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Adsorption and diffusion on a stepped surface: Atomic hydrogen on Pt(211)

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We present density functional theory calculations for atomic hydrogen interacting with a stepped surface, the Pt(211) surface. The calculations have been performed at the generalized gradient approximation level, using a slab representation of the surface. This is the state-of-the-art method for calculating the interaction of atoms or molecules with metal surfaces, nevertheless only few studies have used it to study atoms or molecules interacting with stepped surfaces, and none, to the best of our knowledge, have considered hydrogen interacting with stepped platinum surfaces. Our goal has been to initiate a systematic study of this topic. We have calculated the full three-dimensional potential energy surface (PES) for the H/Pt(211) system together with the vibrational band structure and vibrational eigenfunctions of H. A deep global minimum of the PES is found for bridge-bonded hydrogen on the step edge, in agreement with experimental results for the similar H/Pt(533) system. All the local vibrational excitations at the global minimum have been identified, and this will serve as a helpful guide to the interpretation of future experiments on this (or similar) system(s). Furthermore, from the calculated PES and vibrational band structure, we identify a number of consequences for the interpretation or modelling of diffusion experiments studying the coverage and directional dependence of atomic hydrogen diffusion on stepped platinum surfaces. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1755664]

I. INTRODUCTION

The motivations for studying hydrogen interacting with platinum surfaces are easy to find. Together with palladium, platinum is the most important catalyst for heterogeneous hydrogenation reactions. It is also an interesting model system for developing a better understanding of parts of the intermediate reactions steps in certain fuel cells. But maybe more importantly, it is one of the systems for which the closing of the so-called ''structure gap'' between surface science and heterogeneous catalysis can be investigated both experimentally and theoretically by today's state-of-the-art methods.

In the 1970s it was debated whether the dissociation of molecular hydrogen on platinum surfaces was facilitated by the presence of atomic steps on the surface, with a number of experimental studies on deuterium–hydrogen exchange reactions seeming to indicate that this was indeed the case.[1–8] Very recent molecular beam experiments by Gee *et al.* add convincing evidence to step sites being clearly more reactive towards hydrogen dissociation than terrace sites.[9,10] The experimental evidence from other systems also indicates that the structure gap is ''real,'' supporting the view that ''special'' sites like steps, kinks, defects, or facet edges are more reactive (or exhibit different properties) than sites on the ''perfectly flat'' parts of the surface.[11–22]

The theoretical state-of-the-art method of today for calculating the interactions between atoms or molecules and metal surfaces is considered to be density functional theory (DFT) at the generalized gradient approximation (GGA) level employing a slab or supercell representation of the surface (see e.g., Refs. 23–29). However, most of the studies based on this periodic DFT/GGA approach have so far been performed on defect-free low index single crystalline surfaces, the reason being that the larger unit cells required to treat other systems make the calculations rather expensive computationally. In light of the experimental evidence, the relevance of these studies to heterogeneous catalysis might be questioned. This realization has prompted a few periodic DFT/GGA studies on stepped, rough, or (very) open surfaces (see, e.g., Refs. 14, 15, 18, 20, 21, 30–36), and they all confirm the experimental view that the reactions between atoms/molecules and such surfaces can be appreciably different than the reactions between atoms/molecules and defect-free low index single crystalline surfaces.

As already indicated above there is a considerable experimental literature on hydrogen interacting with both the

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low index and stepped platinum surfaces (for additional references see, e.g., Refs. 9, 10, 37, 38). Theoretical studies on the interaction of hydrogen with the low index platinum surfaces employing the periodic DFT/GGA method for calculating the electronic structure are not so numerous, nor are theoretical studies employing (quasi) classical or quantum dynamical methods to investigate the dynamics of hydrogen atoms or molecules at or close to these surfaces (see, e.g., Refs. 37–44 and references therein). To the best of our knowledge, the periodic DFT/GGA method have so far not been applied to hydrogen interacting with stepped platinum surfaces. This paper is the first in a series with the aim of improving on this situation. The focus in this first contribution will be on atomic hydrogen interacting with a stepped Pt(111) surface, the Pt(211) surface. The choice of the Pt(211) surface is a compromise between computational cost and realistic modelling of a stepped surface: The Pt(211) surface has terraces that are three rows of Pt atoms wide which in the following will be seen to be wide enough to provide distinct terrace and step regions. Still, the unit cell is small enough to make this rather extensive study computationally feasible. To be able to make a direct comparison to the very recent experiments of Gee *et al.* on the H/Pt(533) and H_2/Pt(533) systems[9,10] the Pt(533) surface would have been a desirable choice, but the extra computational cost would in our case have become inhibiting. However, the Pt(211) and Pt(533) surfaces are very similar and we still should be able to make a relevant comparison to the results of Gee *et al.*

Based on a linear combination of atomic orbitals (LCAO) approach, we obtain DFT/GGA results for the H/Pt(211) system using a slab representation of the surface. We use this method to determine the full three-dimensional (3D) potential energy surface (PES) for a hydrogen atom interacting with the Pt(211) surface, together with its vibrational band structure and vibrational eigenfunctions. This will be helpful in determining the position of the more strongly bonded adsorption state close to or at the step edge[9] by providing site-specific vibrational bands that could be probed experimentally. Another issue that will be addressed originates from the knowledge that some experimental effort has gone into determining possible directional anisotropies in the hydrogen mobility due to the presence of atomic steps on a surface,[45–49] and that the theoretical tools to model diffusion on stepped surfaces are rather well developed.[50–56] However, the modelling has been hampered by the lack of accurate PESs describing the diffusion.[54] Our periodic DFT/GGA results might serve as a first step in the direction of developing such a PES for hydrogen diffusion on a stepped platinum surface by providing some detailed information about the important features of the PES.

In the following section some details of the calculational method will be given. Our results for the H/Pt(211) system follow in Sec. III, and these results are discussed in relation to experimental results and other theoretical contributions in Sec. IV. Section V concludes.

TABLE I. The basis sets used in the H/Pt(211) calculations. An NAO is a numerical atomic orbital, and the numbers refer to the exponents (in units of a_0^{-1}) of a Slater-type orbital. Orbitals not indicated were kept frozen.

Element	Basis
Pt	$5d$(NAO,1.8), $6s$(NAO,2.1), $6p$(2.1)
H	$1s$(NAO,1.58), $2p$(1.0)

II. CALCULATIONAL METHOD

The program ADF–BAND[57–59] was used to solve the Kohn–Sham equations[60,61] self-consistently for a H atom adsorbed on a Pt(211) surface, modelling the surface by a slab with translational symmetry in two directions. A combination of numerical atomic orbitals obtained from numerical Herman–Skillman-type calculations[62] and Slater-type orbitals forms a flexible basis set that has been used in the expansion of the one-electron states. It is worth to note that full convergence with respect to the basis set can be obtained without the use of plane waves, as has been demonstrated in the past.[58] The calculations can in principle be performed with all electrons included in the variational space. However, deeper lying electronic levels are kept frozen when explicit tests show that their variational inclusion has negligible effect. Pseudopotentials are not used. The matrix elements of the Hamiltonian are calculated employing an accurate Gauss-type numerical integration scheme,[59] and the **k**-space integration can be done accurately using the quadratic tetrahedron method.[63]

The Vosko–Wilk–Nusair formulas[64] are used to calculate the exchange–correlation energy within the local density approximation (LDA). In this study we have employed a GGA that combines the Becke correction[65] for the exchange energy with the Perdew correction[66] (BP) for the correlation energy. Scalar relativistic corrections are included through the zeroth-order regular approximation (ZORA).[67–69]

The computational parameters have been chosen to ensure that the real space and **k**-space integrations are converged to within 10 meV and 20 meV, respectively, for the adsorption energies and the relative energy differences. The convergence with respect to the basis set (given in Table I) is about 50 meV. This level of accuracy has also been demonstrated for similar basis sets for the CO/Cu(100)[70] and CO/Pt(111)[71] systems. From Fig. 1 it is seen that a three layer slab gives results that are converged to within 50 meV of the four and five layer slabs (note that we here refer to the number of ''full'' layers, see Fig. 2), and this is in accordance with results from a number of studies for flat surfaces.[43,70–72] Our results are given for a slab frozen at a Pt–Pt distance equal to the experimental bulk lattice constant (5.24 bohr), where we have checked that relaxation effects do not change the conclusions reached here (a more detailed discussion of this point is given at the end of Sec. III).

We have used two Cartesian coordinate systems in this study. A ''primed'' system that is spanned by an x' axis along a step edge, a z' axis along the (111)-direction [the surface normal to the (111)-terraces], and a y' axis in the plane of the (111)-terraces, together forming a right-handed system (see Fig. 2). The choice of working (partly) with this primed

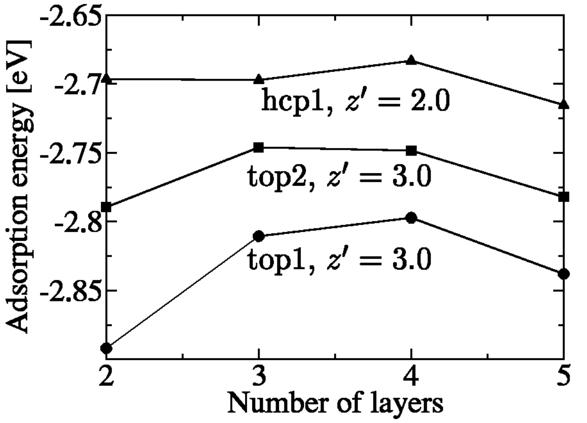


FIG. 1. The convergence of the adsorption energy is shown for the three different sites top1, top2, and hcp1 [see Fig. 2(c)] with respect to the number of layers. The height above the surface (z') is chosen close to the equilibrium position above these sites. Note that the position above the surface is given relative to the "primed" coordinate system, and is thus measuring the height above the terrace plane.

system has been made due to the natural labelling it provides for the sites on the (111)-terrace. It also allows us to demonstrate clearly that the extra barrier we find when moving along the diffusion path from one terrace to the next, is not located at the step itself, but well away from it. The "unprimed" system is the natural one for the Pt(211) surface, and the primed and unprimed systems are connected by the transformation:

$$x = x',$$
$$y = y' \cos\chi + z' \sin\chi, \tag{1}$$
$$z = z' \cos\chi - y' \sin\chi,$$

with

$$\cos\chi = \frac{4}{\sqrt{18}}, \quad \sin\chi = \frac{1}{3}. \tag{2}$$

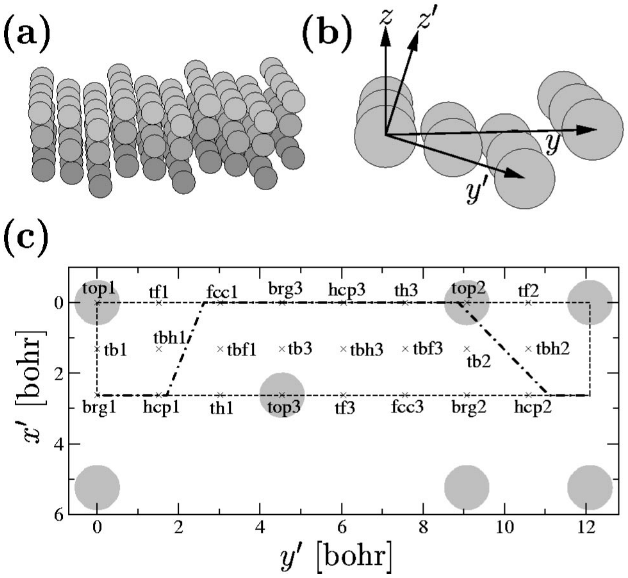


FIG. 2. (a) Three layer representation of a relatively large part of the Pt(211) surface to give an overall impression of this surface, with the three different layers marked by different shades of gray. Three (111)-terraces are separated by atomic steps of a (100)-type. The cell depicted corresponds to a 4×3 surface unit cell. (b) Here a one layer representation of a smaller part of the Pt(211) surface is shown (corresponding to a 2×1 surface unit cell). The directions of the "primed" and "unprimed" y and z axes are indicated (see text). (c) A 1×1 surface unit cell, with the irreducible part of it indicated by the dashed lines. Note that the unit cell has been projected onto a plane with the (111)-direction as a surface normal. The labelling of the sites top, fcc, hcp, and brg (bridge) stems from what would be natural for the (111) surface, with a number added to ensure a unique label. The other labels have been assigned based on a combination of letters from the closest "high" symmetry sites. The dashed–dotted line is a possible diffusion path for moving from a terrace onto the next one. The x' axis lies along a step edge, and the y' direction is normal to the x' axis and the (111)-direction (z' axis).

A full 3D PES for H (adsorbed in a 2×1 unit cell) interacting with the Pt(211) surface has been developed based on the corrugation reducing procedure described in Refs. 73 and 74. The input data set for the employed interpolation scheme consists of more than 850 DFT/GGA calculated points for a range of z' values above/below each of the 24 surface sites indicated in Fig. 2 (between 30 and 40 z' values per site corresponding to the interval $z \in [-7.2, 10.0]$ bohr have been used).

The hydrogen vibrational band structure and vibrational eigenfunctions have been determined for the 3D PES employing the techniques described in Refs. 38 and 39. The basis set used for the diagonalization is of the form $\langle \bar{r}|G\rangle \times \langle z|\Psi_n\rangle$, where $|G\rangle$ are plane waves parallel to the surface, and $|\Psi_n\rangle$ are harmonic oscillator (HO) wave functions with energies corresponding to the average curvature $\partial^2 V/\partial z^2$ on the PES. The centers of the HO wave functions were placed at the average equilibrium position of H along the edge of the unit cell. The matrix elements of the potential, $V_{n,m}(G)$, where obtained by doing a Fourier transform for each z [i.e., $V(G,z)$], and then calculating the matrix elements $\langle \Psi_n|V(G,z)|\Psi_m\rangle$ for each G. We have used 25×49 plane waves for the coordinate $\bar{r} = (x,y)$ for each value of z ($n_z = 201$), and six HO wave functions for the coordinate z. Convergence with respect to all basis set parameters have been checked to ensure that the vibrational eigenvalues are converged to within 1 meV. The diagonalization was done with a parallel code built with the SCALAPACK library.

III. RESULTS

The minimum potential energy along z' for the 3D PES has been calculated on a dense (x',y')-grid and a contour plot of the resulting two-dimensional (2D) PES is shown in Fig. 3. A cut through this 2D PES along a suggested diffusion path [Fig. 2(c)] is shown in Fig. 4, together with the z' value at the minimum and the corresponding minimum distance between the H atom and the Pt surface atoms. The figures show that a rather deep global minimum is found for $(x',y',z') = (2.62, 11.09, 6.03)$ bohr, corresponding to $(x,y,z) = (2.62, 12.47, 1.99)$ bohr [Eq. (1)]. This geometry is very close to what one would call a bridge site on the step edge [$(x,y) = (2.62, 12.83)$ bohr]. We also find an extra barrier for approaching the step edge along the diffusion path from the lower lying terrace—the barrier close to the th3 site

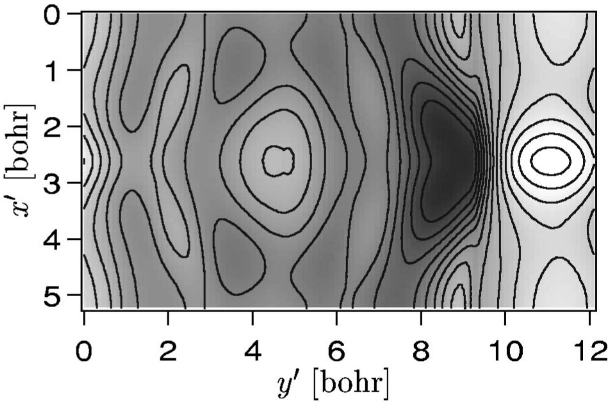


FIG. 3. A contour plot is shown where for each position (x',y') within the 1×1 surface unit cell depicted in Fig. 2 the potential energy has been minimized along z'. The contour spacing is 0.05 eV. The darker the region is shaded, the less stable it is.

is clearly higher than the other barriers between the different local minima on the terrace. Away from the diffusion path this shows up even stronger, with a high barrier hindering motion from the lower terrace towards the step edge. This is clearly shown in Fig. 3, and in Fig. 5 from cuts through the 2D PES along the lines $x'=0$, $x'=1.31\,\text{bohr}$, and $x'=2.62\,\text{bohr}$. Note that this extra barrier is not located in the region where the step is being climbed (moving along z'), but well away from it, as should be clear from Figs. 4 and 5. From Figs. 4(a) and 4(b) it is also seen that there is no extra barrier encountered when climbing the step itself (i.e., there is no Ehrlich–Schwoebel barrier[53,75]).

To better understand the nature of the very rapid (in the sense that it takes place in a very small interval in y') climb of the step, potential energy curves along z' for a number of closely spaced y' values have been shown in Fig. 6. The results are given for the line $x'=0$, but very similar conclusions are reached for all the results in Figs. 4 and 5. The figure clearly shows that the potential along z' develops a double well structure in the region where the step is climbed. This presents a small problem to the simple way we have obtained the 2D PES above by minimizing along z': When the global minimum shifts from a local minimum at “small”

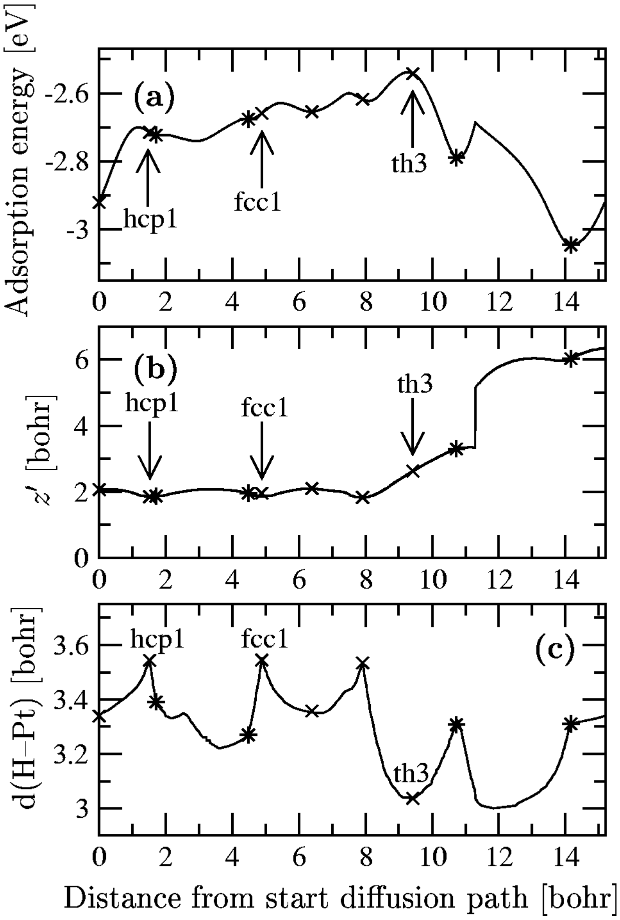


FIG. 4. (a) The adsorption energy, (b) z' value, and (c) the distance to the closest Pt surface atom (d(H–Pt)) for the two-dimensional PES shown in Fig. 3 along the diffusion path indicated in Fig. 2(c). The “bends” in the diffusion path are indicated by stars, and the surface sites from Fig. 2(c) that the diffusion path passes through are marked by crosses (with additional labels for the sites hcp1, fcc1, and th3).

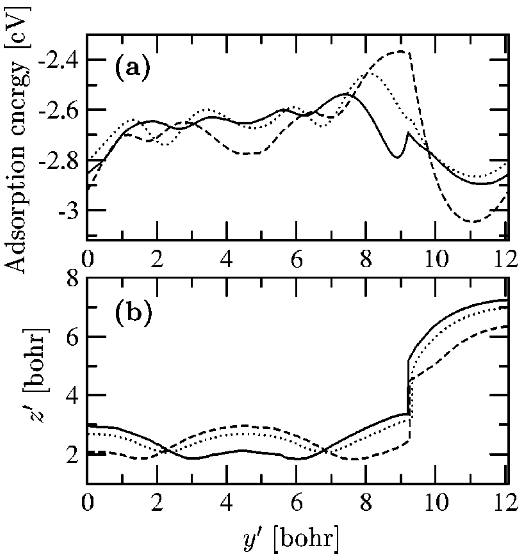


FIG. 5. (a) The adsorption energy and (b) z' value for the two-dimensional PES shown in Fig. 3 along the lines $x'=0$ (full), $x'=1.31\,\text{bohr}$ (dotted), and $x'=2.62\,\text{bohr}$ (dashed).

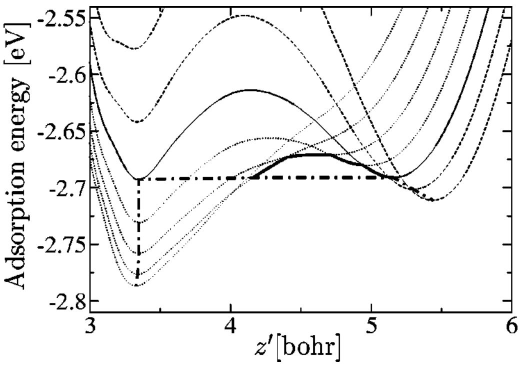
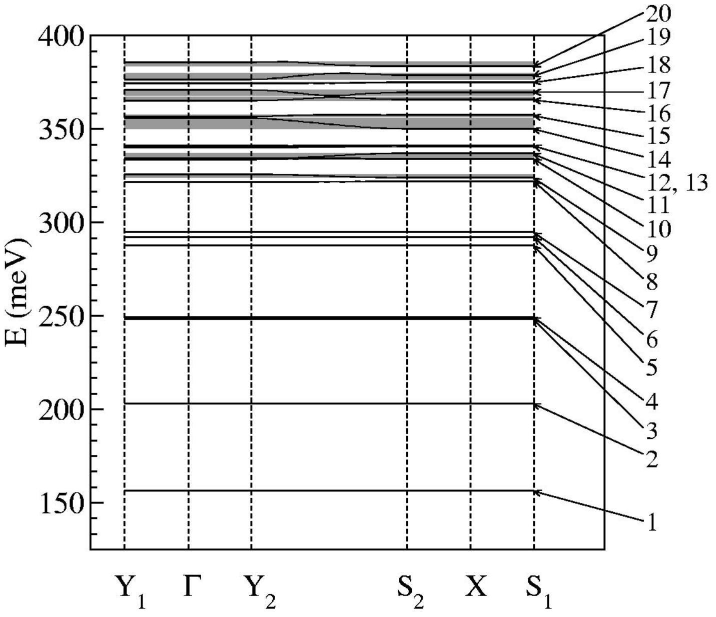


FIG. 6. The adsorption energy along z' for some y' values along the line $x=0$. The thin full line is for $y'=9.21\,\text{bohr}$ where the two local minima are equally stable. The dotted lines are for $y'=8.97$, 9.03, 9.09, 9.15 bohr, and the dashed lines for $y'=9.27$, 9.33 bohr. The thick dashed–dotted line is the results of the minimization procedure used to obtain the results in Fig. 3, and the thick full line shows the barrier missed by this procedure.



n	ϵ_n (meV)	$\Delta\epsilon_n$ (meV)
20	384.8	2.2
19	378.1	3.3
18	374.8	0.7
17	369.8	3.0
16	365.8	1.8
15	357.2	1.0
14	352.9	5.8
13	341.2	0.3
12	340.5	0.8
11	335.7	2.8
10	334.0	0.4
9	324.9	1.9
8	321.8	0.4
7	294.9	<0.1
6	292.3	<0.1
5	287.8	<0.1
4	249.3	<0.1
3	248.4	<0.1
2	203.2	<0.1
1	156.5	<0.1

FIG. 7. The hydrogen vibrational band structure for the 3D PES with the energy E relative to the global energy minimum is shown. The bands are given for straight lines between the points $Y_1=(0,-k_y/2)$, $\Gamma=(0,0)$, $Y_2=(0,k_y/2)$, $S_2=(k_x/2,k_y/2)$, $X=(k_x/2,0)$, $S_1=(k_x/2,-k_y/2)$. The table gives the band index n, the center of the band E_n, and its width ΔE_n (also indicated by the gray shade in the figure).

z' for a given y' to a local minimum at "large" z' for a close lying y', a discontinuous jump in z' will occur. The result is that the minimum energy path for moving from one terrace to the next is not completely followed in this region. However, Fig. 6 also shows that the error made in the energy profile due to this artificial jump is very small, only about 0.02 eV (for all the other cases we have checked the error is smaller). This is the reason for not using a more complex algorithm that would be able to faithfully follow the minimum energy path also in this region.

In Fig. 7 the vibrational band structure for the 3D PES is displayed, where the bandwidths were obtained through diagonalization on a dense grid in the 2D first Brillouin zone (FBZ) of the surface. Cuts along the symmetry lines in the FBZ are shown in Fig. 7 and some eigenfunctions for $k=0$ are shown with respect to the unprimed coordinate system in Fig. 8 (horizontal projections) and Fig. 9 (vertical cuts transversal to the steps, through the brg1 and top3 sites). The first "band" $n=1$ corresponds to the ground state [Figs. 8(a) and 9(a)]; the corresponding Bloch function at $k=0$ is fully localized at the global minimum of the PES and the corresponding band dispersion in the FBZ is essentially zero. Bands $n=2$ through $n=7$ also arise from fully localized states close to the global minimum. They correspond to local parallel vibrational excitations, which we demonstrate below. In a potential minimum, the directions of the oscillations within the harmonic approximation are obtained by diagonalizing the second-derivative matrix evaluated at this given minimum. The second-derivative matrix at the global minimum (as calculated in unprimed coordinate system) has in our case some off-diagonal terms that are nonzero. Diagonalizing this matrix gives the x axis as one of the principal directions (as it should be due to the symmetry of the PES at the global minimum). We denote the other two principal directions found by y'' and z'', and they are shown by dotted lines in Fig. 9. The y'' axis forms an angle of 14.6 degrees with the y axis. The obtained curvature of the potential along y'', $\partial^2V/\partial y''^2$, yields an harmonic approximation of 48 meV for the vibrational frequency in this direction. From Fig. 7 it is seen that the excitation energy for the $n=2$ state is 47 meV. Together with the results from Figs. 8(b) and 9(b) we see that it is reasonable to assign this state to the lowest parallel excitation along y'', suggesting the labelling $\nu_2=(\nu_x,\nu_{y''},\nu_{z''})=(0,1,0)$. Next, $\partial^2V/\partial x^2$ gives a harmonic approximation of 107 meV for the vibrational frequency along x. The excitation energy of the $n=3$ band is 92 meV. The difference between the two is due to the latter including all anharmonic effects. Indeed, we note that Figs. 3 and 5 indicate that the anharmonic effects should be substantially larger in the x direction than in the y'' direction and result in a lowering of the vibrational frequency with respect to the harmonic approximation. The $n=3$ wave function has a nodal plane in the x direction [Fig. 8(c)] and the suggested labelling is therefore $\nu_3=(1,0,0)$. Similar arguments can be used to arrive at the labelling $\nu_4=(0,2,0)$ [Figs. 8(d) and 9(c)], $\nu_5=(2,0,0)$ [Figs. 8(e) and 9(d)], $\nu_6=(1,1,0)$ [Fig. 8(f)], and $\nu_7=(0,3,0)$ [Figs. 8(g) and 9(e)]. At last, from the calculation of normal directions described above, we obtained $\partial^2V/\partial z''^2$ at the global minimum, which gives a harmonic approximation of 166 meV for the vibrational frequency along z''. The excitation energy of the $n=8$ band is 165 meV, it shows little dispersion and has considerable transversal character [Figs. 8(h) and 9(f)]. Together these results suggest that $n=8$ corresponds to the first transversal excitation and the suggested labelling is $\nu_8=(0,0,1)$. We also note that the excitation energy is quite close to what one

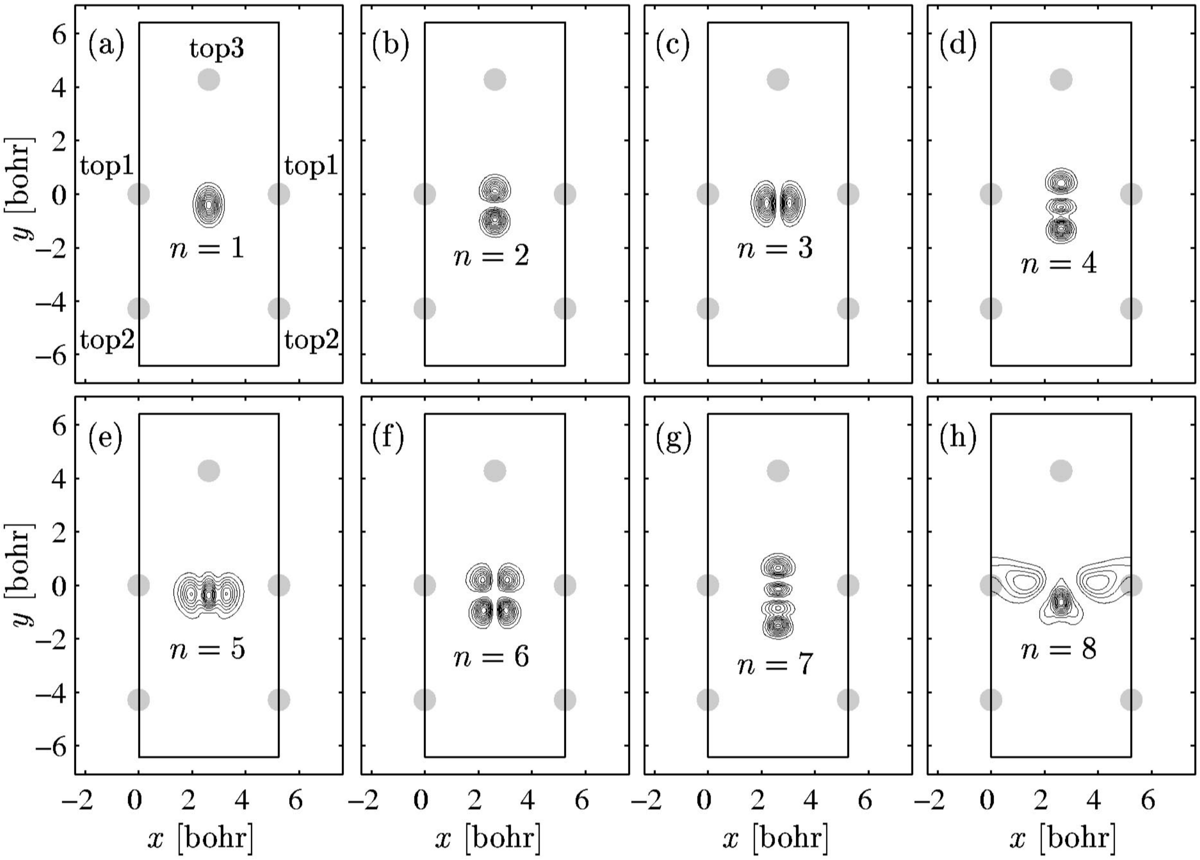


FIG. 8. The vibrational eigenfunctions at Γ for the bands $n=1$ (a), ground state; $n=2$ (b); $n=3$ (c); $n=4$ (d); $n=5$ (e); $n=6$ (f); $n=7$ (g); $n=8$ (h). The probability density, $\int \psi^* \psi \, dz$, is projected onto the $z=0$ plane, and the nearest Pt surface atoms have been indicated [top1, top2, and top3, see also Fig. 2(c)]. Note that the eigenfunctions are shown with respect to the unprimed coordinate system, and that the step edge is located in the middle of the graphs (along the line $y=0$).

would expect for the transversal excitation of a bridge-bonded hydrogen [163 meV on the Pt(111) surface[37]]. The $n=9$ through $n=20$ bands displayed in Fig. 7 are a mixture of medium–wide and wide bands that play a central role in diffusion along the step edge.

The hollow site hcp1 and the top site top3 are two local minima on the terrace, 321 meV and 266 meV above the global minimum, respectively (see Figs. 2 and 3). We found

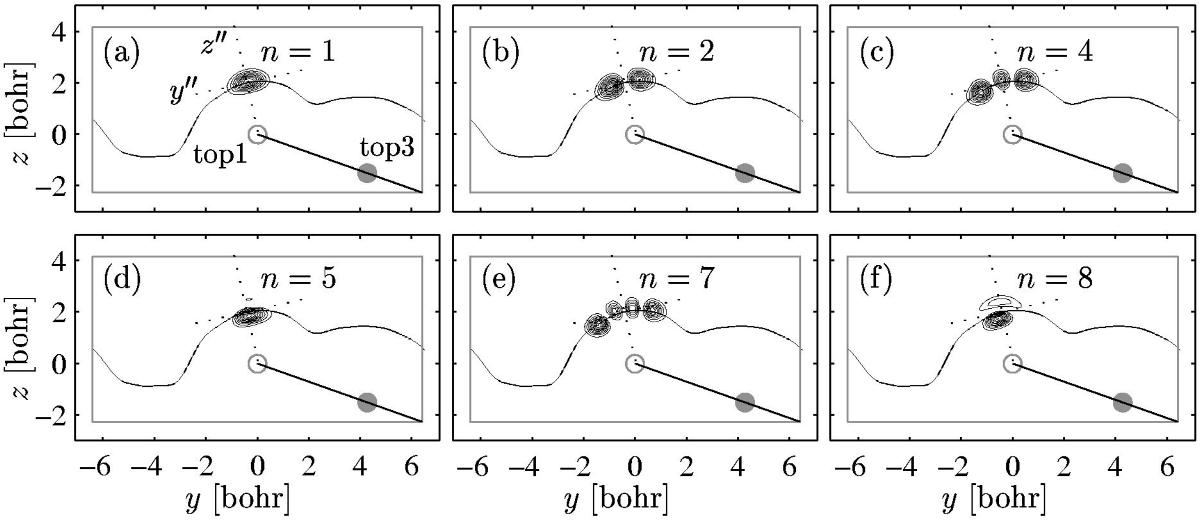


FIG. 9. The probability density $\psi^* \psi$ (at Γ) in the yz plane, for $n=1$ (a), $n=2$ (b), $n=4$ (c), $n=5$ (d), $n=7$ (e), $n=8$ (f). The transversal section plane is given by $x=2.62$ bohr. The open circle represent a top1 Pt atom out of this plane, at $x=0$ bohr [see also Fig. 2(c)], while the filled circle represent a top3 Pt atom contained in this plane. Also depicted is the minimum energy path above the surface in this plane, at constant $x=2.62$ bohr (compare to Fig. 5), together with the tangent line (y'' axis, forming an angle of 14.6° with the y axis) and its normal (z'' axis) at the global minimum of the PES (see text).

the directions of normal oscillations by diagonalizing the corresponding second-derivative matrices. The *x* axis is a normal direction for both minima due to the symmetry. For the hcp1 site, the second principal axis makes an angle of -2.0 degrees with the *y* axis. The harmonic approximations for the vibrational frequencies at this site are 29 meV along *x*, 62 meV along the axis close to the *y* axis, and 152 meV for the third axis, close to the *z* axis, which can be denoted as a transversal direction. The same analysis for the top3 site gives a local principal axis which makes an angle of -21.6 degrees with the *y* axis, the third axis being perpendicular to it. The corresponding harmonic approximations for the vibrational frequencies are 51 meV along *x*, 96 meV along the axis at -21.6 degrees with the *y* axis, and 235 meV along the third axis. The latter axis will be denoted as the transversal axis at the top3 site.

Next, we compare the harmonic estimates just obtained with the energies obtained by the full 3D band structure calculations. The vibrational band states $n=29$ and $n=38$ are localized at the hcp1 and top3 sites with an energy of 420 meV and 444 meV, respectively. They have little dispersion and no clear nodal planes, and could be considered the ‘‘ground states’’ in these local minima. It is worth to note that even if the potential minimum at the top3 site is lower than the hcp1 site by 55 meV, the zero point energy contribution raises the state localized at the top3 site above the state localized at the hcp1 site. For each local potential minimum which confines a localized state, we obtain the zero-point energy (ZPE) by subtracting from the energy of the lowest energy state confined at that site the value of the local potential minimum. For the hcp1 and the top3 sites the ZPE are 99 meV and 178 meV, respectively. The two lowest localized parallel excitations for the hcp1 site have been found at excitation energies of 14 meV ($n=34$) and 17 meV ($n=36$) (the energies are given relative to the local hcp1 ground state), and a local excitation state with considerable transversal character at 153 meV ($n=105$). Two other localized parallel excitations for the hcp1 site were found at 58 meV ($n=53$) and 71 meV ($n=56$). The parallel excitation energies are small with respect to the harmonic estimates found above, which is reasonable taking into account the shallow local minimum at this site and the strong anharmonicity. The transversal mode is in good agreement with the harmonic approximation. For the top3 site the two lowest localized parallel excitations were found to be 48 meV ($n=57$) and 53 meV ($n=61$) (the energies are given relative to the local top3 ground state). The former is an oscillation in the *x* direction and its energy agrees well with the harmonic approximation, while the latter is a lateral oscillation in the y'' direction and its energy does not match with the harmonic approximation, showing that the anharmonic effects are stronger in this direction. We could not isolate a local excitation state with predominantly transversal character at the top3 site. According to the harmonic approximation, such a mode would have a large excitation energy (>650 meV) with respect to the global minimum, which would imply calculating reliably a very large number of eigenstates of the potential. This cannot be achieved with the number of plane waves used in the present study.

TABLE II. The lowest vibrational bands for atomic D on Pt(211) are given relative to the global energy minimum. The table gives the band index n', the vibrational label $\nu_{n'}$, the (center of the) band energy $E_{n'}$, excitation energy with respect to the ground state $E_{n'}-E_1$, and the isotope ratio *R* with respect to the corresponding H state *n* (see text and Fig. 7).

n'	$\nu_{n'}$	$E_{n'}$ (meV)	$E_{n'}-E_1$ (meV)	R	n
1	(0,0,0)	110.1	0.0	1.42	1
2	(0,1,0)	143.7	33.6	1.39	2
3	(0,2,0)	176.9	66.8	1.39	4
4	(1,0,0)	179.5	69.3	1.33	3
5	(0,3,0)	209.9	99.8	1.39	7
6	(0,0,1)	211.1	101.0	1.63	8
7	(1,1,0)	211.8	101.7	1.35	6
8	(0,0,1)	241.2	131.1	1.26	8

Some vibrational band structure results for D at the global minimum are given in Table II. The isotope ratios are very close to the expected value of $\sqrt{2}$ for the ground state and also the parallel excitation states along y'' (where the harmonic approximation was already seen to be rather good). In accordance with our results above, where the anharmonic effects were considerably larger along the *x* direction and lowered the vibrational frequencies relative to the ones obtained within the harmonic approximation, we find a lower isotopic ratio for parallel excitation states along *x*. For the transversal excitation the picture is more complicated. From the harmonic approximation this state should be found at 117 meV, but due to interaction with a parallel mode ($n'=6$) the state is split by ±15 meV.

All the above results have been obtained with a bulk terminated surface, and this is an approximation we should justify. In Fig. 10 we have compared the hydrogen adsorption energy above different sites for a bulk terminated surface based on the experimental lattice constant (5.24 bohr) to the adsorption energy found on a surface based on the GGA BP optimized bulk lattice constant (5.36 bohr) and including top layer relaxations. The figure shows that including surface relaxations does not change the indications (i) for a rather deep global minimum close to the bridge site on the step

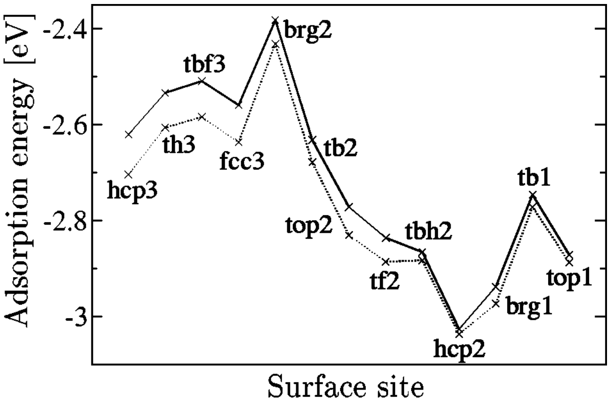


FIG. 10. The adsorption energy is shown for a bulk terminated surface with the experimental lattice constant (full line) and a bulk terminated surface with the GGA BP lattice constant and a relaxed top layer (dotted line) for a number of sites in the surface unit cell [see Fig. 2(c)]. The height above the surface is in each case chosen close to the equilibrium position above these sites.

edge, (ii) that there is an extra barrier for approaching the step edge from the lower terraces along the diffusion path (the difference in the adsorption energy between the hcp3 and th3 sites remain virtually unchanged, see also Figs. 2 and 4), and (iii) that there is a rather large region unfavorable (as compared to the other sites on the surface) for hydrogen adsorption when approaching the step edge from the lower terrace. We also obtained the transversal vibrational frequency within the harmonic approximation at the global minimum for a surface based on the GGA BP optimized bulk lattice constant and including top layer relaxations. Nine DFT points (within 1.0 bohr of the global minimum) were calculated along the z'' axis (Fig. 7) and fitted/interpolated by a cubic spline. The resulting second derivative $\partial^2 V/\partial z''^2$ at the minimum gave a harmonic vibrational frequency of 165 meV, in good agreement with the 166 meV found for the bulk terminated surface with the experimental lattice constant. That surface relaxations do not change the results on the level discussed here is in agreement with what has been reported in other studies where the choice to work with an unrelaxed stepped surface also was made.[31,32]

IV. DISCUSSION

Recent experiments on the Pt(533) surface clearly shows that atomic hydrogen binds more strongly to the steps than to the terraces, as can be seen by a high-temperature peak in the thermal desorption spectra of H_2 that is not present for the Pt(111) surface.[9] Even though we have studied a different surface, Pt(211), a direct comparison to the experimental results for Pt(533) is relevant: They are both surfaces with (111)-terraces separated by (100)-steps, with the difference being that the terraces are four atoms wide in the case of Pt(533), and three atoms wide for Pt(211). The presence of the deep global minimum in the PES found in the preceding section would result in a high-temperature peak in the thermal desorption spectra above a broader low-temperature peak, and this is in good qualitative agreement with what has been found by Gee *et al.* The analysis of their data lead Gee *et al.* to suggest that only half of the available step sites are populated by a strongly adsorbed species. In our case this corresponds to one hydrogen atom adsorbed at the step edge in a 2×1 unit cell (a total coverage of $\theta=1/6$). We have repeated our calculations with two hydrogen atoms in the 2×1 unit cell ($\theta=1/3$), both placed at the most stable geometry found in Sec. III. We find that the second hydrogen atom is about 0.05 eV less stable than the first, but this is still appreciably more stable than all other sites on the Pt(211) surface at $\theta=1/6$ (see Figs. 3, 4, and 5). Thus, our results indicate that all hydrogen atoms adsorbed at the step edge are more strongly bonded to the surface than atoms adsorbed on the terraces, and that all step sites can be populated by this strongly adsorbed species. Additional theoretical and experimental efforts would be needed to resolve this apparent discrepancy.

Based on the results in Sec. III we would expect a quite rich and coverage-dependent hydrogen vibrational band structure that in principle should be detectable with, e.g., high-resolution electron energy-loss spectroscopy (HREELS),[38,39] or quasielastic helium atom scattering (QHAS) employing the new high-resolution spin–echo technique in place of the time-of-flight method.[76–78] By changing the incident direction of the probe specific bands might be preferentially excited, and might lead to more detailed experimental information on the PES. It would also serve as a rather stringent test of the PES that has been developed in this paper—a good agreement between the calculated vibrational band structure and the measured one would indicate the our PES is basically sound, whereas disagreements might give us clues to what the weaknesses in our approach are. We should, however, add that we are well aware of the periodic DFT/GGA approach not being of spectroscopic accuracy (1 meV or better), and that more than a qualitative agreement should not be hoped for at this stage. An error in the well depth for the global minimum of say 0.05–0.1 eV would probably shift most of the bands considerably (in a spectroscopic sense) and the number of localized states might also change. However, the result that the first excitation energy along y'' is considerable smaller (by almost a factor 2 in our calculations) than the first excitation energy along x might be reliably indicated by the periodic DFT/GGA approach. We also believe that the calculated value for the first transversal excitation energy at the global minimum (165 meV) should be less sensitive to the DFT/GGA error. The reason is that the energy differences are large (which is seen from the large frequency), and this would give a smaller relative error in the curvature estimate. Support for this view can be found in, e.g., LDA and GGA giving very similar frequencies for transversal excitations for H/Pt(111) even though the well depths are quite different.[37] A measurement of a vibrational band at low hydrogen coverages with mainly transversal character close to 165 meV could be taken as an indication that the global minimum of the PES is close to the bridge site on the step edge, as predicted by our calculations. Furthermore, the excitation directions suggested in the plots of the vibrational eigenfunctions (Figs. 8 and 9) might be helpful in interpreting maxima and minima in the resulting signal when changing the incident direction of the experimental probe. Note that for a stepped surface the directions of normal oscillations are not dictated by geometry to the same extent as in the case of a flat surface where the adsorption sites (often) have higher symmetry—the directions as determined by diagonalizing the second-derivative matrix can, as in our case, be appreciably different than those determined by the surface plane and surface normal for the terraces.

An older electron energy-loss spectroscopy (EELS) experiment found three hydrogen bands at a stepped platinum surface with (111)-terraces six atoms wide separated by (111)-steps.[79] They assigned a band at 62 meV to a transversal excitation of hydrogen adsorbed on the threefold hollow sites on the (111)-terrace, a band at 140 meV to a transversally excited bridge-bonded hydrogen at the steps sites, and a band at 157 meV to a vibration parallel to the surface. However, recent HREELS experiments and DFT calculations for H on a flat Pt(111) surface[38,39] have shown clearly that a mode at 68 meV is (for all coverages) due to oscillations with large parallel components at the fcc site, while a mode at 153 meV is due to transversal oscillations at the same site.

We suggest here a different assignment of the modes observed by Baró and Ibach.[79] First, the loss peak at 157 meV is most likely a transversal mode at the threefold hollow sites on the (111)-terraces. Support for such an assignment is given by the transversal mode found at the hcp1 site at 153 meV in the preceding section, and by the results of two other studies already mentioned above identifying a transversal mode at 153 meV for Pt(111) as originating from a localized excitation at the fcc site.[38,39] Second, since the 140 meV loss saturates at low coverages it is most likely a vibrational mode at the steps, but the adsorption site is not the same as the bridge-bonded hydrogen on the step edge found in this study which gives a transversal excitation at 165 meV. Baró and Ibach suggested that the mode originates from a localized vibration for a bridge-bonded hydrogen in the corner of the (111)-step. Since the (211) surface has a (100)-step face, and the surface used by Baró and Ibach a (111)-step face, we are not able to check their suggested assignment directly. However, the results in this study giving a mode at 165 meV for bridge-bonded hydrogen at the step edge together with results for H/Pt(111) which gave a transversal excitation energy of 163 meV for bridge-bonded hydrogen[37] (within the harmonic approximation), seems to indicate that 140 meV is too low a frequency to be associated with transversal vibration of a bridge-bonded hydrogen. We suggest that the (effective) coordination for the binding site giving rise to the loss at 140 meV is higher, but theoretical calculations for a surface including (111)-type steps will be needed to provide clear evidence one way or the other. Finally, the loss observed by Baró and Ibach at 62 meV is most likely not originating from a localized transversal excitation at the terraces. The results of the present study as well as those of Refs. 38 and 39 indicates that this loss is due to parallel excitations: In the preceding section two parallel modes at the hcp1 site were found at 58 meV and 71 meV, and in Refs. 38 and 39 a parallel mode at 68 meV localized at the fcc site was found.

We do note that our suggested assignment should be taken *cum grano salis*—the Pt(211) surface we have considered has shorter terraces and a different step face than the surface studied in Ref. 79. We also should note that our PES has been obtained for the low coverage limit and that including lateral hydrogen interactions at higher coverages might influence the suggested assignments considerably.

As already mentioned in the Introduction some experimental effort has been put into investigating directional anisotropies in the hydrogen mobility due to the presence of atomic steps on the surface. However, as we will indicate in the following, a direct comparison between the available experimental results and our H/Pt(211) results is not straightforward. Hydrogen diffusion on two stepped tungsten surfaces, W(123) and W(023), were studied in Refs. 45 and 46, respectively. Very little anisotropy was found, indicating no (or very small) extra barriers for moving from one terrace to the next. However, in the W(123) study the authors noted that there might have been some H present at all times on the surface during the experiments. This ‘‘background’’ of adsorbed hydrogen atoms would most likely alter the PES for hydrogen diffusion considerably, making a comparison to the present H/Pt(211) PES questionable. In the case of W(023) it was believed that substrate distortion was dominating the diffusion process, which also would render a comparison to our PES rather dubious. In Ref. 47 an additional activation energy of about 0.1 eV for climbing the steps was found on a ruthenium surface. However, no trapping of hydrogen at step sites was seen, indicating that the PES governing the diffusion process is quite different from the H/Pt(211) PES. For hydrogen diffusion on Rh(322) the activation energy for crossing a step was found to be about 0.05 eV higher than the activation energy for moving parallel to the step edge.[48] But the measurements were done close to saturation coverage and a comparison to the H/Pt(211) system as studied here might not be very relevant. An upper limit to the additional barrier for hydrogen atoms crossing a step on a 0.1°-miscut Ni(111) surface was reported to be 0.06 eV in Ref. 49. In the light of the very low step density together with a rather high coverage in this study we are not sure we can make a fruitful comparison to the results obtained in Sec. III. The focus in Ref. 80 was to study step effects on diffusion near a substrate reconstructive phase transition for the H/W(100) system, but some indications were found for an extra barrier of about 0.1 eV for moving from one terrace to the next. However, as in many of the cases above, the coverage (with respect to the number of step sites available) was considerably higher than what is considered in the present study.

But even if the above considerations clearly shows that a comparison between existing experimental results and the results of our H/Pt(211) calculations should be done with quite a lot of care, we think there is some support from experiments suggesting that an extra barrier is encountered for a number of systems when hydrogen is moving from one terrace to the next (as compared to moving along a single terrace). The results of Fig. 4 indicate an additional barrier of about 0.1 eV for H/Pt(211), and this seems to be quite reasonable in the light of the experimental values given above. We would be eager to see, e.g., QHAS or STM experiments taking on the challenge of studying surface diffusion for the H/Pt(211) system and possibly verifying our prediction for the presence of such a barrier.

Based on the results in Sec. III we can make a number of other predictions or interesting observations. (i) The activation energy for diffusion on the H/Pt(211) surface is strongly coverage dependent. At low coverage ($\theta = 1/6$ or lower) the barrier should be between 0.15 and 0.2 eV. The diffusion would in this case take place only along the step edges. (ii) After most of the step sites have been occupied by the strongly adsorbed hydrogen, the terrace sites will become occupied and the diffusion barrier decreased to the 0.05–0.1 eV level for diffusion along a single terrace. (iii) In addition to the already mentioned extra barrier of about 0.1 eV, and as a consequence of it, a much lower diffusion constant for moving from one terrace to the next, there might be other interesting features associated with climbing the steps. Since the climbing takes place in a very small interval of y', a modelling of the diffusion on, e.g., a 2D effective PES where the motion along the direction normal to the terrace plane is assumed to evolve adiabatically might give different results than when performing a 3D modelling. Support for such a suggestion can be found from realizing that the inertia of the diffusing H atom is likely to prevent it from following the minimum energy path in the step region, and this would probably lead to a higher effective barrier for moving from one terrace to the next than would be seen in a 2D model. It might also be important to take into account the very repulsive nature of the PES in an extended region close to the step edge when modelling the diffusion. We think that these predictions/observations provide interesting input for new theoretical modelling efforts along the lines already pursued in, e.g., Refs. 50–56.

As indicated in the Introduction we are not aware of any other periodic DFT/GGA studies investigating the interaction of hydrogen atoms with stepped Pt metal surfaces. The efforts so far has mainly been focused on CO, NO, O_2, N_2, H_2, and S interacting with a range of different stepped surfaces (see, e.g., Refs. 14, 15, 18, 20, 21, 30–36, 81). However, some results for atomic adsorption of hydrogen on Pd(210) were given in Refs. 20 and 33. Even if it might be more natural to classify the Pd(210) surface as a (very) open surface and not stepped, the most stable adsorption site is a bridge-bonded species at the ‘‘step edge,’’ i.e., very similar to what we have found for H/Pt(211). Also in Ref. 32 some results for atomic adsorption and diffusion were given. Although the adsorbates were N and O atoms and the surface a ‘‘corrugated’’ ruthenium surface, the trends are very similar to the results in Sec. III: (i) The most stable adsorption site is at the step edge (or close to it), (ii) there is an extra barrier for approaching the step edge from the lower terrace, and (iii) no Ehrlich–Schwoebel barrier is present.

Since a comparison of our results to those of experimental studies is rather difficult (for reasons given above), and a direct comparison to other theoretical studies for hydrogen adsorbed on stepped Pt(111) surfaces is at the moment not possible, a short comparison of different theoretical studies of the H/Pt(111) system might be at its place. In the early DFT/LDA calculations of Feibelman and Hamann[82] only the hollow sites were considered, and the fcc site was found to be about 0.2 eV more stable than the hcp site. In more recent studies at the DFT/GGA level the potential corrugation along a path connecting two fcc sites via bridge and hcp sites is consistently found to be somewhat smaller, in the range 0.03–0.08 eV.[37–43] Also in agreement with each other, these recent studies show the top site to be a rather strong local minimum with a barrier of 0.1–0.15 eV for moving away from it. There are, however, small differences of about 0.1 eV when comparing the depth of the minimum at the top site to the depth of the minimum at the fcc site, but we think this is within acceptable limits—certainly if taking into account the recent debate about the accuracy of different DFT/GGA approaches for the CO/Pt(111) system.[71,83] Based on (i) the favorable comparison between the recent DFT/GGA calculations and experiments for the H/Pt(111) system,[37–43] (ii) the approach followed in this paper being identical to that of Ref. 37, and (iii) all computational aspects pertaining to the method we have applied are shown to be well under control (Secs. II and III), we think our results will be a useful guide for future theoretical and experimental studies on hydrogen interactions with stepped Pt(111) surfaces.

V. CONCLUSIONS

In this study we have presented periodic density functional theory (DFT) calculations at the generalized gradient approximation (GGA) level for atomic hydrogen interacting with a stepped platinum surface, the Pt(211) surface. We have calculated the full three-dimensional (3D) potential energy surface (PES) for the H/Pt(211) system together with the vibrational band structure and vibrational eigenfunctions. A deep global minimum is found for bridge-bonded hydrogen on the step edge, and this is in good qualitative agreement with the thermal desorption spectra on the similar H/Pt(533) system. However, we find a different saturation coverage for this strongly adsorbed species than the experiment for H/Pt(533) suggests—additional theoretical and experimental efforts would be needed to resolve this apparent discrepancy.

All the local vibrational excitations at the global minimum have been identified and will serve as a helpful guide to the interpretation of future experiments on this (or similar) system(s). Based on our results at least two predictions can be made that could be verified by today’s state-of-the-art experimental methods when performed at low coverages: (i) The strongly adsorbed bridge-bonded species at the step edge should give rise to a vibrational band with mainly transversal character at an excitation energy close to 165 meV. (ii) The first parallel excitation energy corresponding to an excitation along the direction normal to the step edge should be considerably smaller (by almost a factor of 2 according to our calculations) than the first excitation energy for an excitation along the step edge.

The vibrational bands that would play an important role in the diffusion between the strong adsorption sites along the step edges have also been calculated. A good agreement between this calculated vibrational band structure and the (to be) measured one would indicate that our PES is basically sound, and therefore be a useful starting point for modelling the diffusive motion. In particular, the calculated PES and vibrational band structure identify a number of consequences for the interpretation or modelling of diffusion experiments studying the coverage and directional dependence of the diffusion of atomic hydrogen on a stepped platinum surface: (i) The activation energy for diffusion on the H/Pt(211) surface is strongly coverage and directional dependent. (ii) The extra barrier encountered when moving from one terrace to the next (as compared to moving along a single terrace) is not found at the step itself, but occurs earlier along the diffusion path (when moving from a lower-lying terrace to a higher-lying one). We find no Ehrlich–Schwoebel barrier. (iii) The climbing of the step takes place over a rather short interval in the direction parallel to the terraces. We therefore expect that modelling the diffusion with, e.g., a 2D effective PES where the motion along the direction normal to the terrace plane is assumed to evolve adiabatically might give different results than when performing a 3D modelling. It might also be important to take into account the very repulsive nature of the PES in an extended region close to the step edge when modelling the diffusion.

When comparing our present results to results from existing experimental and theoretical periodic DFT/GGA studies we find the agreement on the whole rather gratifying. But we would like to stress that there is still a considerable effort to be made for the system of hydrogen interacting with stepped platinum surfaces. On a theoretical level more periodic DFT/GGA calculations are needed, as are efforts to model the diffusion employing realistic PESs. We would also very much encourage new experimental studies on this system by, e.g., high-resolution electron energy-loss spectroscopy, scanning tunneling microscopy, or quasielastic helium atom scattering employing the new high-resolution spin–echo technique in place of the time-of-flight method.

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