Quantum-chemical investigations of phenol and larger aromatic molecules at the TiO$_2$ anatase (101) surface

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Abstract. Adsorption of aromatic molecules at the (101) surface of titanium dioxide anatase is studied by quantum-chemical B3LYP computations, where both cluster and periodic calculations were performed and compared. For phenol different adsorption modes at a TiO$_2$ cluster were mapped out and the energetically most favourable conformation was used for investigation of the electronic structure, for periodic calculations, and as a mould for the adsorption modes of phenylmethanol, phenylethanol, naphthalen-2-ol, phenanthren-2-ol, pyren-2-ol and perylen-2-ol. The alcohols form a H-bond to a surface O and a O(molecule)-Ti bond. For the larger aromatic molecules their increasingly higher HOMO levels decrease the effective band gap of the system. Inclusion of spacer groups as in phenylmethanol and phenylethanol results in higher adsorption energies and larger band gaps. The LUMOs for the adsorbates help visualize the electronic coupling to the surface. Comparison of the cluster with the periodic model indicates that the former describes the electronic coupling in a similar manner as the latter, although the former lacks in the description of the anatase substrate.

1. Introduction

Dye-sensitized solar cells (DSSC) owe their enhanced photovoltaic capability to organic dye molecules that are chemisorbed in a monolayer on a spongy nanocrystalline metal oxide electrode, which allows for absorption of a wider range in the solar light spectrum [1]. The metal oxide is most commonly titanium dioxide with the anatase or rutile crystal structure. The electron excited by the photon in the dye is subsequently injected into the conduction band of the semiconductor. Part of the efficiency of the cell depends on a sufficiently high rate of this injection, which can be related to the degree of overlap between the dye LUMO level with the metal oxide’s conduction band. This makes it of interest to study systematically the electronic coupling between aromatic molecules and the TiO$_2$ surface. During the last few years several experimental [2-6] and theoretical [7-12] studies have been performed for different aromatic organic molecules at the titanium oxide surface, with e.g. various conjugated-system sizes or anchor groups. In this paper we study the adsorption at the anatase surface for aromatic alcohols from phenol to perylenol, and for phenol with CH$_2$ and C$_2$H$_4$ spacer groups.

2. Method

The adsorption of molecules on the anatase (101) surface of titanium dioxide was studied both using a cluster and a periodic model. The cluster consists of 8 Ti, 14 O and 4 OH-groups (figure 1a) chosen to represent the outermost atoms of a (101) surface. The OH-groups were added at the corners

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to neutralize the cluster. In the geometry optimization these OH groups, the four Ti they bind to, and the two O between these Ti, were kept fixed. The periodic model consists of a slab of basically two interconnected sheets of TiO$_2$ units (the slab thus is about twice as thick as for the cluster) with a rectangular surface cell of dimensions 7.67 $\times$ 10.27 Å containing 16 Ti and 32 O atoms (figure 1b) from [8,9]. In the periodic calculations all atoms were allowed to relax. The computations were performed using the hybrid density functional B3LYP and the double-zeta basis set used in [7-10, 13-14]. The Gaussian03 [15] program was used for the cluster and the CRYSTAL [16] program for the periodic computations, with visualization of crystal orbitals as described in [10].

![Figure 1](image1.png)

**Figure 1.** The anatase (101) surface used: a) cluster model b) periodic model.

Phenol was attached to the cluster at different initial positions and the structure was energy-minimized to elucidate the optimal way of adsorption. Both the undissociated and the dissociated (deprotonized) forms of phenol were tested. The energetically most favorable mode was then selected as adsorption mode also for the larger molecules (figure 2) and for phenol in the periodic computations. CH$_2$ spacer groups were added in phenol (phenylmethanol and phenylethanol, figure 2) to vary the distance between the conjugated system and the surface. Alternatively, the conjugated system was extended by merging additional benzene rings to phenol (naphthalen-2-ol, phenanthren-2-ol, pyren-2-ol and perylen-2-ol, figure 2). The molecule plus cluster was geometry-optimized while keeping the surface fixed at the optimized structure from the phenol plus surface calculation.

![Figure 2](image2.png)

**Figure 2.** The adsorbates: phenol, with spacer groups added, and larger aromatic molecules.

Adsorption geometries, energies, and the electronic structures were analyzed, and the HOMO and LUMO orbitals and the lowest unoccupied orbital mainly located on the adsorbate, LUMO(ads), were visualized and investigated.

3. Results and discussion

3.1. The adsorption geometry for phenol

The different adsorption geometries for phenol at the cluster surface and the corresponding energies are given in figure 3 and table 1. The undissociated phenol forms a H-bond to a O(surf) and usually a
monodentate bond from the adsorbate-O to Ti, whereas the deprotonized phenol may form bi- or tridentate bonds to different Ti atoms. The undissociated phenol is generally more strongly bound to the surface than the deprotonized form.

In the energetically most favorable mode phenol forms a monodentate bond to Ti1 and a H-bond to O6 in figure 1a. The adsorption energies (table 1) from the periodic slab computations (figure 4) for the two most stable modes agree well with those from the cluster. For mode “a” the distance from the O in the hydroxyl group to Ti1 is 2.37 Å/2.32 Å and the H-O6 distance is 1.85 Å/2.16 Å for the cluster and periodic model, respectively. The surface Ti1-O6 distance is 3.89 Å/3.93 Å. The H in the OH group is somewhat more twisted out from the benzene ring plane in the cluster than in the periodic case (7° and 2° respectively). For both models the benzene ring is tilted ~30° from the normal of the surface.

Figure 3. The different geometries for phenol attached at the cluster surface.

Table 1. Coordination properties and adsorption energy for the different modes. The adsorption sites for the OH-group of phenol at the surface are given. Bold numbers are for the periodic model.

| Geometry | O(ads) to Ti number | H to O(surf) number | State of the alcohol group | Adsorption energy (kJ/mol) |
|----------|------------------|--------------------|--------------------------|---------------------------|
| a        | 1                | 6                  | undissociated            | 92, **96**                |
| b        | 1                | 8                  | undissociated            | 82, **91**                |
| c        | 1                | 8                  | undissociated            | 78                        |
| d        | 1,2,4            | 10                 | deprotonized             | 43                        |
| e        | 1,4              | 8                  | deprotonized             | 56                        |
| f        | 1,2              | 8                  | deprotonized             | 26                        |

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3.2. The electronic structure of phenol at the anatase surface

For the most stable adsorption mode of phenol the electronic density of states, DOS, and molecular orbitals were calculated for both the cluster and periodic models (figure 5). The DOS for the cluster model has a considerably larger band gap than the periodic, but the projected DOS (PDOS) on the adsorbate AOs are similar. The MOs are shown in figure 6. The HOMO (just below -6.0 eV) is localized at the adsorbed molecule while LUMO consists of d orbitals of Ti. The lowest unoccupied MO localized on the adsorbate, LUMO(ads) lies at 0.0 eV for both models, and shows a non-negligible coupling with the surface, as evidenced foremost by the Ti d orbital amplitudes.

![Figure 4. Phenol in adsorption mode “a” at the periodic surface.](image)

![Figure 5. DOS for the cluster and periodic models of phenol@anatase, and PDOS for the molecule (filled area). Smoothed by Gaussian function convolution.](image)

![Figure 6. HOMO, LUMO and LUMO(ads) for phenol at the cluster (a) and at the periodic surface (b).](image)

| Adsorbed molecule | Adsorption energy kJ/mol |
|-------------------|--------------------------|
| phenol            | 92                       |
| phenylmethanol    | 118                      |
| phenylethanol     | 116                      |
| naphthalenol      | 91                       |
| phenanthrenol     | 93                       |
| pyrenol           | 94                       |
| perylenol         | 95                       |
3.3. Adsorption of larger molecules

The adsorption energies for the molecules with spacer groups and larger aromatic ring systems are shown in Table 2. Increasing the aromatic systems does not change the adsorption energy compared to phenol significantly. Interestingly, inclusion of CH$_2$ or C$_2$H$_4$ spacer groups results in notably higher adsorption energies, possibly due to the breakage of conjugation to the alcohol O. This was not seen in previous studies where phosphonic and carboxylic instead of alcoholic anchor groups were used [10].

The molecular orbitals HOMO, LUMO and LUMO(ads) for phenylethanol, naphthalenol and perylenol adsorbed at anatase are shown in figure 7. The situation is similar to that of phenol in that the HOMO is localized on the adsorbate and the LUMO on the surface, and LUMO(ads) is well localized on the molecule but with a surface Ti d coupling.

![Figure 7. HOMO, LUMO and LUMO-ads for a) phenylethanol b) naphthalenol and c) perylenol at the anatase cluster.](image)

The DOS for the molecules with spacer groups (figure 8) show that the HOMO level is stabilized compared to that in phenol, resulting in a slightly larger band gap. The LUMO(ads) is approximately unaffected by the spacer group. In the DOS for the larger aromatic molecules (figure 9) more occupied adsorbate levels with successively higher energies are introduced into the anatase band gap with increasing aromatic system size, thereby reducing the LUMO-HOMO difference. For example, for the pure anatase cluster the band gap is 5.59 eV (table 3), and with phenol respective perylenol adsorbed the band gap becomes 4.12 eV and for 2.83 eV, respective. One can also see from figure 9 that the LUMO(ads) moves to lower energies with increasing aromatic size. For phenol LUMO(ads) is located 32 orbitals above the LUMO level but for the perylenol it lies only three orbitals above. From table 3 it
also appears that exciting an electron from HOMO to LUMO(ads) will require approximately the same amount of energy in the adsorbate-surface system as in the free molecule.

Table 3. The LUMO-HOMO energy difference (in eV and nm) for the free molecules, the anatase cluster, the molecules at the surface, and within the adsorbed molecule.

|                        | LUMO - HOMO | LUMO(ads) - HOMO | LUMO - HOMO |
|------------------------|-------------|------------------|-------------|
|                        | E (eV)  | λ (nm) | E (eV)  | λ (nm) | E (eV)  | λ (nm) |
| anatase, cluster       | 5.59    | 222    | 3.91    | 317    |         |        |
| anatase, periodic      | 4.12    | 301    | 6.21    | 200    | 6.02    | 206    |
| phenol                 | 4.69    | 265    | 6.42    | 193    | 6.50    | 191    |
| phenylmethanol         | 4.47    | 278    | 6.53    | 190    | 6.59    | 188    |
| phenylethanol          | 3.23    | 384    | 4.47    | 277    | 4.61    | 269    |
| naphthalenol           | 3.56    | 348    | 4.75    | 261    | 4.65    | 267    |
| phenanthrenol          | 3.16    | 393    | 3.85    | 322    | 3.85    | 322    |
| pyrenol                | 2.83    | 439    | 3.02    | 410    | 3.06    | 406    |
| perylenol              | 2.19    | 567    |         |        |         |        |

3.4. Rotation of the benzene ring in phenol

The effect of how the relative ring position in phenol influences the band gap and the molecular orbitals was studied. The OH-group was kept fixed at the cluster surface while the benzene ring was rotated around the CO-axis. The energy variation relative the energy minimum upon rotation is shown in figure 10. The minimum is at 0°, and at approximately 75° and 115° the rotation energy has
maxima and at 90° a faint local minimum. When the benzene ring is rotated the band gap varies between 4.1 to 4.5 eV (figure 11), which correspond to wavelengths from 301 to 274 nm. It is foremost the variation of the HOMO energy that affects on the band gap.

![Figure 10. Energy required to rotate the ring.](image1)

![Figure 11. MO energies during rotation.](image2)

The molecular orbitals HOMO, LUMO and LUMO(ads) for phenol upon rotation of the benzene ring are shown in figure 12. The appearance of the HOMO and LUMO are not much affected by the rotation, but for LUMO(ads) the orbital distribution changes from being located at the molecule to be delocalized over both the molecule and the anatase cluster. When the ring is rotated by 90° and 135° a noticeable part of the orbital is delocalized to the anatase cluster.

![Figure 12. HOMO, LUMO and LUMO(ads) when the ring is rotated in steps of 45°.](image3)
4. Conclusions
In the energetically most favored adsorption mode of phenol at the anatase (101) surface according to the present B3LYP calculations, phenol is chemisorbed in an undissociated manner and forms an O(alcohol) – Ti(surface) bond and a H-bond with a surface oxygen. The HOMO is localized at the adsorbed molecule while LUMO is localized at the surface (Ti d orbitals). If spacer groups are introduced between the alcoholic group and the benzene ring, the adsorption energy increases. The effective band gap also increases due to stabilization of the HOMO orbital. When the aromatic ring system of the molecule is augmented the adsorption energy is relatively unaffected. The band gap decreases due to the increased amount of higher energy adsorbate orbital levels introduced into the anatase band gap. When the benzene ring of the phenol adsorbate is rotated, the degree of localization of the LUMO(ads) orbital changes from being mainly localized to phenol to being significantly delocalized to the surface, which points to the possibility of manipulating the electronic coupling by molecular construction [7]. This may be of importance when novel dye-sensitized solar cell devices are to be created.

When the rather crude cluster model is compared to the periodic model, it is seen that the cluster model for example exaggerates the band gap, but it still manages to capture some of the essential features of the electronic LUMO(ads)-surface coupling.

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