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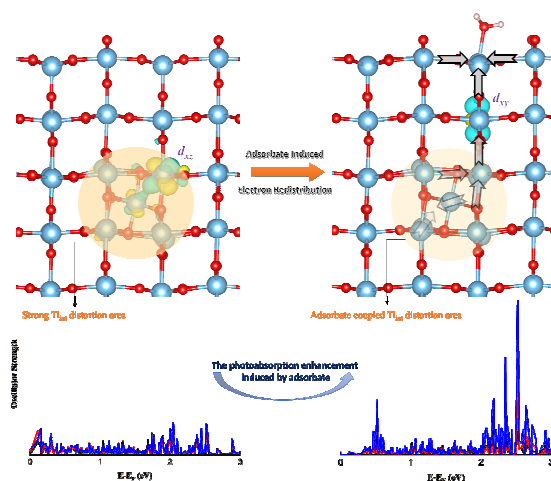
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Abstract

We investigate the effect of adsorbates on the structure and photoabsorption of reduced TiO₂ by first-principles calculations of rutile TiO₂(110) in the presence of both titanium interstitials (Ti_{int}s) and adsorbed water or methanol. Our results show that, while Ti_{int}s prefer to reside in deep inner layers when the surface is clean, they tend to diffuse toward the surface in the presence of water or methanol. This migration is due to the mutual stabilization of the adsorbates and Ti_{int} defects in the near surface region. We also find that adsorbed water/methanol change the orbital character and localization sites of the excess electrons associated with the Ti_{int}. These results can explain why the adsorption of water and methanol enhances the photoabsorption of the reduced TiO₂(110) surface.

TOC Graphic:



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4 The interaction of water with TiO₂ surfaces is of great interest in many fields of science and
5 technology¹⁻¹⁴. In particular, much attention has been focused on the character, molecular vs
6 dissociated, of adsorbed water, which has an important role in photocatalytic water splitting.
7 While it is well established that water dissociates at surface oxygen vacancies (O_vs) to form
8 bridging hydroxyls (O_{br}Hs),¹⁵⁻¹⁸ the effect of other intrinsic defects, notably Ti interstitials (Ti_{int}s),
9 is not as well understood.

10
11 Many physical and chemical properties of TiO₂ surfaces are strongly affected by intrinsic
12 defects. Both O_vs and Ti_{int}s give rise to excess electrons (two and four, respectively), which tend to
13 form localized polaronic Ti³⁺ states in the band gap.^{4, 18-31} Based on photoemission spectroscopy
14 (PES) measurements, Wendt et al.¹⁸ suggested that excess electrons in TiO₂ mainly originate from
15 Ti_{int}s. These defects can be dragged to the surface by adsorbed oxygen, with which they react to
16 form small TiO₂ islands²⁶. On the other hand, Yim et al performed combined PES and STM
17 experiments on TiO₂ surfaces containing various amounts of oxygen vacancies.³² They observed
18 that the intensity of the PES peak depended linearly on the O_v density and thus proposed that the
19 gap states originate mainly from O_vs. Similar to O_vs and Ti_{int}s, surface bridging hydroxyls (O_{br}H)
20 also induce gap states^{21, 33}. Using UPS measurements combined with first-principles calculations,
21 Mao et al. investigated hydroxylated TiO₂ with different coverages of hydroxyls, and concluded
22 that both hydroxyls and bulk intrinsic defects are responsible for the Ti³⁺ gap states in TiO₂.³⁴

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24 The effect of Ti³⁺ ions on TiO₂'s optical absorption has also been investigated. Based on
25 photoluminescence measurements, Santara et al suggested that Ti_{int} could enhance the light
26 absorption in the visible region.²⁹ Recent two-photon photoemission (2PPE) measurements
27 combined with first principles calculations showed that, in addition to the well-known gap states,
28 Ti³⁺ ions introduce also resonant excited states in the conduction band, which can extend the
29 optical adsorption to the visible.³⁵ On the other hand, various 2PPE experiments^{36, 37} have found
30 that such resonant excited states at about 2.3-2.5 eV above Fermi energy (E_F) are greatly affected
31 by water adsorption, their observed intensity strongly increasing with increasing water coverage
32 up to one monolayer (ML).³⁶ However, the origin of this effect and the interplay between Ti³⁺
33 defect states and adsorbates are still unclear.

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35 In this work, we use hybrid density functional calculations to investigate the effect of water
36 and methanol on the structure, electronic properties and photoabsorption of rutile TiO₂(110)
37 containing reducing Ti_{int} defects. We find that both adsorbates, especially when dissociated, can
38 modify the relative stability of Ti_{int} at different sites. They also affect the states of the excess
39 electrons, strongly enhancing the contribution of Ti³⁺ ions to the photoabsorption, in agreement
40 with experimental observations.

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42 Spin-polarized DFT calculations were performed with the CP2K/Quickstep package,³⁸ which
43 uses a hybrid Gaussian and plane-waves approach to describe the electrons' wave functions. It is
44 known that Ti_{int} introduce gap states below TiO₂'s conduction band minimum (CBM).^{34, 39, 40} To
45 properly describe these states, the hybrid functional of Heyd, Scuseria, and Ernzerhof
46 (HSE06)⁴¹⁻⁴³ was chosen for all the calculations. Van der Waals corrections were not included.
47 Norm-conserving Goedecker, Teter, and Hutter (GTH) pseudopotentials were used to describe the
48 core electrons.⁴⁴ The wave functions of the valence electrons were expanded in terms of Gaussian
49 functions with molecularly optimized double-zeta polarized basis sets (m-DZVP)⁴⁵ while plane
50 waves with a 280 Ry cut-off in energy were used for the auxiliary basis sets. Due to the large size
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of the models used in our calculations, the Brillouin zone sampling was restricted to the Γ point. All atoms in the slab were relaxed (i.e. no atom or layer is fixed) until the maximum residual force was less than 0.02 eV/Å.

The rutile-TiO₂ (110) surface was modeled using a repeated slab geometry with slabs of four (Figure S1) or six TiO₂ tri-layers (Figure 1a, b) and a (4×2) surface supercell of dimensions (11.836 Å×12.949 Å). The vacuum separation between slabs was around 12 Å. On this surface, bridge bonded O (O_{2c}) and alternate rows of Ti_{5c} and O_{3c} are present. Water mainly adsorbs on the Ti_{5c} rows and can dissociate into O_{br}H and Ti_{5c}-OH as shown in Figure 1a. Water coverages of 1/8 or 1/4 monolayer (ML) were considered by adding one or two H₂O molecules above the Ti_{5c} site on the TiO₂ (110). The adsorption energy, E_a , was calculated from the expression:

$$E_a = E_{slab} + E_{adsorbate} - E_{slab+adsorbate} \quad (1)$$

where E_{slab} and $E_{adsorbate}$ are the total energies of clean surface and adsorbate molecule, respectively, while $E_{slab+adsorbate}$ is the total energy of the slab with an adsorbate molecule on its surface. With the above definition, a positive E_a value means that adsorption is favorable, and larger (more positive) E_a indicates stronger binding.

The oscillator strength was calculated as follows:⁴⁶

$$f_{cv}^{\mu} = \frac{2}{m_e(E_c - E_v)} |\langle v | p_{\mu} | c \rangle|^2 \quad (2)$$

Here f_{cv}^{μ} is the oscillator strength in the \vec{e}_{μ} polarization direction, $\langle v |$ and $| c \rangle$ denote the Kohn-Sham orbitals corresponding to the occupied gap states (or valence band) and unoccupied MOs above E_F , respectively, and E_c and E_v are the corresponding eigenvalues. p_{μ} is the momentum operator along \vec{e}_{μ} .

a. Structure and energetics of Ti interstitials and adsorbed water/methanol at TiO₂(110)

Three possible sites for a Ti_{int} defect in a 6 tri-layers TiO₂(110) slab model are shown in Figure 1. Here, L1 corresponds to the region between the surface and subsurface, L2 is between subsurface and the third layer, and L3 is between the third and fourth layers (Figure 1c-e). As reported in previous computational studies, layers of rutile TiO₂ (110) slabs tend to pair up to form bi-layers.⁴⁷ As a result, the average Ti-O bond length in regions L1 and L3 ranges from about 1.80 Å in the absence of the Ti interstitial to 1.85-1.91 Å when Ti_{int} is present; the corresponding values in region L2 are 2.10-2.20 Å in the absence of Ti_{int} and 2.21-2.28 Å with a Ti interstitial. As shown in Figure 2a and Table S1, Ti_{int} is energetically most stable in L2 (0.46 eV more stable than L1), followed by L3 (0.35 eV more stable than L1). The result that Ti_{int} prefers subsurface or even deeper sites in the case of a clean surface agrees well with previous reports.^{2, 48}

To determine how water affects the stability of titanium interstitials, we computed the relative energies of a Ti_{int} at different sites in the presence of one adsorbed water molecule per surface unit cell (1/8 ML). When the water molecule is adsorbed in intact form, L2 is 0.40 eV more stable than L1, thus remaining the most favorable site for Ti_{int}, while L3 is only 0.13 eV more stable than L1. When the adsorbed water is dissociated, L1 becomes 0.24 (0.22) eV more stable than L2 (L3), but Ti_{int} at L2 with adsorbed water in molecular form is still ~ 0.15 eV more stable than Ti_{int} at L1 with dissociated water. For a Ti_{int} in the presence of two adsorbed water molecules (1/4 ML), the most stable configuration is again Ti_{int} at L2 with all water in molecular form, but Ti_{int} at L1 with one of the two water molecules dissociated is only ~ 0.01 eV higher in energy (Table S1). When

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3 the coverage further increases to 3/4 ML, the configuration with Ti_{int} at L1 and one of the six
4 adsorbed water molecules dissociated is 0.07 eV more stable than the one with six intact water
5 molecules (**Table S1**). These results clearly show that water affects the relative stability and
6 therefore the distribution of Ti_{int} defects in the slab. Moreover, this influence is more pronounced
7 at higher adsorbed water coverage.
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9 In turn, we can consider how Ti_{int} affects the water adsorption state. Our computed adsorption
10 energies for molecular and dissociated water in the presence of Ti_{int} are shown in **Figure 2b** and
11 **Table S1**. On the defect-free surface, the molecular (M) state is about 0.10 eV more stable than the
12 dissociated one (D), as found in previous studies.^{47, 49-51} A Ti atom on the surface can easily
13 dissociate water into hydroxyls, also in agreement with previous reports²⁸. With a Ti_{int} in the
14 subsurface at L1, the water D state is 0.25 eV more stable than the M state, whereas the D state is
15 0.38 eV less stable than M when Ti_{int} is at L2. For Ti_{int} at the L3 site, the energy difference
16 between dissociated and molecular water is very similar to that on defect-free TiO_2 . These results
17 imply that the presence of Ti_{int} can change the water adsorption state. When Ti_{int} is at L1, water
18 prefers to dissociate, as observed also in ab initio molecular dynamic (AIMD) simulations of
19 water on the anatase (101) surface.⁵²
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22 To find out whether the interplay between interstitial and water exists also for other
23 adsorbates, we further investigated the adsorption of methanol (1/8 ML) in the presence of a Ti_{int}
24 at various sites. Our results show that a Ti_{int} at L2 or L3 is only 0.05 eV more stable than one at L1
25 when methanol is adsorbed in molecular form on $\text{TiO}_2(110)$ (**Table S1** and **Figure 2**). The
26 difference with respect to a Ti_{int} in a clean (adsorbate-free) slab is even larger when methanol is
27 dissociated, as L1 is in this case 0.27 (0.28) eV more stable in energy than L2 (L3). Altogether, the
28 adsorption of methanol appears to make the migration of Ti_{int} to L1 even more favorable than
29 found in the case of water adsorption. In turn, subsurface Ti_{int} s strongly affect the methanol
30 adsorption state. While methanol prefers to adsorb in molecular form in the absence of Ti_{int} ,
31 dissociated methanol with Ti_{int} at L1 is about 0.3 eV more stable than any molecular adsorption
32 state (**Table S2**).
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36 Altogether, our results for water/methanol adsorption in the presence of a subsurface Ti
37 interstitial (**Figure 2**) show that there is a significant interaction between defects and adsorbates,
38 which favors dissociation of the adsorbates together with migration of the Ti_{int} toward the
39 subsurface L1 site. On the other hand, previous DFT studies have predicted an activation barrier
40 of 0.75 (0.84) eV for Ti_{int} diffusion from L2 to L1 in the presence of adsorbed O_2 ¹⁸ (in vacuum⁵³),
41 and 1.2 (1.4) eV for Ti_{int} migration from L1 to the surface. By comparison with reference¹⁸, where
42 the onset temperature for the formation of TiO_x islands on the surface was ~ 400 K, we may infer
43 that a significant fraction of Ti_{int} should be present at the L1 site at temperature of around 300 K,
44 the desorption temperature of water from $\text{TiO}_2(110)$.³
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48 **b. Effect of adsorbed water/methanol on the electronic structure and photoabsorption** 49 **of Ti interstitials**

50 Adsorbed water on the $\text{TiO}_2(110)$ surface appears to have only minor effects on the projected
51 DOS (PDOS) of the Ti^{3+} ions introduced by Ti_{int} (**Figure S2**). In contrast, the effects on the
52 photoabsorption of the Ti^{3+} ions are quite prominent. We find indeed a large difference between
53 the oscillator strengths of the transitions from the gap states to the CB calculated without and with
54 adsorbed water (see **Figure 3** and **S3**; note that Ti_{int} at L1 was used for all these calculations). As
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3 shown previously,¹⁹ the transitions from the VBM to the CB states are all very small, with no
4 remarkable peak (see also **Figure S3a**). The transitions from the gap states to the CB show a
5 similar behavior, with no obvious peak, on the clean surface. In the presence of adsorbed water,
6 instead, the oscillator strengths of the transitions from the gap states to the CB show a prominent
7 peak near ~2.5 eV. The peak is present in the spin down channel only in the case of molecularly
8 adsorbed water (**Figure 3b** and **3e**), whereas the oscillator strength is greatly enhanced for both
9 spin up and spin down transitions in the case of dissociated water (**Figure 3c** and **3f**).

10
11 To understand the reason of this enhancement, we examined the spin density of slab models
12 without and with H₂O at the coverage of 1/8 ML. As shown in **Figure 4**, the states occupied by the
13 Ti_{int}'s excess electrons have the character of d_{xz} , d_{yz} and d_{z^2} orbitals on the clean surface.
14 Interestingly, one gap state is changed to d_{xy} in the presence of molecularly adsorbed water
15 (**Figure 4b**). Even more so, two gap states acquire d_{xy} character when the adsorbed water is
16 dissociated (**Figure 4c** and **S4**). At the same time, there is a strong enhancement of the oscillator
17 strengths of the transitions involving these states, indicating that the d_{xy} gap states can couple
18 much more effectively with the Ti³⁺ resonance in the CB than the d_{xz} , d_{yz} and d_{z^2} states. In fact,
19 the transitions from the gap states to the CB depend on the polarization of the incident light: the
20 transitions induced by a field polarized along [110] (z) have a much larger oscillator strength
21 compared to those along the [001] (x) or [1 $\bar{1}$ 0] (y) directions on the rutile TiO₂(110) surface¹⁹.
22 This adsorbate-induced change of the orbital character of the gap states may be the main reason
23 why water adsorption can enhance the photoabsorption of the reduced TiO₂(110) surface. Note
24 that this effect is not unique to a Ti_{int} at L1 with 1/8 ML of water: we observed indeed the same
25 effect also for Ti_{int} at L2 and L3 (see **Figure S4**), as well as with higher water coverage (1/4 ML)
26 (see **Figure S5**) and in the case of methanol adsorption (see **Figure S6**).

27
28 We can further investigate why the d_{xz} , d_{yz} and d_{z^2} gap states tend to transform to d_{xy} in the
29 presence of water and methanol. This change may be related to a decrease of the electron trapping
30 ability of Ti_{int} caused by the adsorbates. As shown in **Figure 5**, a Ti interstitial induces a strong
31 local distortion that favors the trapping of the excess electrons close to the defect site. This local
32 structure is changed in the presence of adsorbates, which in turn reduces the ability of Ti_{int} to trap
33 the excess electrons. This can be seen from the average distance d_{av} between Ti_{int} and the sites
34 where the excess electrons are localized. As shown in **Table 1**, d_{av} changes from 2.998 Å on the
35 clean surface to 3.663 Å and 3.709 Å with adsorbed water and methanol, respectively. As an
36 excess electron moves farther away from Ti_{int}, the structure is less distorted and the electron tends
37 to acquire d_{xy} character, which is more stable than all other d orbitals in rutile.^{19,35} To estimate the
38 electron localization, we also calculated the spin moments of the Ti³⁺ ions where the excess
39 electrons are (mainly) localized (**Table S3**). For each Ti_{int} site (L1/L2/L3), two of the four Ti³⁺
40 ions have spin moments larger than 0.8 μ_B on the clean surface, whereas there are often three spin
41 moments > 0.8 μ_B for the cases of 1/8 ML adsorbed water or methanol, suggesting that the excess
42 electrons tend to become more localized in the presence of these adsorbates.

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44 We can interpret the above process as an adsorbate induced excess electron redistribution
45 (AIER; see **Figure 5**), an effect that may be quite common in TiO₂ and other reducible oxides as
46 well. For example, using electron-stimulated desorption Zhang et al found that the defect electrons
47 can redistribute when there are adsorbates on the surface.⁵⁴ Similarly, using PBE+U calculations,
48 Wang et al found that water adsorption can induce the migration of excess electrons originating
49 from hydroxyls or O_vs in TiO₂.⁵⁵ Both these results can be understood in terms of the AIER
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scheme in **Figure 5**.

Table 1 Average distances d_{av} (in Å) between the trapping sites of the excess electrons (e^-) and Ti_{int} at different sites on the clean surface and in the presence of 1/8 ML adsorbed water or methanol in either molecular or dissociated form. The electron trapping sites are separated in two groups, based on the character, d_{xy} vs. non- d_{xy} , of the excess electron's state. Note that d_{xy} electrons are always farther away from Ti_{int} than non- d_{xy} electrons.

d_{Ti-e}	<i>Clean</i>	<i>H₂O</i>	<i>CH₃OH</i>
<i>non-d_{xy}</i>	2.062	1.807	1.431
<i>d_{xy}</i>	4.869	5.680	5.637
<i>all</i>	2.998	3.663	3.709

In summary, in this work we have shown that the coupling between adsorbates such as water and methanol and Ti_{int} defects can not only affect the distribution of Ti_{int} s, but also the locations and orbital character of the excess electrons and the photoabsorption of TiO_2 . On the clean surface, Ti_{int} defects prefer to reside well below the surface, making a relatively small contribution to the photoactivity. When water and methanol molecules are present on the surface, instead, they interact with the Ti_{int} s and tend to drag the defects close to the surface, while simultaneously undergoing partial dissociation. Importantly, the coupling between defects and adsorbates can change the orbital character of the excess electrons around the defect and transform them into more stable d_{xy} states. This leads to a substantial enhancement of the photoabsorption and therefore of the photoactivity of reduced TiO_2 .

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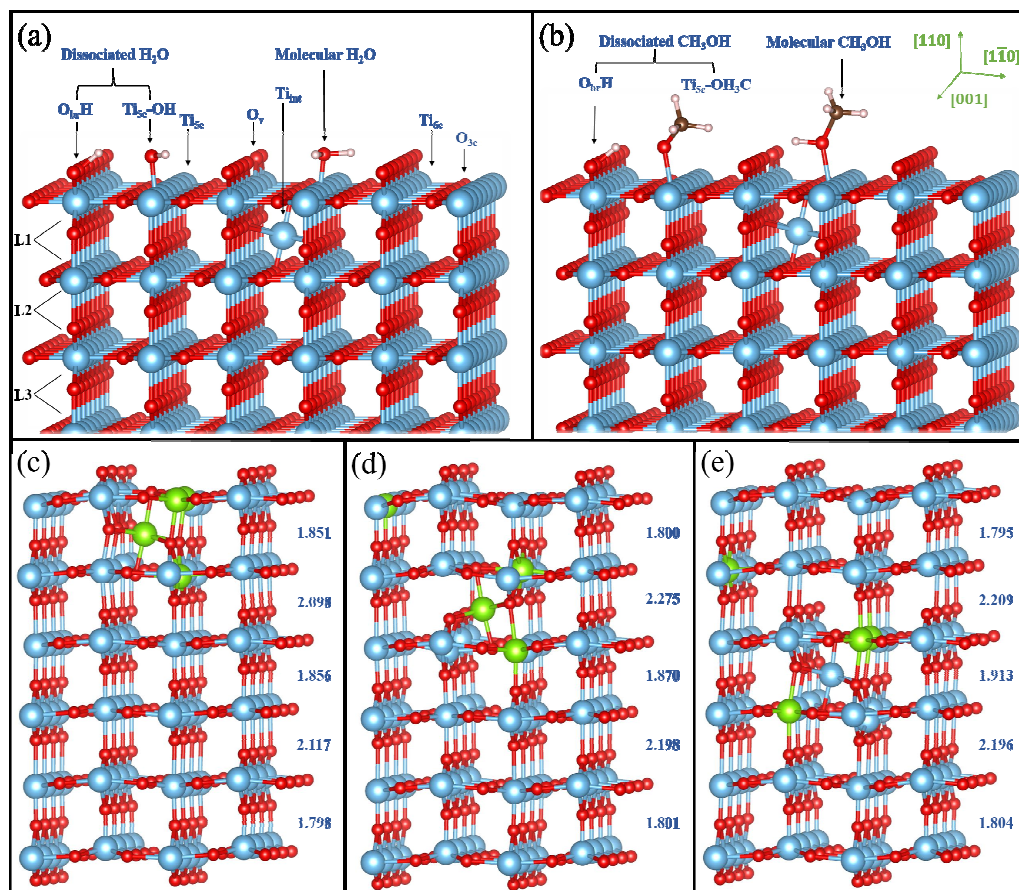


Figure 1 *Top*: defective rutile-TiO₂ (110) surface with subsurface Ti interstitials and adsorbed water (a) or methanol (b). Both molecular and dissociated adsorbates as well as typical structural features are indicated, e.g. Ti_{5c}, Ti_{6c}, O_{3c}, O_v and Ti_{int} denote 5-coordinated Ti, 6-coordinated Ti, 3-coordinated O, bridging O vacancy and interstitial Ti, respectively. Dissociated water includes a bridging hydroxyl (O_{br}H) and Ti_{5c} hydroxyl (Ti_{5c}-OH), while dissociated methanol includes O_{br}H and Ti_{5c}-OH₃C. *Bottom*: optimized structure of a six-layers rutile (110) slab with Ti_{int} at L1 (c), L2 (d) and L3 (e). The red, light blue and light pink spheres represent O, Ti and H atoms, respectively. The green spheres represent Ti³⁺ ions.

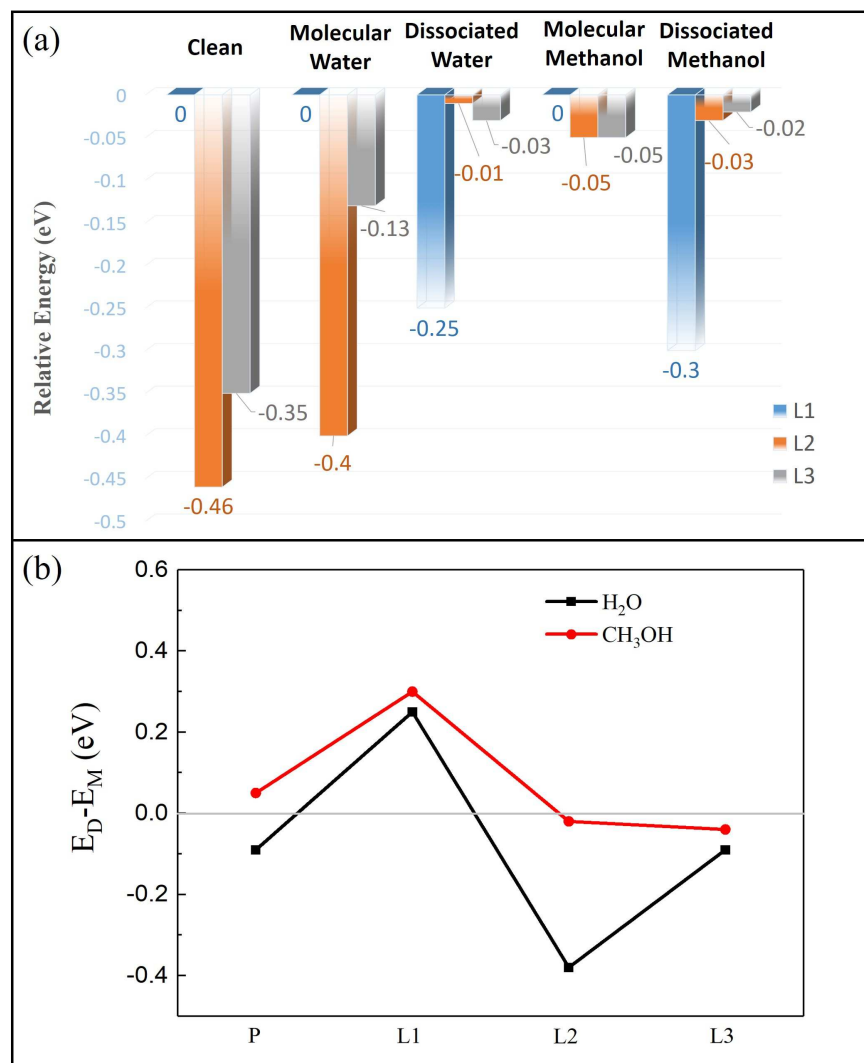


Figure 2 (a) Relative energies of Ti interstitials at L1, L2 and L3 sites of a six-layers TiO₂(110) slab in the absence (clean) and with 1/8 ML intact or dissociated adsorbed water or methanol. In all cases, energies are referred to the total energy of Ti_{int} at L1 with an intact adsorbed molecule. (b) Difference between the energies of 1/8 ML molecular (E_M) and dissociated (E_D) water (black) or methanol (red) on defect-free (P) or defected TiO₂(110) slab with a Ti_{int} in different locations (L1, L2 or L3); a positive value indicates that the dissociated state is more stable. See Table S1 and S2 for detailed data.

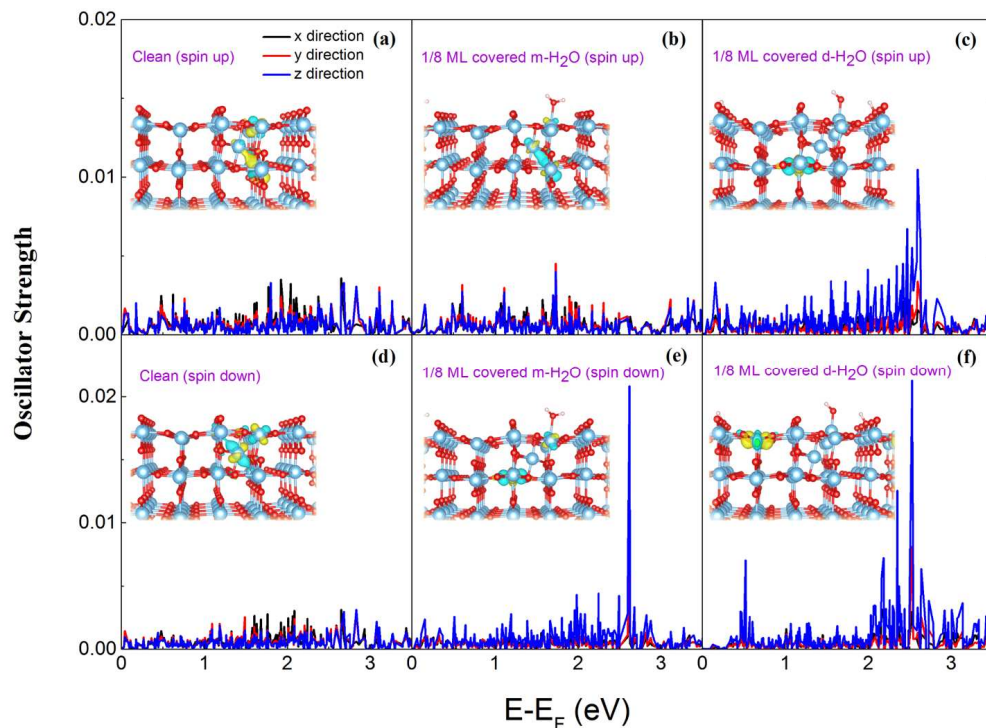


Figure 3 Calculated oscillator strengths of the transitions from the Ti_{int} -induced gap states to the CB for reduced rutile $TiO_2(110)$: (a, d) clean surface; (b, e) 1/8 ML adsorbed water in molecular form; (c, f) 1/8 ML dissociated water. Transitions of spin up (a, b, c) and spin down (d, e, f) states are shown separately, with the spin density of the gap states shown in the inset. The iso-surface for the spin density contour is 0.06 a.u.. To compare the oscillator strengths of different characteristic orbitals, each panel shows only the contribution of one spin up and one spin down states. The black, red and blue lines refer to transitions with the dipole moment along the $[001]$ (x), $[1\bar{1}0]$ (y) and $[110]$ (z) directions, respectively. The red, light blue and light pink spheres represent O, Ti and H atoms, respectively. The energy zero correspond to E_F that is assumed to coincide with the CBM.

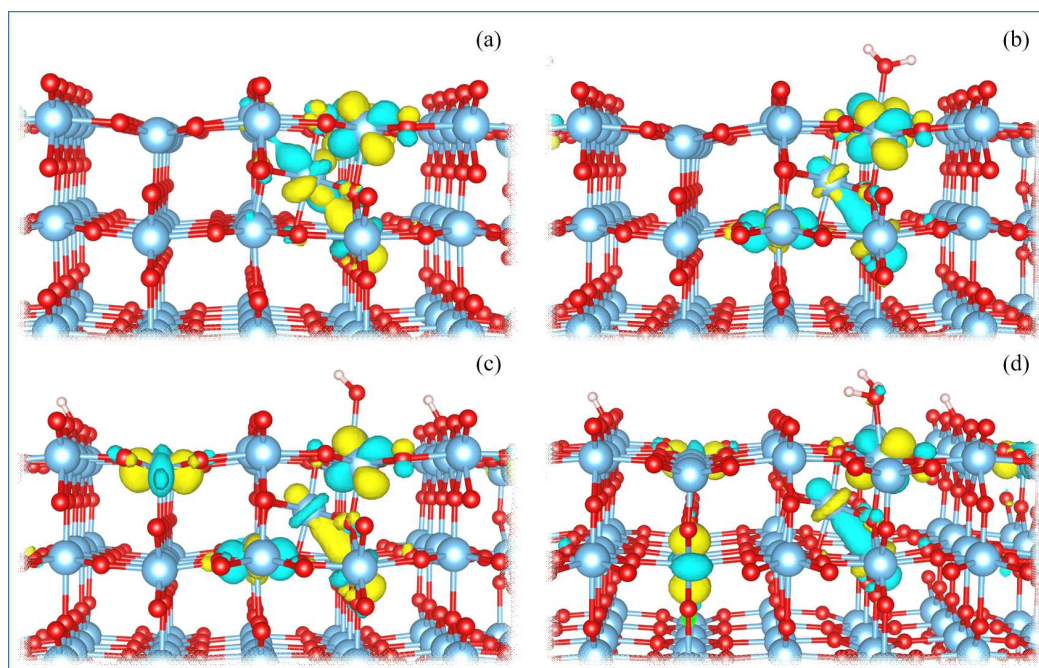


Figure 4 Spin density of defect states for Ti_{int} at L1 site: (a) clean surface; 1/8 ML adsorbed water in (b) molecular and (c) dissociated forms; (d) 1/4 ML dissociated water. The red, light blue and light pink spheres represent O, Ti and H atoms, respectively. The iso-surface for the spin density contour is 0.06 a.u..

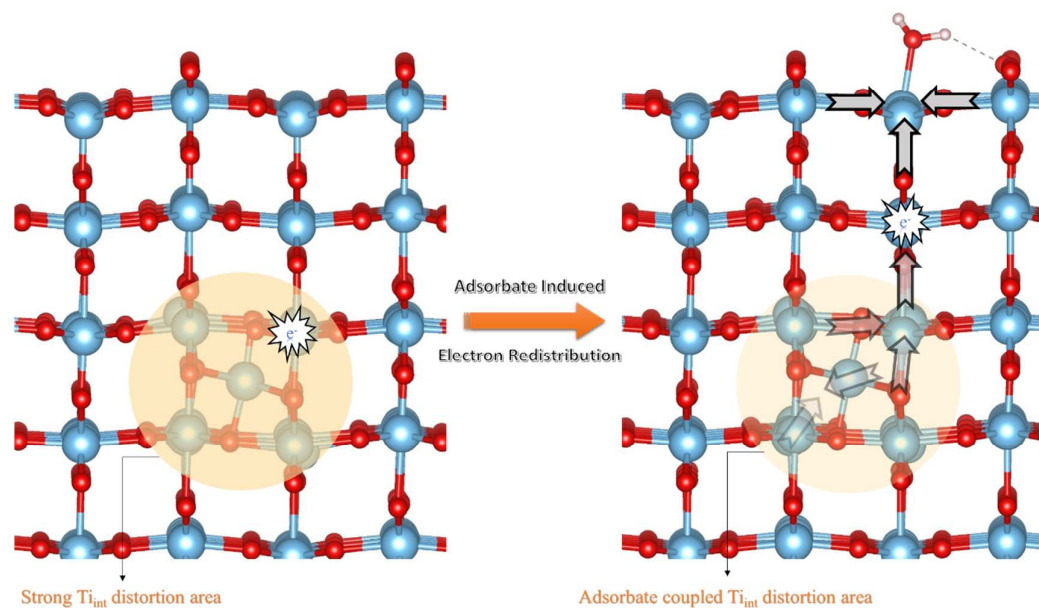


Figure 5 Sketch of adsorbate induced electron redistribution (AIER). As an example, the electron path in the case of a Ti_{int} at L3 with an adsorbed water molecule is shown. The arrows indicate the displacements of some of the atoms in the slab, and the semi-transparent orange circle highlights the area of the Ti_{int} induced distortion. The red, light blue and light pink spheres represent O, Ti and H atoms, respectively.