

The structure of water on rutile TiO₂(110) for applications in solar hydrogen production: towards a predictive model using hybrid-exchange density functional theory

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ABSTRACT

Periodic hybrid-exchange density functional theory (DFT) simulations are used to develop a predictive model of the structure of water on the rutile TiO₂(110) surface ($\Theta \leq 1$ ML). A description of the adsorbed species is given: dissociated water molecules and either mixed or dissociative dimers. The behaviour of the adsorbates is rationalised by considering both direct intermolecular and surface-mediated interactions. Some of these results are then compared with those from water adsorption on the rutile SnO₂(110) surface, isostructural to TiO₂(110). Lastly, the electronic structure of the surface in contact with monolayer water ($\Theta = 1$ ML) reveals the contributions of adsorbate states involved in the photocatalytic reaction that controls the water oxidation process.

INTRODUCTION

Current challenges in the hydrogen economy are the storage and transport of hydrogen, the efficient conversion of hydrogen into electrical energy in fuel cells, and the carbon-free and economically-viable generation of hydrogen. Photoelectrochemical water splitting over semiconductor materials such as titanium dioxide (TiO₂) provides a carbon-free renewable route to hydrogen production [1]. The reaction mechanisms that occur at the crystal surfaces are debated [2, 3]: identifying and understanding them in detail could potentially lead to the suggestion of engineering and design rules for more efficient systems.

TiO₂ is a transition metal oxide that adopts a variety of crystal structures, three of which are rutile, anatase and brookite. The (110) surface of rutile TiO₂ is the most stable [4], and is considered to be a quintessential model metal oxide system for the study of water chemistry. The question of whether water molecules are adsorbed molecularly or dissociatively on the rutile TiO₂(110) surface is a continuing issue, as well as the conditions under which each mode of adsorption takes place.

The majority of experimental measurements support the concept that molecular adsorption dominates in the first layer of water ($\Theta \leq 1$ ML) on nearly-perfect surfaces at low temperatures (< 350 K) [5]. Various levels of theory have been applied for periodic and cluster simulations of water adsorption on this surface. Theoretical studies mostly predict that the dissociation of water is energetically favoured on the defect-free TiO₂(110) surface at all coverages up to one monolayer (1 ML) [6]. Many of these simulations are based on models characterised by constraints (either point group or translational symmetry): neighbouring adsorbates are restricted to be at fixed orientation and separation. The important role of intermolecular interactions has been emphasised, suggesting a more complex pic-

ture at monolayer coverage, in which both molecular and dissociated water coexist on the surface, stabilised by hydrogen bonding [7].

In this work, water adsorption on the defect-free rutile $\text{TiO}_2(110)$ surface has been explored using periodic hybrid-exchange DFT calculations. The possible adsorption mode – molecular, dissociative or mixed (one dissociated and one molecularly adsorbed water molecule interacting directly through hydrogen bonding) – has been studied as a function of coverage and arrangement of adsorbed species. The effects of the separation of adsorbates on the intermolecular interactions have also been studied by considering the isostructural rutile $\text{SnO}_2(110)$ surface. SnO_2 is widely used in gas-sensing devices [8]. Experimental and theoretical water adsorption studies on $\text{SnO}_2(110)$ are less extensive; nevertheless, the presence of both molecularly and dissociatively adsorbed water molecules on the surface has been deduced [9]. The model systems in the current study benefit from symmetry-breaking induced by the interactions between adsorbates on the surface, allowing the interactions between adjacent adsorbates to be analysed.

COMPUTATIONAL DETAILS

All calculations have been performed using the CRYSTAL09 software package [10], based on the expansion of the crystalline orbitals as a linear combination of a local basis set (BS) consisting of atom-centred Gaussian orbitals. The titanium, tin, oxygen and hydrogen ions are described by a triple valence all-electron BS: an 86-411d(41) contraction (one s , four sp and two d shells), a 976-311d(331) contraction (one s , five sp and three d shells), an 8-411d(1) contraction (one s , three sp and one d shells), and a 6-31G** contraction (two s and one p shells), respectively [11–13]. Electronic exchange and correlation are approximated using the hybrid-exchange B3LYP functional [14], resulting in an accurate description of the energetics and the electronic structure of periodic systems [15], particularly for transition metal oxides [22]. The self-consistent field procedure was converged up to a tolerance in the total energy of $\Delta E = 1 \cdot 10^{-7} E_h$ per unit cell.

The rutile (110) surface was simulated using a 9-atomic-layer (9AL) slab cut from the optimised bulk [23]. Adsorbates were introduced symmetrically on each each surface of the slab. The effects on the stability of the system have been explored in terms of the binding energy (BE) per molecule of the adsorbate-substrate system with respect to the clean surface and the isolated molecule [24]. The convergence of the BE with respect to slab thickness can be studied by adopting slabs composed of a greater number of AL [16]. In this work, using a 9AL slab has facilitated a systematic and computationally-viable study of the coverage and arrangement of adsorbates, rationalising the behaviour of molecules and hydroxyls on the surface. We focus on the interactions between adsorbates at ML and sub-ML coverage, demonstrating the types of interactions involved and the sensitivity of these interactions to coverage and arrangement. A 1x1 unit cell was extended in the \mathbf{a}_{slab} and \mathbf{b}_{slab} directions, corresponding to the [001] and [1 $\bar{1}$ 0] directions of the bulk, respectively, to form 2x1, 3x1, 4x1, 1x2 and 2x2 cells, to decrease the coverage and increase the distance between adsorbates [25]. Projection of density of states was carried out following a Mulliken analysis. For a more detailed description of the methods see Ref. [17].

RESULTS AND DISCUSSION

Water adsorption on rutile $\text{TiO}_2(110)$: Geometry and energetics

The rutile (110) surface is characterised by five-coordinated Ti atoms (Ti_{5c}) and two-coordinated O atoms (O_{2c}). Ti_{5c} and O_{2c} are adsorption sites for molecularly and dissociatively adsorbed water (Fig. 1). In the dissociative case, the bonding of a hydrogen atom, detached from the water molecule, to O_{2c} results in an hydroxyl group, defined as the bridging hydroxyl (BH). This is to be distinguished from the terminal hydroxyl (TH), formed by the adsorption of OH from the molecule onto the surface Ti_{5c} atom. The outermost surface atoms undergo more notable structural changes upon dissociative adsorption than molecular adsorption. Our calculations have shown that to understand the water-water interactions and to predict the structure of water on this surface, it is sufficient to consider the interactions in the \mathbf{a}_{slab} direction (along rows of Ti_{5c} , 2.979 Å) only, since along \mathbf{b}_{slab} the level of interaction between adsorbates is negligible.

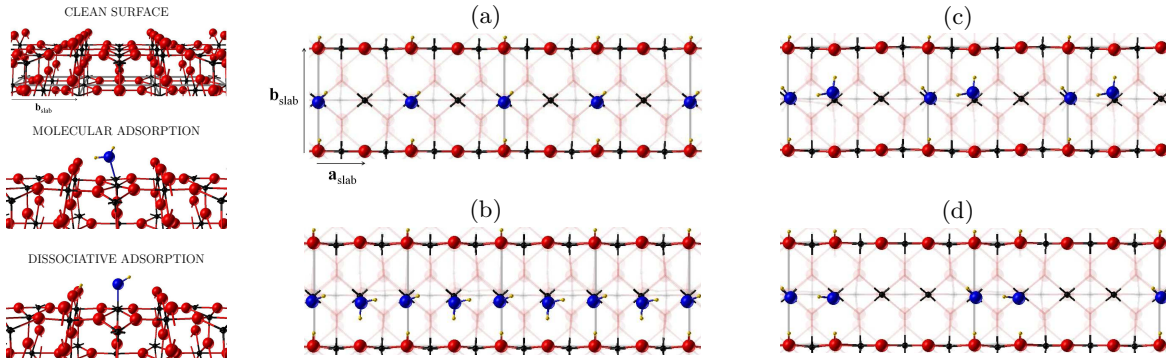


FIG. 1: Left: Perspective views of (from top to bottom) the clean rutile $\text{TiO}_2(110)$ surface, the molecular (M) and the dissociative (D) adsorption modes of water. Right: Top views of the adsorbate-substrate system corresponding to the scenarios that describe the structure of water on this surface: (a) $\Theta = 1/2$ ML, dissociative, D; (b) $\Theta = 1$ ML, mixed, DM; (c) $\Theta = 2/3$ ML, mixed, DM; (d) $\Theta = 1/2$ ML, dissociative, DD. O, Ti, adsorbate O and adsorbate H atoms are represented by red, black, blue and yellow spheres, respectively.

The simulations predict that, in \mathbf{a}_{slab} , there are two adsorption scenarios: (i) isolated adsorbates in the absence of neighbours and (ii) the formation of one of three types of dimers (MM, DD and DM), depending on the separation between them. In the absence of neighbours, the dissociative mode is most favourable, as shown in Fig. 1(a) ($\text{BE} = -1.21$ eV). The dissociative mode remains the most favourable when well-separated dimers form ($\text{BE} = -1.24$ eV): the separation must be adequate – 8.939 Å – to allow for the structural distortion imposed by surface hydroxyls upon adsorption (Fig. 1(d)). Finally the mixed adsorption mode becomes important when dimers are neighbouring (Fig. 1(b)) or separated by a short distance (Fig. 1(c)) – ≤ 5.959 Å – as this is when the strong hydrogen bonding comes into play ($\text{BE} = -1.03$ and -1.15 eV, respectively). The atomic displacements induced by adsorbed hydroxyls propagate further through the surface, since a particular separation is required for the dissociative dimer to form. Previous calculations have suggested that the benefit of having a neighbouring adsorbate is greatest in the mixed mode, and that the order of strength of the hydrogen bond between adsorbates in a dimer on this surface is: $\text{D}\cdots\text{D} < \text{M}\cdots\text{M} < \text{D}\cdots\text{M}$ [17]. The type of dimer that

forms is dependent on both the strength of the hydrogen bond and on the separation of dimers at the surface, suggesting that the interactions between adsorbates are not only direct, but also mediated by the surface through the atomic displacements.

Water adsorption on SnO₂(110): Comparison with TiO₂(110)

As discussed above, on TiO₂(110) the mixed adsorption mode is the most stable at $\Theta = 1$ ML, with a BE of -1.03 eV, which is 0.18 eV and 0.04 eV more energetically favourable than the dissociative and molecular modes, respectively. On SnO₂(110), dissociative adsorption is the most stable mode, with a BE of -1.86 eV: -0.18 eV more stable than the mixed mode (see Table I). Both molecular and mixed adsorption on TiO₂(110) are stabilised by hydrogen bonding interactions in the \mathbf{a}_{slab} direction, where $\mathbf{a}_{\text{slab}} = 2.979$ Å. Adjacent adsorbates on the SnO₂(110) surface are 0.275 Å further apart, since $\mathbf{a}_{\text{slab}} = 3.254$ Å, which seems to sufficiently suppress the formation of strong hydrogen bonding interactions between them. As a consequence of this, the calculated BE for molecular adsorption on SnO₂(110) has not been reported.

TABLE I: The binding energies (BE) per molecule for molecular (MM), dissociative (DD) and mixed (DM) adsorption on TiO₂(110) and SnO₂(110) are shown ($\Theta = 1$ ML; 2x1 cell).

Surface	Molecular MM	Dissociative DD	Mixed DM
rutile TiO ₂ (110)	-0.99	-0.85	-1.03
rutile SnO ₂ (110)	-	-1.86	-1.68

Electronic structure

Proposed water splitting mechanisms indicate that the first step is the oxidation of surface hydroxyls/adsorbed water molecules by photogenerated holes, resulting in the formation of hydroxyl radicals, Ti – OH_{ads}[•] [3]. To gain insight into this reaction, the density of states (DOS) of the surface in contact with ML water is considered for mixed adsorption, with separate projections onto the O_{2c} and Ti_{5c} atoms, alongside the contributions of the adsorbate O and H atoms. The states of the molecularly adsorbed molecule, the BH and the TH have been identified relative to the surface Ti and O states (see Fig. 2).

The mixed adsorption mode shows characteristics of both molecular and dissociative adsorption: the contributions of the molecularly and dissociatively adsorbed molecules are indicated within the DOS plot in Fig. 2(a). The lower valence band (VB), upper valence band, and conduction band (CB) of the surface are made up largely of O-2s, O-2p, and Ti-3d states, respectively [26]. O-2p states associated with both the TH and BH are present at the valence band maximum (VBM), whereas those of the adsorbed water molecule appear further from the VBM. This evidence suggests that the photogenerated holes at the surface are unlikely to react with molecularly adsorbed water, while it is possible that they react with both terminal and bridging hydroxyls.

Additionally, the projected DOS of the analogous adsorption on SnO₂(110) is shown in Fig. 2(b). The VB and CB of the surface are made up of O-2p/Sn-4p and Sn-5s/Sn-5p

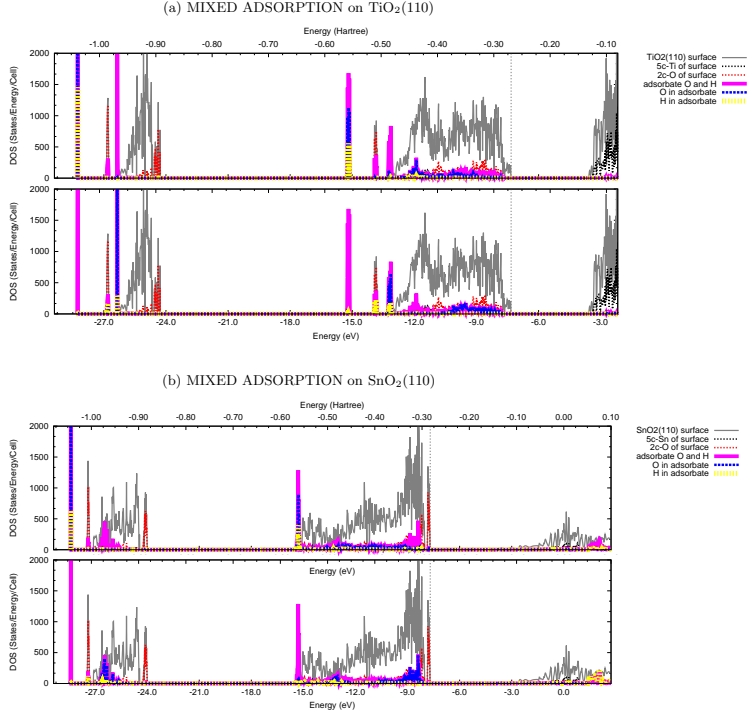


FIG. 2: Projected density of states (DOS) for the mixed adsorption onto (a) rutile $\text{TiO}_2(110)$ and (b) rutile $\text{SnO}_2(110)$ ($\Theta = 1 \text{ ML}$; 2×1 cell). The DOS is projected onto the O and H atoms in the molecularly (top) and dissociatively (bottom) adsorbed water molecules, separately. In both cases, the states at -28.5 eV and -15.2 eV are characteristic of intact molecules on the surface. On $\text{TiO}_2(110)$ [$\text{SnO}_2(110)$], the states at -27.0 eV and -14.5 eV [-27.5 eV] characterise the bridging hydroxyls (BH), and above these peaks lie the terminal hydroxyl (TH) states at -26.5 eV and -14.0 eV [-26.8 eV and -15 to -9 eV]. The vertical dotted line denotes the position of the Fermi energy. All energies are referred to vacuum zero as 2D periodic boundary conditions are used: $V(z)=0$ when $z=\infty$, where V is the electrostatic potential and z is the distance from the surface.

states, respectively [27]. The O- $2p$ and O- $2s$ states of the adsorbed water molecule have distinct peaks at $\sim -28.5 \text{ eV}$ and $\sim -15.2 \text{ eV}$, similar to those in $\text{TiO}_2(110)$, but with very little mixing with the states of the surface in the VB. The states associated with the BH and TH are much more delocalised in nature, hybridising strongly with both the upper and lower VBs. This element in the electronic structure could be a factor coinciding with the high stability of the dissociative adsorption mode on $\text{SnO}_2(110)$, as well as indicating that the production of distinct $\text{Ti} - \text{OH}_{\text{ads}}^\bullet$ is less likely than on TiO_2 .

CONCLUSIONS

The structure of water on the rutile $\text{TiO}_2(110)$ surface has been studied by means of periodic hybrid-exchange density functional theory calculations. Water binds readily to the surface with strong interaction between the adsorbate and the surface Ti_{5c} atom. A description of the most favourable adsorption scenarios has been given: (i) isolated dissociated water molecule in the absence of neighbours, (ii) mixed adsorption dimers and (iii) dissociative dimers. The arrangement and separation between adsorbed species affect the nature of the intermolecular interactions, consisting of both direct and surface-mediated interactions. In turn, these interactions influence the most energetically favourable adsorption mode. The separation between adsorbates has been studied further by considering

water adsorption on the SnO₂(110) surface. The larger size of the \mathbf{a}_{slab} lattice parameter compared to TiO₂(110) means that the molecules on the surface are unable to form strong hydrogen bonds to one another, and water dissociation becomes more favourable.

Through analysis of the DOS of the surface in contact with water, the positions of the adsorbate states relative to the VB and CB of TiO₂(110) have been identified, revealing that O-2*p* states associated with both hydroxyls are present at the VBM. This could play an important role in the proposed water oxidation mechanisms.

The adsorption scenarios described can be used to develop a predictive model of the structure of water on rutile TiO₂(110), based on the evaluation of a set of parameters to describe the main energy contributions governing water adsorption on this surface. When considering multilayer water adsorption, the matter then involves the interaction of water with a surface consisting of a mixture of adsorbed hydroxyls and water molecules [28].

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- [1] M. Grätzel, *Nature* **414**, 338 (2001).
- [2] R. H. Wilson, *J. Electrochem. Soc.* **127**, 228 (1980).
- [3] P. Salvador, *Prog. in Surf. Sci.* **86**, 41 (2011).
- [4] V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, 1994).
- [5] M. Batzill, *Energy Environ. Sci.* **4**, 3275 (2011).
- [6] C. Sun, L. Liu, A. Selloni, G. Lu, and S. Smith, *J. Mater. Chem.* **20**, 10319 (2010).
- [7] P. J. D. Lindan, N. M. Harrison, and M. J. Gillan, *Phys. Rev. Lett.* **80**, 762 (1998).
- [8] K. F. T. Seiyama, A. Kato and M. Nagatani, *Anal. Chem.* **34**, 1502 (1962).
- [9] M. Batzill, *Sensors* **6**, 1345 (2006).
- [10] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, et al., *CRYSTAL09*, Università di Torino (Torino, 2010).
- [11] J. Muscat, N. M. Harrison, and G. Thornton, *Phys. Rev. B* **59**, 2320 (1999).
- [12] M. Habgood and N. Harrison, *Surf. Sci.* **602**, 1072 (2008).
- [13] D. Feller, *J. Comp. Chem.* **17**, 1571 (1996).
- [14] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [15] J. Muscat, A. Wander, and N. Harrison, *Chemical Physics Letters* **342**, 397 (2001).
- [16] G. T. L. Liu, C. Zhang and A. Michaelides, *Phys. Rev. B* **82**, 161415 (2010).
- [17] M. Patel, G. Mallia, L. Liborio, and N. M. Harrison, *Phys. Rev. B* **86**, 045302 (2012).
- [18] J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson, and J. V. Smith, *J. Am. Chem. Soc.* **109**, 3639 (1987).
- [19] F. Labat, P. Baranek, C. Domain, C. Minot, and C. Adamo, *J. Chem. Phys.* **126**, 154703 (2007).
- [20] J. Scaranto, G. Mallia, and N. Harrison, *Comp. Mater. Sci.* **50**, 2080 (2011).
- [21] H. Tang, F. Levy, H. Berger, and P. E. Schmid, *Phys. Rev. B* **52**, 7771 (1995).
- [22] Reciprocal space sampling for the bulk structure was performed on a Pack-Monkhorst net with a shrinking factor IS=8 along each periodic direction. The predicted structural parameters for bulk TiO₂ are: $\mathbf{a}_{\text{bulk}}=\mathbf{b}_{\text{bulk}}=4.639\text{\AA}$, $\mathbf{c}_{\text{bulk}}=2.979\text{\AA}$ and $u=0.306$. For bulk SnO₂, $\mathbf{a}_{\text{bulk}}=\mathbf{b}_{\text{bulk}}=4.822\text{\AA}$, $\mathbf{c}_{\text{bulk}}=3.254\text{\AA}$ and $u=0.307$. These structures agree well with experiment [18] and are consistent with that predicted in previous calculations [19].
- [23] The corresponding TiO₂ and SnO₂ lattice parameters are as follows. TiO₂: $\mathbf{a}_{\text{slab}}=2.979\text{\AA}$, $\mathbf{b}_{\text{slab}}=6.561\text{\AA}$; SnO₂: $\mathbf{a}_{\text{slab}}=3.254\text{\AA}$, $\mathbf{b}_{\text{slab}}=6.820\text{\AA}$.
- [24] The counter-poise correction to the BE was applied to take into account the basis set superposition error (BSSE) [20].
- [25] The respective shrinking factors [8,8], [4,8], [4,8], [2,8], [8,4], and [4,4] were adopted in order to ensure consistent k-space sampling.
- [26] The calculated band gap of the clean TiO₂(110) surface is 2.90 eV, which is in good agreement with the experimental gap of 3.03 eV (polarised optical transmission measurements) [21].
- [27] The calculated band gap of the clean SnO₂(110) surface is 2.80 eV.
- [28] This work made use of the high performance computing facilities of Imperial College London and - via membership of the UK's HPC Materials Chemistry Consortium funded by EPSRC (EP/F067496) - of HECToR, the UK's national high-performance computing service, which is provided by UoE HPCx Ltd at the University of Edinburgh, Cray Inc and NAG Ltd, and funded by the Office of Science and Technology through EPSRC's High End Computing Programme.