

Initial stages of oxidation of (100) and (110) surfaces of iron caused by water

Michael Eder* and Kiyoyuki Terakura

Joint Research Center for Atom Technology and National Institute for Advanced Interdisciplinary Research, Higashi 1-1-4,
Tsukuba 305-0046, Japan

Jürgen Hafner

Institut für Materialphysik and Center for Computational Materials Science, Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria
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The initial stages of the oxidation of the (100) and (110) surfaces of iron caused by the adsorption of water have been investigated using *ab initio* local-spin-density functional calculations including generalized gradient corrections. It is shown that at low coverages water dissociates spontaneously into hydrogen atoms and hydroxyl groups. Further adsorption of water molecules in the presence of preadsorbed H and OH does not lead to spontaneous dissociation. On both surfaces dissociation is a weakly activated process. This explains the presence of molecular water as observed experimentally. Especially on the (110) surface H₂O dissociation in the presence of preadsorbed H and OH is found to be a complex process involving the formation of an intermediate molecular species.

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I. INTRODUCTION

The interaction of water with iron surfaces, especially the oxidation mechanism, has been the subject of extensive interest for many years. Water chemistry on iron surfaces is of importance in electrochemistry, corrosion (rust), and catalysis (Haber-Bosch synthesis, Fischer-Tropsch reaction). The investigation of the initial stages of the dissociation process of water on iron provides the basis of an understanding of these fundamental reactions. Of particular interest is the nature of the adsorbed species, the molecular orientation with respect to the surface and the determination of the reaction barrier.

In this work we present a first-principles analysis of the initial stages of iron-oxidation caused by water on the Fe(100) and the Fe(110) surfaces. The adsorption geometry and the adsorption energies have been calculated for all the atoms and molecules involved in the dissociation process H₂O→OH+H. With the aid of the nudged elastic band method, calculations to determine the transition state were performed. To show the coverage dependence of the energy barrier for the H₂O→OH+H process, the interaction of a second water molecule with the Fe surfaces has been investigated.

Experimentally it has been found by Dwyer *et al.*¹ and Baró *et al.*² for the Fe(110) surface that water dissociates on the surface spontaneously at 130 and 160 K. Dwyer *et al.*¹ reported spontaneously dissociated water up to an exposure of 0.2 L. For higher water-coverage adsorbed molecular water was detected.

In contrast to these results, Wei-Hsiu Hung *et al.*^{3,4} observed adsorbed molecular water on the Fe(100) surface for low exposure (0.05 L) as well as for high exposure (1.2 L) at a temperature of 100 K. This is somewhat surprising considering that the Fe(100) surface is not as closed packed as the Fe(110) surface and is therefore expected to be more reactive. It is also in contradiction to our results (as shown later) and might be explained by the existence of local water clus-

ters at the Fe surface, where one would be locally in high coverage regime, where molecular adsorbed water should be expected.

II. METHODOLOGY

Our calculations have been performed using a spin-polarized version of the Vienna *ab initio* simulation program (VASP).⁵ VASP performs an iterative solution of the generalized Kohn-Sham equations of local-spin-density (LSD) theory via an unconstrained minimization of the norm of the residual vector to each eigenstate and optimized routines for charge and spin-density mixing. The calculations are performed in a plane-wave basis, using fully nonlocal Vanderbilt-type ultrasoft pseudopotentials^{8,9} to describe the electron-ion interaction. Exchange and correlation are described by the functional proposed by Perdew and Zunger,⁶ adding nonlocal corrections in the form of the generalized gradient approximation (GGA) of Perdew *et al.*⁷ The wave functions are expanded in terms of plane waves with an energy cutoff of 270.2 eV (553.7 eV for the augmentation charges). The Brillouin zone integrations have been performed on grids of 4×4×1 and 5×5×1 **k** points. The surface has been described with a repeated slab approach. The supercell contains five layers of Fe and water molecules on both both sides of the symmetric slab. A *p*(2×2) surface structure was used as the surface geometry for both the Fe(100) and Fe(110) surfaces. The vacuum spacing is for both surfaces [Fe(100) and Fe(110)] at around 12 Å. Convergence tests for the Fe(100) and the Fe(110) surface have shown that this setup is converged with respect to slab thickness, vacuum spacing, and **k**-point sampling. As lattice constants we used the theoretically determined equilibrium value of *a*=2.856 Å for body-centered-cubic Fe.

To determine the activation energies of the reactions, the transition states have been determined using the nudged elastic band method.¹⁰ In this method the total energies of a series of intermediate states distributed along the reaction

TABLE I. Comparison of the calculated properties of clean Fe(100) and Fe(110) surfaces (interlayer relaxations Δ_{12} and Δ_{23} of the top layers and magnetic moment m_1 at the surfaces) and of a water molecule in the gas phase (O-H bond length d_{OH} and H-O-H bond angle) with experiment and previous calculations.

	Current calc.	Other calc./exp.
clean Fe(100) surface:		
Δ_{12}	-3.5%	-1% (Ref. 19) / $-5 \pm 2\%$ (Ref. 18)
Δ_{32}	2.3%	+5% (Ref. 19) / $5 \pm 2\%$ (Ref. 18)
m_1	$3.05\mu_B$	$3.01\mu_B$ (Ref. 16) /
clean Fe(110) surface:		
Δ_{12}	-0.2%	0% (Ref. 19) / $-0.5 \pm 2\%$ (Ref. 17)
m_1	$2.71\mu_B$	
H ₂ O		
O-H	0.96 Å	1 Å (Ref. 15)
H-O-H	104.5°	104.5° (Ref. 15)

path connecting the starting and final states are simultaneously minimized, restricting the atomic motions to the hyperplane perpendicular to the reaction path. As the starting configuration we considered molecular water adsorbed at Fe(100) or Fe(110) and as the end configuration OH+H coadsorbed at the iron surfaces. As an initial guess of the reaction path, a linear approximation between start and end configuration was used.

Comparison of known properties for Fe and water. As a test of the pseudopotentials we calculated structures of the water molecule in the gas phase and of the clean Fe(100) and Fe(110) surfaces. Table I compares some of the calculated properties such as the geometry of the molecule in the gas phase, and the interlayer-relaxations of the first two iron layers and the magnetic moments of these layers with the values obtained by other groups with experiments or other calculations. All of these known properties could be reproduced using our ultrasoft pseudopotentials.

III. H, O, OH ON THE Fe(100) AND Fe(110) SURFACES

As the first step we calculated the energetically most stable configurations of the atoms and molecules which are expected to be found on the surface after the dissociation process occurred (H, OH). To complete the picture we performed also calculations where only oxygen was adsorbed at the surface. This corresponds to the complete dissociation process of water which was experimentally observed for the

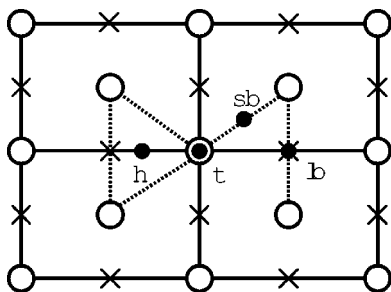


FIG. 1. Definition of on-top (t), bridge (b), short-bridge (sb), and hollow (h) absorption sites on Fe(110). Circles, surface atoms; crosses, subsurface atoms.

Fe(100) surface at higher temperatures (310 K).³

As adsorption sites on the Fe(100) surface we considered the high-symmetry position: the fourfold hollow (*h*), the twofold bridge (*b*), and the on-top (*t*) position. For the Fe(110) we considered the twofold long-bridge (*lb*) site, the twofold short-bridge (*sb*) site, the pseudo-three-fold hollow (*h*), and the on-top (*t*) position (Fig. 1). We optimized the adsorption geometry and allowed also the first iron-layer to relax. Relaxations have been performed until the forces acting on the atoms were smaller than $0.02 \text{ eV}/\text{Å}$.

Table II shows the calculated adsorption energies and geometries for the different adsorption sites for H, O, and OH. Hydrogen is found to be adsorbed at the bridge or hollow position of the Fe(100) surface (both positions have almost the same adsorption energy) and on the threefold hollow site in the case of Fe(110). H is stronger bound on the Fe(110) surface where the system gains 0.69 eV when H is adsorbed [compared to 0.34 eV for Fe(100)]. This result is in agreement with experiments and with calculations performed by other groups.^{11,12} The first iron layer relaxes inwards on the Fe(100) surface (-2.7% if H is adsorbed on the hollow site) and only very slightly outwards on the Fe(110) surface (only the on-top configuration has an relaxation of the first layer of 1.5%, but at this adsorption-site the reaction of H with Fe is not exothermic).

In the case of the adsorption of atomic O, the fourfold hollow site for the Fe(100) surface is the energetically most stable position, where it has a slightly higher adsorption energy than oxygen on the Fe(110) surface, where oxygen sits preferably on the twofold long-bridge site. The short-bridge and the pseudo-three-fold hollow site are found to be unstable, the atom moves into the twofold long-bridge site. The calculated adsorption energies for H and O in Table I are the energies per adsorbed atom which are gained if molecular H₂ or O₂ are dissociated and adsorbed on the iron surface. The adsorption energies are with -3.72 eV [Fe(100)] and -3.69 eV [Fe(110)] quite similar for both iron surfaces. For Fe(110) no stable configuration could be obtained if we tried to put oxygen over the short bridge and pseudo-three-fold adsorption sites.

TABLE II. Adsorption energy E_{ad} per atom/molecule, normal distance z of the adsorbate to the averaged Fe surface, relative relaxation Δ_{12} of the first Fe layer for H, O, OH on Fe(100) and Fe(110). The adsorption energies for O and H have H_2 and O_2 as a reference. For Fe(100) the top (t), bridge (b), and hollow (h) and for Fe(110) the top (t), short-bridge (sb), long-bridge (lb), and the pseudo-three-fold hollow (h) were considered. For OH adsorption we report also the O-H bond-length $d(\text{O-H})$ and the angle between the O-H bond and the surface normal.

	Fe(100)			Fe(110)			
	t	b	h	t	sb	lb	h
H							
E_{ad} [eV]	+0.17	-0.36	-0.35	+0.06	-0.51	-0.63	-0.69
z_{H} [\AA]	1.63	1.08	0.35	1.52	1.16	0.94	0.95
$\Delta_{12}\text{Fe}$ [%]	-1.0	-1.5	-2.7	+1.5	+0.5	+0.7	+0.3
O							
E_{ad} [eV]	-2.19	-3.16	-3.72	-2.03		-3.69	
z_{O} [\AA]	1.67	1.32	0.63	1.69		1.03	
$\Delta_{12}\text{Fe}$ [%]	-2.4	+2.30	+2.53	+0.9		1.7	
OH							
E_{ad} [eV]	-3.71	-4.12	-3.86	-3.19	-3.74	-4.05	
z_{O} [\AA]	1.99	1.56	1.22	1.95	1.53	1.30	
$d(\text{O-H})$ [\AA]	0.91	1.01	1.01	0.99	1.00	1.00	
OH angle [$^\circ$]	47	53	0	0	0	5	
$\Delta_{12}\text{Fe}$ [%]	-0.8	+0.8	+1.9	+0.5	+0.8	+0.6	

An isolated hydroxyl group has a 0.08 eV larger adsorption energy on the Fe(100) surface than on Fe(110). The adsorption energy for OH on Fe(100) would be 4.04 eV with OH oriented perpendicular to the iron surface but the [Fe(100)+OH] system gains some energy if the hydroxyl-group is tilted towards the surface by 53° . In contrast to this result, OH cannot do this on the Fe(110) surface because of the dense packing and symmetry of the surface. The tilted configuration is in an agreement with experiment³ where this configuration has been proposed after measuring the EELS spectrum of this surface. However, a tilted configuration could only be found for the top and the bridge sites. For the hollow site only a metastable geometry could be found, which is unstable if we tilt the OH molecule even slightly. We also tried to find a stable adsorption geometry with OH on Fe(110) for the threefold site but as for pure oxygen no stable configuration could be found, because OH moved immediately towards the long-bridge site.

These results show some important difference between the two iron surfaces. For the Fe(110) surface, oxygen is going to stay at its twofold long-bridge site, whether or not hydrogen is removed from the OH group (complete dissociation) or the adsorbed atomic oxygen is hydroxylated (e.g., if an additional water molecule approaches the surface). The situation is completely different on the Fe(100) surface. Here oxygen has to move from the fourfold hollow site to the twofold bridge site if an additional H is adsorbed at the oxygen atom, back to the fourfold hollow if the hydroxyl group is dissociated. Both processes (complete dissociation and hydroxylation) have been found experimentally on Fe(100).^{3,4}

IV. ADSORPTION OF MOLECULAR H_2O AND COADSORPTION OF OH AND H

As the next step we performed calculations to determine the start and end position for the reaction $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$.

There are early reports by Simmons and Dwyer^{13,14} that water dissociates via a mobile precursor on the Fe(100) surface. Our results show that on Fe(100) the adsorption energies with the water oxygen on the on-top site has the same adsorption energy as on the bridge site on this surface (the bridge site is slightly more stable but the difference is smaller than the accuracy of the calculation). Also water on the hollow site has a similar adsorption energy. If we rotate the water molecule slightly towards the surface or rotate it slightly along the z axis we found adsorption geometries with stable water molecules on the surface with the same adsorption energy as on the highly symmetric sites. The adsorption energy on Fe(100) is always around 0.3 eV.

A similar result could be found also for the Fe(110) surface (see Table III). The potential-energy-surface seems to be very flat for both surfaces. The bridge position for the Fe(100) surface and the on-top position for the Fe(110) surface are a little bit more favorable than the other adsorption sites, but as mentioned above the difference is sometimes smaller than the accuracy of our calculations. To fix the starting configuration we choose the bridge positions for water on Fe(100) and the on-top position for water on Fe(110) as the start-configuration for the dissociation process, which is needed to perform calculations using the nudged-elastic-band method. We conclude that water is very mobile on the iron surfaces, and that it can move to the considered starting configurations very easily, even if it is initially adsorbed on a different site. The geometry of the adsorbed molecule is only slightly different from its gas-phase configuration. The OH distance is unchanged, only the H-O-H angle is about 6° bigger than in gas phase. This is valid for both surfaces.

To calculate the end configuration of the water-dissociation process—when we have only OH and H on the surface—we considered all possible combinations of the

TABLE III. Adsorption site, adsorption energy E_{ad} , and geometry of H_2O and $OH+H$ on $Fe(100)$ and $Fe(110)$. Distances to the Fe surfaces are measured as the normal distance from the atom to the average first iron layer.

	Fe(100)	Fe(110)
H ₂ O on Fe:		
adsorption site	bridge	top
E_{ad} [eV]	0.35	0.26
H ₂ O geometry	OH=1.01 Å, HOH=111°	OH=1.01 Å, HOH=112.1°
z_O [Å]	1.87	2.29
OH+H on Fe		
appr. adsorption site	bridge(OH)/bridge(H)	<i>p</i> threefold(OH)/ <i>p</i> threefold(H)
diss. energy	1.13 eV	1.38 eV
$d(O-H)$ [Å]	1.01	1.00
OH angle [°]	64	2
z_O [Å]	1.47	1.33
z_H [Å]	0.99	1.03

highly symmetric adsorption sites for OH and H. Many of these combinations are not stable because the distance between hydrogen and the OH group is too small, leading to strong lateral repulsions between the coadsorbates. However, out of all locally stable configurations the energetically most favorable configuration could be clearly determined (in contrast to the case where we considered H_2O on the surfaces). The preferred adsorption sites for OH and H do not change very much if both species are coadsorbed on the surface (compare Table II with Table III). For example, OH moves slightly from the long-bridge site towards a pseudo-threefold hollow in the case of $Fe(110)$. The OH group is again tilted on $Fe(100)$, and remains perpendicular to the surface for $Fe(110)$. The only significant change could be found for coadsorption of $OH+H$ on $Fe(100)$ where the OH molecule is more strongly tilted towards the iron surface as compared to the case where we have only OH on the surface.

Dwyer *et al.*¹ reported additional intensity in the ultraviolet

photoemission (UPS) spectrum for water on $Fe(110)$ compared to the clean surface at binding energies of 6 eV and 10 eV. After heating the sample they found that after all hydrogen was desorbed and only oxygen remained on the surface, the only significant difference in the UPS spectra was the peak at 6 eV. They concluded that water dissociates spontaneously, that the 6 eV peak corresponds to the adsorbed oxygen (in the form of atomic oxygen or of a hydroxyl group), and that the 10 eV peak is only present if hydroxyl is adsorbed on the surface. This interpretation can be confirmed by your calculations if one approximates the UPS spectrum by the local density of states on the first two iron layers and the adsorbed atoms or molecules weighted with the atomic photoionization cross sections. The cross sections computed by Yeh and Lindau²⁰ for photon energies of $h\nu=21.2$ eV [$\sigma(H-1s)=1.9, \sigma(O-2p)=10.67, \sigma(Fe-3d)=4.83$] show that the oxygen contribution has the largest weight, explaining the high sensitivity of

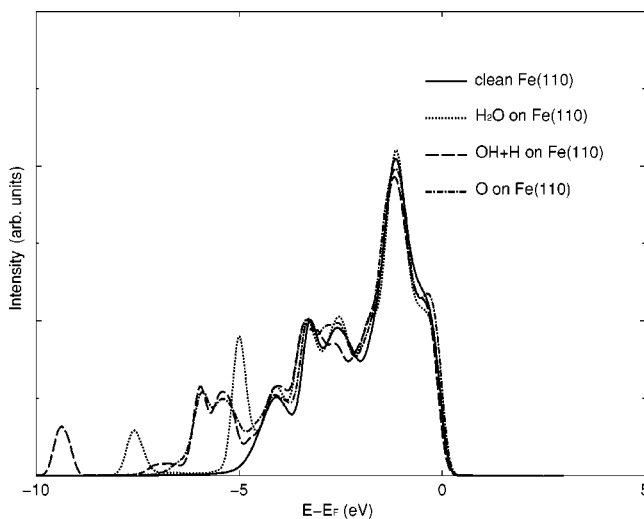


FIG. 2. Calculated UPS spectra for O, $OH+H$, and H_2O on $Fe(110)$.

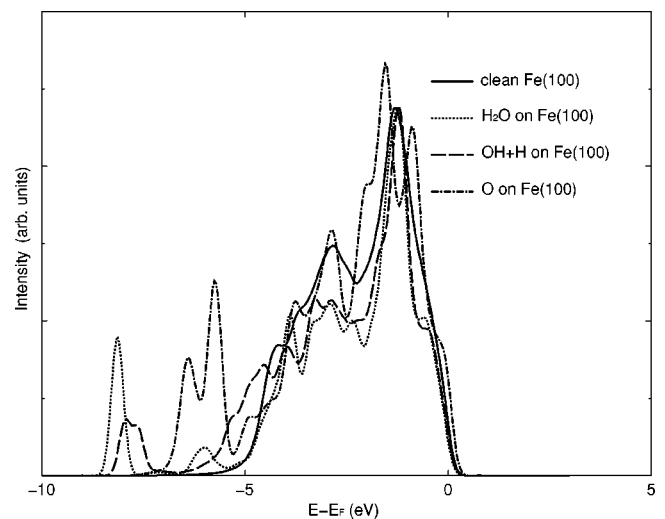


FIG. 3. Calculated UPS spectra for O, $OH+H$, and H_2O on $Fe(100)$.

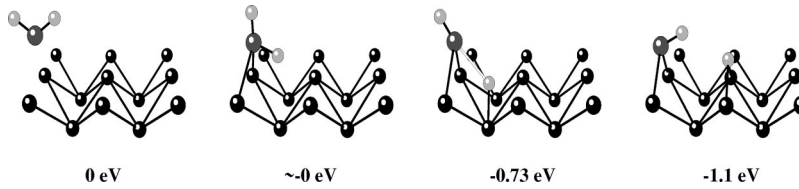


FIG. 4. Four representative configurations for the dissociation reaction $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ on Fe(100). The total energy of the start-configuration is used as the energy zero. The reaction proceeds from the left to the right. Atoms and molecules, which should be on the picture because of the periodic boundary conditions are not displayed.

the UPS experiment. To sum over all occupied states, a Fermi-Dirac distribution at 100 K was assumed, the finite resolution of the experiment was simulated by a Gaussian broadening with a width of 0.2 eV. The results for Fe(110) are shown in Fig. 2. For H_2O on Fe(110) we observed additional intensity below the d -band edge at ≈ -5 and ≈ -7.8 eV originating from the $3a_1$ and $1b_2$ molecular eigenstates of water, states with lower binding energies merge with the d -band of the substrate. After dissociation both bands are shifted to higher binding energies due to the stronger interaction with the substrate in the pseudo-three-fold site assumed by both the hydroxyl group and the H atom. The double-peaked structure of the band near ≈ -6 eV reflects a spin-up–spin-down splitting induced by the magnetic surface. After desorption of H, the peak near -9.5 eV disappears, in striking agreement with experiment.

Also for the Fe(100) case a UPS spectrum was calculated (see Fig. 3), but no recent experiment could be found to be compared with these results. For the more open Fe(100) surface we find also more pronounced adsorbate-induced changes in the DOS near the surface. Since water is now adsorbed in a bridge position, the strong adsorbate-substrate interaction leads to higher binding energies for the H_2O -derived bands. After dissociation both OH and H are in bridge positions and consequently we find only modest change in the electronic states—hence in this case H_2O dissociation is difficult to monitor in an UPS experiment, in contrast to $\text{H}_2\text{O}/\text{Fe}(110)$. After complete H desorption, the adsorbed oxygen shifts from the bridge to the hollow position. The increased O substrate interaction is reflected by an intense spin-split O band at about -6.5 eV. Pictures of the geometrical configurations of the start and end positions of the water dissociation process can be seen in the first and last pictures of Figs. 4 and 5.

V. DETERMINATION OF THE TRANSITION PATH FOR DISSOCIATION

We used the nudged-elastic-band method¹⁰ to calculate the transition state for the dissociation of water. First we

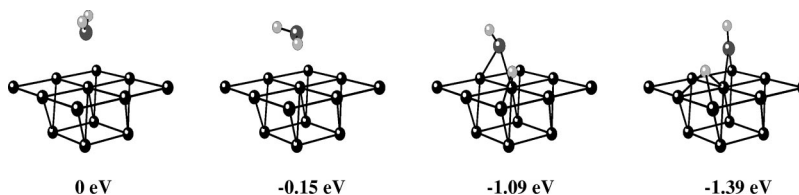
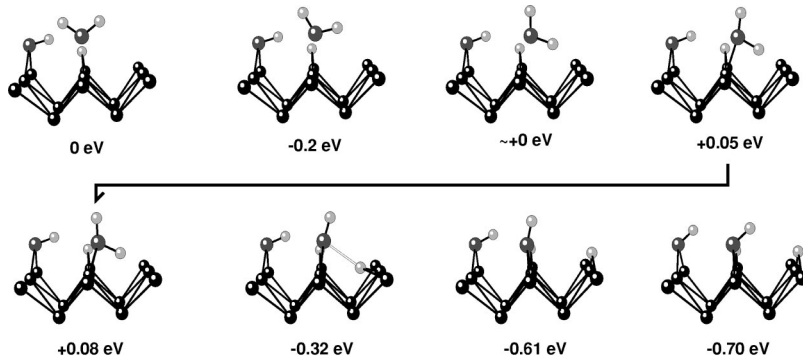


FIG. 5. Four representative configurations for the dissociation reaction $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ on Fe(110). The total energy of the start-configuration is used as the energy zero. The reaction proceeds from the left to the right. The first layer is drawn larger than the actual unit cell [$p(2 \times 2)$].

calculated only eight configurations between the start and end configurations, but after an initial optimization of the reaction path we inserted another eight between the two configurations where we suspected an eventual energy barrier. However, we could not find any configuration along the transition path with an energy higher than the starting position using the nudged elastic band method for both surfaces. This means that there is no barrier or the barrier is so small that it could not be determined by this method. We found the total energy gain (without considering any barrier) for the dissociation process to be 1.1 eV for Fe(100) and 1.4 eV for the Fe(110) surface (see Figs. 4 and 5). The dissociation process for both surfaces is quite similar. First the water molecule starts to rotate around the O atom to break the initial symmetry of the system (which it can do without any energy loss because of the flat energy surface) to a position where one hydrogen approaches the iron surface and breaks the O-H bond to form a Fe-H bond with the substrate. As seen by comparing Figs. 4 and 5, this rotation is more complex for Fe(110) because the oxygen previously bound on the top position has to move to the long-bridge position during the dissociation process. Immediately following dissociation OH is first adsorbed on the short-bridge site, from where it moves to its end position on the long-bridge site.

In experiments on the Fe(110) surface no molecular H_2O could be found, whereas for the Fe(100) surface, molecular H_2O was detected.² This is not what we would expect because the Fe(100) surface should be more reactive than the Fe(110) surface because of the less dense packing. But as our calculations show, there is a coverage dependence of the energy barrier of the dissociation process for both surfaces [in the case of Fe(110) it has also been experimentally confirmed in Ref. 2]. It is possible that in the experimental situation considered in Refs. 3,4, clustering of H_2O molecules plays an important role leading to a locally increased coverage which is the reason that molecular water was observed. To clarify this situation one must perform calculations at a higher coverage.



VI. DISSOCIATION OF WATER IN THE PRESENCE OF PRE-ADSORBED OH AND H

To show the coverage dependence of the energy barrier we performed another nudged-elastic-band calculation with two water molecules involved in this process. The first water molecule was considered as already dissociated according to our previous calculations. The second water molecule was initially adsorbed molecularly. At the end of this reaction both water molecules were dissociated. We investigated all different combinations of start and end positions of the involved atoms and molecules. The most stable configurations can be seen in Figs. 6 and 7. Again, the calculations have been performed with eight images between the start and the end configuration. But to determine the energy barrier more accurately another eight images were calculated between the two configurations where we suspected the barrier. The reaction path is quite different for the Fe(100) surface compared to the Fe(110) case if we have a second water molecule on the surface.

First we kept the first iron layer on Fe(100) fixed and found an energy barrier of around 0.15 eV. But after relaxing also the first layer this value was reduced to 0.08 eV (Fig. 6). This means we have an energy barrier (although t is rather small) for the water dissociation process if we consider a higher coverage of water on the surface. The dissociation process for the Fe(100) surface looks quite similar to the case where we have only a single water molecule on the surface. However, now it costs around 0.1 eV to move the water molecule into a position where one hydrogen atom can form a bond with the surface and break the O-H bond. The existence of a barrier demonstrates that it is possible to find at low temperatures molecular water adsorbed on the Fe(100) surface. The precise value of the reaction barrier might depend on the choice of the GGA functional, but it is clearly shown

that the dissociation process depends on the water coverage on the surface. So if one adsorbs water at very low temperatures where the formation of islands with increased coverage is possible, one should find water molecularly adsorbed on Fe(100) where the water coverage is increased locally.

In the case of Fe(110) the situation is more complicated. First we tried to adsorb the water molecule on the top position, but the molecule moved to a position where it forms a hydrogen bond with the hydrogen of the preadsorbed OH group (Fig. 7), which is now tilted by 38° . Also the end configuration is quite different from the case where we had only OH+H on the surface. The preadsorbed OH group moves to the short-bridge position, which was previously not stable. In this position the OH group is now 67° tilted towards the iron surface (Fig. 7). It is clear that to perform the transformation from this start configuration to the end configuration, one expects a quite large energy barrier in contrast to the Fe(100) case. In fact, the water molecule hydrogen bonded to the hydroxyl groups undergoes very interesting transformations before it dissociates into OH+H. Due to the large tilt of the OH groups and to the orientation of the H_2O molecule attached to it, one of the H atoms of the molecule comes quite close to the surface where it is absorbed in a pseudo-three-fold hollow. At the same time where the hydrogen-bonded H_2O loses one of its hydrogen atoms to the surface, the hydrogen bond between the two OH groups is strengthened, leading to the formation of a new H_2O molecule which is hydrogen-bonded to the oxygen atom of the former preadsorbed OH. This proton transfer allows to reduce the energy barrier. The newly formed H_2O molecule adsorbs to the surface through the O atom without breaking the H bond to the coadsorbed oxygen. After adsorption, the H atom returns to the O atom so that we are left with two OH groups and two H atoms coadsorbed on Fe(110). The com-

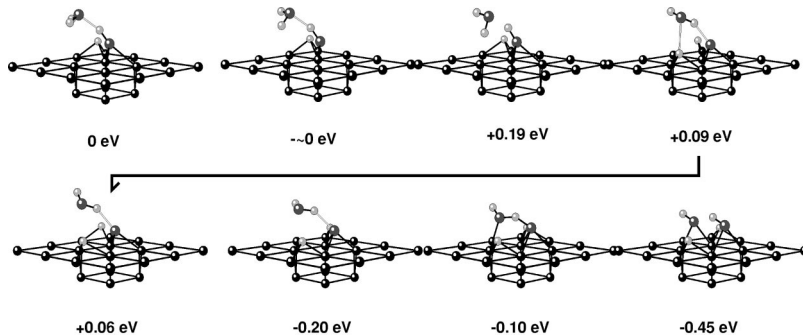


FIG. 7. Eight representative configurations for the reaction dissociation of water in the presence of coadsorbed H and OH: $OH+H+H_2O \rightarrow 2OH+2H$ on Fe(110). The total energy of the start configuration is used as the energy zero, cf. Fig. 5.

plete reaction is visualized in Fig. 7. The observed energy-barrier for this process on the Fe(110) is 0.19 eV. It is quite high compared to the Fe(100) surface, but one has to keep in mind that for Fe(110) all atoms have to rearrange quite substantially to transform to the end geometry from the starting configurations.

VII. CONCLUSIONS

To describe the dissociation process of water on the Fe(100) and Fe(110) surfaces, we have calculated the adsorption energies and adsorption geometries for all molecules and atoms involved in this process using *ab initio* density functional methods. We predict the adsorption geometry, and the transition path for the dissociation process $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$ for both iron surfaces. Our results are in agreement with experiments and previous calculations, and provide a fundamental understanding of the initial stages of iron oxidation.

The adsorption energies on the two considered surfaces are not very different. However, they differ significantly in their adsorption geometries. Whereas OH is tilted on the

Fe(110) surface for low and for high coverage, the OH group is tilted on the Fe(110) surface only in the high coverage regime. Oxygen can remain in its initial position on the Fe(110) surface even in the case of complete dissociation, whereas it moves from the bridge site to the hollow site on Fe(100). We could not find any energy barrier within the GGA approximation for both surfaces if we consider only one water molecule per unit cell [$p(2 \times 2)$]. However, if we increase the water coverage per unit cell (a second water molecule), we found a small energy barrier to dissociation on both surfaces. This shows the strong dependence of the dissociation barrier on the water coverage. This should be also valid in the case where we have clustering at low temperatures at the surface. The energy barrier in the case of Fe(110) is higher than on Fe(100) because a lot of rearrangement of the atomic geometry has to occur. An hydrogen transfer from and to the preadsorbed OH group to the new water molecule helps to decrease this barrier but it is still higher than on Fe(100). Our calculation shows also that the closed packed Fe(110) is chemically less reactive the more open Fe(100) surface as one would expect.

*On leave from the Center for Computational Materials Science, Wien.

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