

Adsorption of Catechol on TiO₂ Rutile (100): A Density Functional Theory Investigation

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We have used DFT calculations to investigate the binding of catechol, one of the smallest sensitizing chromophores, to the rutile TiO₂(100) surface. On the clean surface, we find that monodentate adsorption is favored over molecular adsorption. An oxygen defective site strongly favors the fully dissociative bidentate adsorption, which is otherwise found not to be stable. Regardless of the protonation form of catechol, however, occupied molecular states are introduced into the band gap of rutile (100). The lowest unoccupied levels are localized exclusively on the substrate.

Introduction

Due to its photostability, nontoxicity, and low cost, titanium dioxide (TiO₂) is widely used as a semiconductor in dye-sensitized solar cells (DSSCs).^{1,2} In these devices, a monolayer of an organic or metal-based dye, with an absorption spectrum in the visible region, is attached to a film of TiO₂ nanoparticles. After photoexcitation has taken place in the dye, an electron is transferred to the conduction band (CB) of the oxide. The dye is then regenerated by a redox couple present in solution, which in turn is reduced by the electrons passed through the load. The efficiency of the electron transfer will depend strongly on the binding of the dye to the nanoparticle. In this paper, we present DFT calculations of the energetics and electronic structure for catechol bound to the rutile TiO₂(100) surface.

Among the many dyes which have been studied, catechol has received considerable attention.^{3–11} Despite its lowest excitation energy (4.1 eV) being larger than TiO₂ band gap, catechol shifts the energy absorption of TiO₂ into the visible region (from 3.2 to 2.9 eV).^{12,13} Semiempirical quantum chemical calculations have in fact shown that catechol introduces an occupied π state at the lower end of the anatase TiO₂ band gap, and the shift in the absorption has been attributed to a direct charge-transfer excitation from this level to the Ti levels at the bottom of the CB.¹⁴ In addition, a TDDFT investigation of catechol bound to a single titanium has revealed that the lowest excitation is dominated by the (catechol $\rightarrow$ Ti) transitions HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+2.⁴

The interest in this small sensitizer is also motivated by the achievement of incident photon to current efficiency (IPCE) values of up to 50% with Ru(II)–polypyridyl complexes containing a pendant catechol on TiO₂ anatase.¹⁵ This has suggested that new and more effective photosensitizers which bind through a catechol ring could be designed.

To date, the anatase form of TiO₂ has been preferred to rutile for the use in DSSCs.^{16–19} This is due to the larger surface to volume ratio of anatase nanoparticles, as well as the higher CB edge of anatase, which allows larger photovoltages to be achieved than in rutile. However, when compared to anatase, rutile presents some advantages; it is chemically more stable,

potentially cheaper to produce, and has superior light-scattering properties because of its higher refractive index.²⁰ Moreover, rutile performances in DSSCs have been shown to be comparable to those of anatase at one sun light intensity.²¹

Although the (110) plane is the most stable surface of rutile,^{22,23} it covers only the 64% of the crystal surface, with the remaining part covered equally by the (100) and (101) planes.²⁴ It is therefore important to study the dye–semiconductor interface also on these surfaces. Indeed, using atomically flat rutile (110) and (100) surfaces²⁵ as a substrate to adsorb the merocyanine dye, much larger IPCE values were obtained for the (100) plane than the (110) one, probably due to the larger surface density of anchoring (five-coordinated) Ti sites.²⁶ Tsujiko et al. have also shown that the photoetching of *n*-TiO₂ rutile in aqueous H₂SO₄ produces rectangular holes along [001], with a (100) face at the walls irrespective of the electrode surface used,²⁷ and that this is accompanied by an increase of the IPCE²⁸ when the resulting nanoporous material is used in DSSCs.

The study of defective surfaces is also important. It is well-known that oxygen vacancies at the surface are formed if rutile crystals are heated in ultrahigh vacuum at $T > 870$ K.²⁹ The associated reduction of the surface has strong effects on the electronic structure.³⁰ Water dissociation on the (110) face, for example, takes place exclusively on this type of defect sites.³¹

In a recent combined theoretical and experimental study of the catechol on the rutile (110) surface at saturation, it was found that two structures are simultaneously present, one with only partially dissociated (monodentate) and another with alternating monodentate and fully dissociated (bidentate) adsorbates.³² Here, we use a density functional theory (DFT) approach to characterize the interaction of catechol with the less investigated rutile (100) face. Four different adsorption modes will be modeled, with results presented for geometry, energetics, and electronic structure. In the next section, computational details are given. We then present the results, starting with the substrate and moving on to the different adsorption modes and their electronic structure, and finally, we conclude.

Computational Details

All of the calculations have been performed with the package VASP,^{33,34} which solves the Kohn–Sham (KS) equations of the system through a self-consistent procedure. We chose the

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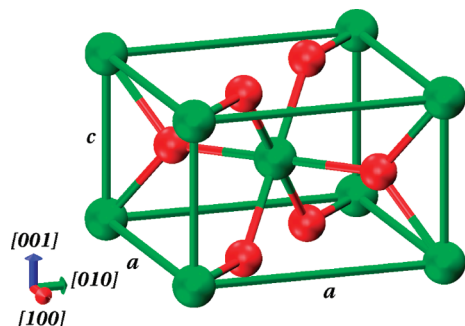


Figure 1. Primitive cell of the rutile TiO_2 . Ti atoms are represented in green, O in red. The lattice vectors a and c are also shown.

TABLE 1: Calculated Values of Bulk Rutile Parameters and a Comparison with the Experimental Results by Abrahams et al.³⁹

	a (Å)	c (Å)	u
experiment	4.594	2.959	0.305
this work	4.645 (+1.11%)	2.991 (+1.08%)	0.305

generalized gradient approximation (GGA) for the exchange and correlation term, in the formalism of Perdew and Wang (PW91).³⁵ A plane wave basis set with a cutoff of 400 eV was adopted, enough to converge the energy of the unit cell of bulk rutile within 3 meV/atom. Ultrasoft Vanderbilt pseudopotentials³⁶ were used to represent the effect of the inner electrons. Specifically, the 1s, 2s, 2p, 3s, and 3p electrons of Ti and the 1s of O and C were considered core electrons and not treated explicitly. Since VASP implements a periodic boundary conditions scheme, we introduced a vacuum of at least 8 Å between adjacent slabs to avoid spurious interactions between replica atoms. Relaxations of structures were performed with the conjugate gradient method and stopped when the force acting on each ion was less than 0.03 eV.

In the calculations with a (1×1) unit cell, a Monkhorst–Pack grid³⁷ of $(1 \times 5 \times 5)$ was used to sample the Brillouin zone. In order to adsorb the dye, the substrate was modeled by a (3×3) supercell, with dimensions of 13.935 and 8.973 Å. A supercell with an O vacancy (1/9 of a monolayer) was also employed (described below). The optimizations of the adsorptions were performed with the Γ point (more dense grids and higher cutoff energies were tested with differences in energy of less than 3 meV/atom). However, for density of states (DOS) calculations, we adopted a grid of $(1 \times 8 \times 8)$. In every relaxation, the bottom three planes of rutile were constrained to their bulk positions.

All the figures were made with VMD.³⁸

Results and Discussion

Bulk Rutile and Its (100) Surface. Rutile tetragonal cell is defined by the primitive vectors a and c (Figure 1). Each Ti is coordinated to six neighboring O, with two Ti–O bonds longer than the other four. Each O is coordinated to three Ti atoms, and all three bonds lie in the same plane.

Table 1 compares with some experimental values³⁹ the lattice parameters a and c and the internal parameter u , obtained after the optimization of the unit cell. The discrepancy is around 1% for both a and c . The overestimation of the lattice parameters is typical of the GGA.

The rutile (100) surface is formed of alternating layers, that is, O–Ti–O stoichiometric units (Figure 2). Its termination can be easily derived by Tasker⁴⁰ and LaFemina⁴¹ rules; the extreme layer contains (besides a plane of three-fold O ions) a plane of five-fold-coordinated Ti and a plane of two-fold-coordinated O ions.

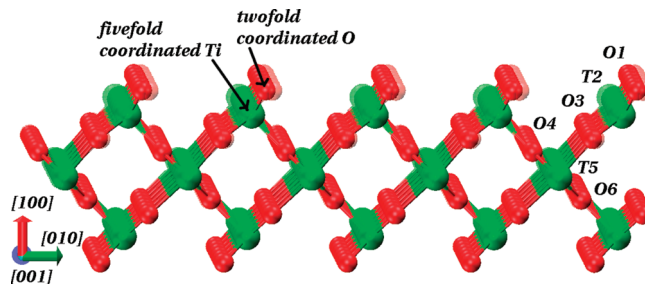


Figure 2. Geometry of the rutile (100) surface before (transparent) and after (opaque) the structural relaxation. Ti atoms are represented in green, O in red.

TABLE 2: Calculated Displacements (Å) of the Rutile (100) Surface Relative to the Optimized Bulk Terminated Structure along [010] and [100] for Different Numbers of Layers n^a

label	number of layers n							
	3		4		5		6	
	[010]	[100]	[010]	[100]	[010]	[100]	[010]	[100]
O1	−0.25	0.01	−0.31	0.07	−0.27	0.06	−0.26	0.04
Ti2	0.17	−0.08	0.14	−0.03	0.16	−0.04	0.18	−0.06
O3	−0.10	0.00	−0.12	0.05	−0.13	0.06	−0.10	0.03
O4	0.02	−0.03	−0.02	0.02	−0.02	−0.02	0.00	−0.02
Ti5	0.09	−0.03	0.08	0.02	0.10	0.01	0.11	0.00
O6	0.05	−0.01	−0.02	0.01	0.03	0.01	−0.01	−0.02

^a Labels refer to Figure 2.

In order to find a converged thickness for the adsorption, the geometry and the formation energy of the (1×1) relaxed surface were studied with respect to the number of layers. Displacements from the bulk truncated structure along [010] and [100] are reported in Table 2 (for reason of symmetry, no displacements could be observed along [001]). The most important changes occur in the topmost layer. Here, in the six-layer slab, O1 and O3 move, respectively, by -0.26 and -0.10 Å along [010] as Ti2 moves by 0.18 Å. Opposite displacements between titaniums (upward) and oxygens (downward) occur also along [100]. The net result is that Ti2 increases its coordination toward the oxygens. Though with some differences, this pattern has been previously reported^{30,42–44} and is reproduced at a good level also with a three-layer slab.

The unrelaxed surface formation energy E_{unrel} was evaluated according to the formula

$$E_{\text{unrel}} = \frac{1}{2A}(E_n - nE_{\text{bulk}}) \quad (1)$$

where A is the area of the slab, E_n is the energy of the surface unit cell containing n layers, and E_{bulk} is the energy per TiO_2 unit in the infinite bulk system. The energetic gain after the optimization, E_{gain} , was added to the unrelaxed surface energy to obtain the relaxed surface formation energy E_{rel}

$$E_{\text{rel}} = E_{\text{unrel}} + E_{\text{gain}} \quad (2)$$

We found that the surface energies of a three-layer slab are already converged to better than 0.05 J/m² with respect to the values of 1.57 (unrelaxed) and 0.74 J/m² (relaxed) of the six-layer slab. These results are in good agreement with literature^{42,43} and, together with the qualitatively correct pattern for the displacements, made us choose a three-layer substrate model.

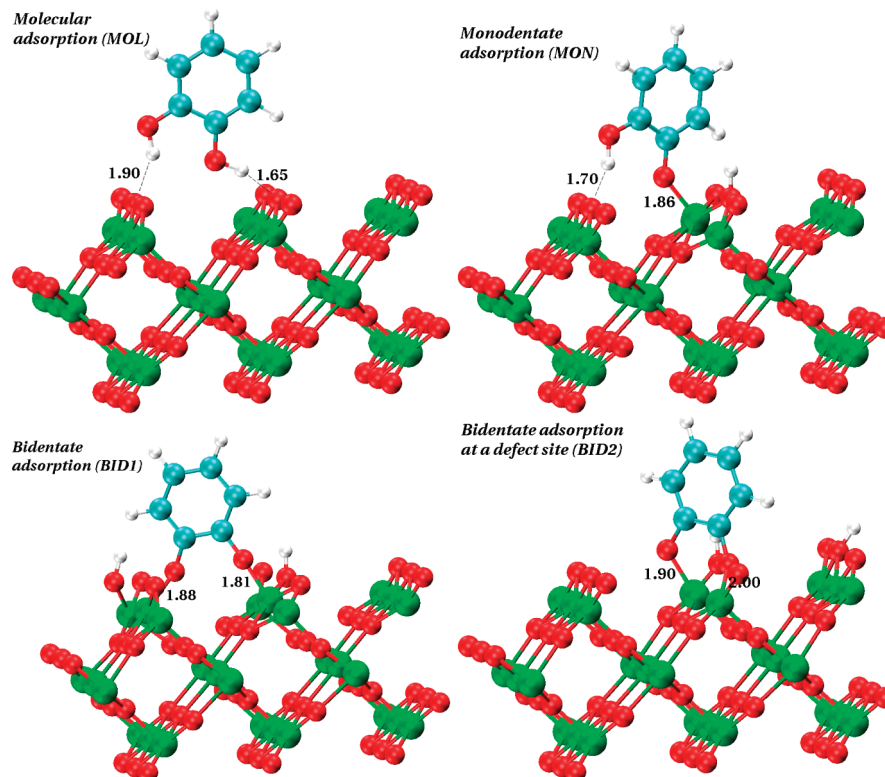


Figure 3. Geometries of the optimized four adsorption modes. Ti atoms are represented in green, O in red, C in cyan, and H in white. Hydrogen bonds are indicated by dashed lines, and bond lengths are expressed in Å.

Interaction Catechol–TiO₂. Here, we will illustrate the results for the adsorption of the catechol on TiO₂. This small dye can be present in solution as a neutral, partially dissociated, or fully dissociated species. For each of them, we investigated a possible type of interaction.

Adsorption Geometries. A molecular (MOL), a partially dissociative monodentate (MON), and two fully dissociative bidentate adsorption modes (BID1, BID2) were studied. When removed from catechol, hydrogens were bonded to the nearest two-fold-coordinated oxygens at the surface.

The four optimized structures are shown in Figure 3. In every mode, the Ti ions bonded to catechol are displaced outward, so as to favor the interaction. In MOL, both of the OH groups of the neutral catechol form two hydrogen bonds with distances of 1.90 and 1.65 Å to two two-fold-coordinated O atoms of the substrate. In MON, one oxygen of catechol bonds to a five-fold-coordinated Ti with a distance of 1.86 Å. The OH group interacts by a hydrogen bond with a two-fold-coordinated oxygen at a distance of 1.70 Å. The two bidentate modes, BID1 and BID2, differ in the adsorption site. In BID1, both oxygens of catechol bond to two five-fold-coordinated Ti of the stoichiometric surface, with distances of 1.88 and 1.81 Å. To study BID2, the dye was adsorbed at a defect site of the (3 × 3) unit cell (cf. Figure 2 with one oxygen removed). Here, a neutral O is removed from the top plane, causing the reduction of the surface and the formation of two four-fold-coordinated Ti. Before adsorbing the dye, this new supercell was relaxed, which resulted in diffusion of a subsurface oxygen; however, upon adsorption of catechol, this diffusion was reversed. Details of the defect structure will be presented in a separate publication as it is not relevant for the bound catechol. After being adsorbed with its two O's bonded to the same four-fold-coordinated Ti, the dye underwent a rotation of 27° around [100], which caused both of the four-fold-coordinated Ti's to bond the OH groups with distances of 1.90 and 2.00 Å. As pointed out in earlier

TABLE 3: Adsorption Energies (eV) of the Four Interaction Modes^a

mode	supercell size			
	(3 × 3)	(3 × 4)	(4 × 3)	(4 × 4)
MOL	−0.33	−0.39	−0.37	−0.39
MON	−0.88	−0.93	−0.87	−0.92
BID1	+0.11	+0.00	+0.14	+0.04
BID2	−2.05	−2.09	−2.06	−2.10

^a See text for the abbreviations of modes.

studies on rutile surfaces,^{44–46} a correct description of the oxygen vacancies would require spin-polarized calculations. The removal of a neutral oxygen, in fact, introduces two more electrons in the surface, which distribute on Ti ions below. Accordingly, spin-polarized calculations were also carried out. The relaxed structure, however, was identical to the (starting) spin-paired one, with a difference between the positions of correspondent ions of less than 0.01 Å and a negligible change in the energy of the supercells (0.12 eV) and in the DOS.

Adsorption Energies. The adsorption energies E_{ads} were evaluated according to the formula

$$E_{\text{ads}} = E_{\text{cat+rut}} - E_{\text{rut}} - E_{\text{cat}} \quad (3)$$

Here, $E_{\text{cat+rut}}$ is the energy of the supercell containing the adsorbed structure, while E_{rut} and E_{cat} are the energies of the same supercell with, respectively, only the dye or the substrate.

Table 3 reports the adsorption energies relative to the different modes. Very similar results are given by supercells bigger than a (3 × 3), which gives confidence in its use in the following calculations on the electronic structures. Moreover, we repeated the calculations for one of the modes (MON) using a thicker five-layer slab. The adsorption energy that we found in this case

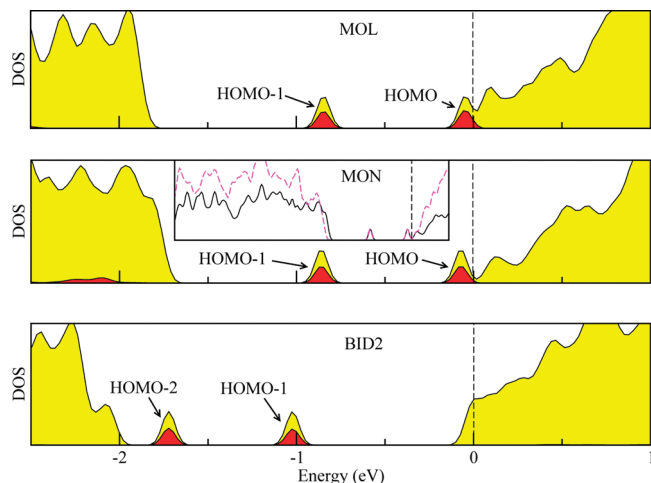


Figure 4. Electronic structures of the three adsorption modes. In yellow is plotted the total DOS, and in red is its projection on catechol. The Fermi energies are marked by dashed lines. Inset: total DOS of MON on a three-layer (black) compared with a five-layer (purple) slab.

is -0.83 eV, which is close to the -0.88 value obtained for the three-layer, suggesting that the slab thickness has little effect on the adsorption energy. We found BID1 to have a positive adsorption energy (for various starting configurations and positions of hydrogens in the surface) and did not investigate it further. This result seems to be a peculiarity of the rutile (100) surface since the same interaction is energetically favored on the five-fold-coordinated Ti of rutile (110)³² and anatase (101).⁴⁷ Similarly to what has been found for the (110) face,³² MON is the most favored in the stoichiometric (100), followed by MOL.

Even though an experimental estimate of the oxygen vacancy concentration on the stoichiometric (100) surface is lacking in the literature, it has been reported several times that the more characterized (110) face presents a typical range of 5–10%.⁴⁸ Since the oxygen vacancy formation energies for the (110) and (100) are very close to each other (3.66 and 3.73 eV, respectively⁴⁹), we believe it is reasonable to suppose that, under typical experimental conditions, the oxygen vacancy concentration, and hence the fraction of catechol in BID2 when a monolayer dye coverage is reached, will also be around 5–10%. For this interaction, much greater values of E_{ads} are obtained. This is not totally unexpected since the removal of an O atom from the top layer increases the reactivity of the Ti atoms below. Moreover, a similar result has been obtained for the adsorption of catechol on anatase (101).⁴⁷

Electronic Structures. First, we would like to stress that there is little justification for identifying KS eigenvalues from DFT calculations with system eigenvalues (except for the highest occupied one, which corresponds to the negative of the lowest ionization potential). However, they have already been successfully employed in the study of the dye–TiO₂ interface,^{47,50,51} giving useful information about the electronic structure of systems otherwise too large to be treated with more sophisticated approaches such as time-dependent DFT (TDDFT).

Figure 4 shows the total DOS for the different modes of adsorption, together with the projected DOS (PDOS) on catechol. In MOL and MON, HOMO–1 is located inside of the band gap of TiO₂, while the HOMO is very close to the CB. In BID2, the surface has been reduced, and the two electrons coming from the removal of the surface O occupy the HOMO at the bottom of the CB. HOMO–2 and HOMO–1 represent now the highest occupied states on catechol, and their localization is, without any ambiguity, inside of the band gap. We note that the position of the HOMO can be related to the increase of the adsorption energy; it constitutes the edge of the CB in MOL ($E_{\text{ads}} = -0.39$ eV), is pushed toward the gap in MON ($E_{\text{ads}} = -0.92$ eV), and is located inside of the gap in BID2 ($E_{\text{ads}} = -2.10$ eV).

In order to evaluate any possible effect of the finite slab thickness on the electronic structure, we compared the DOS of MON with that resulting from a five-layer slab (Figure 4, inset). While the use of the thicker slab causes the valence band of the oxide to be pushed down by about 0.1 eV, the qualitative shape of the DOS and, most important of all, the relative position of HOMO and CB remain unaltered.

It is generally recognized that, due to the discontinuity of the exchange and correlation potential,⁵² HOMO–LUMO gaps are systematically underestimated by DFT. For this reason, we are not able to determine the relative position of the gap states and the bottom of the CB. The HOMO, in particular, may be located well inside of the semiconductor gap. However, our electronic structures, predicting that both HOMO–1 and HOMO are two dye states inside of the band gap, are consistent with the TDDFT-PW91 finding that the lowest excitation in the catechol–Ti system is dominated by the (catechol $\rightarrow$ Ti) transitions HOMO–1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO+2.⁴ Furthermore, there are no contributions from the adsorbate to the lowest unoccupied levels in any of the three modes. This is in agreement with the attribution of the lowest unexpected absorption at 420 nm to a direct charge-transfer excitation from the dye to the Ti levels at the bottom of the CB.¹⁴

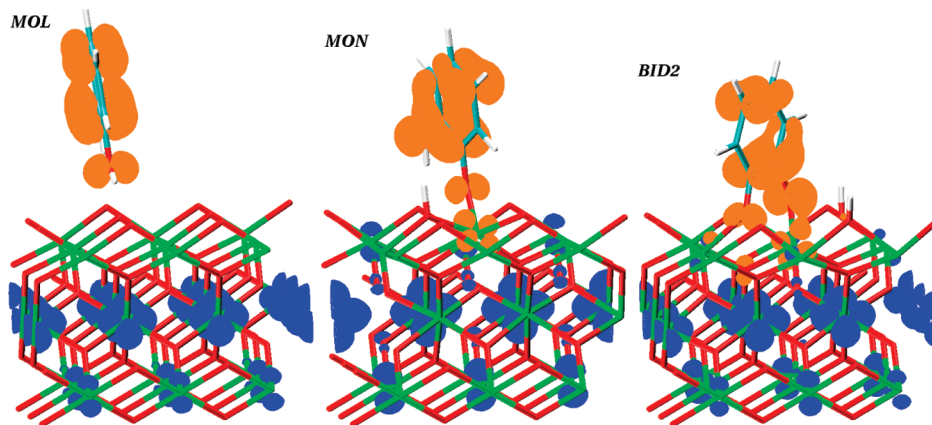


Figure 5. Isosurfaces of $0.03 \text{ e}/\text{\AA}^3$ relative to the HOMO–CATs (orange) and LUMOs (blue) of the three modes viewed from [010]. (Left) molecular adsorption; (middle) monodentate adsorption; (right) bidentate adsorption at a defect site. Ti atoms are represented in green, O in red, C in cyan, and H in white.

In a recent publication,³² Li et al. have reported that when the stoichiometric (110) rutile face constitutes the substrate for catechol, only a bidentate adsorption can introduce occupied band gap states. Here, we find that all of the stable adsorptions investigated in the (100) plane are potentially able to do that, a favorable characteristic for the light harvesting of the catechol–TiO₂ system.

For every interaction mode, the highest occupied molecular orbitals whose projection is localized on catechol (HOMO–CATs, that is, HOMO, HOMO, and HOMO–1, respectively, for MOL, MON, and BID2 in Figure 4) are displayed in Figure 5, together with the respective LUMOs. As predicted by the previous PDOS analysis, HOMO–CATs (and HOMO–CATs–1, not shown) are localized on catechol. On the contrary, LUMOs (and more generally all levels at the bottom of the CB, not shown) are centered exclusively on the substrate, particularly on Ti ions at the second layer.

Conclusions

We have investigated, within a DFT approach, four different adsorption modes of the catechol dye on the TiO₂ rutile (100) surface. Results from these calculations show that, differently from what has been reported in the literature on other TiO₂ faces, the bidentate adsorption of catechol is not stable on the stoichiometric (100). A bidentate interaction on a partially reduced surface, where a single oxygen in the topmost layer has been removed, is found to be the most favored. On the clean surface, monodentate interaction is more stable than molecular physisorption. Our study suggests that the monodentate mode is the most likely, if the assumption of typical oxygen vacancy density is made.

Regardless of the type of interaction, however, the lowest unoccupied states of the system present contributions only from the substrate, while two occupied molecular states are introduced into the band gap. The electronic structure for these binding modes fit into the general understanding of the charge-transfer mechanism at the catechol–TiO₂ interface, which is thought to be direct from catechol to the semiconductor and not to involve any excited states of the dye.

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