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Water Adsorption on Ideal Anatase-TiO$_2$(101) – An Embedded Cluster Model for Accurate Adsorption Energetics and Excited State Properties

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Abstract: A combined theoretical approach towards the accurate description of water on anatase-TiO$_2$(101) was pursued in this study. Firstly, periodic slab calculations on the basis of density hybrid functionals (PBE0, HSE06) were performed in order to gain insight into the adsorption sites and geometric structure of the surface. For submonolayer coverage of H$_2$O, the molecular adsorption of water is found to be the most stable one with quite similar energetics in PBE0 and HSE06. Moreover, the transition states towards the less preferred dissociative adsorption forms are predicted to be greater than 0.7 eV. Thus, water will not spontaneously dissociate and based on the Computational Hydrogen Electrode model an overpotential of about 1.71 V is needed to drive the overall oxidation. In addition, to validate our results for molecular adsorption of H$_2$O, an embedded cluster model is carefully evaluated for the a-TiO$_2$(101) surface based on the periodic slab calculations. Subsequent high-level DLPNO-CCSD(T) results are in close agreement with our periodic slab calculations since the interaction is found to mainly consist of electrostatic contributions which are captured by hybrid functionals. Finally, first results on optimized geometries in the excited state based on the photogenerated charge-transfer state are presented.

Keywords: anatase; DFT; excited states; periodic slab calculation; titanium dioxide; water splitting.

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1 Introduction

In photocatalytic reactions, several intermediates occur due to charge-transfer processes induced through the interaction of incident light with the photocatalyst. Especially concerning photocatalytic water splitting, subsequent electron transfers lead to different intermediates such as hydroxo-, peroxo- and oxo-species [1]. To identify the key reaction steps, an accurate description of the interaction of the adsorbate-substrate system is one of the main prerequisites. In this regard, many studies focus on understanding the chemical behavior of water on titanium dioxide (TiO$_2$). Due to its well-known crystal structure, the overall goal consists not only of enhancing its photocatalytic properties but also the adaption of the knowledge towards other, promising materials [2, 3].

In this study, we focus on the anatase modification of titanium dioxide (a-TiO$_2$). In recent years, this modification became most widely studied due to its preferential appearance in commercially available Degussa P25 TiO$_2$ powder [4] and in nanoparticles [5] and moreover due to its higher photocatalytic activity due to longer charge carrier lifetimes compared to rutile-TiO$_2$ [6–8]. The (101) surface termination of a-TiO$_2$ was found to be the most dominant one experimentally [9]. Theoretical analysis of the underlying surface energies of the different a-TiO$_2$ facets further confirmed this result [10]. Thus, several experimental and theoretical studies investigated the adsorption behaviour of water on a-TiO$_2$(101). At first, molecular adsorption of the water molecule was found to be the thermodynamically preferred form as indicated by scanning tunnel microscopy (STM) and temperature-programmed desorption (TPD) measurements [11, 12] as well as periodic slab calculations based on the GGA-PBE functional [13–15]. However, more recent experiments focusing on monolayer adsorption of water revealed that mixed adsorption forms are present [16–18]. This observation was only recently explained theoretically by employing a rather large periodic slab model and density functional hybrid theory [19]. Still, the adsorption behaviour is not yet entirely understood from a theoretical point of view since different density functionals yield different results and energetics. Thus, the application of more sophisticated wave function based methods is demanded.

One alternative in this instance is provided by establishing non-periodic cluster models for the surface. Few studies were already pursued with such models for TiO$_2$ in the context of clarifying the reaction pathway of water oxidation on nanoparticles [20–25]. The advantage provided by cluster models is the availability of all quantum chemical methods, especially those based on wave function theory (WFT) which can be improved systematically. In comparison, periodic slab calculations are usually restricted to density functional theory (DFT) due to their
large system size and experimental data for proving the reliability of the applied 
method. However, experimental data is often difficult to access for short-lived 
intermediate reaction products and excited state properties present in photocat-
alytic reactions. As pointed out by Rodriguez et al., cluster models provide an 
insight into the reaction mechanism by sampling of an overall potential energy 
surface (PES) for ground and excited states in this regard on an equal theoret-
ical footing [23]. Additionally, high-level methods such as Coupled Cluster (CC) 
became feasible for larger system sizes and were already successfully applied to 
the H_2O/rutile-TiO_2(110) system [26].

The present study therefore aims to establish an embedded cluster model 
that accurately describes the interaction with a single water molecule and the 
underlying electronic properties. By firstly employing periodic slab calculations 
with exchange-correlation functionals with Hartree–Fock exchange, a detailed 
picture of the adsorbate-induced relaxation and the energetics of the a-TiO_2(101) 
surface are gained. Next, an embedded cluster model will be cut out of the relaxed 
surface structure by an external Fortran program. A careful evaluation of the 
adsorption energetics with different methods will subsequently be compared to 
our periodic slab calculations. Moreover, first results on excited state properties 
by time-dependent DFT (TD-DFT) and wave function based Complete Active Space 
Self-Consistent Field (CASSCF) methods will be presented.

2 Periodic slab calculations

2.1 Computational details

Periodic slab calculations were performed using the CRYSTAL17 program package 
based on a linear combination of atomic gaussian type orbitals (LCAO-GTO) [27]. 
Hybrid density functional theory in the scheme of PBE0 [28] and HSE06 [29, 30] 
was employed throughout. In order to allow a direct comparison to our embed-
ded cluster model later on, the empirical parameters of these functionals like 
Hartree–Fock exchange were not adjusted. For all atoms the triple-zeta valence 
basis set introduced by Peintinger et al. (pob-TZVP) was applied [31]. In corre-
spondence to this basis set, tolerances of the integral thresholds were set to 10^{-8}, 
10^{-8}, 10^{-8}, 10^{-18}, 10^{-27}. For adsorption studies, a slab consisting of four layers 
with 2 Ti and 4 O atoms each was cut from the anatase-TiO_2 bulk structure per-
pendicular to the (101) plane using CRYSTAL17. While the topmost three layers 
were relaxed, the bottom layer was fixed at the atomic bulk positions to ensure a 
transition towards bulk properties. All forces were optimized until a convergence
in energy of $8 \times 10^{-3}$ eV Å$^{-1}$ as implemented by default in the program package. The Monkhorst-Pack grid method with a Γ-centered k-point sampling of $6 \times 6 \times 1$ was used [32]. Frequencies were calculated at the Γ-point [33]. The adsorption energy of water on this a-TiO$_2$(101) slab model was calculated according to Eq. (1) throughout this study:

$$E_{\text{ads}} = E_{\text{opt(H}_2\text{O/surface)}} - E_{\text{opt(surface)}} - E_{\text{opt(H}_2\text{O)}}$$  \hspace{1cm} (1)

with $E_{\text{opt(H}_2\text{O/surface)}}$ as the total energy of the water molecule in its geometrical minimum on the surface, $E_{\text{opt}}$ (surface) as the energy of the surface before adsorption and $E_{\text{opt(H}_2\text{O)}}$ as the energy of an isolated water molecule optimized in the respective surface cell. Thus, a more negative value of the adsorption energy corresponds to a stronger interaction of the water molecule with the surface. In addition, due to the LCAO treatment, all interaction energies need to be corrected for the basis set superposition error (BSSE). The Counterpoise method as introduced by Boys and Bernadi [34] was applied for this purpose:

$$E_{\text{corr(ads)}} = E_{\text{ads}} - (E_{\text{AB(H}_2\text{O)}} + E_{\text{AB(surface)}} - E_{\text{A(H}_2\text{O)}} - E_{\text{B(surface)}})$$  \hspace{1cm} (2)

where $E_{\text{AB}}$ denotes the energy of the species given in parenthesis in the basis of molecule A (H$_2$O) and B (surface). Note, that in Eq. (2) the geometries of adsorbate and substrate are kept fixed at the optimum geometry corresponding to $E_{\text{opt(H}_2\text{O/surface)}}$.

### 2.2 Bulk and surface structure

Anatase titania crystallizes in a tetragonal space group ($I4_1/amd$) with 12 atoms in the unit cell [35]. The results for the relaxed bulk structure are given in Table 1. Our results are in reasonable agreement with previously published literature [10]. Note, that despite a small deviation in the lattice vectors $a$ and $c$, the band gap substantially differs for each functional. Due to the long-range HF exchange in PBE0, the band gap is overestimated [36]. The long-range corrected functional

| Tab. 1: Lattice vectors $a$ and $c$ as well as optical band gap $E_{\text{gap}}$ of the relaxed bulk structure of a-TiO$_2$ for different methods (pob-TZVP). |
|-------------------|--------|-------|-----------------|
| Functional        | $a/\text{Å}$ | $c/\text{Å}$ | $E_{\text{gap}}/\text{eV}$ |
| PBE0              | 3.748  | 9.673 | 4.29            |
| HSE06             | 3.749  | 9.678 | 3.65            |
| PW1PW [10]        | 3.765  | 9.545 | 3.74            |
HSE06 introduces two error functions in place of the Coulomb operator to only treat the problematic Coulomb potential from HF at short ranges, which results in a reasonable band gap compared to the experimental value [37].

Afterwards, the a-TiO$_2$(101) surface model was cut from the relaxed bulk structure. The slab used in this study consists of four Ti$_2$O$_4$ layers. Its surface energy was calculated as 0.67 J m$^{-2}$ and 0.69 J m$^{-2}$ for PBE0 and HSE06 functionals, respectively. These values are in excellent agreement with a literature value of 0.64 J m$^{-2}$ PW1PW [10]. Details concerning the evaluation of surface energies for different slab models are given in SI-I of the Supporting Information.

### 2.3 Adsorption of water

As a next step, water adsorption was studied over a five-fold coordinated Ti-atom exposed at the surface. The size of the surface unit cell was increased gradually in order to neglect adsorbate-adsorbate interactions. This leads to two stable adsorption forms (molecular and dissociative forms) for a coverage of 1 ML (c.f. Figure 1) and to three adsorption forms (one additional dissociative form) for coverages below 1 ML as shown in Figure 2. The calculated adsorption energies starting from one monolayer (ML) adsorption above each five-fold coordinated Ti-atom up to 1/6 ML are given in Table 2.

At 1 ML coverage, adsorbate-adsorbate interactions prevail, which lead to a formation of hydrogen bonded water molecule chains on the surface. As the coverage decreases, the molecularly adsorbed water molecule establishes hydrogen bonds towards the bridging oxygen atom row (see Figure 2). Out of this form, the dissociative adsorption form 1 is formed by abstraction of a proton to one bridging oxygen atom which is not directly bonded the central adsorption site (interpair dissociation). Additionally, a rotation of the water molecule and subsequent abstraction of a proton towards the directly neighbouring bridging oxygen atom gives the dissociative adsorption form 2 (intrapair dissociation). These three adsorption sites were also identified in literature [14, 19].

![Fig. 1: Adsorption forms of H$_2$O on a-TiO$_2$(101) at 1 ML coverage (PBE0/pob-TZVP) (Ti: grey, O: red, O$_{ads}$: blue, H: yellow). (a) Molecular adsorption, (b) Dissociative adsorption.](image-url)
Fig. 2: Adsorption forms of H$_2$O on a-TiO$_2$(101) at 1/4 ML coverage (PBE0/pob-TZVP). The size of the surface unit cell was enlarged by a factor of two in each direction ($X = 7.50$ Å and $Y = 10.37$ Å, for directions see Figure 1). (a) Molecular adsorption, (b) Interpair dissociation (1) and (c) Intrapair dissociation (2).

Tab. 2: Influence of coverage $\Theta$ on adsorption energy $E_{ads}$ of the most stable adsorption forms of H$_2$O/a-TiO$_2$(101) (pob-TZVP).

<table>
<thead>
<tr>
<th>Method</th>
<th>Coverage $\Theta$/ML</th>
<th>Mol. $E_{ads}$/eV</th>
<th>Diss. 1 $E_{ads}$/eV</th>
<th>Diss. 2 $E_{ads}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE0</td>
<td>1</td>
<td>−0.61</td>
<td>−0.44</td>
<td>−0.48</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>−0.73</td>
<td>−0.32</td>
<td>−0.47</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>−0.78</td>
<td>−0.42</td>
<td>−0.47</td>
</tr>
<tr>
<td></td>
<td>1/6</td>
<td>−0.77</td>
<td>−0.41</td>
<td>−0.47</td>
</tr>
<tr>
<td>PBE0-D3</td>
<td>1</td>
<td>−0.84</td>
<td>−0.62</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>−1.03</td>
<td>−0.59</td>
<td>−0.62</td>
</tr>
<tr>
<td>HSE06</td>
<td>1</td>
<td>−0.62</td>
<td>−0.45</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>1/2</td>
<td>−0.74</td>
<td>−0.38</td>
<td>−0.46</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>−0.77</td>
<td>−0.40</td>
<td>−0.46</td>
</tr>
<tr>
<td></td>
<td>1/6</td>
<td>−0.77</td>
<td>−0.42</td>
<td>−0.47</td>
</tr>
<tr>
<td>HSE [19]</td>
<td>1</td>
<td>−0.77</td>
<td>−0.75</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>−0.84</td>
<td>−0.49</td>
<td>−0.54</td>
</tr>
<tr>
<td>GGA-PW91 [5]</td>
<td>1</td>
<td>−0.56</td>
<td>−0.48</td>
<td>−</td>
</tr>
<tr>
<td>PW-PBE [14]</td>
<td>1/6</td>
<td>−0.72</td>
<td>−0.32</td>
<td>−0.34</td>
</tr>
</tbody>
</table>

All values were corrected for BSSE (for the uncorrected values see SI-II of the Supporting Information).
In Table 2 the adsorption energetics of the aforementioned stable geometries are given for further exchange-correlation functionals and coverages. All values were corrected for the BSSE by employing Eq. (2) (for a discussion of the influence of the BSSE correction see Table 2 in Supporting Information SI-II). Throughout all coverages the molecular adsorption form stays the most stable one. Considering monolayer coverage, only one bridging oxygen atom is exposed at the surface unit cell which solely allows for one dissociation pathway. Interestingly, the difference in reaction energy from molecular to dissociative adsorption form for PBE0 and HSE06 is less when comparing monolayer adsorption (0.17 eV) with lower coverages (e.g. 0.31 eV at 1/4 ML). This can be attributed to a more stable molecular adsorption form due to weaker adsorbate-adsorbate interactions. In general, our results show that adsorbate-adsorbate interactions on a-TiO$_2$(101) can be neglected at a coverage of 1/4 ML and below. When comparing the dissociative adsorption forms at these low coverages, it is observed that form 2 (intrapair dissociation) is preferred by about 0.05 eV compared to the interpair dissociation. Interestingly, both our applied density hybrid functionals in general yield the same adsorption energies with a maximum deviation of 0.06 eV for the interpair dissociation at 1/2 ML coverage. Although, as shown in Table 1, HSE06 describes the band gap of anatase titania more accurately, the influence of the long-range HF correction on the adsorption energy is rather negligible. This leads to the conclusion that in terms of reaction pathways on titania, the PBE0 functional already leads to accurate results at a much lower computational cost compared to HSE06.

By adding dispersion correction in the scheme of Grimme’s D3 approach [38], the adsorption energy is lowered throughout all adsorption forms. For 1/4 ML, the molecular adsorption form and intrapair dissociation are stabilized by 24%, the interpair dissociation by 28%. Since these values are rather equal in difference, we do not assume a drastic influence on the reaction pathway discussed further on.

Comparing with previously published results based on plane wave calculations with the PBE functional [14] at 1/6 ML coverage our results for molecular adsorption are in reasonable agreement. However, the dissociative adsorption forms are more stabilized by −0.10 eV for the interpair and −0.13 eV for the intrapair dissociation. Since our results are comparable to previous HSE studies [19], the more simplified generalized gradient approximation (GGA) PBE functional presumably underestimates the adsorption strength after dissociation. Though our HSE06 values are comparable to the published HSE ones [19], the authors do not state if a correction for the BSSE was done in their study. We therefore assume, that the adsorption energies are underestimated compared to our values due to the BSSE.
In addition to the adsorption sites of molecular and dissociative water, the transition state in between was calculated to elucidate the reaction barrier (c.f. Figure 3 for the structures and Figure 4 for their relative energetics). To investigate the coverage dependence of the reaction barrier, we performed scan calculations on the $1 \times 1$ and $2 \times 2$ surface unit cell corresponding to 1 ML and 1/4 ML coverage, respectively. At low coverages of 1/4 ML, the activation barrier is slightly lowered by 0.07 eV compared to 1 ML. Additionally, the two possible dissociation mechanisms at this coverage are almost identical in height of the activation barriers with the intrapair dissociation only preferred by 0.02 eV. From a physical point of view, both dissociations pathways of the initially bound intact water molecule are equally favoured. Thus, the hydrogen bonds towards the bridging oxygen atoms are rather weak in the molecular state and a rotation or diffusion of the adsorbate over the five-fold coordinated titanium atom is likely to happen.

In Table 3 a comparison to previously calculated dissociation barriers is given. Interestingly, no study investigated both dissociation pathways present at low coverages, which makes a direct comparison difficult. However, since most reaction pathways are calculated on the more approximate generalized-gradient PBE level of theory, a comparison with hybrid density functional theory is required. Our calculated results based on PBE0 and HSE06 are almost identical by value, as already

![Fig. 3: Transition state structures of H$_2$O on a-TiO$_2$(101) at 1 ML and 1/4 ML coverage (PBE0/pob-TZVP). (a) 1 ML, (b) 1/4 ML, Interpair diss. (1) and (c) 1/4 ML, Intrapair diss. (2).]
Fig. 4: Energy profile for first step of water dissociation on a-TiO$_2$(101) (PBE0/pob-TZVP) for coverages of 1 ML (dashed, red line) and 1/4 ML (straight, blue and dashed-dotted, green lines). For the respective dissociation and recombination barriers see Table 3. (1) and (2) denote the interpair (straight, blue line) and intrapair (dashed-dotted, green line) dissociative adsorption forms, respectively, as indicated in Figure 2.

Tab. 3: Influence of coverage $\Theta$ on the dissociation (recombination) barrier of the initial reaction step of H$_2$O/a-TiO$_2$(101) (pob-TZVP).

<table>
<thead>
<tr>
<th>Method</th>
<th>Cov. $\Theta$/ML</th>
<th>Activation (recombination) Barrier $E_{\text{act}}$ ($E_{\text{recomb}}$)/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TS 1</td>
</tr>
<tr>
<td>PBE0</td>
<td>1</td>
<td>0.77 (0.60)</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>0.70 (0.34)</td>
</tr>
<tr>
<td>HSE06</td>
<td>1</td>
<td>0.76 (0.59)</td>
</tr>
<tr>
<td></td>
<td>1/4</td>
<td>0.70 (0.34)</td>
</tr>
<tr>
<td>PW-PBE [14]</td>
<td>1/4</td>
<td>0.52 (0.12)</td>
</tr>
<tr>
<td>PW-PBE [39]</td>
<td>1/4</td>
<td>0.50 (0.15)</td>
</tr>
<tr>
<td>PW-PBE [40]</td>
<td>1/4</td>
<td>–</td>
</tr>
<tr>
<td>PW-PBE+U [41]</td>
<td>1/4</td>
<td>–</td>
</tr>
</tbody>
</table>

All values were corrected for the BSSE (for the uncorrected values see SI-II of the Supporting Information).

stated concerning the stable adsorption geometries. Moreover, our dissociation and recombination barriers are in general higher by roughly 0.2 eV. Albeit recent results based on PBE+U [41] are able to recover this energetic difference by about 0.1 eV, hybrid density functional theory is still needed to provide accurate activation barriers. In this instance, we also performed exemplary spin-polarized PBE0
calculations on the optimized geometries of initially bound water, dissociated water and the transition state in between. Bearing in mind that a charge-transfer between adsorbate and surface might influence the dissociation process energetically, the spin density of titania 3d orbitals was inspected in particular. However, none of our calculations revealed a significant population of these orbitals. Moreover, the final energetics were identical to the ones obtained by spin-restricted PBE0. Thus, the charge-transfer probably constitutes a higher excited state of the adsorbate-substrate complex which is not easily accessible by spin-polarized DFT in our study but requires a theoretically more sophisticated approach. Regarding the periodic slab calculations, we therefore stick to spin-restricted DFT as it nevertheless provides a reasonable insight into ground state dissociation pathway of water on the surface.

Generally, the activation barrier with over 0.70 eV is rather high, which is consistent with literature data stating that the first proton removal of the water molecule is the rate-determining step in the overall water dissociation pathway [42]. Thus, an initially bound water molecule will not spontaneously dissociate without an external force. The Computational Hydrogen Electrode (CHE) model provides a way to study the influence of the overpotential on the reaction barriers of the overall water oxidation [43–45]. For that purpose, the reaction intermediates according to Eq. (3)–(6) were optimized on the a-TiO$_2$(101)-(1×1) surface unit cell and a subsequent frequency calculation was performed. For the frequency calculations, the first layer of the slab and the respective adsorbate were taken into account. The energy of the remaining proton and electron was replaced by the energy of half a hydrogen molecule [46] using the standard hydrogen electrode conditions (pH = 0, p = 1013 hPa and T = 298.15 K). Additionally, the free energy change $\Delta G_4$ in Eq. (6) was shifted by 1.24 eV to reproduce the experimentally known Gibbs free energy of 4.92 eV for the formation of oxygen from two water molecules [46]. Due to the poor description of O$_2$ in DFT calculations, this reaction free enthalpy is generally overestimated. The resulting standard free energy diagram is depicted in Figure 5.

$$
\begin{align*}
\text{H}_2\text{O}(l) + ^* &\rightarrow \text{HO}^* + \text{H}^+ + e^- \\
\Delta G_1 &= \Delta G_{\text{HO}^*} - \Delta G_{\text{H}_2\text{O}} - e \ U + k_B \ T \ \ln a_H \\
\text{HO}^* &\rightarrow \text{O}^* + \text{H}^+ + e^-
\end{align*}
$$

$$
\begin{align*}
\Delta G_2 &= \Delta G_{\text{O}^*} - \Delta G_{\text{HO}^*} - e \ U + k_B \ T \ \ln a_H \\
\text{O}^* + \text{H}_2\text{O} &\rightarrow \text{HOO}^* + \text{H}^+ + e^-
\end{align*}
$$

$$
\begin{align*}
\Delta G_3 &= \Delta G_{\text{HOO}^*} - \Delta G_{\text{O}^*} - e \ U + k_B \ T \ \ln a_H
\end{align*}
$$
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\[
\text{HOO}^* \rightarrow \text{O}_2(\text{g}) + \text{H}^+ + e^- \\
\Delta G_a = \Delta G_{\text{O}_2} - \Delta G_{\text{HOO}^*} - e \ U + k_B \ T \ \ln a_H \tag{6}
\]

Ideally, all four reaction steps should possess the same magnitude of 1.23 eV since the reaction free energies at an equilibrium potential of 1.23 V should then become zero. Regarding a-TiO$_2$(101), the first two reaction steps dominate the overall reaction with barriers of 2.94 eV and 2.23 eV, respectively. At equilibrium potential of $U = 1.23$ V these two reaction steps still remain uphill whereas the OOH and O$_2$ generation become feasible. An overpotential of $U_{OP} = 1.71$ V is needed to get all steps downhill. This results is close to literature values of 1.39 V at PBE+U level of theory [47].

To gain insight into the influence of the different adsorption forms on the photocatalytic behaviour, the contribution of each orbital type to the overall density of states was analyzed (c.f. Figure 6 for 1/4 ML coverage and SI-II for 1 ML coverage). To provide a reasonable agreement with the experimental band gap of titania, the HSE06 optimized geometries are used. The dispersive features at the valence band edge (VBE) and conduction band edge (CBE) of the total DOS arise from lower-lying layers of the slab model which constitute the band gap of 3.36 eV. A photoexcitation in the bulk corresponds to a O(2p) $\rightarrow$ Ti(3d) transition in the lowest layer (not shown here). As expected, the main contributions below the valence band edge stem from oxygen 2p orbitals of the surface, whereas above the conduction band edge mainly titania 3d orbitals are present. Hence, a

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**Fig. 5:** Standard free energy $\Delta_{R}G$ diagram of the overall water oxidation on a-TiO$_2$(101) at different potentials $U$ (PBE0/pob-TZVP). Standard hydrogen electrode conditions were used throughout ($\text{pH} = 0, \ p = 1013$ hPa and $T = 298.15$ K). At an overpotential of $U_{OP} = 1.71$ V (dashed-dotted, blue line) all steps become downhill.
Fig. 6: Density of states (DOS) at a coverage of 1/4 ML (HSE06/pob-TZVP). For the contribution of atomic orbitals, only the first layer of the slab was investigated. Note, that O(2p) (dashed-dotted, red lines) and H$_2$O (straight, blue lines) orbitals mainly contribute to the valence band, whereas Ti(3d) unoccupied orbitals (dashed, green lines) constitute the conduction band. The energy values were referenced to the normal hydrogen electrode (NHE) potential in vacuum of $E = -4.44$ eV.

Photogenerated electron-hole pair will presumably dissociate in the way that the electron will migrate to empty titania 3d orbitals and the hole will diffuse to filled oxygen 2p orbitals. This behaviour is already proven by other theoretical [19] and experimental studies [3]. Upon adsorption, the occupied orbitals of water arise within the valence band. For molecular adsorption an additional band is present at about $-5.3$ eV below NHE potential whereas for dissociative adsorption a band at $-3.6$ eV is developed. Considering the photocatalytic activity, a photogenerated hole is thus more likely to migrate towards the orbitals of the dissociated species and photooxidize the terminal OH group above the five-fold coordinated titanium atom. This can be explained by Mulliken analysis of the electronic charge on the adsorbed oxygen atom of the water molecule which is more negative for the dissociative form 1 ($-0.64$ e) compared to the molecular form ($-0.53$ e) and thus electrostatically attracts the hole more strongly.

To conclude the first part of our work, the periodic slab calculations revealed that water initially binds intact to the stoichiometric a-TiO$_2$(101) surface and that the dissociation barrier with over 0.7 eV is too high to initiate spontaneous dissociation throughout all coverages. In addition, though the long-range corrected HSE06 functional generally yields more accurate band gaps for semiconducting...
materials, the energetics in terms of reaction pathways of water on the anatase titania surface do not differ from PBE0 results. Thus, to elucidate the reaction pathway of adsorbates on this class of materials in future work hybrid density functional theory on the PBE0 level of theory gives reasonable results with feasible computational costs. After optimization, single-point calculations on the optimized geometry using HSE06 can be applied to correct for the band gap. In consistency with previous studies, the DOS revealed that a photogenerated hole is more likely to oxidize the dissociated terminal OH group rather than the molecular bound adsorbate.

3 Embedded cluster calculations

3.1 Methodology

Our periodic slab results provide a valuable insight into the ground state properties of water on a-TiO$_2$(101). However, due to the large system size of these slab models the application of hybrid density functional theory is already a computational highly demanding task. Moreover, the explicit calculation of excited states is not yet implemented in periodic slab calculations. Though some approximations involve the introduction of a compensating negative background charge to generate a photooxidized adsorbate [48, 49] or make use of spin-polarized DFT calculations to treat the charge-transfer state as a triplet [50], it is not clear from a theoretical point of view that these approximations are justified.

To allow for the usage of high-level wave function based methods to tackle these problems, we next employ an embedded cluster approach to describe the adsorption of water on a-TiO$_2$(101). This approach was already successfully applied to the H$_2$O/rutile-TiO$_2$(110) system [51–53] and to the adsorption of various other adsorbates such as CO [54, 55], CO$_2$, NH$_3$ and CH$_3$OH [26]. In a nutshell, a cluster model is cut from the relaxed surface structure which can fully be treated quantum mechanically. To account for the long-range Coulomb interactions of the bulk material, the cluster is surrounded by a point charge field (PCF). In accordance with Mulliken charge analysis of the bulk a-TiO$_2$ unit cell, we assign a point charge of +2.0650 e to titania and a negative charge of −1.0325 e to oxygen ions. Due to covalent interactions, this values differ from the formal oxidation numbers of the compound [56]. Consequently, a boundary region between cluster and PCF is needed to prevent the flow of the molecular orbitals (and by association electron density) of the cluster towards the point charges. Whereas in previous work [51, 54] magnesium cations with a minimal basis set were used instead of titania atoms as boundary region, we apply a modified embedding procedure based
on capped effective core potentials (c-ECPs) in this work as proposed by Berger et al. [26, 57]. SDD c-ECPs for titania with an effective charge of $+2.0650 \, \text{e}$ obtained from the pseudopotential library of the Stuttgart/Cologne group were used for this purpose [58]. A sketch of the overall approach is shown in Figure 7.

### 3.2 Computational details

Our calculations using the embedded cluster model were performed with the ORCA 4 program package [59]. Several convergence test were done in order to find an appropriate cluster model. Most importantly, the cluster size and the basis set need to be studied carefully. To evaluate their performance, the adsorption energy of water in its molecular state was calculated using the PBE0 functional with the RIJCOSX approximation for Coulomb and Exchange integrals using the def2/J [60] auxiliary basis as implemented in the ORCA software package [61]. The adsorption energy was determined according to Eq. (1) with the adsorbate optimized on the cluster model. Note, that the geometry of the embedded cluster was adopted from the periodic slab calculations and being kept fixed at the optimized structure of the adsorbate-substrate system throughout our calculations. To efficiently cut several cluster models with their boundary region and respective PCF, a FORTRAN90 program was written that uses the CRYSTAL17 output files. Its work flow is given in the Supporting Information SI-III.

The adsorption energies for various cluster models of growing size are depicted in Figure 8. The pob-TZVP basis set of the CRYSTAL17 calculations was adopted for this study. An illustration of the cluster models can be found in the

![Fig. 7: Illustration of the embedded cluster procedure used in this work. A half-spherical point charge field was adopted as compared to previous studies on the rutile-TiO$_2$(110) surface [57] (Ti: grey, O: red, c-ECPs: light blue).](image-url)
Fig. 8: Adsorption energy $E_{\text{ads}}$ for different cluster sizes $\text{Ti}_n\text{O}_{2n}$ (PBE0/pob-TZVP). The respective cluster models can be found in the Supporting Information SI-IV. Note, that the CRYSTAL17 values are referenced to non-interacting distance of water on the relaxed surface to be consistent with our embedded cluster calculations.

Supporting Information SI-IV. As shown, the adsorption energy for our $\text{Ti}_9\text{O}_{18}$ cluster model underestimates the adsorption energy compared to our periodic slab calculations by about $-0.34$ eV ($-0.36$ eV for the BSSE uncorrected value) and is far from converged. However, the remaining cluster models rapidly converge within an error of $-0.11$ eV ($-0.12$ eV) for a size of $\text{Ti}_{13}\text{O}_{26}$ up to almost no deviation for $\text{Ti}_{26}\text{O}_{52}$. Regarding the savings of computational effort, the $\text{Ti}_{13}\text{O}_{26}$ cluster model thus represents the most promising alternative and will be used from here on in this study.

Concerning the adsorption energies, changing neither the number of c-ECPs in the boundary region nor the number of point charges resulted in a significant change. For our $\text{Ti}_{13}\text{O}_{26}$ cluster model 29 c-ECPs and about 43,000 point charges were found to give reasonable results. For a more detailed analysis, the reader is referred to the Supporting Information SI-IV.

More importantly, the basis set needs to be further evaluated. Generally, the use of too diffuse atomic centered basis functions in calculations with periodic boundary conditions is prohibited. Due to the problematic overlap in crystalline systems, this rapidly leads to an increase of the exchange and coulomb integrals by which means numerical problems arise [31]. On the contrary, our embedded cluster allows to systematically add basis functions up to the basis set limit. Starting from the double-zeta (DZ) quality def2-SVP basis set [62] the basis set influence on the adsorption energy was investigated (c.f. Figure 9). A full def2-SVP basis set exhibits an error of $-0.18$ eV ($-0.40$ eV) and is therefore not reliable. Next, when going from double to triple (TZ) and quadruple (QZ) zeta quality, the
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Fig. 9: Adsorption energy $E_{\text{ads}}$ for different basis sets from the def2-family [62] for our $\text{H}_2\text{O}/\text{Ti}_{13}\text{O}_{26}\text{ECP}_{29}$ system (PBE0). The final basis set (fin) consists of a combined def2-TZVPD/def2-TZVP/def2-SVP basis set (see SI-IV for details).

Adsorption energy rapidly converges within a deviation of $-0.10$ eV ($-0.05$ eV) as for def2-TZVP. Finally as expected, the BSSE for a full QZ basis set almost vanishes (0.05 eV). Moreover, additional diffuse functions at the adsorbate and the central titania and bridging oxygen atoms provide results in reasonable agreement with TZ/QZ basis sets at a much smaller number of contracted functions. Thus, the final basis set adopted in this work consists of a combined def2-TZVP(D) basis for the central atoms close to the adsorption center and a def2-SVP basis set for the peripheral cluster atoms with resulting in a total of 1120 contracted basis functions (for a detailed listing see SI-IV).

### 3.3 Methodological study

The use and evaluation of an appropriate cluster model now eventually provides the basis to use more sophisticated methods compared to the exchange-correlation functionals available in the periodic slab calculations. For a variety of different methods, the adsorption energy was calculated as previously (see Figure 10). Interestingly, when going up Jacob's ladder to the stairs of the double-hybrid functional B2PLYP, the adsorption strength decreases by 0.06 eV compared to PBE0. In contrast, wave function based methods predict a stronger adsorption. Considering Coupled Cluster theory as the most accurate method, the Direct Local Pair Natural Orbital (DLPNO) approximation [63] allows for calculating an adsorption energy of our cluster model of $-1.17$ eV ($-1.59$ eV). The
value obtained by PBE0 of $-1.10$ eV ($-1.23$ eV) is very close, thus this functional already provides a good description of the adsorption energetics. The difference in both energies can be attributed to the missing dispersion treatment in density functional theory in general. By performing a local energy decomposition (LED) scheme on top of the DLPNO-CCSD(T) wave function [64, 65], we found that the dispersion interaction contributes about 23% to the overall interaction energy. This value is slightly lower than the dispersion contribution calculated by Neese et al. for the H$_2$O/rutile-TiO$_2$(110) system (27%) [66], which can be attributed to the stronger hydrogen bonding towards the bridging oxygen atoms on a-TiO$_2$(101). In contrast, applying empirical dispersion correction based on the Grimme approach [38] with Becke–Johnson damping (D3BJ) [67] overestimates the adsorption energy by 0.11 eV in the case of PBE0-D3BJ. Interestingly, this error almost cancels out in the instance of PBE-D3BJ with only 0.04 eV deviation compared to DLPNO-CCSD(T). The lack of electrostatic interaction due to the missing Hartree–Fock ratio is hence recovered by the overestimation of the dispersion correction in D3BJ. Though this might result in reasonable adsorption energetics, one should be aware that PBE is not able to accurately describe the electronic properties such as band gaps of this class of materials properly [36]. Moreover, note that the BSSE correction is mandatory in the case of RI-MP2 and DLPNO-CCSD(T), which exhibit the largest BSSE with 0.41 eV and 0.39 eV, respectively.
Consequently, our cluster model allows for the application of methods to treat excited state properties. For instance, TD-DFT provides access to the absorption spectrum of our material (c.f. Figure 11). In comparison to the band gap of the bulk material estimated by our periodic slab calculations (4.29 eV in Table 1), reasonable agreement with the peak transitions at 3.4 eV and 4.1 eV (solid, red line) is given. Note, that the two major peaks indicate the indirect and direct band gaps, respectively [68]. Additionally, the absorption spectrum for the PBE0-optimized adsorbate on the cluster model is given (dashed, blue line), which influences the peak region of the direct band gap by a blue-shift and increase in intensity.

Though the charge-transfer state can be identified through TD-PBE0 at a single-point geometry, optimizing the adsorbate on this specific state results in severe difficulties: as several roots with cluster-cluster excitations lie within a small energy range, root flipping occurs. Thus, in order to identify the most favoured geometry of the charge-transfer, we rely on a wave function based approach based on CASSCF theory, which was already successfully applied to the H$_2$O/r-TiO$_2$(110) system [51]. Within this method, an active space consisting of the three highest occupied molecular orbitals, the two lowest unoccupied orbitals of the adsorbate and the LUMO of the cluster was constructed (CAS(6,6)). The first excited state in this set-up corresponds to an electron transfer from the HOMO of the water molecule to the LUMO of the cluster. By state-averaging over the ground and this charge-transfer state the resulting SA-CAS(6,6) state can be optimized with respect to the molecular geometry. The resulting structure (c.f. Figure 12) exhibits the lowest excitation energy of 3.15 eV. The charge-transfer is most likely

![Fig. 11: Absorption spectra of the H$_2$O/Ti$_{13}$O$_{26}$ECP$_{29}$ system (TD-PBE0/def2-TZVP(D)/def2-SVP) at non-interacting distance of the adsorbate (solid, red line) and at the optimum adsorption geometry (dashed, blue line). A total of 250 roots were included in the TDDFT method.](image)
to proceed over the bridging oxygen atom and hydrogen atom. This is consistent with experimental studies that expect the photogenerated hole to be trapped at surface oxygen atoms [3].

To summarize, we established an embedded cluster model that is able to accurately describe the adsorption of water on anatase-TiO$_2$(101). By performing state-of-the-art wave function based methods based on Coupled Cluster level of theory the adsorption behaviour of water was found to consist of mainly electrostatic (77%) compared to dispersive (23%) contributions to the overall interaction. Moreover, excited state properties such as absorption spectra and charge-transfer states are now accessible by our cluster model. We could further reveal the most favoured geometry of the adsorbate for the charge-transfer to occur, which is bound to the bridging oxygen atoms over its protons.

4 Conclusion and outlook

In comparison to most previous theoretical studies, our work comprises a combination of periodic slab and embedded cluster approaches to gain a deep insight into the adsorption of water on anatase-TiO$_2$(101). By applying accurate exchange-correlation functionals with Hartree–Fock exchange we could reveal in our periodic slab calculations that water favourably adsorbs in its molecular form on top of a five-fold coordinated titanium atom. Decreasing the coverage from 1 ML to 1/4 ML furthermore does not substantially affect the dissociation barrier which remains rather high with about 0.7 eV. Thus, water does not dissociate spontaneously in the ground state. In order to study whether the applied PBE0 functional was accurate enough to describe the adsorption, an embedded cluster model was developed. A Ti$_{13}$O$_{26}$ cluster model in combination with additional diffuse basis functions on the adsorbate and the central surface atoms was found to perform
well for this purpose. High-level DLPNO-CCSD(T) theory revealed that the adsorption is already described quite precisely by PBE0 since the missing dispersion interaction of adsorbate and substrate only accounts for 23% in total. In addition, excited state properties such as the absorption spectrum of our \( \text{H}_2\text{O}/\text{Ti}_{13}\text{O}_{26} \) model system on TD-PBE0 level of theory and the charge-transfer state by SA-CASSCF are now accessible. Optimization of the structure using the latter method revealed the charge-transfer of the photogenerated hole to most likely occur over the bridging oxygen atom.

So far, this work almost solely dealt with the stationary points of the water adsorption on a-\( \text{TiO}_2 \)\,(101) with a special emphasis on the molecular adsorption on the embedded cluster model. Though our periodic slab results revealed that the dissociation barrier is rather high, their behaviour in the excited state due to the charge-transfer process are not yet included in these calculations. Prospectively, our embedded cluster will constitute the basis for the calculation of an overall potential energy surface for ground and charge-transfer state on CASSCF level of theory. This will allow for the evaluation of the kinetics of the water desorption and dissociation in the excited state to clarify the possible photo-induced processes in this reaction step.

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**References**


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