hydrogen adsorption on metal surfaces also has interest in itself, due to the quantum behaviour of the light H atoms.

In understanding the formation of a hydride phase it is important to know how the hydrogen enters the metal and how it is transferred from the surface to the bulk. Therefore a number of studies has been investigating the role played by subsurface sites. In Section II we summarize and discuss some of the experimental and theoretical data related to subsurface sites on Pd. In Section III we use this to construct a model PES for H\(_2\) impinging on a Pd(111) surface. Section IV describes the techniques used for the dynamical calculations, and a discussion of the model PES and results follow in Section V. Section VI concludes.

II. SUBSURFACE SITES ON Pd

Subsurface occupation connected with surface reconstruction has been observed for Pd(110) for coverages (\(\Theta\)) larger than 1 monolayer (ML) and at low temperatures (100–200 K) [4]. Besenbacher et al. [5] found a saturation coverage of 1 ML on the Pd(100) surface in the same temperature regime when considering deuterium adsorption. They also noted that the results of Ref. [6] are consistent with no hydrogen occupying subsurface sites at low temperatures. The theoretical calculations of Ref. [8] support this. Refs. [9–11] also agree that at low temperatures, 1 ML is the expected saturation coverage. But they also state
that at higher temperatures the subsurface sites play an important role in understanding the adsorption energy’s dependence on coverages above 1 ML.

In the case of Pd(111), Eberhardt et al. [12] were the first to postulate occupation of subsurface sites. After adsorbing hydrogen on a low temperature substrate and then heating it to room temperature, they concluded that the warming up caused a phonon assisted conversion of hydrogen from the surface sites to lower energy sites; the subsurface sites. The experimental results of Felter et al. [13] showed hydrogen to form two distinct phases with $\sqrt{3} \times \sqrt{3}R30^\circ$ symmetry and with low order-disorder transition temperatures; 85 and 105 K. To establish agreement between the experimental results and their calculations with the embedded atom method (EAM), they found that occupation of subsurface sites was crucial. When allowing the lattice to relax, the surface and subsurface sites were found to be very close in energy and separated by a small barrier. They also found the energies to be coverage dependent, with subsurface sites being lowest for coverages larger than 0.1 ML. For the two ordered phases with $\Theta = 1/3$ and $2/3$ ML, all the hydrogen was expected to go subsurface at 0 K. At the critical temperature for the order-disorder transition, approximately 60% of the hydrogen occupied the subsurface sites for both phases. These findings are consistent with electron-stimulated desorption measurements of Kubiak and Stulen [14].

In Ref. [15] Daw and Foiles gave a more detailed description of their EAM results presented in Ref. [13]. They found only the following sites energetically favorable for hydrogen occupation: surface tetrahedral ($A^+$), surface octahedral ($B^+$), subsurface octahedral ($A^-$) and subsurface tetrahedral ($B^-$). The classical energies, i.e. not including zero point energies, of these sites were found to be from $-2.905$ to $-2.950$ eV. This is in good agreement with the experimental value for the adsorption energy $-2.85$ eV of Conrad et al. [16] (the zero of the energy scale is set to be that of a free hydrogen atom, and we have neglected the zero point energies of the $H_2$ molecule and the adsorbed H atom). They again stressed that the energetical ordering of the four sites was coverage dependent. Further they stated that lattice relaxations are much more important for the $B^-$ sites (relaxation energy 0.36 eV) than the $A^+$, $A^-$ and $B^+$ sites (relaxation energies on the order of a few hundredths
of an eV). The calculated barrier height between the surface and subsurface sites for low coverages was only 50 meV when including lattice relaxations. It increased significantly with increasing coverage. For $\Theta = 0.64$ ML they found only $A^-$ occupation at 0 K, 50% subsurface occupation above the critical temperature and almost no occupation of $B^-$ sites at any temperature. Felter et al., using low-energy-electron-diffraction (LEED) measurements, returned to study the $\Theta = 2/3$ ML phase at 82 K in Ref. [17] and found the results to be consistent with a subsurface occupation in the range 0–60%.

Cluster calculations of Rochefort et al. [18] found the $A^-$ sites to be 0.3–0.4 eV higher in energy than the $A^+$ sites and the barrier height between the two sites to be 0.8 eV (for an unrelaxed surface). Ezzehar et al. [19], using a tight binding scheme not including lattice relaxations, found the energy of the $A^+$ sites to be $-2.880$ eV, considerably lower than the $A^-$ and $B^+$ sites ($-2.521$ and $-2.376$ eV, respectively). This gave no support for subsurface occupation, but they stated that this could be caused by the fact that they only looked at isolated impurities. Rick et al. [20] gave some EAM values for the barrier height between surface and subsurface sites. The $A^+$ and $A^-$ sites were separated by a 67 meV barrier, $B^+$ and $B^-$ by 37 meV. These are the adiabatic values, i.e. allowing for lattice relaxations. The static lattice had 181 and 148 meV for the two barriers, respectively. Chakraborty et al. [21] also found the in-plane relaxations, i.e. relaxations of metal atoms within the top metal layer, to be very important for the barrier height. Recently Ezzehar et al. [22] pointed out a tendency to $\sqrt{3} \times \sqrt{3}R30^\circ$ superstructure formation with hydrogen in both $A^+$ and $A^-$ sites, bringing them more in line with the experiments of Felter et al. [17].

Also recently, Löber and Hennig [23] used the full-potential linear muffin-tin orbital (FP-LMTO) method to study the Pd(111) surface. They found the $A^+$ and $B^+$ sites (their notation ffc or F and hcp or H, respectively) to be very close in energy, $-2.67$ and $-2.69$ eV, for $\Theta = 1$ ML. A slight coverage dependence was found for the adsorption energies since for $\Theta = 1/3$ ML the respective energies were $-2.74$ and $-2.80$ eV. These are in good agreement with the already mentioned experimental value of $-2.85$ eV [10]. For the subsurface $A^-$ (their notation $O_1$) sites they found the absorption energy to be $-2.60$ eV ($\Theta = 1$ ML)
when allowing for interlayer relaxations. The barrier height for the \( A^+ \) to \( A^- \) transition was calculated to 0.74 eV and found to be independent of interlayer relaxations. In Ref. [24] the barrier height was given as 0.82 eV under slightly different considerations.

Thus for Pd(111), the following picture emerge:

- There is good experimental and theoretical support for occupation of subsurface sites, even at low temperatures and low coverages.
- Interlayer relaxations are important for the depth of the subsurface well, but not for the barrier height.
- In-plane relaxations are very important for the barrier height between surface and subsurface sites.

However, this doesn’t necessarily mean that the inclusion of subsurface sites is important in a dissociative chemisorption calculation. The population of subsurface sites could be a result of thermally activated diffusion which is a slower process. We will come back to this in Section V.

III. THE PES

In the last years methods have been developed which, together with the increasing computing power, now make it feasible to do \textit{ab initio} calculations of many points on the PES [25–28], and then use a set of fit functions to interpolate between these values. These fit functions are not necessarily chosen because of their simplicity, but because they are flexible enough to allow a good fit to the \textit{ab initio} calculated points [27, 29]. There would be little gained if the fit functions were chosen too simple to accommodate the information of the \textit{ab initio} data.

However, in the cases where the full PES is not available from \textit{ab initio} calculations, it makes sense to choose a model potential which is simple, yet reproduces the main expected features of the true PES. Then one can use experimental data together with \textit{ab initio}
calculated points to construct the model PES. The London-Eyring-Polanyi-Sato (LEPS) potential, first introduced in dissociative chemisorption by McCreery and Wolken [30] and later used by others [31–34], is well suited to this. Fig. 1a shows the three interactions that go into the ordinary LEPS construction. Since we want to include subsurface sites in our model PES, this form will not suffice. We therefore extend the LEPS formalism by introducing an additional interaction representing the hydrogen interaction with the subsurface and bulk metal layers as shown in Fig. 1b. The resulting three-dimensional model PES is then given by

\[ V(r, z_1, z_2) = U_{HH}(r) + U_{HM}(z_1) + U_{HM}(z_2) \]

\[ + \sqrt{Q_{HH}(r)^2 + (Q_{HM}(z_1) + Q_{HM}(z_2))^2} - Q_{HH}(r)(Q_{HM}(z_1) + Q_{HM}(z_2)). \]

Here \( r \) is the hydrogen-hydrogen separation, and \( z_1 \) and \( z_2 \) are the heights above/below the surface plane for the two hydrogen atoms (\( z_1 \) and \( z_2 \) take positive values above the plane, negative below). The hydrogen-hydrogen (HH) interaction is described by the two functions

\[ U_{HH}(r) = U(r, r_{0HH}, \alpha_{HH}, \Delta_{HH}, D_{HH}) \]

\[ Q_{HH}(r) = Q(r, r_{0HH}, \alpha_{HH}, \Delta_{HH}, D_{HH}), \]

with the parameters chosen to be those of a hydrogen molecule far away from the surface (Table I). The hydrogen-metal (HM) interactions are chosen as the sum of the hydrogen-surface (HS) interaction and the hydrogen-subsurface (HSS) interaction:

\[ U_{HM}(z) = U(|z|, r_{0HS}, \alpha_{HS}, \Delta_{HS}, D_{HS}) + U(z + d_0, r_{0HSS}, \alpha_{HSS}, \Delta_{HSS}, D_{HSS}) \]

\[ Q_{HM}(z) = Q(|z|, r_{0HS}, \alpha_{HS}, \Delta_{HS}, D_{HS}) + Q(z + d_0, r_{0HSS}, \alpha_{HSS}, \Delta_{HSS}, D_{HSS}). \]

The surface-subsurface spacing is denoted \( d_0 \) and is equal to 4.24 \( a_0 \) for Pd(111). The standard LEPS form follows for \( U \)

\[ U(r, r_0, \alpha, \Delta, D) = \frac{D}{4(1 + \Delta)} \left( (3 + \Delta) \exp\{-2\alpha(r - r_0)\} - (2 + 6\Delta) \exp\{-\alpha(r - r_0)\} \right) \]

and \( Q \)
\[ Q(r, r_0, \alpha, \Delta, D) = \frac{D}{4(1 + \Delta)} \left( (1 + 3\Delta) \exp\{-2\alpha(r - r_0)\} - (6 + 2\Delta) \exp\{-\alpha(r - r_0)\} \right). \] (5)

The parameters for the hydrogen-metal interactions in Table II are chosen to fit values for atomic hydrogen approaching the Pd(111) surface above the surface tetrahedral (A\textsuperscript{+}) site, and going down to the subsurface octahedral (A\textsuperscript{-}) site. We have constructed two different PESes 1 and 2 with barrier heights \( E_B = 0.8 \) and 0.4 eV per H atom, respectively. The motivation for this is given in Section V. Both PESes mimic the H\(_2\) molecule approaching the surface with the molecular axis parallel to the plane of the surface and dissociating above a bridge site into the threefold hollow sites. This is a favorable adsorption geometry and also allows the hydrogen atoms to go to the subsurface sites (A\textsuperscript{-}, B\textsuperscript{-}) directly below the threefold surface sites (A\textsuperscript{+}, B\textsuperscript{+}). For simplicity we have assumed the same energetics for the B and A sites. In the dynamical calculations we only have two degrees of freedom: \( r \) and \( Z \), the height of the center of mass above the surface. This means that we are restricted to that both atoms in the molecule either go to the surface or to the subsurface. Fig. II shows a contour plot of the resulting PES 1, given by \( V(r, Z, Z) \).

IV. DYNAMICAL CALCULATIONS

The two-dimensional Hamiltonian operator governing the motion of a hydrogen molecule impinging on a flat, rigid metal surface is

\[ \hat{H} = \frac{1}{2M} \frac{\partial^2}{\partial Z^2} + \frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + V(r, Z, Z). \] (6)

We use atomic units unless otherwise explicitly stated, which gives the total mass \( M = 3674.4 \) and the reduced mass \( \mu = 918.6 \). \( V(r, Z, Z) \) is the model PES described in the previous section. The time independent Hamiltonian gives the formal solution to the Schrödinger equation

\[ \Psi(r, Z, t + \delta t) = e^{-i\hat{H}\delta t} \Psi(r, Z, t). \] (7)
We use a 34.5 by 15.0 grid, with $Z$ ranging from $-6.5$ to 28.0 and $r$ from 0 to 15.0. 512 and 64 points are used in the $Z$ and $r$ directions, respectively. The numerical time evolution of the wave function is obtained by expanding the time evolution operator $e^{-i\hat{H}t}$ according to the Chebychev technique [35]. The action of the potential energy operator on the wave function is found by multiplying the wave function by the potential energy at each grid point. Added to this is the kinetic energy part of the Hamiltonian, obtained by the FFT technique of Kosloff and Kosloff [36]. The initial wave function is chosen to be a product of the vibrational ground state of the hydrogen molecule, $\chi_0(r)$, and a Gaussian in $Z$:

$$\Psi(r, Z, t_0) = \chi_0(r) \left( \pi\delta^2 \right)^{-1/4} \exp \left\{ -\frac{(Z - Z_0)^2}{2\delta^2} + ik_0Z \right\}. \quad (8)$$

The shape of the vibrational ground state wave function was obtained analytically from Ref. [37], whereas the normalisation constant is found numerically. $Z_0$ and $k_0$ define the initial position and momentum, respectively. For all the runs we start the wave packet at $Z_0 = 15.0$. This far away from the surface the PES has obtained its asymptotic value in the $Z$ direction. Choosing $Z_0$ smaller would cause the wave packet to miss a part of the drop in potential energy towards the surface, thus reducing the kinetic energy with which the wave packet is approaching the barrier.

Since we have not performed an asymptotic analysis of the wave packet in line with Refs. [38–40], we want to have a narrow energy distribution in our initial wave packet, thus $\delta = 3.0$. We will then take $E_0 = k_0^2/2M$ to be the initial kinetic energy of the wave packet. To avoid problems with the wave function at the boundary of the grid, we multiply it by an exponential damping function after each time step. The damping function is 1 in the entrance channel and the interaction region. In the exit channel it is continuously decreasing from 1 to 0 towards the $r = 15.0$ boundary of the grid. The direct subsurface absorption probability, $\eta_{SS}$, is found by accumulating the removed norm for $Z$ less than 0. Norm conservation is checked.

The Chebychev method is known to be most efficient for long time steps [35]. But since we only damp the wave function after each time step (as opposed to the use of optical
potentials, where the damping function effectively is a part of the Hamiltonian \([41–43]\), a too long time step would allow the wave function to reach the boundary of the grid. We have found that a time step of 300 a. u. is short enough to avoid this problem, yet long enough for the Chebychev technique to be efficient. Repeated runs with different initial kinetic energies then give the energy dependence of \(\eta_{SS}\).

V. DISCUSSION

The simple form of our model PES carries some limitations. Even though there are quite a few tunable parameters in our model PES, the Morse form of \(U\) and \(Q\) in Eqs. 4 and 5 limits how many points we can accurately fit. The positions of the surface and subsurface minima, \(r_S\) and \(r_{SS}\), are bound to be close in absolute value. Felter et al. [17] gave values from 1.5 to 1.6 for \(r_S\) and from \(-2.2\) to \(-2.3\) for \(r_{SS}\), whereas our model PES has \(r_S = 1.5\) and \(r_{SS} = -1.7\). Also the subsurface absorption minimum \((E_{SS})\) always lies slightly below the surface adsorption minimum \((E_S)\). This fits in the case of a relaxed lattice [13,15,20], but not for the static lattice [18,19] where \(E_{SS}\) is significantly higher than \(E_S\). However, we think this is not too important for our dynamical calculations. The most important quantity in determining whether the hydrogen goes to the surface or to the subsurface is the barrier height. The values of \(E_{SS}\) and \(r_{SS}\) will be more important when discussing thermally activated diffusion between surface and subsurface sites. This process is however many orders of magnitude slower than the dissociative adsorption/absorption process, as is indicated by the low surface to subsurface rates of Rick et al. [20].

Another possible problem with our model PES is the cusp at \(Z = 0\) introduced by the dependence of \(|Z|\) in Eq. 3. It yields a barrier that is somewhat narrower than that of the expected smooth physical PES. At the same time, we see that the barrier height is somewhat larger near the entrance channel than in the asymptotic region (large \(r\) values). We have fitted our model PES to values for atomic hydrogen interacting with a metal surface, and the details of the interaction region are not yet known. Thus, our barrier height should be
taken *cum grano salis*. Having said this, the increasing barrier height for small \( r \) values is easy to understand physically. For the hydrogen molecule to dissociate and absorb, the atoms have to move towards the favorable absorption sites. Fig. 3 shows a snapshot of the wave function when it is crossing the barrier, obtained from the dynamical calculations. We can see that it crosses the barrier around \( r = 4 \), about the same as the distance between two neighboring hollow surface sites which the atoms pass close to on the way subsurface. We therefore believe that our model PES has the qualitatively correct features for describing direct subsurface absorption.

In Section II we mentioned the diverging results when it comes to the values of the barrier heights. For a static lattice the calculated barrier heights vary from 148 and 181 meV [20] to 0.74 and 0.76 eV [23], 0.8 eV [18], and 0.82 eV [24] per H atom. Clearly this will have drastic effects on the probability of subsurface absorption. Löber [24], Löber and Hennig [23], and Rochefort *et al.* [18] all work within the local density approximation (LDA). It has been shown by others [25–27] that LDA is not able to reproduce the experimental barrier height of the \( \text{H}_2/\text{Cu} \) system. This barrier is different from the one we are considering in the respect that it is located in front of, and not within, the surface. But if the trends of the \( \text{H}_2/\text{Cu} \) system is followed by the \( \text{H}_2/\text{Pd} \) system, it means that \( E_B = 0.74 \text{ eV} \) [23] is too low. But Löber and Hennig state that this value is already too high when compared to available experimental data. This, in addition to the large discrepancies between the LDA barrier heights [18,23,24] and the EAM values of Rick *et al.* [20], shows that more effort is needed to determine a more reliable value. For our model PES 1, we have chosen the parameters to give a barrier height \( E_B = 0.8 \text{ eV} \) per H atom.

In Section II we also saw that allowing for in-plane relaxations gave much lower values for the barrier height. Therefore it is important to answer the question: does the lattice have time to relax? The estimated surface Debye temperature of Pd is \( T_D = 164 \text{ K} \) [20]. This gives a measure of the maximum surface phonon frequency \( \omega_D \) and sets a typical time scale \( (t_s) \) for the surface phonons to \( t_s = 2\pi/\omega_D = 2\pi/k_B T_D = 12000 \text{ a. u.} \). We suppose that this is about the same time requested to perform the in-plane relaxation, since both
the relaxation length and the amplitude of the phonon vibration are typically a few percent of $d_0$. Next we have to know how much time the wave packet spends in the barrier region. Studying snapshots of the wave function like Fig. 3 reveals that this time varies from about 1000 a. u. for the highest initial kinetic energies to more than 5000 a. u. for the lowest ones. Thus when $E_0$ is high the wave packet spends a shorter time in the barrier region than it would take the nearby substrate atoms to relax, thence it is reasonable to use a barrier height representing a static lattice. Nevertheless, since the time needed for relaxation is much shorter than the diffusion time scale, the interlayer relaxed value for $E_{SS}$ should be used when discussing diffusion back to the surface. For a lower $E_0$, the wave packet spends more time in the barrier region and the nearby substrate atoms should have time to at least partially relax. This will cause the barrier height to drop. The longer the wave packet spends in the barrier region, the more the surface has time to relax, and the larger this drop will be. The parameters of our model PES 2 have been chosen to give a barrier height $E_B = 0.4$ eV per H atom, which we will think of as that of a partially relaxed lattice valid for a small $E_0$.

With this low barrier height, the barrier actually lies below the energy of the free hydrogen molecule, so most of the wave function is expected to go directly to the subsurface. If we had used even lower values for the static lattice barrier height, the barrier would have been so small compared to the kinetic energy that is gained on the way towards the surface, that the wave function would be smeared out between the surface and subsurface site even for small kinetic energies. It would not be localized before the thermalization occurred. At that time the relaxation also should have finished, so that $E_S$ and $E_{SS}$ are almost degenerate. With a low barrier height, we could thus expect equal probabilities for finding hydrogen at the surface and subsurface, independent of $E_0$.

Fig. 4 shows the results of the dynamical calculations for the two PESes. For a static lattice (PES 1) the subsurface gets appreciably populated only for $E_0$ above 0.7 – 0.8 eV. The partially relaxed lattice, represented by PES 2, shows almost 70% subsurface occupation already for the smallest initial kinetic energies. If the lattice was allowed to relax during
the dynamical calculations, the resulting $\eta_{SS}$ is expected to be a combination of the curves for PES 1 and PES 2. Without introducing a time dependent PES and allowing for energy exchange between the hydrogen molecule and substrate atoms, only qualitative trends can be given. For low $E_0$, there are two competing effects. Firstly, an increase in $E_0$ makes it easier for the wave packet to cross the barrier. Secondly, the nearby substrate atoms get a shorter time to relax, so that the effective barrier height increases. The net result is a decrease in $\eta_{SS}$. As we continue to raise the initial kinetic energy, the lattice gets even shorter time to relax. At a certain point, the increasing kinetic energy is more important than the increasing barrier height, and $\eta_{SS}$ then starts to grow. This qualitative trend is suggested by the dashed line in Fig. 4.

As pointed out by the referee, also the barrier width will change when the surface has time to relax. This might affect the behaviour of $\eta_{SS}$ for low energies, since the tunneling wave packet has a complicated interaction in the intermediate region. The size of this effect is difficult to estimate without going through a full time dependent analysis. However, we do not believe that the barrier width will change substantially due to the in-plane relaxation, since then the positions of the surface and subsurface minima are fixed. In Fig. 4 we can see a small effect of the change in barrier width following a lower barrier height: the slope of the curve for PES 2 is slightly steeper than for PES 1 in the same region of $\eta_{SS}$. Interplane relaxations typically increases the interplane distance and hence the barrier width with only a few percent, not enough to make any major contributions to $\eta_{SS}$. The upper energy limit should moreover be unaffected, so we believe that the global trend will have the same qualitative features as the suggested curve in Fig. 4.

In Section 11 we mentioned that the experimentally observed occupation of subsurface sites could be a result of thermally activated diffusion from surface sites. Even though our results are dependent on the particular geometry we have chosen for the incoming molecule, we have demonstrated the possibility for direct subsurface absorption taking place on the same time scale as dissociative adsorption. This possibility is seen both for low and high barrier heights, the only difference is in the dependency on $E_0$. 

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VI. CONCLUSION

The most important quantity when discussing direct subsurface absorption is the barrier height between the surface and subsurface. This is however not known experimentally, and the calculated values vary a lot. Calculations have further shown that in-plane relaxations lowers the barrier height significantly, and it is therefore crucial to decide whether the surface has enough time to relax. Our dynamical calculations have shown that high-energetic molecules may be viewed in the static limit, that is with a high barrier height. When the hydrogen molecule has lower kinetic energy, however, the time spent in the barrier region is comparable to the time needed to perform a relaxation of the metal lattice. For a barrier height of 0.8 eV per H atom, we suggest that this results in a probability of direct subsurface absorption that is decreasing for low initial kinetic energies due to the increasing barrier height. For higher energies, the barrier height stabilizes, and the probability of overcoming the barrier thus increases. For barrier heights below 0.4 eV per H atom, we expect that about 50% of the hydrogen is found subsurface after thermalization, independent of the initial kinetic energy.

The phonon mode associated with the variation of the barrier height has been identified by Chakraborty et al. [21] and Rick et al. [20]. With the total energy calculations techniques now available, it should in a future study be possible to calculate the frequency of this phonon excitation. This would clarify the extent of the coupling between the dissociation process and this phonon mode, and thus check the validity of using the static limit.

Our results are of course dependent on the limitations of the two-dimensional calculations and the particular geometry chosen. To obtain more reliable results it would be necessary to work with at least three dimensions. It would also be valuable to have more points to the fitting of the PES. We therefore believe that total energy calculations to create a full three- or higher-dimensional PES in the line of Refs. [25, 28] should be taken on.
VII. ACKNOWLEDGMENTS

We would like to thank Geert-Jan Kroes for helpful discussions and suggestions on the dynamical calculations and Runa Löber, Axel Gross and Steffen Wilke for sending us their results prior to publication. R.A.O. would like to thank George Darling and Stephen Holloway for organizing the Dynamics Workshop in Chester, U.K., which offered a very good opportunity to discuss the most recent ideas on quantum dynamical calculations and potential energy surfaces. Many thanks to the participants of this workshop as well, especially Rick Mowrey for being so positive and encouraging. Finally, we would like to thank John Rekstad for his support. This work has been financed by the Norwegian Research Council.
FIGURES

FIG. 1. The interactions used in a) the ordinary and b) our modified LEPS potential energy surface. Solid, dashed and dotted lines specifies the hydrogen-surface, the hydrogen-hydrogen, and the hydrogen-subsurface interactions, respectively.

FIG. 2. The potential energy surface 1 for H$_2$ on Pd(111) used in the calculations. The barrier height is $E_B = 0.8$ eV per H atom, and the contour spacing is 0.5 eV. The model parameters are listed in Table I.

FIG. 3. A snapshot of the absolute square of the wave function taken at $t=4200$ a. u. The initial kinetic energy was 0.89 eV, the initial width in the Z direction was $\delta=3.0$ $a_0$, and it started at $Z_0=15.0$ $a_0$. The potential energy surface 1 with barrier height $E_B = 0.8$ eV per H atom was used in the dynamics.

FIG. 4. The probability of direct subsurface absorption $\eta_{SS}$ as a function of initial kinetic energy $E_0$ for the static (PES 1) and partially relaxed (PES 2) lattice. The dashed curve indicates qualitatively how we think the curve would go if the lattice was allowed to do in-plane relaxations during the dynamical calculations.
TABLE I. Parameters for the two different potential energy surfaces 1 and 2 used in the dynamical calculations. PES 1 gives a barrier height $E_B = 0.8$ eV per H atom. PES 2 has $E_B = 0.4$ eV per H atom. Both surfaces have $E_S = -2.85$ eV per H atom, $E_{SS} = -2.95$ eV per H atom, $r_S = 1.5 \, a_0$, and $r_{SS} = -1.7 \, a_0$.

|        | $r_0[a_0]$ | $\alpha [a_0^{-1}]$ | $\Delta[1]$ | $D[^{\text{eV}}]$ |
|--------|------------|---------------------|-------------|-----------------|
| H-H    | 1.4002     | 1.0282              | 0.05        | 4.745           |
| H-S (PES 1) | 1.613   | 0.29                | 0.2         | 2.694           |
| H-SS (PES 1) | 2.0     | 0.29                | 0.2         | 0.272           |
| H-S (PES 2)  | 1.613   | 0.214               | 0.2         | 2.656           |
| H-SS (PES 2) | 2.0     | 0.214               | 0.2         | 0.272           |
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