

Quantum chemical modeling study of adsorption of benzoic acid on anatase TiO₂ nanoparticles

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Received: 22 August 2011 / Accepted: 24 October 2011 / Published online: 25 November 2011
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Abstract The semi-empirical MSINDO method has been used to investigate the mode of adsorption of benzoic acid on the nano anatase TiO₂ (100) surface. The (100) surface is modeled with a Ti₃₆O₉₀H₃₆ cluster. Molecular dynamics simulations for the adsorption behavior of benzoic acid indicate it is linked to the TiO₂ surface through interactions from the oxygen atoms of the carboxylic acid moiety with surface titanium atoms. The benzoic acid may be positioned with its aromatic ring either parallel or perpendicular relative to the surface, however the perpendicular adsorption mode is more stable. The calculated substrate-surface interaction energy is influenced by the number of linkages between the substrate and the surface as well as the degree of hydrogen bonding between the acid hydrogen and lattice oxygen atom. The greater stability of the perpendicular adsorption orientation is ascribed to the higher number of linkages between the substrate and the surface. It is concluded that the simplified model is sufficiently detailed to elucidate surface interactions.

Keywords Adsorption · Benzoic acid · Model calculations · Molecular dynamics · Titanium oxide

Introduction

In recent years, molecular modeling has gained increasing importance in the study of environmental, chemical and biological processes from a molecular basis [1, 2]. Modeling offers a complementary approach to experimental studies and may be used to gain further insight into the mechanism of such reactions and molecular interactions. This is particularly for the investigation of adsorption processes on a microscopic scale, for which molecular modeling has proven to be a powerful tool [3–5].

The adsorption of aromatic substrates on TiO₂ surfaces may occur through a range of geometries of the aromatic ring. The chemisorptions of benzoic acid [6] and 4-chlorophenol [7] are reported to favor a conformation with the aromatic benzene ring perpendicular to the surface. Robert et al. [8], in their diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic study of phenol and p-nitrophenol chemisorption, have suggested the possibility of a parallel orientation of the aromatic ring relative to the surface.

It has been observed that there is a clear relationship between the photocatalytic oxidation and adsorbability of organic substrates [9]. Moreover, there is evidence that the degradation of organic moieties often occurs on the surface of the photocatalyst [9, 10]. It is therefore logical to expect that adsorption of the organic substrate is an important factor in the efficiency of the detoxification process [10].

The present work is focused on investigating the adsorption of aromatic molecules on the anatase TiO₂ surface, for which benzoic acid (BZA) has been selected as a model compound, in part due to its environmental impact as a common recalcitrant contaminant [11]. We have carried out computational modeling in order to simulate different

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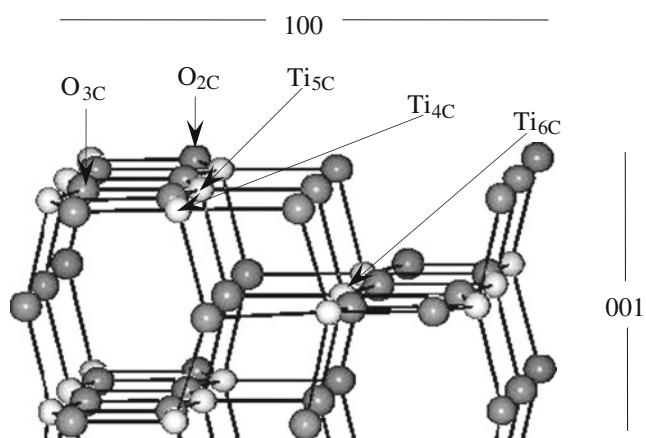
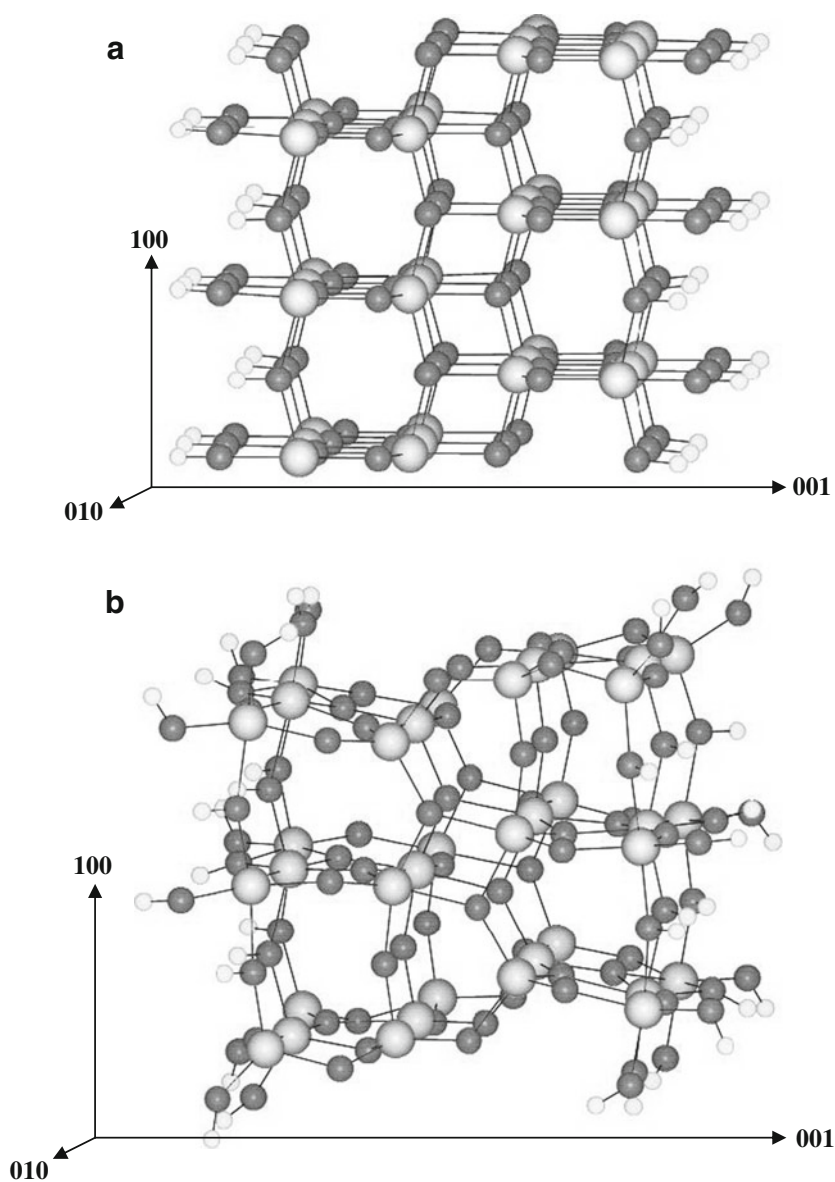


Fig. 1 Anatase TiO_2 (100) surface modeled from $\text{Ti}_{36}\text{O}_{72}$: Light spheres represent titanium atoms and the dark spheres represent oxygen atoms

Fig. 2 (a) Non-relaxed saturated $\text{Ti}_{36}\text{O}_{90}\text{H}_{36}$ cluster; (b) minimum energy structure of $\text{Ti}_{36}\text{O}_{90}\text{H}_{36}$



modes of adsorption of BZA onto the anatase TiO_2 surface, and to probe the electronic properties and stability of the various modes of adsorption. To the best of our knowledge, molecular modeling has not previously been employed for a quantitative analysis of the mode of adsorption.

The combination of reliable accuracy for structures and energies and the speed of computation for large systems make the semi-empirical MSINDO a useful tool for the current study. A study of the scope of a complicated surface reaction mechanism [12] is not feasible with *ab initio* or density functional theory (DFT) methods.

The paper is organized as follows. The computational method is summarized in the next section. Results follow, firstly from a simulation of the cluster adsorption surface and secondly, for the adsorption models of BZA molecule on the anatase TiO_2 surface. Finally, conclusions are reported.

Computational methodology

The quantum chemical model calculations are performed with the MSINDO semi-empirical MO method, which is extensively documented for the first and second row elements [13, 14], and the third row transition metal elements [15]. The transition metal atoms are described by a pseudo minimal Slater basis set (3d,4s,4p), while the first row elements are described by a (2s,2p) basis set with different Slater exponents for intra- and inter-atomic integrals comparable to the Pople 6–31 G basis set.

The first step in the computational approach is to perform a full geometry optimization for all of the isolated systems; the substrate (benzoic acid molecule), TiO₂ clusters and the cluster-substrate complex. The molecular orbital calculations are carried out with the self-consistent field (SCF) method. An energy convergence threshold of 10⁻⁹ Hartree was used in all calculations.

The next step involved the calculation of adsorption energies (E_{ads}) for different BZA adsorption modes according to the following formula [16],

$$E_{ads} = E_b^{TiO_2-BZA} - (E_b^{BZA} + E_b^{TiO_2}), \quad (1)$$

where $E_b^{TiO_2-BZA}$ is the binding energy of the TiO₂-BZA system, E_b^{BZA} is the binding energy of BZA, and $E_b^{TiO_2}$ binding energy of TiO₂. A negative value for E_{ads} indicates a stabilization of the TiO₂-BZA system due to adsorption.

Molecular dynamics (MD) modeling has been used to study the dynamics of certain cluster-substrate (TiO₂-BZA) models, in which the statistical average of the kinetic energy of the system becomes constant when the simulation has reached constant temperature. The MD simulations were carried out for 2000 femtoseconds (2000 steps) at a temperature of 300 K, with a time step of one femtosecond (1 fs). Constant temperature dynamics were performed using the Nosé-Hoover-Chain thermostat.

A saturated Ti₃₆O₉₀H₃₆ cluster model has been employed for modeling the anatase TiO₂ nanoparticle, which is subsequently used as a model of the adsorption surface. In order to circumvent the spin localization phenomenon due to the coordinative unsaturated sites, a similar water saturation strategy was followed, which has been reported in a previous study [17]. This relatively small cluster is utilized in order to avoid excessive computational expense in the subsequent adsorption calculations.

For the sake of clarity and simplification, fixed sizes of the spheres are used for the representation of the atoms for the exhibited models unless otherwise stated; large light spheres for titanium atoms, small light spheres for hydrogen atoms, large dark spheres for carbon atoms and medium dark spheres for oxygen atoms.

Results and discussion

Simulation of the adsorption surface

The extended three layer free cluster, Ti₃₆O₇₂, has been simulated using the MSINDO method. This cluster was subsequently used for modeling the (100) nano anatase surface (Fig. 1), which is normally observed in powder materials [18]. Cluster models are often selected for local processes such as adsorption of single atoms and molecules [16]. In order to avoid boundary effects that often accompany free clusters, the peripheral oxygen and titanium atoms of the free Ti₃₆O₇₂ cluster have been saturated with hydrogen atoms and OH groups, respectively, so that the cluster, Ti₃₆O₉₀H₃₆, is formally saturated with water (Fig. 2a). This technique is often applied to metal oxides of partially covalent nature [19], and is particularly appropriate for semiconductors.

The appropriateness of this model cluster for modeling the adsorption process has previously been verified by comparing calculated anatase bulk properties, heats of atomization and lattice parameters with available accurate literature data [20]. On the nano-sized anatase TiO₂ (100) surface (Fig. 1), which is employed in this work, the exposed atoms are the five-fold-coordinated titanium atoms (Ti_{5C}), representing Lewis acid sites, and the two- (O_{2C}) and three-fold (O_{3C}) coordinated oxygen atoms, which act as Lewis base sites. This unique surface conformation may be in part the source of the mutual reactivity of titanium and oxygen atoms [21]. In the channel along the (010) direction, six-fold coordinated titanium (Ti_{6C}) and O_{3C}

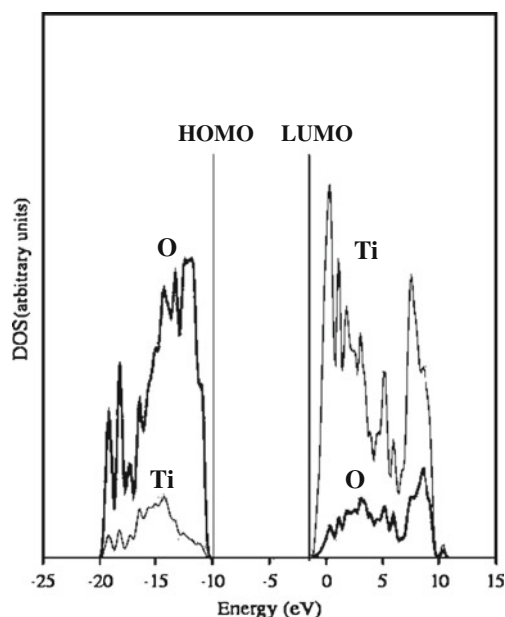
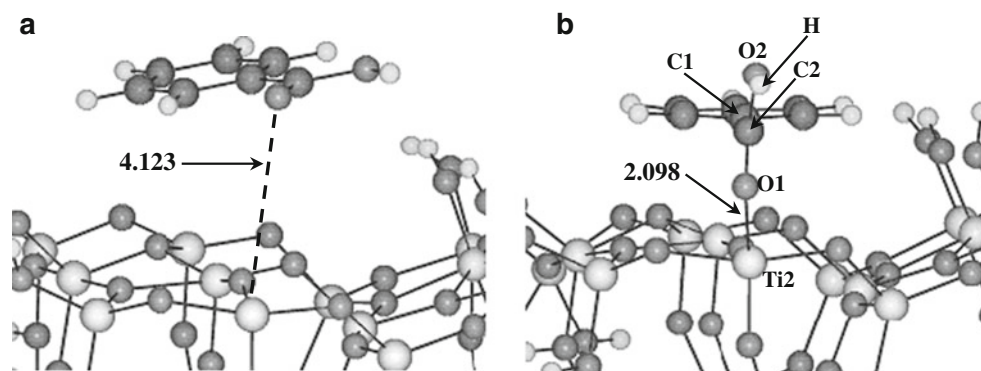


Fig. 3 Density of states (DOS) for the saturated Ti₃₆O₉₀H₃₆ cluster

Fig. 4 MD simulation for the parallel mode of BZA molecule adsorption on TiO_2 (100) surface; **(a)** initial structure and **(b)** minimum energy structure. Dashed lines represent distances



atoms are also present. Moreover, the $(100) \times (010)$ edge contains four-fold coordinated titanium ($\text{Ti}_{4\text{C}}$), which are also Lewis acid sites (Fig. 1).

As long as the surface is explicitly a part of the particle (semi-conductor model), full relaxation of the particle will implicitly relax all the surfaces. The relaxed surfaces exhibit different morphologies and buckled geometries, as is depicted in Fig. 2b.

Further scrutiny of the model surface is provided from the density of states (DOS) of the dual lattice titanium and oxygen atoms (Fig. 3). This analysis reveals that the upper part of the TiO_2 valence band is dominated by oxygen (O 2p) orbitals with small contributions from titanium. The lower conduction band is composed mainly of titanium orbitals (Ti 3d) with a slight anti-bonding (O 2p) character. Accordingly, the contribution of both Ti and O atoms ought to be on one hand proof of the partial covalence of Ti-O bonds, and on the other hand an indication of their simultaneous reactivity.

Adsorption models

There exist several ways that the aromatic ring of BZA may align relative to the TiO_2 surface. In this study we have limited our focus to parallel, perpendicular and hydrogen-bonding conformations, which may be expected to be the most common arrangements.

For the fully relaxed BZA molecule, the C = O and C-O bond lengths are calculated to be 1.219 and 1.374 Å, respectively. These values are in good agreement with

experimental (1.228 and 1.316 Å) and theoretical B3LYP/6-31 G* values (1.224 and 1.356 Å) [22].

Parallel adsorption model

The initial and equilibrated structures for the parallel adsorption geometry of BZA onto the anatase TiO_2 (100) surface are depicted in Fig. 4. The computed E_{ads} of BZA is $-30.27 \text{ kcal mol}^{-1}$ (Table 1). It can be seen that the substrate (BZA) approaches the surface with the carbonyl oxygen atom linking to the $\text{Ti}_{4\text{C}}$ atom, preserving the parallel conformation of the aromatic ring relative to the surface. Zhao and Fang [23] have reported a parallel adsorption configuration of the benzoate ion as a possible adsorption geometry on silver nanoparticles, which was further confirmed theoretically using DFT-B3PW91/lan12dz calculations.

An interesting observation during the MD simulation of BZA adsorption was the tilting of the -COOH group prior to adsorption. This tilting resulted in a variation in the H-O-C = O and C-C-C = O dihedral angles (Table 2). This phenomenon of tilting of an organic ring structure has also been observed by Lee and co-workers [24] in their study of the chemisorption of 4-picoline on the Cu (110) surface.

Löwdin net charges for the initial and adsorbed structures are collated in Table 3. The charges of the carbonyl oxygen and surface $\text{Ti}_{4\text{C}}$ atoms are lower upon adsorption, which suggests the possibility of charge transfer from the non-bonding electron pair of an oxygen atom (O1) into the partially empty d orbital of TiO_2 (Ti_2). Confirma-

Table 1 Computed energies for different adsorption modes of benzoic acid

| Energy | Substrate BZA | Cluster $\text{Ti}_{36}\text{O}_{90}\text{H}_{36}$ | Parallel adsorption mode | Perpendicular adsorption mode | H-bonding adsorptionmode |
|---|---------------|--|--------------------------|-------------------------------|--------------------------|
| E_{T} , a.u. | -76.5147 | -1579.1275 | -1655.7320 | -1655.7839 | -1655.7470 |
| E_{b} , a.u. | -2.8073 | -34.2841 | -37.1396 | -37.1963 | -37.1812 |
| E_{ads} , kcal/mol | - | - | -30.2691 | -65.8762 | -56.3935 |
| ΔH_{f} , kcal/mol At 298 K | -71 | -9820 | -9918 | -9988 | -9922 |
| DM, Debye | 2.1 | 2.8 | 3.9 | 9.9 | 6.4 |

Table 2 The computed geometry parameters for the isolated and adsorbed BZA molecule

| Parameter | Isolated relaxed molecule, Å | Parallel adsorbed relaxed molecule, Å | Perpendicular adsorbed relaxed molecule, Å | H-bonding adsorbed relaxed molecule, Å |
|---------------------------|------------------------------|---------------------------------------|--|--|
| C=O | 1.219 | 1.245 | 1.235 | 1.246 |
| C-O | 1.364 | 1.347 | 1.382 | 1.339 |
| O-H | 0.965 | 0.972 | 0.971 | 0.981 |
| O = C-O angle, degrees | 121.546 | 121.098 | 113.899 | 124.746 |
| C-O-H angle, degrees | 109.393 | 110.775 | 112.853 | 112.347 |
| C-C-C = O, dihedral, deg. | -0.226 | 82.793 | 85.263 | -89.759 |
| H-O-C = O, dihedral, deg. | 0.157 | 1.777 | 177.762 | -1.795 |

tion of this conclusion is provided by the O-Ti2 linkage distance of 2.098 Å in the adsorption model (Fig. 4b).

Perpendicular adsorption model

The initial and equilibrated structures for the perpendicular adsorption geometry of BZA onto the nano-sized TiO₂ (100) surface are depicted in Fig. 5. The MD simulation started from a vertical (perpendicular) non-optimized geometry (Fig. 5a). Upon adsorption the plane of the aromatic ring preserved the perpendicular conformation relative to the surface. The carboxyl group oxygen, O1 and O2, atoms' lone pairs point toward the surface lattice Ti_{5C} and Ti_{4C} atoms respectively, with the shortest interaction being with the carboxylic oxygen (O1) atom. In the same manner as with the parallel adsorption mode, aromatic plane twisting was observed (Fig. 5b), which was confirmed by the variation of the H-O-C = O and C-C-C = O dihedral angles (Table 2). The E_{ads} is -65.88 kcal mol⁻¹, which is double the magnitude of E_{ads} for the parallel mode.

The perpendicular adsorption configuration is linked to the surface lattice titanium atoms via both oxygen atoms of the carboxylic acid group, resulting in a bridged adsorption geometry with (C=)O-Ti1 linkage of 2.210 Å, and (C-)O-Ti2 linkage of 2.245 Å. This observation is in excellent agreement with data reported by other researches [23, 25].

A closer look at Fig. 5b reveals a hydrogen-bonding interaction between the carboxylic hydrogen and the surface lattice O_{2C} atom, with a bond distance of 2.593 Å.

Löwdin net charges have been calculated in order to provide a more quantitative analysis of the interaction between BZA and the TiO₂ surface. Charges for the active surface titanium and oxygen sites and the constituents of the COOH group are presented in Table 3. Upon adsorption there is a decrease in the net charge of the COOH group components and an increase in the net electronic charge of the TiO₂ surface lattice partners involved in adsorption process. Again, this suggests the possibility of charge transfer from the unshared electron pair of the BZA oxygen atoms into the empty d orbital of the TiO₂ cluster. Accordingly, the twisting, electronic charge variation and the negative value for E_{ads} (Table 1) indicate stabilization of the perpendicular TiO₂-BZA system due to adsorption.

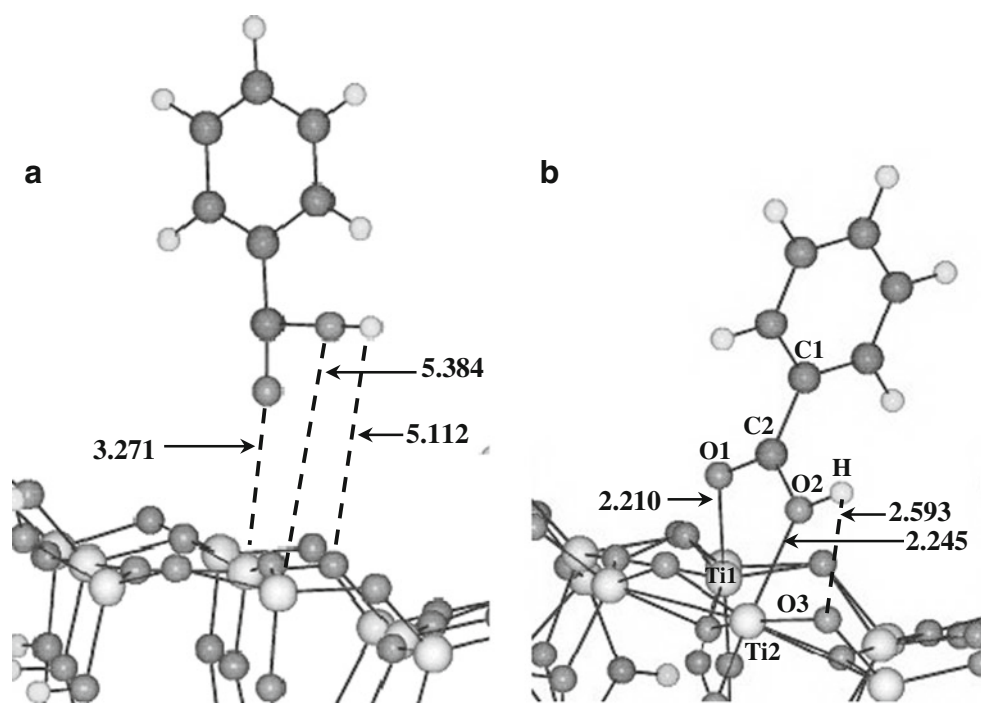
Adsorption model via hydrogen-bonding

After ensuring the description of the parallel and perpendicular modes of BZA adsorption onto nano TiO₂ (100) surface, examination of the feature of BZA adsorption through hydrogen-bonding was carried out (Fig. 6). At first, the BZA molecule was modified from the perpendicular adsorption configuration in such a way that it is adsorbed

Table 3 Computed net Löwdin charge (a.u.) changes of selected atoms in isolated and adsorbed BZA molecule on TiO₂ (100) surface

| Atom | Relaxed isolated molecule | Parallel adsorbed molecule | Perpendicular adsorbed molecule | Adsorbed molecule via H-bonding |
|------------------------------|---------------------------|----------------------------|---------------------------------|---------------------------------|
| Phenyl carbon C1 | -0.0800 | -0.0729 | -0.0761 | -0.0750 |
| Carboxyl carbon C2 | +0.6306 | +0.6838 | +0.7213 | +0.7137 |
| Carboxyl oxygen O1 | -0.4615 | -0.4346 | -0.4392 | -0.4358 |
| Carboxyl oxygen O2 | -0.4896 | - | -0.4665 | - |
| Carboxyl hydrogen H | +0.2677 | - | +0.3367 | +0.3567 |
| Surface lattice oxygen O3 | -0.6423 | - | -0.6681 | -0.6998 |
| Surface lattice titanium Ti1 | +1.3419 | - | +1.3130 | +1.3271 |
| Surface lattice titanium Ti2 | +1.3058 | +1.2332 | +1.2630 | - |

Fig. 5 MD simulation for the perpendicular mode of BZA molecule adsorption on TiO_2 (100) surface; (a) initial structure and (b) minimum energy structure. Dashed lines represent distances



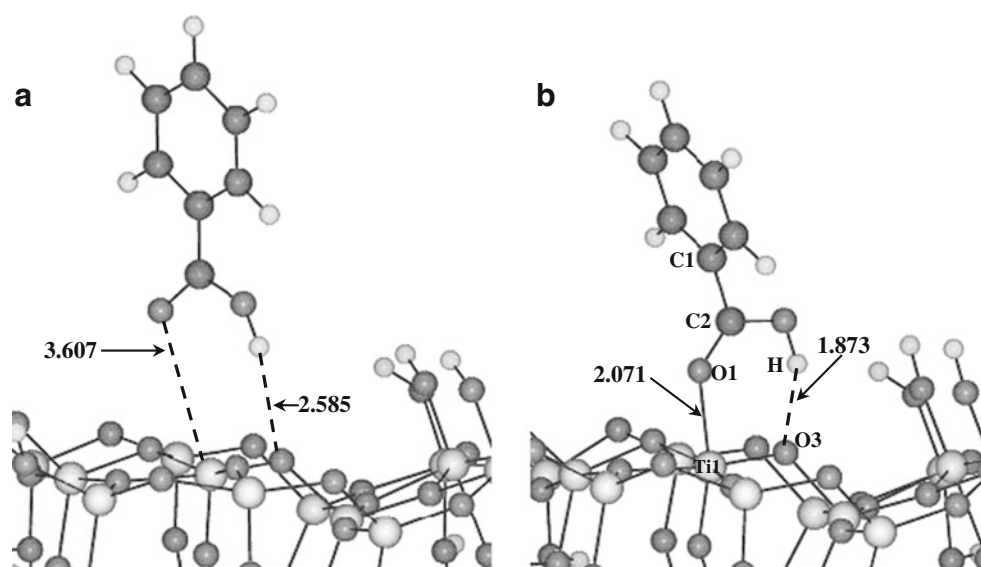
2.585 Å away from the $\text{O}_{2\text{C}}$ via the carboxyl hydrogen atom (Fig. 6a). MD equilibration produced a structure whereby the aromatic ring migrated toward the surface and linked to the $\text{Ti}_{5\text{C}}$ atom with (C=)O-Ti1 linkage of 2.071 Å (Fig. 6b). Further, hydrogen bonding with the $\text{O}_{2\text{C}}$ site is preserved, although it is stronger than the pre-relaxation ones (shorter bond length of 1.873 Å).

An interesting observation from the data in Table 3 is that the computed Löwdin charges for oxygen and hydrogen atoms that participated in hydrogen bonding (Fig. 6b), reveal a remarkable difference in charges upon adsorption. In accordance with the observation, the variation in the Löwdin net charges (Table 3) of the H-bond

partners ($-\text{COOH}\dots\text{O}_{2\text{C}}$) and (C=)O-Ti1 linkage components, and further the negative E_{ads} value (Table 1) indicates the energetic favorability of the adsorption process. Moreover, the adsorbed molecule has preserved the non-dissociative perpendicular conformation at the TiO_2 surface, where the aromatic ring is tilted toward the cluster surface. This tilting action has contributed in the variation of H-O-C = O and C-C-C = O dihedral angles (Table 2).

It was also observed during simulation that as BZA approached the surface, the COOH group rotated freely along the vertical axis before it obtained its final position. This phenomenon of COOH group internal rotation has also been observed by Neuber and co-workers in their

Fig. 6 MD simulation for the adsorption of BZA molecule via H-bond on TiO_2 (100) surface; (a) initial structure; (b) minimum energy structure. Dashed lines represent distances



adsorption geometry study of benzoic acid on Ni (110) [26]. These authors reported that the ring is rotated 30° relative to the (110) azimuth and is tilted approximately 30° with respect to the surface.

Results from Table 1 indicate the relative adsorption energies for the parallel, perpendicular and via hydrogen-bonding adsorption modes. It is noted that the bridged adsorption (perpendicular) mode has the largest negative E_{ads} and E_{b} values (Table 1). This is most likely attributable to higher number of atom-atom contacts of the accommodated BZA molecule on the TiO_2 cluster surface, regardless of the chemisorption or physisorption process that takes place. The transfer of electron density to two or even more Ti sites has also been reported by Bermudez [27].

The decreasing order of preference of adsorption modes is perpendicular, hydrogen-bonding and parallel configurations. The primary means of differentiating between each model is the calculated reaction energies [28]. These findings are further supported by the E_{T} and ΔH_{f} values reported in Table 1, and also are in accordance with Wheland's localization approach [29], which states that the energy of the species determines the path of the reaction.

Vibrational density of states

The vibrational density of states (VDOS) provides support for the proposed adsorption mechanisms illustrated in Figs. 4, 5 and 6. The VDOS are calculated relative to the reference free (non-adsorbed) BZA molecule by means of the optimized coordinates and trajectories using post-MD software within the MSINDO framework. The estimated VDOS for those selected atoms in the reference BZA molecule and the parallel, perpendicular and hydrogen-bonding adsorption models are presented in Fig. 7.

The spectrum shown in Fig. 7a includes bands located at 1249, 1876 and 3619 cm^{-1} , which can tentatively be assigned to C-O, C = O and O-H stretches in BZA, respectively. The spectra in Fig. 7b, c and d depict a relatively similar shift in the band located at 1876 cm^{-1} ($\Delta\nu = 27\text{--}30$). The shift in the band located at 1249 cm^{-1} is much higher in the case of the bridged adsorption (perpendicular mode) ($\Delta\nu = 31$) in comparison to the monodentate parallel mode ($\Delta\nu = 17$) and the hydrogen-bonding mode ($\Delta\nu = 7$). This may be attributed to the participation of C-O implicitly in the adsorption mechanism of the bridged mode. These calculated $\Delta\nu$ values generally lie within the range expected for bridged-bonded coordination [30]. On the other hand, the shift in the band located at 3619 cm^{-1} follows an increasing sequence of $\Delta\nu = 23, 53$ and 98 cm^{-1} , which belong to the parallel, perpendicular and hydrogen-bonding adsorption modes, respectively. The appearance of O-H bands at different locations as a result of adsorption could most likely be due to different bonding

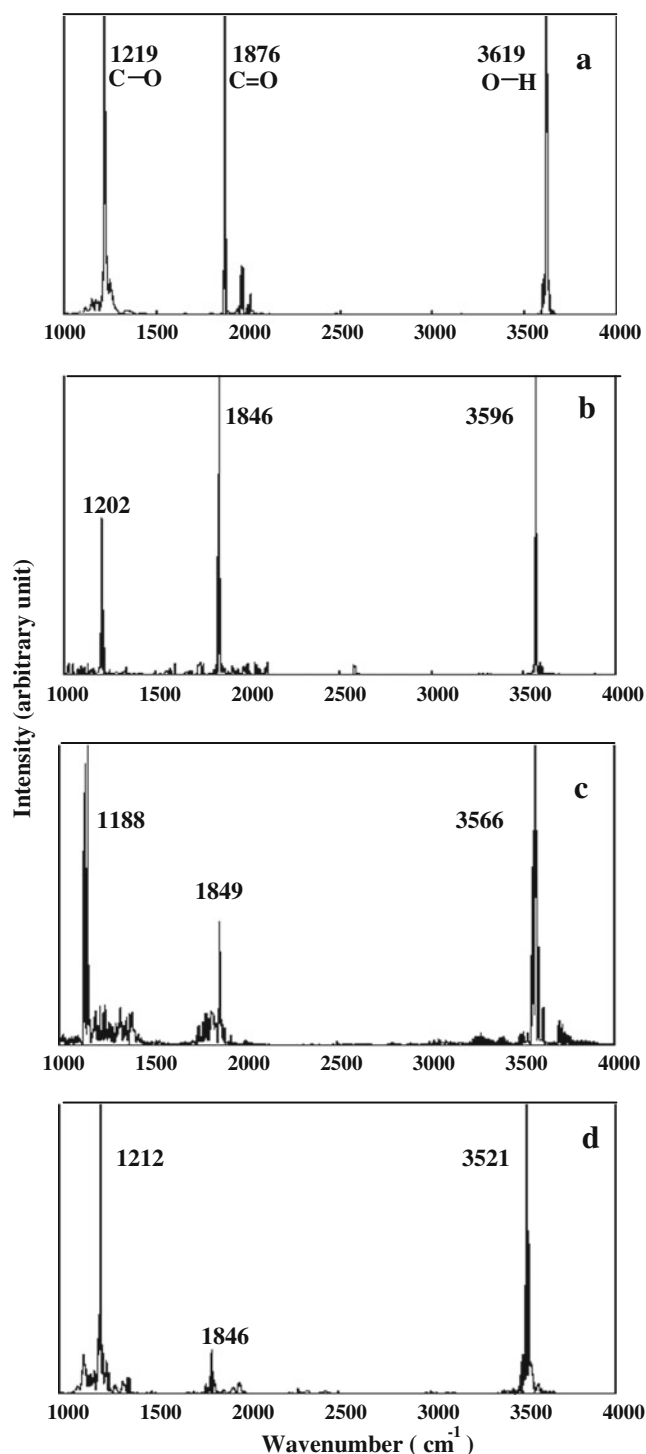


Fig. 7 The VDOS of selected atoms for BZA molecule adsorption modes on TiO_2 (100) surface; (a) free BZA molecule as a reference; (b) parallel adsorption; (c) perpendicular adsorption; (d) adsorption via H-bonding

features, which emerge as a result of hydrogen bonding between the carboxyl group hydrogen and surface $\text{O}_{2\text{C}}$ atom that is explicitly illustrated in Figs. 5 and 6. The red shift of these bands and lowering of the corresponding

intensities may be attributed to the weakening of the relevant bonds upon the adsorption process, in which the C=O, C-O and O-H bond distances have become relatively longer (Table 2).

No experimental evidence for the adsorption configuration of BZA onto TiO₂ (100) surface has been yet reported. However, Dobson and McQuillan [30] concluded that there is weak adsorption of BZA onto the TiO₂ surface from their study of the adsorption of aromatic carboxylic acids onto TiO₂ and Ta₂O₅. Unfortunately no reference to the type of crystallographic plane was given.

Conclusions

Benzoic acid adsorbs to anatase TiO₂ (100) surface in molecular form through the interaction between the carboxyl group and surface active sites. The adsorption results in parallel or perpendicular configuration of the aromatic ring relative to the surface, with however greater stability of the perpendicular adsorption mode.

The mechanism of the intermolecular interaction between BZA and TiO₂ surface is mediated through the donation of electron lone pair from -COOH group into the partially empty d orbital of TiO₂. Furthermore, hydrogen bonding may also play an important role in the stabilization of molecular BZA adsorption.

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