Incipient adsorption of water and hydroxyl on hematite (0001) surface

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Abstract

The adsorption of submonolayer coverages of water and hydroxyl molecules on hematite (0001) surface is investigated using density functional theory with Hubbard correction U (DFT+U). The effect of adsorption on the structural, energetic, and electronic properties of both iron and oxygen terminated hematite surfaces is examined. The influence of the van der Waals interactions on the adsorption binding energy and geometry is also considered. It is found that tilted orientations of molecules are energetically more favored than planar ones, because the hydrogen bond stabilizes molecules on the surface. Bonding of H2O is more than twice weaker than that of OH. For both molecules adsorption on the iron-rich termination is much stronger than on the oxygen-terminated surface. The differences in bonding properties of water and hydroxyl molecules to the hematite surfaces are explained by different character of the charge transfer in the molecule–oxide system.

1. Introduction

During the last three decades or so, adsorption of water on iron oxide surfaces has attracted substantial research interest [1–7]. This is due to its important role played in the initial stages of reaction processes occurring at the oxide surfaces in an ambient environment leading to corrosion and reduction of iron oxides [7], and in photoelectrochemical water splitting devices for solar energy conversion [8]. Majority of these studies have focused on the interaction of water with the hematite (α-Fe2O3) (0001) surface and have revealed many interesting features occurring upon adsorption of water and hydroxyl molecules thereon. One of the basic questions from the beginning was about molecular or dissociative character of water adsorption. The earliest experimental studies [1, 2, 4] pointed to the conclusion that water does not bind strongly to the α-Fe2O3(0001) surface and that water dissociation is not favored under ultra-high vacuum (UHV) condition. X-ray photoelectron spectroscopy (XPS) studies by Liu et al [6] suggested a threshold for hydroxylation at a pressure of 10−4 Torr. Below the threshold, only a small amount of dissociated water was found, mostly at surface defect sites. Surface x-ray scattering studies of the hydrated iron and oxygen terminated surfaces of hematite, combined with density functional theory (DFT) calculations performed by Trainer et al [9] showed that water weakly associates at the surface and rather dissociates, thus the surface is hydroxylated. Yamamoto et al [10] studied water adsorption on iron-terminated α-Fe2O3(0001) surface at near ambient conditions and showed that adsorption of water molecules is preceded by surface hydroxylation, which is initiated at very low relative humidity, and molecular water starts to adsorb at higher relative humidity. On the theory side DFT studies of Yin et al of the initial stages of adsorption and hydroxylation of water on the perfect [11] and defective [12] Fe-terminated surfaces of hematite showed that even at perfect surface dissociation is strongly favored over molecular adsorption at low coverage. They were followed by several DFT+U studies. Souvi et al [13] found that first water molecule is adsorbed dissociatively, while second and third water adsorb associatively. Calculations of low-coverage water adsorption and dissociation on various surface terminations of α-Fe2O3(0001) performed by Nguyen et al [14] revealed very low energy barriers (0.06—0.3 eV) for water dissociation. Their later work [15]...
showed that upon contact with water the surface can easily be covered with O atoms and/or OH groups. Low energy barriers for water dissociation on iron-rich hematite surface were confirmed by a combined *ab initio* molecular dynamics and experimental studies [16]. Calculation of the isolated water molecule on an Fe- and O-terminated (0001) surfaces yielded the adsorption energy of merely 0.49eV for the O-terminated surface [17]. Stability of two hydroxylated, iron and oxygen terminated surfaces has been studied using surface-specific DFT+U approach [18]. The effects of OH adsorption at different coverages on the structure of Fe-terminated α-Fe₂O₃(0001) surface was also studied [19]. Calculations of Negreiros *et al* [20], including the van der Waals correction, of the interaction of very low coverage of water with this surface, showed that a negatively charged surface reduces the energy barrier and enhances substantially the water binding and inhibits water dissociation. A similar theoretical framework was recently applied to study water adsorption on defective Fe-terminated hematite surfaces [21], and different terminations of hematite [22].

All those calculations concluded that water dissociation is favored over molecular adsorption at low coverage. This seem to contradict experimental observation of molecular water adsorption on the partially covered hematite surface under UHV condition [1, 2, 6]. However, the existing DFT simulations do not show a spontaneous H₂O dissociation at the low coverages considered. Thus, the picture they convey is that initially water adsorbs intact and subsequently it dissociates.

Interaction of water and/or hydroxyl with hematite surfaces has been usually studied for only one and relatively high coverage, and adsorption on the Fe-terminated surface. A quite a large scatter in the calculated adsorption energies is seen due to the use of partially constrained or fully relaxed slab [23]. It is also likely that iron- and oxygen-rich terminations of α-Fe₂O₃(0001) surface coexist [24]. All this calls for a more systematic comparison of the initial H₂O and OH adsorption on the two terminations. Therefore, in this work we apply DFT+U to investigate in detail the influence of very low-coverages of H₂O and OH molecules on surface geometry and composition, electronic structure, and energetics and stability of these two terminations of hematite (0001) surface. We also examine the influence of the correction for the long-range van der Waals interactions on the structure and properties of the two terminations upon adsorption of H₂O and OH.

2. Computational details

The calculations were performed within the spin-polarized density functional theory as implemented in the Vienna *ab initio* simulation package (VASP) [25, 26]. The electron ion-core interactions were described by the potentials generated by the projector augmented wave (PAW) method [27, 28] with Fe 3d⁴4s¹, O 2s²2p⁴, and H 1s¹ states, treated as valence states. A plane waves basis with cut-off energy of 500eV and the conjugate gradient grid for the calculations of the generalized gradient approximation (GGA) to exchange and correlation energy functional was used. To account for the on-site Coulomb repulsion of the Fe 3d electrons the Hubbard correction term U was included using the rotationally invariant approach of Dudarev *et al* [30]. Following our previous studies [31] the effective parameter $U_{eff} = U - J = 4.0$ eV was adopted. The integrations over the Brillouin zone were performed using the k-point sampling method with a $6 \times 6 \times 1$ Monkhorst-Pack [32] grid for the calculations using a $1 \times 1 \times 1$ surface unit cell, and $3 \times 3 \times 1$ mesh for $2 \times 2 \times 1$ cell. A Gaussian broadening of the Fermi surface of 0.1eV was applied to improve the convergence of the solutions. This PBE+U calculation of antiferromagnetic bulk yields the following lattice parameters of the hexagonal unit cell, $a = 5.072$ Å and $c = 13.892$ Å [33, 34]. In order to examine an influence of the van der Waals (vdW) interactions on the water and hydroxyl adsorption the empirical D3 functional proposed by Grimme and co-workers [35] has been used. With vdW D3 correction included, $a = 5.057$ Å, and $c = 13.840$ Å.

Iron Fe₁ terminated (Feₙ – Feₙ) and oxygen Oₙ-terminated (Oₙ – Feₙ – Feₙ) (0001) surfaces of α-Fe₂O₃ were simulated by symmetric slabs consisting of 18 (12 Fe and 6 O) and 16 (10 Fe and 6 O) atomic layers, respectively, with a symmetry plane in the middle of the Fe bilayer [31], separated from their periodic images by a vacuum region of 23 Å. The positions of all atoms were optimized until the forces on atoms were smaller than 0.05 eV/Å. The molecules were adsorbed on both sides of the slab, and the adsorption binding energy was calculated from the expression

$$E_{ad} = - (E_{X/\text{hem}} - E_{\text{hem}} - 2nE_X)/n,$$  \(1\)

where a minus sign yields positive $E_{ad}$, so larger adsorption energy means more favored binding. $E_{X/\text{hem}}$ is the total energy of the substrate slab covered with adsorbed molecule species, $X$, $E_{\text{hem}}$ represents the energy of the relaxed bare oxide surface, $E_X$ is the energy of a free molecule, and $n$ is the number of molecules per surface cell. The gas-phase H₂O and hydroxyl molecules were calculated in a large rectangular box by using PBE and PBE +D3. They yielded same geometry: 0.97 Å for the H–O bond length, and 104.50° for the H–O–H angle in H₂O molecule, in good agreement with experiment [3] and theory [36]. The H–O bond length in the gas-phase hydroxyl is 0.99 Å. The work function was calculated as a difference between electrostatic potential far in the
vacuum and the Fermi energy. The charges on atoms were calculated using the Bader analysis as implemented by Henkelman et al.\[37\].

3. Results and discussion

In adsorption studies we adopted the convention in which a single molecule adsorbed in a $1 \times 1$ surface cell corresponds to 1/3 monolayer (ML) coverage [2, 38], because there are three oxygen atoms in an oxygen layer in $1 \times 1$ surface cell. Thus, using a $2 \times 2$ surface cell in which up to four molecules can be placed in four equivalent adsorption sites allows to study molecular coverages varying from 1/12 ML (cf figure 1) to 1/3 ML. Note that even at the highest coverage of 1/3 ML, the molecules are laterally separated from each other by $\approx 5 \, \text{Å}$, which excludes formation of the ice structure in case of water adsorption. The deposited molecule was originally placed above one of the surface sites and the initial distance between topmost surface atom and molecule’s oxygen atom ($O_{m}$) was at least 2.3 Å. In order to determine preferred adsorption geometries, differently oriented water and hydroxyl molecules: vertical, flat, or tilted were used as starting configurations, in several possible adsorption sites.

3.1. Fe1-terminated surface

On the Fe1-termination we considered adsorbate positions above the atom of the surface Fe layer, and above the threefold coordinated subsurface Fe atoms, labeled respectively as A, and B, C, in figure 1. The position above, and in the vicinity of the surface iron atom (site A), appeared to be the most stable for both molecules. The other two surface sites, B and C, are much less stable.

3.1.1. $H_{2}O$ adsorption

Geometry. Upon adsorption on the Fe1-terminated $\alpha$-$Fe_{2}O_{3}(0001)$ surface, regardless of the initial configuration, after structure optimization the adsorbed water molecule prefers tilted orientation, with one of its
hydrogens closer to the surface than the other one (figure 1(a)). With the coverage increased up to 1/3 ML the orientation and geometries of adsorbed water molecules remained unchanged. As can be seen from figure 1(a), at the lowest coverage (1/12 ML) the tilted H$_2$O molecule forms a 1.75 Å long bond between its H atom and the surface oxygen (O$_{surf}$). This causes that O$_{surf}$ atom is slightly, by 0.1 Å, pulled out of the oxygen layer. The O$_m$ atom of the molecule is shifted from the surface site by 1.4 Å and forms a 2.15 Å long bond with the surface Fe atom.

When adsorbed on the surface, the geometry of the water molecule (1/12 ML) changes compared to the gas-phase. The bond length between the O$_m$ and H atoms, pointing towards the surface, is extended by 5% to 1.02 Å. Fe atom.

However, as is seen from figure 2, with a further increase of H$_2$O coverage the calculated adsorption energy significantly decreases, to 0.88 eV for 1/3 ML (for other numerical values see SI). This $E_{ad}$ value agrees well with recent PBE+U results (0.75 eV [14]; 0.82 eV [22]) for molecularly adsorbed water. Figure 2(a) also shows that the account for vdW interactions enhances $E_{ad}$ values by nearly same amount of 0.2 eV, at all water coverages. The lowest coverage (1/12 ML) value, $E_{ad}$ = 1.19 eV, agrees well with PBE+U+D3 result, 1.26 eV [20]. The overall relative adsorption energy variation between the different coverages is rather small which indicates that the molecule-surface interaction is dominant over the molecule-molecule interaction. The lowering of the adsorption energy with increasing coverage and shortening of the hydrogen bonds with the substrate oxygen

**Energetics.** A single H$_2$O molecule (1/12 ML coverage) binds relatively strong to the Fe1-terminated (0001) surface, with $E_{ad} = 0.97$ eV. With the coverage increased to 1/6 ML the adsorption energy is only slightly increased (by 0.016 eV) which is connected to the above mentioned changes in the surface local structure.

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**Figure 2.** Adsorption energy per H$_2$O molecule (a), and work function change (b), versus H$_2$O coverage for the Fe1-terminated (0001) surface of α-Fe$_2$O$_3$. 
atoms, support the picture of adsorption of molecular H₂O, which precedes the surface hydroxylation that occurs above the pressure threshold [6].

**Charge transfer.** A qualitative information about charge transfer on the surface is provided by the work function change \(\Delta \Phi\), with respect to the clean surface value. Compared to that of the clean Fe1-terminated surface \(4.35\) eV, PBE+U \(4.51\) eV, PBE+U+D3) at small H₂O coverages the work function increases by \(0.30\) eV for 1/12 ML, and \(0.43\) eV for 1/6 ML (figure 2). At 1/4 ML water coverage the work function is almost unchanged (within 0.09 eV) but decreases by \(-0.20\) eV for 1/3 ML (see SI). Calculations using the vdW functional give the same initial trend of \(\Delta \Phi\) change which is reduced by \(0.05−0.13\) eV; for higher H₂O coverages work function is lower than that of the clean Fe1-termination. These \(\Delta \Phi\) changes correlate well with the electron charge transfer in the adsorbate–oxide system. The calculated Bader charges on surface atoms are small. For the three lowest coverages, each H₂O molecule loses \(-0.018e, -0.025e, and -0.006e\), respectively, while at 1/3 ML it becomes slightly cationic by gaining 0.003e. The surface Fe atom loses even more charge than the water molecule \((-0.04−0.05e)\). The majority of the charge \((-0.04−0.05e)\) is transferred to the surface oxygen atoms which form bonds with H atoms. The amount of charge transfer upon water adsorption resulting from PBE+U + D3 calculations is nearly the same as that calculated within PBE+U.

**Electronic structure.** Figure 3 presents the calculated partial density of states (PDOS) for molecular adsorption on the Fe1-terminated surface resulting from PBE+U. The electronic structure is slightly modified by additional peaks from H₂O which appear in the energy region below the main conduction band minimum (figure 3). The modifications are nearly independent of H₂O coverage. The effect of magnetism of hematite on adsorbed water is weak. The magnetization of H₂O molecules adsorbed on the Fe1-termination is small for all calculations. The magnetic moment on the O₂⁻ atoms varies slightly, from 0.03 to 0.04 \(\mu_B\), and is negligible on hydrogen atoms, for all considered coverages of H₂O.

**3.1.2. OH adsorption**

**Geometry.** On the Fe1-terminated surface, the adsorbed hydroxyl group binds with the topmost surface Fe atom through its oxygen and forms a bond of 1.84 Å, tilted with respect to the surface plane (figure 1(b)). The hydrogen atom points out from the surface, even though the initial geometry was with H pointing to the surface. For all coverages considered, the O–H bond length is shortened to 0.97 Å, compared to its length (0.99 Å) in a gas phase. The Fe–Oₐ bond length shrinks a little bit with increasing coverage, from 1.84 Å to 1.81 Å for 1/3 ML. The OH configuration on the Fe1-termination excludes bond formation between H and surface atoms. It is worth noting that the hydrogen atom has no preferred position with respect to the surface. It means that there are other similar OH configurations with degenerated energies, which suggests that OH can rotate around the O₂⁻ atom of the adsorbed molecule pinned over the surface Fe atom. The geometries of adsorbed OH on the Fe1-termination obtained from PBE+U+D3 calculations are nearly the same as those resulting from PBE+U (cf. SI).

**Energetics.** The binding of OH to the Fe1-terminated surface is twice as strong as that of H₂O molecule. For the smallest OH coverage (1/12 ML) the adsorption energy is 2.28 eV. Thus, our results support the conclusion of previous studies [9, 10] that hydroxylation of hematite surface is energetically favored. \(E_{ad}\) decreases by 0.09 eV in the range of OH coverages considered (figure 4(a)) to 2.19 eV for 1/3 ML. This agrees well with recent PBE+U result (2.31 eV [19]). Adsorption energies calculated by using PBE+U+D3, i.e. with the contribution of vdW interactions included, are larger by 0.14 eV, but their relative variation for the considered coverage range is the same. Similar to water adsorption this indicates that the OH–surface interaction dominates over the OH–OH interaction in adsorbed layer.

**Charge transfer.** The calculated work function changes induced by OH adsorption are significantly larger than upon H₂O adsorption. \(\Delta \Phi\) amounts to 1.52 eV for 1/12 ML, and it increases gradually with coverage up to 2.69 eV for 1/3 ML (figure 4(b)). This results from a larger charge transfer between adsorbed OH and the hematite surface atoms which is by an order of magnitude larger than in case of H₂O adsorption. An analysis of Bader charges shows that at the lowest coverage the hydroxyl O atom loses \(-0.37e\). With increasing coverage the loss increases to \(-0.46e\) for 1/3 ML. Also the Fe and O atoms of the topmost oxide layer lose some charge (up to \(-0.11e\) and \(-0.08e\), respectively) by transferring electrons to subsurface layers. The charges on atoms calculated using PBE+U+D3 do not differ from those resulting from PBE+U calculations.

**Electronic structure.** In contrast to H₂O, adsorption of OH substantially modifies the electronic structure of the Fe1-termination. As can be seen in figure 3, in the presence of adsorbed OH, even at the smallest OH coverage, the Fe 3d and O 2p bands are shifted by about 0.5 eV to higher energies, and the surface becomes metallic. The metallic character of this termination is further enhanced by the OH states present just below the Fermi energy, which hybridize with Oxsurf 2p and Fe 3d states. Figure 3 shows that compared to water adsorption, there is much larger asymmetry in the density of majority and minority spin states which results in the magnetization of adsorbed OH molecules substantially enhanced. The magnetic moment on the hydrogen atom is 0.01 \(\mu_B\) while on the hydroxyl oxygen it rises from 0.16 \(\mu_B\) at 1/12 ML coverage, to 0.21 \(\mu_B\) at 1/3 ML A
similar value of the magnetic moment on the hydroxyl oxygen, which is much larger than in the water molecular state, was also noticed in [14]. The magnetic moments calculated using the vdW corrected functional are unaltered with respect to those obtained from PBE+U.

3.2. O3-terminated surface
On this surface the most stable position both for H₂O and OH molecule is site A, in a deep hollow left by the surface Fe atom removed from the Fe-termination during formation of the O3 termination (figure 5). Other, less stable sites, are the threefold coordinated hollow sites, above Fe atoms of the second and first subsurface Fe layer.

3.2.1. H₂O adsorption
Geometry. On the O3-terminated surface a water molecule binds flat-like over the surface hollow site A with both its hydrogens pointed towards the surface (figure 5). The molecule is shifted by 0.48 Å from the hollow
center towards one of the surface oxygens and forms three bonds. A 2.15 Å long bond between O_{m} and O_{surf} atoms, and two bonds between hydrogen and surface oxygen atoms. One of the two H–O_{surf} bonds is significantly shorter (1.70 Å) than the other (1.76 Å). However, the length of the H–O_{m} bonds within the molecule is the same (1.00 Å). The H–O–H angle in the adsorbed H_{2}O is reduced by 3° compared to the free water molecule. The same geometry of H_{2}O was obtained from PBE+U+D3.

Figure 4. Adsorption energy per OH molecule (a), and work function change (b), versus OH coverage for the Fe1-terminated (0001) surface of α-Fe_{2}O_{3}.

Figure 5. As figure 1, but for H_{2}O (a) and OH (b) adsorption on the O3-terminated (0001) surface of hematite.
Energetics. The PBE+U calculated adsorption energy shows very weak coverage dependence. For the lowest H$_2$O coverage (1/12 ML) $E_{ad}$ amounts to 0.67 eV and decreases with the increasing coverage to 0.61 eV at 1/3 ML (figure 6(a)). This is distinctly higher than that reported by other PBE+U calculations (0.51 eV [14]; 0.49eV [17], and 0.41 eV [22]). With vdW corrections included, the calculated $E_{ad}$ is 0.3–0.5eV higher and its decreasing trend with the coverage is more distinct. Nevertheless, H$_2$O binds 30% weaker to the O3-terminated surface than to the Fe1-termination. The much weaker bonding of H$_2$O to the O3-termination allows to distinguish between different terminations of the hematite (0001) surface which may be useful for the interpretation of experimental measurements on these surfaces.

Charge transfer. The presence of adsorbed H$_2$O molecules reduces the surface dipole moment, and consequently the work function is lowered compared with the clean O3-termination values (8.40 eV, PBE+U; 8.42 eV, PBE+U+D3). Even for the smallest coverage the work function is significantly reduced ($-0.24$ eV) and the reduction is larger with growing H$_2$O coverage, reaching $-0.78$ eV for 1/3 ML (figure 6(b)). The work function changes obtained from the calculations accounting for vdW interactions are very similar (within 5%). This is quantitatively different from H$_2$O adsorption on the Fe1-termination, where even a small coverage of H$_2$O leads to an increase of the work function. The different work function change upon water adsorption can be understood by comparing very different orientation of the dipolar H$_2$O molecules adsorbed on the two terminations (figure 1(a) and 5(a)) which contribute differently to surface dipole moment. Calculated Bader charges show that the amount of charge transferred from a single H$_2$O molecule ($-0.38$ e) adsorbed on the O3-termination is more than twice as large as that on the Fe1-terminated surface. Most of the electrons are transferred to the surface oxygen layer of the oxide, but also atoms of deeper subsurface layers gain some small charge (up to 0.04 e). The charge transfer does not depend much on the H$_2$O coverage and is almost the same for all coverages. The charges on the atoms obtained from PBE+U+D3 are almost the same as those calculated without the vdW correction included.

Electronic structure. As can be seen from the PDOS plotted in figure 7, water adsorption does not affect much the surface electronic structure of the O3 termination. The presence of water opens a narrow energy gap, just below the Fermi energy, which widens with increasing H$_2$O coverage. Additional peaks from adsorbed water molecules appear also at energies far below the Fermi level. Increasing of H$_2$O coverage affects mostly unoccupied surface O 2p states above the Fermi level (figure 7). In contrast to the Fe1-terminated surface, adsorption of H$_2$O on the O3-termination enhances significantly the magnetic moment on the oxygen atom of the molecule ($0.36 \mu_B$) and leads to a significant magnetization of water, 0.41 $\mu_B$, which was also noticed in [14]. The magnetization is almost independent of H$_2$O coverage and is the same when calculated with PBE+U or PBE+U+D3.

Figure 6. Adsorption energy per H$_2$O molecule (a), and work function change (b), versus H$_2$O coverage for the O3-terminated (0001) surface of $\alpha$-Fe$_2$O$_3$. 

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3.2.2. OH adsorption

Geometry. On the O3-termination of the α-Fe₂O₃(0001) surface the OH molecule binds with the surface by forming O_m–O_surface and H–O_surface bonds, in a flat-like geometry with respect to the surface (figure 5(b)). The O_m atom binds with two neighboring surface oxygens at a distance of 2.08 Å and 2.12 Å, while the H–O_surface bond length is 1.65 Å, so the OH molecule lies closer to the surface than H₂O. These geometries do not change much with increasing coverage and do not alter when calculated within PBE+U+D3.

Energetics. The adsorption binding of OH is almost 0.5 eV stronger than that of H₂O. At the lowest coverage (1/12 ML) it amounts to 1.09 eV. Similarly as for H₂O, with increasing coverage of OH to 1/3 ML, E_ad decreases only by about 0.05 eV (figure 8(a)). PBE+U+D3 calculations predict 0.2–0.5 eV larger adsorption energies and a more pronounced coverage dependence. Again, OH binds much weaker (by 1 eV) to the O3− than to the Fe1-termination of hematite (0001).

Charge transfer. The work function of the O3-terminated surface decreases with increasing amount of adsorbed OH. At the smallest coverage (1/12 ML) the work function change is −0.16 eV and increases up to −0.65 eV at 1/3 ML (figure 8(b)). The vdW calculations yielded slightly smaller values (by 0.03—0.11 eV) of

![Figure 7](image-url)
The calculated Bader charges on atoms are smaller than in the case of H$_2$O adsorption. The OH molecule loses up to 0.21 e at the highest coverage (1/3 ML). The electron charge transfer calculated within PBE+$U$+$D3$ is almost the same.

Electronic structure. The changes in the surface electronic structure induced by the presence of OH on the O$_3$-termination can be seen in the PDOS plots displayed in figure 7. Similarly as for H$_2$O, at higher coverages adsorption of OH leads to an opening of the energy gap just below the Fermi energy. Additional peaks from adsorbed hydroxyl are present, however, at 2 eV closer to the Fermi level. With increasing coverage, the OH states dominate in the unoccupied minority states. Interestingly, the magnetic moment on the oxygen atom of the adsorbed hydroxyl is greatly increased to 0.98 $\mu_B$ and is the largest of all systems considered in this work. On the surface oxygen atoms it does not exceed 0.17 $\mu_B$ and is almost independent of coverage both when calculated with or without vdW correction.

3.3. Surface stability

The stability of different bare terminations of the $\alpha$-Fe$_2$O$_3$(0001) surface as a function of oxygen partial pressure was considered based on the thermodynamic approach $[39]$ in several previous works (see for instance $[14, 18, 21, 31]$). The stoichiometric Fe1-termination is the most stable one in the available range of the chemical potential of oxygen. The clean O$_3$-terminated surface is unstable. In order to determine the effect of adsorption on stability of surface terminations we consider the relative variation of the Gibbs free energy, $\Delta G$, with respect to the energy of the bare hematite surface termination. Upon adsorption of molecule X, X = H$_2$O or OH, $\Delta G$ can be approximately expressed as

$$\Delta G = E_{X/\text{hem}} - E_{\text{hem}} - 2n\mu_X,$$

where $E_{X/\text{hem}}$, $E_{\text{hem}}$, and $n$ have the same meaning as in equation (1), while $\mu_X = E_X$ is standing for the chemical potential of the molecule. Hence, the surface energy change upon adsorption of molecule can be written as $\Delta \gamma = \Delta G/(2A)$, where A is the surface cell area.

The variations of surface energy of the two hematite (0001) terminations versus H$_2$O or OH coverage are plotted in figure 9. As is seen, the presence of adsorbed water or hydroxyl molecules distinctly lowers the surface energy and thus enhances the stability of the surface. The variation of $\Delta \gamma$ with coverage is nearly linear. The lowering of $\gamma$ is stronger for adsorption on the Fe1 than on the O3 termination and stronger for PBE+$U$+$D3$ than for PBE+$U$. At 1/3 ML of H$_2$O the surface energy of the Fe1 termination is lowered by about 40 meV/Å$^2$ (50 meV/Å$^2$) as calculated with PBE+$U$/PBE+$U$+$D3$). On the O3-terminated surface the variation of $\Delta \gamma$ upon H$_2$O adsorption is 30% weaker. Upon OH adsorption the variation of $\Delta \gamma$ is nearly 2.5 times stronger than that due to H$_2$O. At the OH coverage of 1/3 ML, $\Delta \gamma$ of Fe1 termination is ~99 meV/Å$^2$, and is nearly the same independent of whether calculated using PBE+$U$ or PBE+$U$+$D3$. Added to the clean Fe1-termination value (67 meV/Å$^2$ $[31, 40]$) it gives for the surface energy ~32 meV/Å$^2$, which is in very good agreement with the PBE+$U$ result calculated in $[18]$. On the O3 termination the variation of $\Delta \gamma$ upon OH adsorption is weaker compared to that on the Fe1-terminated surface, which reflects a weaker binding of OH to this surface.
4. Summary and conclusion

We have presented results of investigation of submonolayer coverages of water and hydroxyl on iron, and oxygen terminated α-Fe₂O₃ (0001) surfaces. On the Fe1-terminated surface, both water and hydroxyl molecules prefer adsorption on the topmost Fe ion through molecule oxygen, in a tilted geometry. In the case of H₂O adsorption, an additional hydrogen bond with surface oxygen is formed, which stabilizes the molecule on the surface. Such a configuration may be considered as an initial stage for dissociation of an adsorbed water molecule. For all coverages studied, the calculated adsorption energy of hydroxyl is more than twice as large as that of water. On the Fe1-terminated surface the work function change increases with increasing amount of adsorbed hydroxyls. This result may be helpful in analysis of experimental data to distinguish different termination domains. Adsorption of OH substantially modifies the electronic structure of the Fe1-termination and makes it metallic. On the oxygen termination, both water and hydroxyl bind weaker than on the Fe1-terminated surface. However, the binding of hydroxyl is much stronger than water. Both molecules prefer formation of O and H bonds with surface oxygens, and consequently their geometry is rather flat. At higher coverages, adsorption of H₂O and OH leads to an opening of the narrow energy gap around the Fermi energy. The adsorption of H₂O and OH lowers the surface energy of the α-Fe₂O₃(0001) surfaces. Our results show that taking into account van der Waals interactions affects mainly the adsorption binding and surface energies, and to lesser extent work functions, while the geometry of the adsorbate–oxide system and their electronic and magnetic structures are almost unaffected.

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References

[1] Hendewerk M, Salmeron M and Somorjai G A 1986 Water adsorption on the (001) plane of Fe₂O₃: an XPS, UPS, Auger, and TPD study Surf. Sci. 172 544–56

[2] Kurtz R I and Henrich V E 1987 Surface electronic structure and chemisorption on corundum transition-metal oxides: α-Fe₂O₃ Phys. Rev. B 36 3413–21
[3] Thiel P A and Maday T E 1987 The interaction of water with solid surfaces: fundamental aspects Surf. Sci. Rep. 7 211–385
[4] Junta-Rosso J L and Hochella M F 1996 The chemistry of hematite 001 surfaces Geochim. Cosmochim. Acta 60 305–14
[5] Henderson M A, Joyce S A and Rustad J R 1998 Interaction of water with the (1 × 1) and (2 × 1) surfaces of α-Fe2O3(012) Surf. Sci. 417 66–81
[6] Liu P, Kendelevicz T, Brown G E, Nelson E J and Chambers S A 1998 Reaction of water vapor with α-Fe2O3(001) and α-Al2O3(001) surfaces: synchrotron x-ray photoemission studies and thermodynamic calculations Surf. Sci. 417 53–65
[7] Parkinson G S 2016 Iron oxide surfaces Surf. Sci. Rep. 71 272–365
[8] Seriani N 2017 Ab initio simulations of water splitting on hematite J. Phys.: Condens. Matter 29 463002
[9] Trainor T P, Chaka A M, Eng P J, Neville M, Waychunas G A, Catalano J G and Brown G E Jr 2004 Structure and reactivity of the hydrated hematite (0001) surface Surf. Sci. 573 204–24
[10] Yamamoto S et al 2010 Water adsorption on α-Fe2O3(001) at near ambient conditions J. Phys. Chem. C 114 2236–66
[11] Yin S, Ma X and Ellis D E 2007 Initial stages of H2O adsorption and hydroxylation of Fe-terminated α-Fe2O3(001) surface Surf. Sci. 601 2426–37
[12] Yin S and Ellis D E 2008 H2O adsorption and dissociation on defective hematite (001) surfaces: a DFT study Surf. Sci. 602 2047–54
[13] Souvi S M O, Badawi M, Paul J-F, Cristol S and Cantrel L 2013 A DFT study of the hematite surface state in the presence of H2, H2O and O2 Surf. Sci. 610 7–15
[14] Nguyen M T, Seriani N and Gebauer R 2013 Water adsorption and dissociation on α-Fe2O3(001); PBE+U calculations J. Chem. Phys. 138 194747
[15] Nguyen M-T, Seriani N, Piccinin S and Gebauer R 2014 Photo-driven oxidation of water on α-Fe2O3 surfaces: an ab initio study J. Phys. Chem. 118 046703
[16] English N J, Rahman M, Wadnerkar N and MacElroy J M D 2014 Photo-active and dynamical properties of hematite (Fe2O3)-water interfaces: an experimental and theoretical study Phys. Chem. Chem. Phys. 16 14445–54
[17] Pan H, Meng X and Qin G 2014 Hydrogen generation by water splitting on hematite (0001) surfaces: first-principles calculations Phys. Chem. Chem. Phys. 16 25442–8
[18] Huang X, Ramadugu S K and Mason S E 2016 Surface-specific DFT+U approach applied to α-Fe2O3(001) J. Phys. Chem. C 120 4919–30
[19] Pang Q, DorMohammadi H, Isgor O B and Arnadóttir L 2017 Density functional theory study on the effect of OH and Cl adsorption on the surface structure of α-Fe2O3 Comput. Theor. Chem 1100 91–101
[20] Negreiros F R, Pedroza L S and Dalpian G M 2016 Effect of charges on the interaction of a water molecule with the Fe2O3(001) surface J. Phys. Chem. C 120 11918–25
[21] Ovcharenko R, Voloshina E and Sauer J 2016 Water adsorption and O- and Fe-formation on Fe2O3(001) surfaces Phys. Chem. Chem. Phys. 18 25560–8
[22] Wang B R and Hellman A 2018 Initial water adsorption on hematite (α-Fe2O3) (001): A DFT+U study J. Chem. Phys. 148 094705
[23] Corum K W, Huang X, Bennett I W and Mason S E 2017 Systematic density functional theory study of the structural and electronic properties of constrained and fully relaxed (001) surfaces of alumina and hematite MOL. SIMULAT. 43 406–19
[24] Kiejna A and Pabisiak T 2013 Mixed termination of hematite (α-(Fe2O3)) (001) surface J. Phys. Chem. C 117 24339–44
[25] Kresse G and Hafner J 1993 Ab initio molecular dynamics for liquid metals Phys. Rev. B 47 558–61
[26] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86
[27] Blochl P E 1994 Projector augmented-wave method Phys. Rev. B 50 17953–79
[28] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758–75
[29] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8
[30] Dudarev S L, Botton G A, Savrasov S Y, Humphreys C J and Sutton A P 1998 Electron-energy-loss spectra and the structural stability of nickel oxide: an LSDA + U study Phys. Rev. B 57 3505–9
[31] Kiejna A and Pabisiak T 2012 Surface properties of clean and Au or Pd covered hematite (α-(Fe2O3)) (001) J. Phys.: Condens. Matter 24 095003
[32] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188–92
[33] Pabisiak T, Winiarski M and Kiejna A 2016 CO adsorption on small Au(1) (n = 1–4) structures supported on hematite: I. adsorption on iron terminated α-Fe2O3(001) surface J. Chem. Phys. 144 044704
[34] Pabisiak T, Winiarski M and Kiejna A 2016 CO adsorption on small Au(n = 1–4) structures supported on hematite: II. adsorption on O-rich terminated α-Fe2O3(001) surface J. Chem. Phys. 144 044705
[35] Grimme S, Antony J, Ehrlich S and Krieg H 2010 A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu J. Phys. Chem. 132 154104
[36] Eder M, Terakura K and Hafner J 2001 Initial stages of oxidation of (100) and (110) surfaces of iron caused by water Phys. Rev. B 64 115426
[37] Henkelman G, Arnaldsson A and Jónsson H 2006 A fast and robust algorithm for Bader decomposition of charge density Comput. Mater. Sci. 36 354–60
[38] Jones F, Rohl A L, Farrow J B and van Bronswijk W 2000 Molecular modeling of water adsorption on hematite Phys. Chem. Chem. Phys. 2 3209–16
[39] Reuter K and Scheffler M 2001 Composition, structure, and stability of rutile(110) as a function of oxygen pressure Phys. Rev. B 65 035406
[40] Lewandowski M, Groot I M N, Qin Z-H, Ossowski T, Pabisiak T, Kiejna A, Pavlovska A, Shaikhutdinov S, Freund H-J and Bauer E 2016 Nanoscale patterns on polar oxide surfaces Chem. Mater. 28 7433–43