

# Comparative Study of the Adsorption of Aromatic Pollutants onto TiO<sub>2</sub> (100) Surface via Molecular Simulation

Hilal S. Wahab<sup>A,C</sup> and Andreas D. Koutselos<sup>B</sup>

<sup>A</sup>Al-Nahrain University, College of Science, Department of Chemistry, PO Box 64090, Al-Jadriya, Baghdad, Iraq.

<sup>B</sup>National and Kapodistrian University of Athens, Chemistry Department, Zografou 15771, Athens, Greece.

<sup>C</sup>Corresponding author. Email: hswahab@gmail.com

The adsorption mode of benzoic acid onto the anatase TiO<sub>2</sub> (100) surface has been studied through the semi-empirical self-consistent field molecular orbital method MSINDO and is compared with previously determined modes of four aromatic compounds: chlorobenzene, aniline, *p*-chlorophenol and nitrobenzene. The simulation results reveal that aniline and *p*-chlorophenol molecules are adsorbed with their aromatic ring positioned parallel to the surface although they are linked to a surface lattice titanium atom via the amino nitrogen and phenolic oxygen respectively. In contrast, chlorobenzene, nitrobenzene and benzoic acid are found in perpendicular configurations and they are attached to the surface via the chlorine and oxygen atoms of the NO<sub>2</sub> and COOH groups respectively. The calculated substrate–surface interaction energy is influenced by the degree of basicity of the lone pair of the donating atoms, the number of linkages between the substrate and the surface and, further, the hydrogen bonding between the acidic hydrogen and lattice oxygen atom. The computed vibrational density of states for these adsorbed organic pollutants is in reasonably good agreement with available experimental data and previous theoretical results.

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## Introduction

Organic moieties are widely distributed pollutants in the environment. They are classified as high-priority pollutants owing to their toxicity, persistence, carcinogenicity and low biodegradability.<sup>[1–4]</sup> Several authors have observed that there is a clear relationship between the adsorbability of organic molecules onto the surface of TiO<sub>2</sub> and their photocatalytic oxidation.<sup>[5,6]</sup> Furthermore, there is some evidence to indicate that the degradation of organic pollutants occurs on the surface of the photocatalyst.<sup>[7]</sup> It is therefore logical to expect that the adsorption of organic substrates is an important factor for a detoxification process to be highly efficient.<sup>[8]</sup>

The surface of a solid corresponds to a fracture of the lattice. Consequently, the surface atoms do not have their full arrangement of neighbours as in the bulk and their coordination number is smaller. As a result, when in contact with a gaseous or liquid phase, a clean surface will spontaneously accumulate molecules from the fluid phase through chemisorption or physisorption processes.<sup>[9]</sup> Moreover, the adsorption of organic compounds onto TiO<sub>2</sub> surfaces is generally governed by several parameters.<sup>[10]</sup> For instance, the inductive or mesomeric effect of the substituted groups on the aromatic ring plays a significant role.<sup>[11]</sup> Vasudevan and Stone<sup>[12]</sup> have investigated the adsorption of aromatic compounds possessing pairs of ligand donor groups, viz. catechol, 2-aminophenol and 1,2-phenylenediamine, onto the TiO<sub>2</sub> surface. The authors concluded that the organic

molecules possessing donor groups with the highest ionic contribution to bonding adsorb to the greatest extent owing to the high ionic properties of TiO<sub>2</sub> surface. This conclusion was confirmed by other researchers<sup>[13,14]</sup> whose results have shown a higher percentage of degradation on the TiO<sub>2</sub> surface for 4-chlorocatechol than for 4-chlorophenol, because catechol is adsorbed through two donor groups<sup>[13]</sup> whereas 4-chlorophenol is adsorbed only through a single hydroxyl group.<sup>[14]</sup> Further, the adsorption and photodegradation of aniline and *N,N*-dimethylaniline, in acidic and alkaline media, have been examined by Canle et al.<sup>[15]</sup> using three TiO<sub>2</sub> powders: anatase, rutile and Degussa P25. Their results indicated that the main interaction between the surface of the catalyst and aniline or *N,N*-dimethylaniline takes place through the non-bonding electron pair of the amino group.

The adsorption of aromatic substrates on TiO<sub>2</sub> surfaces usually exhibits different geometries. Some researchers<sup>[16,17]</sup> have found a perpendicular conformation of the benzene ring on the surface for the chemisorption of benzoic acid<sup>[16]</sup> and 4-chlorophenol.<sup>[17]</sup> In contrast, Robert et al.,<sup>[10]</sup> from their diffuse-reflectance Fourier infrared spectroscopic (DRIFT) chemisorption study of phenol and *p*-nitrophenol, have suggested the possibility of a parallel adsorption of the aromatic ring.

Substantial literature investigations on the treatment of organic pollutants by advanced oxidation processes have been published.<sup>[4,8,11–15,18]</sup> Although most of the studies have

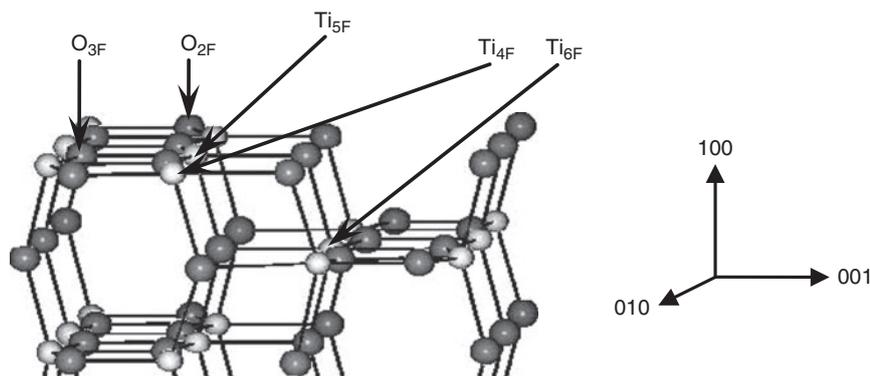


Fig. 1. The anatase  $\text{TiO}_2$  (100) surface. Light spheres represent titanium atoms and dark spheres represent oxygen atoms.

focused on the role of adsorption in the photocatalytic degradation of organic moieties, limited literature is available on their adsorption geometries onto the  $\text{TiO}_2$  surface. Here, we study the adsorption configuration obtained for benzoic acid (BZA) onto the  $\text{TiO}_2$  (100) surface through a computational method. The results are compared with previous work on chlorobenzene (CB),<sup>[19]</sup> aniline (AN),<sup>[20]</sup> *p*-chlorophenol (*p*-CP)<sup>[21]</sup> and nitrobenzene (NB).<sup>[22]</sup>

### Computational Approach

In order to simulate the adsorption of small molecules onto an extended crystal structure of the anatase  $\text{TiO}_2$  (100) surface, we employed the molecular orbital (MO) method MSINDO, which is based on a semi-empirical simplification of complex molecular matrix elements. The method has been extensively documented for the first-, second- and third-row main group elements and first-row transition metal elements.<sup>[23–25]</sup> The main group elements are described by (s, p) basis sets and the transition metal atoms by a (3d, 4s, 4p) pseudo minimal Slater basis set. The intra- and inter-atomic integrals require the use of variable exponents in the Slater basis functions, as in the case of the Pople 6-31G basis set. The anatase  $\text{TiO}_2$  (100) surface is modelled as a three-layer cluster of molecular structure  $\text{Ti}_{36}\text{O}_{90}\text{H}_{36}$ . The extension of the cluster is large enough to acquire the surface properties of the crystal but sufficiently small to ensure efficient computation with the MSINDO method (see Accessory Publication).

The chemical model calculations start with full optimization of all initial geometries of isolated systems, substrate and  $\text{TiO}_2$  surface, and continue with relaxation of the substrate–surface complex to an optimum state. When the two sets of results are compared, conclusions can be drawn for the mechanism of adsorption of a substrate onto the surface. The MO calculations were carried out at the level of the self-consistent field (SCF) method, with convergence criterion better than  $10^{-9}$  Hartree for the energy throughout the calculation. Finally, the inner-shell electrons are taken into account through the use of Zerner pseudo potentials.<sup>[26]</sup>

The direct output of the computation is the structure of the substrate–cluster complex and the energies of the involved species, substrate ( $E^{\text{substrate}}$ ), cluster ( $E^{\text{cluster}}$ ) and substrate–cluster complex ( $E^{\text{substrate-cluster}}$ ). The structure depicts the geometry of the adsorbed complex and the energies can be used for the calculation of the adsorption energy,  $E_{\text{ads}}$ .<sup>[27]</sup>

$$E_{\text{ads}} = E^{\text{substrate-cluster}} - E^{\text{substrate}} - E^{\text{cluster}} \quad (1)$$

Table 1. Adsorption energies,  $E_{\text{ads}}$  ( $\text{kJ mol}^{-1}$ ), for the adsorption of chlorobenzene, aniline, nitrobenzene, *p*-chlorophenol and benzoic acid molecules on the anatase  $\text{TiO}_2$  (100) surface

Molecule	$E_{\text{ads}}$ [ $\text{kJ mol}^{-1}$ ]
Chlorobenzene	–121
Aniline	–192
<i>p</i> -Chlorophenol	–110
Nitrobenzene	–230
Benzoic acid	–276

When the adsorption energy is negative, the complex substrate–cluster is stabilized and adsorption takes place.

In order to estimate the vibrational density of states (VDOS) for the geometries under consideration for the purpose of comparison with the available experimental and theoretical data, isokinetic molecular dynamics (MD) simulations for 2000 fs (2000 steps) at 300 K were performed using the Nose–Hoover Chain thermostat. The VDOS of the selected atoms (carbon, hydrogen, nitrogen and oxygen) in the system were obtained by calculating the Fourier transform of their velocity auto correlation function (VACF) available in the MSINDO framework.

### Results and Discussion

#### Adsorption of Chlorobenzene

The adsorption sites of the anatase  $\text{TiO}_2$  (100) surface consist of two-fold,  $\text{O}_{2\text{F}}$ , and three-fold,  $\text{O}_{3\text{F}}$ , -coordinated O (Lewis base) sites, as well as five-fold,  $\text{Ti}_{5\text{F}}$ , -coordinated Ti (Lewis acid) sites. In addition, four-fold,  $\text{Ti}_{4\text{F}}$ , -coordinated Ti sites, located at the  $(100) \times (010)$  edge, act as Lewis acid sites, though six-fold,  $\text{Ti}_{6\text{F}}$ , -coordinated Ti atoms located in the bulk far from the exposed surface remain inactive (Fig. 1). The interest in the  $\text{TiO}_2$  (100) surface stems from its significant occurrence in anatase powder.<sup>[28,29]</sup> In addition, the (100) surface is isostructural with the (010) surface of  $\text{TiO}_2$ .<sup>[28,30]</sup>

The bonding of the CB molecule to the  $\text{TiO}_2$  (100) surface has been inferred from a study of substrate–cluster optimization starting from a perpendicular initial orientation.<sup>[19]</sup> The attachment develops through the interactions of chlorine atoms to unsaturated surface titanium, in accordance with experimental observations on the catalytic degradation of trichlorophenol.<sup>[31]</sup> The substrate is positioned perpendicularly to the lattice surface and is adsorbed with a release of a rather small energy of  $121 \text{ kJ mol}^{-1}$  (Table 1). However, in this complex, the chlorine

atom is easily detached on excitation, with a weak energy barrier of 27 kJ mol<sup>-1</sup>. Eventually, the phenyl ring is attached to the surface through a bond between a substrate C and a surface O atom. These results are in accordance with experimental analysis of the photocatalytic degradation of chlorinated benzenes in the air.<sup>[32]</sup>

#### Adsorption of Aniline

In order to study the adsorption of AN onto the TiO<sub>2</sub> surface in the past, we initially positioned the molecule in a rather general perpendicular configuration to the surface.<sup>[20]</sup> The simulation of the whole structure showed that the adsorption energy,  $E_{\text{ads}}$ , is negative (Table 1), revealing the exothermic nature of the process. The final relaxed structure is positioned parallel to the surface and is linked to the surface at a five-fold coordinated Ti atom (Ti<sub>5F</sub>) through the amino nitrogen. The bonding thus occurs through the donation of the electron lone pair of nitrogen to an empty d orbital of Ti. This conclusion is in accordance with the results of Canle et al.,<sup>[15]</sup> who suggested that the interaction of aniline and *N,N*-dimethylaniline, in the dark, with the TiO<sub>2</sub> surface is not mediated through the  $\pi$  interaction of the aromatic ring but rather through the amino group.

Additional information about the adsorption process was provided by the comparison of the VDOS calculated for selected atoms in the free (reference) and adsorbed AN. Most of the frequencies of the peaks observed in the VDOS were assigned to vibration modes through comparison with the frequencies of experimental bands.<sup>[33]</sup> Similar bands have been calculated through an *ab initio* MO theory at the HF/6-31+G\* level of accuracy<sup>[34]</sup> in agreement with our results.

By analysing the changes in the frequencies of the N–H and C–N vibration modes between free and adsorbed AN, we obtained local information about the adsorption process. Specifically, the C–N band was found to be shifted on adsorption of AN from 1300 to 1250 cm<sup>-1</sup>. The shift was attributed to the observed weakening and lengthening of the C–N bond.

A second major change occurred for the N–H mode around 3400 cm<sup>-1</sup>, which was found to split into two bands at 3355 and 3398 cm<sup>-1</sup>. This change can be explained by comparing the environment of the hydrogen atoms of the amino group of free and adsorbed AN. Initially, both H atoms are equivalent but on adsorption differentiate, with one of the hydrogen atoms participating in hydrogen bonding with the oxygen of the boundary hydroxyl group. This interaction can explain the red-shift of the stretching band, from 3400 to 3355 cm<sup>-1</sup>. Then, the splitting of the band should be due to the fact that the adsorbed amino group exhibits two different types of hydrogen atoms owing to the difference in their bonding features. In addition, it was confirmed from the VDOS spectra that the AN molecule is adsorbed to the surface through the amino group.

For further support, the net Löwdin charge changes on adsorption were computed. These charges are preferred because they are obtained by a Löwdin analysis of a symmetrically orthogonalized basis calculated through MSINDO and acquire reasonable values of smaller magnitude than the Mulliken ones. It has been observed that the net charge of amino nitrogen decreases on relaxation of the adsorption and the net charge of surface titanium atom slightly increases. Moreover, the net charge of the amino hydrogen atoms has varied noticeably owing to adsorption, because they are impacted by the proximity of the amino nitrogen.

#### Adsorption of *p*-Chlorophenol

In the case of *p*-CP, the molecule was arranged in a perpendicular position to the surface.<sup>[21]</sup> On relaxation, a gradual movement of the substrate was observed, which led eventually to binding of *p*-CP to the surface lattice titanium atom with a negative  $E_{\text{ads}}$  value (Table 1). Further, the plane of the phenolic ring was oriented in a way exhibiting a parallel conformation for the aromatic ring to the surface linked via phenolic oxygen to the surface lattice Ti<sub>5F</sub> atom. This finding is in accordance with the results of Stafford et al.,<sup>[35]</sup> who reported that *p*-CP was adsorbed on dry TiO<sub>2</sub> powder through the formation of a phenolate linkage based on DRIFT spectrometry measurements.

The estimated VDOS of reference and adsorbed *p*-CP molecules indicates primarily weakening of the OH bond owing to red shift of the stretching vibration frequency, which is in accordance with the observed disappearance of the O–H bond by Stafford et al.<sup>[35]</sup> due to the phenolate linkage formation on adsorption.

In addition, the Löwdin charge variation due to adsorption shows a decrease in the charge of phenolic oxygen on relaxation of the adsorption model, and a slight increase in the net charge of the surface titanium atom. This confirms the donation of the electron lone pair of oxygen into an empty d orbital of Ti on adsorption via the phenolic O atom when in a parallel configuration.

#### Adsorption of Nitrobenzene

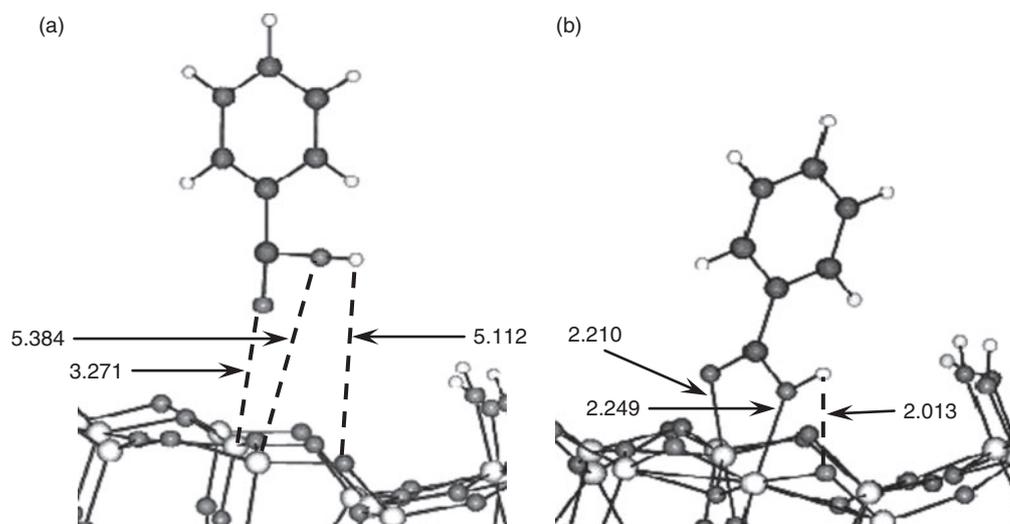
When NB was initially set in an unbound perpendicular configuration away from the anatase TiO<sub>2</sub> (100) surface, the simulation procedure produced a structure with the aromatic ring positioned in a vertical configuration. The NO<sub>2</sub> group was linked to the surface lattice five-fold-coordinated titanium atoms. In addition, it was observed that during relaxation, as the NB molecule approached the surface, the NO<sub>2</sub> group rotated before acquiring its final position. The phenomenon of NO<sub>2</sub> internal rotation has also been observed by Shlyapochnikov et al.<sup>[36]</sup> in their *ab initio* calculations for the vibrational frequencies of the C–NO<sub>2</sub> moiety. The computed  $E_{\text{ads}}$  value of the adsorption mode is negative (Table 1), which indicates the energetic favourability of the adsorption process.

The binding of the substrate onto the TiO<sub>2</sub> (100) surface took place again through the interaction of the oxygen atoms of the NO<sub>2</sub> group with Ti and not through the  $\pi$  interaction of the aromatic ring. We mention that adsorption of NB onto TiO<sub>2</sub> has been inferred indirectly by Bhatkhande et al.<sup>[37]</sup> from photocatalytic experiments.

The adsorption mechanism was also analysed through comparison of the VDOS of selected atoms in the free and adsorbed NB substrate, primarily by the bands at 1348 cm<sup>-1</sup> ( $\Delta\nu = 34.5$ ), 1500 cm<sup>-1</sup> ( $\Delta\nu = 50$ ) and 1535.5 cm<sup>-1</sup> ( $\Delta\nu = 35.5$ ), which show a red shift indicating weakening of C–N and N–O bonds in accordance with the observed increase of bond lengths.<sup>[22]</sup>

The net Löwdin charge variation that stemmed from relaxation of the adsorption model reveals a decrease in the net charge of the nitro oxygen atoms and, further, an increase in the net charge of surface titanium atoms. This is again in accordance with the donation of the electron lone pair of oxygen into an empty d orbital of Ti on adsorption.

From Table 1, we observe that the NB molecule has a lower  $E_{\text{ads}}$  value in comparison with the AN and *p*-CP molecules. This is expected owing to the higher number of linkages between the NB molecule and the anatase TiO<sub>2</sub> (100) surface. However, the



**Fig. 2.** Adsorption of the benzoic acid (BZA) molecule on the  $\text{TiO}_2$  (100) surface: (a) starting conformation; (b) equilibrated conformation. Dashed lines represent distances. Ti, large light; H, small light; O, small dark; C medium dark spheres.

AN moiety has a lower  $E_{\text{ads}}$  value than the *p*-CP molecule, which is attributed to the higher basicity of the amino N atom in comparison with the phenolic O atom.

#### Adsorption of Benzoic Acid

After having described the adsorption of organic moieties that contain chlorine, basic nitrogen, and one and two oxygen atoms interacting with the  $\text{TiO}_2$  surface, we proceed here to examine the mechanism of adsorption of BZA, which contains two oxygen atoms and a rather strongly acidic hydrogen.

As in the previous cases, the molecule was initially positioned perpendicular to the cluster surface (Fig. 2a). On optimization, it was observed that the substrate approached the surface with the two oxygen atoms bridged-bonded to lattice  $\text{Ti}_{4\text{F}}$  and  $\text{Ti}_{5\text{F}}$  sites, after free rotation of the  $-\text{COOH}$  group had taken place along the vertical axis. Further, the acidic hydrogen atom is involved in hydrogen bonding with the unsaturated two-fold-coordinated,  $\text{O}_{2\text{F}}$ , site. Additionally, the adsorbed molecule has preserved the associative perpendicular conformation at the  $\text{TiO}_2$  surface, with the benzene ring tilting towards the cluster surface (Fig. 2b). The optimization of the BZA molecule exhibited the most negative  $E_{\text{ads}}$  value (Table 1) in comparison with the previously considered organic moieties. This is most likely attributed to the higher number of atom-atom contacts between the substrate and the cluster surface, regardless of the physisorption or chemisorption process taking place.

Sheka et al.<sup>[38]</sup> reported, from a quantum chemical study for the adsorption of carboxylic species on  $\text{TiO}_2$  nanoparticles, that the BZA adsorption pattern over anatase  $\text{TiO}_2$  presented both associative and dissociative modes. A closer look at Fig. 2b reveals the significant role of hydrogen bonding. On one hand, hydrogen bond formation ( $\text{COOH} \cdots \text{O}_{2\text{F}}$ , which probably acts as a precursor to dissociation,<sup>[39]</sup> is induced by the approach of the carboxyl hydrogen atom to the surface lattice oxygen atom. On the other hand, the hydrogen-bonded BZA molecule enhances the interaction, leading to an increase in the adsorption energy.<sup>[30]</sup>

From Table 2 and Fig. 2b, we notice an elongation in the  $\text{COO-H}$  bond and a decrease of the distance between the carboxyl hydrogen atom and the surface  $\text{O}_{2\text{F}}$  oxygen atom respectively.

**Table 2.** Computed geometry parameters for the isolated and adsorbed benzoic acid (BZA) molecule (all parameters are in Å and refer to the relaxed structure)

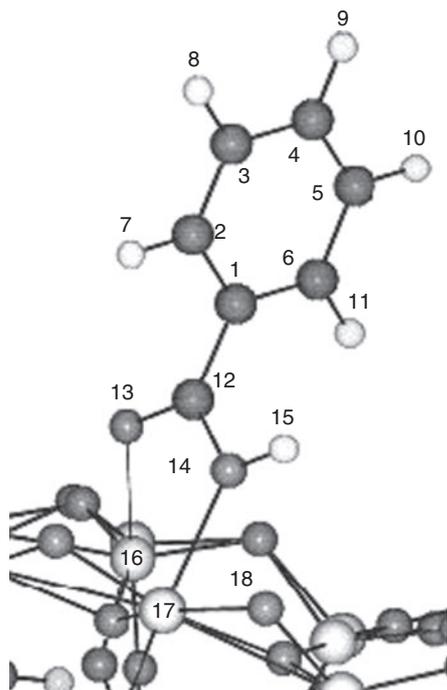
Parameter	Isolated molecule [Å]	Adsorbed molecule [Å]
C=O length	1.219	1.235
C-O length	1.374	1.382
O-H length	0.965	0.975
O-C-O angle [°]	121.6	113.9
C-O-H angle [°]	109.4	112.8
O-C-O-H, dihedral [°]	0.157	177.8

Further information about the adsorption process of BZA onto the  $\text{TiO}_2$  (100) surface is provided through computation of the net Löwdin charge changes due to adsorption (Fig. 3). From the results in Table 3, we observe a decrease in the net charge of carboxylic oxygen and hydrogen atoms on optimization of the vertical adsorption mode of BZA shown in Fig. 2a, and a slight increase in the net charge of the surface lattice titanium and oxygen atoms. This is likely ascribed to the charge-transfer process during adsorption, which has also affected the aromatic-ring carbon atom ( $\text{C}^{12}$ ). The transfer of electron density to two or even more Ti sites has also been reported by Bermudez.<sup>[40]</sup>

An interesting observation from Table 3 is that the computed Löwdin charges for oxygen and hydrogen atoms ( $\text{H}^{15}$  and  $\text{O}_{2\text{F}}^{18}$ ), which participated in hydrogen bonding (Fig. 2b), reveal a remarkable difference in charges due to adsorption. In agreement with this observation, the adsorption of the BZA molecule exhibits a more negative  $E_{\text{ads}}$  value, and hence higher stability, than the NB molecule (Table 1).

No experimental evidence for the adsorption configuration of BZA onto the  $\text{TiO}_2$  (100) surface has been yet reported. However, Dobson and McQuillan<sup>[41]</sup> have concluded, from their analysis of the adsorption of aromatic carboxylic acids on  $\text{TiO}_2$  and  $\text{Ta}_2\text{O}_5$ , a weak adsorption of BZA on the  $\text{TiO}_2$  surface.

Further support for the above findings is provided by the VDOS for selected atoms in the model seen in Fig. 2b together with the free reference (non-adsorbed) BZA molecule. The resulting VDOS are presented in Fig. 4a and b. The spectrum of the reference BZA molecule, Fig. 4a, includes bands located

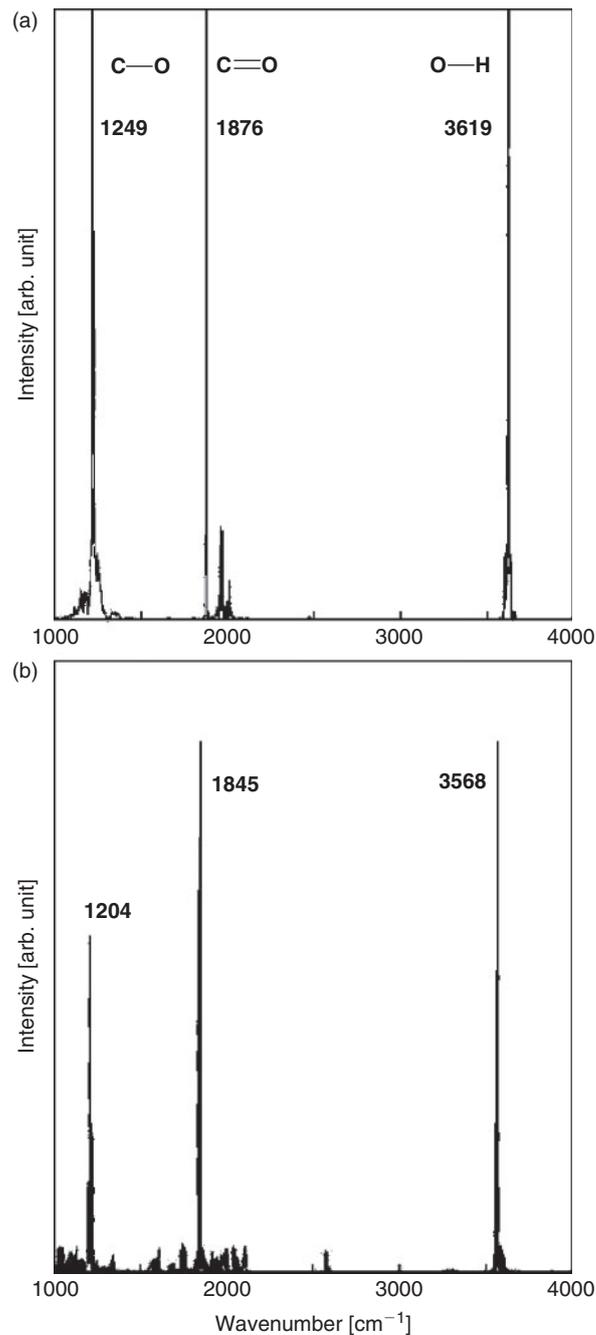


**Fig. 3.** Model of the adsorbed benzoic acid (BZA) molecule at the surface lattice titanium atom.

**Table 3.** Computed net Löwdin charge changes (au) of atoms in the isolated and adsorbed benzoic acid (BZA) molecule on the TiO<sub>2</sub> (100) surface (atom numbering is indicated in Fig. 3)

Atom	Isolated	Adsorbed
C <sub>1</sub>	-0.020	-0.106
C <sub>2</sub>	-0.028	+0.003
C <sub>3</sub>	-0.036	-0.029
C <sub>4</sub>	+0.002	+0.001
C <sub>5</sub>	-0.051	-0.031
C <sub>6</sub>	+0.005	+0.005
H <sub>7</sub>	+0.038	+0.070
H <sub>8</sub>	+0.043	+0.055
H <sub>9</sub>	+0.039	+0.048
H <sub>10</sub>	+0.049	+0.054
H <sub>11</sub>	+0.102	+0.050
C <sub>12</sub>	+0.631	+0.721
O <sub>13</sub>	-0.439	-0.358
O <sub>14</sub>	-0.593	-0.497
H <sub>15</sub>	+0.268	+0.337
Ti <sub>16</sub>	+1.342	+1.313
Ti <sub>17</sub>	+1.316	+1.304
O <sub>18</sub>	-0.642	-0.666

at 1249, 1876 and 3619 cm<sup>-1</sup>, which can be assigned to C–O, C=O and O–H respectively. The relevant spectrum of the adsorbed BZA (Fig. 4b) shows shifted bands at 1204 cm<sup>-1</sup> ( $\Delta\nu = 45$ ), 1845 cm<sup>-1</sup> ( $\Delta\nu = 31$ ) and 3568 cm<sup>-1</sup> ( $\Delta\nu = 51$ ). This modification and the accompanying lowering of the corresponding intensity could be attributed to the weakening of the relevant bonds on adsorption causing the C–O, C=O and O–H bonds to elongate (Table 2). Moreover, the observed  $\Delta\nu$  values generally lie within the range expected for bridged-bonded coordination.<sup>[41]</sup>



**Fig. 4.** The vibrational density of states (VDOS) of selected atoms for benzoic acid (BZA) molecule adsorption on the TiO<sub>2</sub> (100) surface: (a) VDOS of free BZA molecule as reference; (b) VDOS of the adsorbed BZA molecule.

## Conclusions

The presented computational results clearly show the organic molecules are adsorbed at the Lewis acid sites of the TiO<sub>2</sub> surface via charge-transfer for the non-bonding electron pair of the Lewis-basic atoms contained in the organic moieties into the empty d orbital of TiO<sub>2</sub>. Further, the adsorbed molecules are oriented in parallel or perpendicular conformations relative to the surface, and the mechanism of the intermolecular interaction between a substrate and a cluster may follow monodentate, bridged-bonding and hydrogen-bonding paths depending on the functional groups of the aromatic moieties.

The substrate–cluster interaction energy is influenced by the degree of basicity of the lone-pair donating atoms and the number of linkages, including hydrogen bonding, between the substrate and the cluster surface.

### Accessory Publication

The simulated three-layer  $\text{Ti}_{36}\text{O}_{90}\text{H}_{36}$  cluster can be found on the Journal's website.

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