

# Carboxylic species adsorption on TiO<sub>2</sub> nanoparticles

© E.F. Sheka\*, E.A. Nikitina\*, V.A. Zayets, I.Ya. Ginzburg\*\*, J. Schoonman\*\*\*

\* Peoples Friendship University of Russia,  
117302 Moscow, Russia

\*\* Institute of Chemical Physics Problems, Russian Academy of Sciences,  
142432 Chernogolovka, Moscow district, Russia

\*\*\* Delft University of Technology, Laboratory for Inorganic Chemistry,  
Delft, The Netherlands

E-mail: sheka@icp.ac.ru

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We present the results of a quantum-chemical study of the interface formed by titania nanoparticles and a set of carboxylic moieties, namely, benzoic and bi-isonicotinic acids and tris-(2, 2'-dcbipyridine) Fe (II) complex placed on the surface of either rutile or anatase polymorphs. The calculations were performed in the *spd*-basis using semi-empirical quantum-chemical codes, both sequential and parallel. The results are mainly addressed to the geometry optimization of the adsorbed molecules on the surface as well as to the adsorption mechanism and the energy of adsorption.

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## 1. Introduction

TiO<sub>2</sub> nanoparticles covered by organic dyes are the main photosensitive elements of solar cells [1]. Usually, organic dyes are presented by ruthenium (II) complexes with carboxylated didentate, tridentate, and tetradentate ligands. Little is known about the structure of the formed interface as well as of the nature and strength of the intermolecular interaction between the particles and organic dyes. At the same time, it is absolutely obvious that the nature of the latter plays a crucial role not only in chemical stability of the cell components but considerably influences the kinetic behavior of the solar element as well. Widely accepted, the dyes are anchored to the particle surface by carboxylic units [2]. The adsorption is evidently strong, and is undoubtedly caused by the formation of the intermolecular chemical bonds that connect dye molecules with the particle surface. However, no experimental evidences about both the disposition of the dye molecules over the surface and the type of the bond formed are available. Experimental data are restricted to the estimation of the contact area only. Basing on the dye concentration, which provides a monolayer covering of particles, the contact area, or landing area, can be evaluated as of  $\sim 150 \text{ \AA}^2$  [3].

The current study is aimed at throwing light on the interface formed by organometallic dyes, whose ligands involve carboxylic units, and TiO<sub>2</sub> nanoparticles as well as at highlighting the mechanism of their adsorption on the surface of both rutile and anatase crystalline modifications. The study has been performed in two stages. The first stage, or the ligand stage, is dedicated to the study of the adsorption of the bi-isonicotinic acid (BNA), or dcbipyridine H<sub>2</sub> (dcbpyH<sub>2</sub>), which is the most popular ligand that

anchors organometallic dyes to the particles in the „Grätzel cells“ [1]. This stage involves as well a part, which concerns the benzoic acid (BZA), as „a half“ of the ligand that is of a great assistance in understanding and generalizing the adsorption mechanism. An organometallic molecular carboxylated bidentate complex tris-(2, 2'-dcbipyridine) Fe (II) (Fe(dcbpyH<sub>2</sub>)<sub>3</sub>, or Fe-dye below) has been considered at the second stage of the study, or dye stage, which well simulates similar ruthenium complex commonly used in practice.

When looking for a support of the validity of obtained results, it is naturally to apply to experimental data. However, experimentally, particle science concerning adsorption events at atomic level is extremely difficult and practically not available. At the same time, that is the very point where the difference between the particle science and surface science disappears and where all knowledge gathered when studying molecules on single-crystalline surfaces is of valuable assistance. At first glance, the case related to the TiO<sub>2</sub> surfaces seem to be quite promising. Actually, the phenomenon has been studied rather thoroughly (see overwhelming review [4] and references therein), particularly for complex organic molecules involving carboxylated acids. However, the review statement that the latter species have become the most investigated organic molecules on single-crystalline TiO<sub>2</sub> surfaces (about half hundred references are cited in [4]) is related to the formic acid mainly. As for BZA and BNA, the results are rather scarce [5–8] and they are related to the rutile modification of the crystal only. As for organometallic dyes, no results are available at all. The lack of both experimental and theoretical data has forced us to perform an extended computational study, which involves the adsorption of the above three

molecules on (110) and (101) surfaces of rutile and anatase modifications, respectively, which mainly facet TiO<sub>2</sub> crystalline nanoparticles [9]. Different degree of distortion and/or defectness under the surface relaxation has been taken into account therewith. The obtained results allow exhibiting main features of the adsorption processes under study.

Quantitative characteristics of adsorption are usually a measure of the intermolecular interaction between an adsorbate and adsorber. To get the quantities in due course of computational experiment means to perform three sets of calculations related to non-interacting components, considered separately, as well as to their ad-mixture. Obviously, all calculations have to be carried out at the same computational footing. Such an approach has been implemented in the current study. Part 1 [10] presents results concerning adsorbents, or titania surfaces. Molecular adsorbates and the relevant ad-complexes are considered in the current paper. Partially, the results were presented in [11,12].

The paper is organized in the following way. Section 2 is devoted to a design of the TiO<sub>2</sub>-carboxylic species interface and involves the study of adsorbate molecules as constituents of the interface. Adsorption of benzoic and bi-isonicotinic acids is considered in Sections 3 and 4. Section 5 is devoted to the adsorption of tris-(2, 2'-dcbipyridine) Fe (II) complex. Conclusion completes the paper.

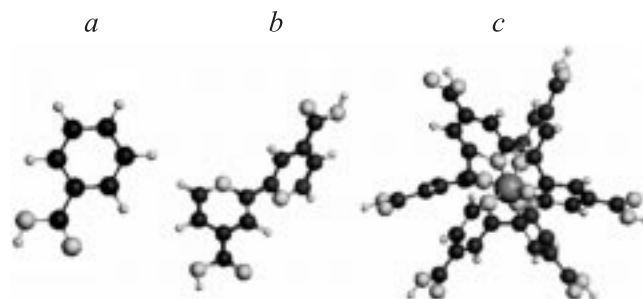
## 2. TiO<sub>2</sub>-carboxylic species interface design

To provide a large bulk of calculations, close to *ab initio* semi-empirical quantum-chemical software ZAVA (improved CLUSTER-Z2) has been chosen which is based on the NDDO-weighted factors (NDDO-WF) approximation [13–17], suitable for the calculations in the *spd*-basis. The SCF HF calculations have been performed for the singlet ground state in the close shell approximation. Both sequential [18] and parallel [19] codes of the program have been used.

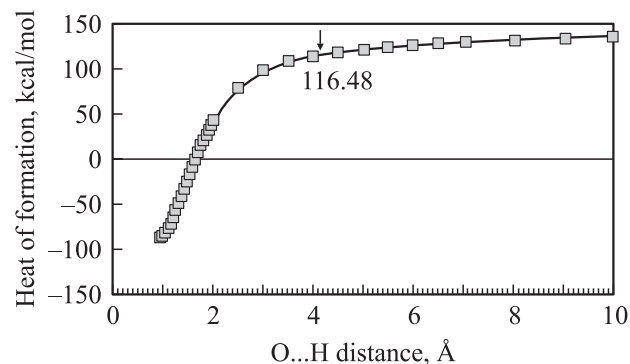
**Table 1.** Molecular energetic characteristics

Molecules	Heat of formation, kcal/mol		Energy of dissociation, kcal/mol
	molecular form	dissociative form <sup>1</sup>	
Benzoic acid	-83.54	116.48	200.02
Bi-isonicotinic acid (two OH units are dissociated)	-148.47	325.97	474.44
Fe (dcbpyH <sub>2</sub> ) <sub>3</sub> (evaluation for two OH units dissociation)	-1160.39	~ -685	~ 475

<sup>1</sup>Energies are taken at averaged distances related to the dissociative adsorption of the molecules on the surfaces.



**Figure 1.** Molecule equilibrated structures: *a* — BZA, *b* — dcbpyH<sub>2</sub>, *c* — Fe(dcbpyH<sub>2</sub>)<sub>3</sub>.



**Figure 2.** Dissociation curve for the benzoic acid along the coordinate of reaction related to the -COO...H unit.

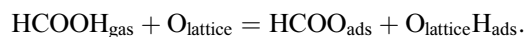
2.1. Molecular adsorbates. Equilibrated structures of the three studied molecules are shown in Fig. 1. Fe atom instead of Ru in the Fe-dye has been chosen as a close analogue to the latter with the available parameters [17]. By using the coordinate-of-reaction approach (see, for example, Fig. 2 for BZA), the heat of formation in both associative (molecular) and dissociative forms of the molecules as well as the dissociation energy has been determined. The relevant data are listed in Table 1.

Looking at the equilibrated structures in Fig. 1, a rather complex structure of both BNA and Fe-dye should be noted. Benzene rings of both BNA and each ligand in the second case do not lie in one plane and form a roof-like scrambled composition with carboxylic units directed down. The structure of the BNA differs from that one considered in [7,8]. As seen from Table 1, the dissociation energy of one COO...H unit of the BZA molecule is rather significant. One had to expect that a simultaneous dissociation of two COO...H units would result at least in doubling the value. This occurs, indeed. The energy of two units dissociation therewith is practically the same if the units belong to either an individual ligand (BNA) or to one of three ligands of the Fe-dye.

2.2. Ad-complexes. As shown in Part 1 [10], bare surfaces of both rutile and anatase crystallographic modifications are subjected to a severe distortion under relaxation. This inevitably results in a high density

of defects through over the surface and a pronounced diversity of the structure of the contact area, to which the relevant molecular adsorbate is attached. Consequently, a large dispersion in values of the energy of intermolecular interaction (adsorption energy) between adsorbate and substrate should be expected. The fact has been actually characteristic of the titania surfaces that has been proved by a large number of adsorption studies involving both simple molecules like water and complex organic molecules (see Table 16 in [4] and references therein). Due to the fact, no canonical values of the adsorption energy for TiO<sub>2</sub>-based ad-complexes are available. These circumstances greatly complicate the computational experiment due to clear understanding that a rather large set of model ad-complexes should be investigated. Not pretending to be fully complete, the current study was designed in such a way to cover the formulated problem as full as possible. The diversity of the contact area structures has been taking into account by using a number of clusters of different levels of the distortion and defectness of the relaxed surfaces studied in Part 1 [10].

The second circumstance concerns the adsorption of carboxylic-unit molecules. A detailed investigation of the phenomenon involving formic acid has shown (see review [20] and references therein) that generally the acid dissociates on the titania surfaces giving a formate so that the acid is adsorbed on the surface dissociatively in the form



A detailed investigation of the phenomenon has allowed suggesting its characteristic meaning for any carboxylic-unit species on the titania surfaces. As shown later [5], the tendency has been actually preserved for BZA, although not only dissociative and strong, but associative and weaker adsorption has been recorded in this case. The trend of the two-mode adsorption for molecules, which are more complex than a formic acid, occurred to be true for BNA [8] as well with prevailing dissociative mode. Evidently, the same behaviour might be expected for organometallic dyes with carboxylic-unit ligands. This circumstance greatly complicates computational study causing a duplication of any adsorption events with respect to its two-mode behaviour.

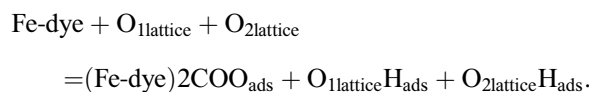
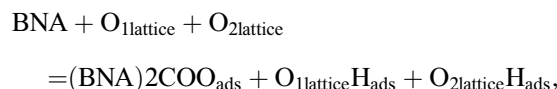
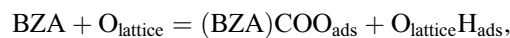
Design of starting configurations of the studied ad-complexes and choice of the optimisation procedure have been subordinated to the following assumptions.

1) The contact between the surface and molecular adsorbates is provided via one (BZA, one-dentant contact) or two (BNA and Fe-dye, bidentant contact) carboxylic units of the relevant molecules.

2) The unit oxygen atoms, doubly bonded to carbon, are always located above either one (one-dentant contact) or two (bidentant contact) Ti(5) atoms at a preset starting O–Ti<sub>lattice</sub> distance of 1.78 Å.

3) Similarly to the above presentation of the formic acid, the dissociative adsorption for the studied molecules has

been configured as



4) The starting configuration of the surface correspond to the non-relaxed cut off clusters in all cases.

5) The relaxation modes of the surface [10] involve:

a) one-center and top-layer modes in the case of one-dentant contact of the surface with the BZA adsorbate;

b) two-center and top-layer modes in the case of bidentant contact of the surface with the BNA and Fe-dye molecule.

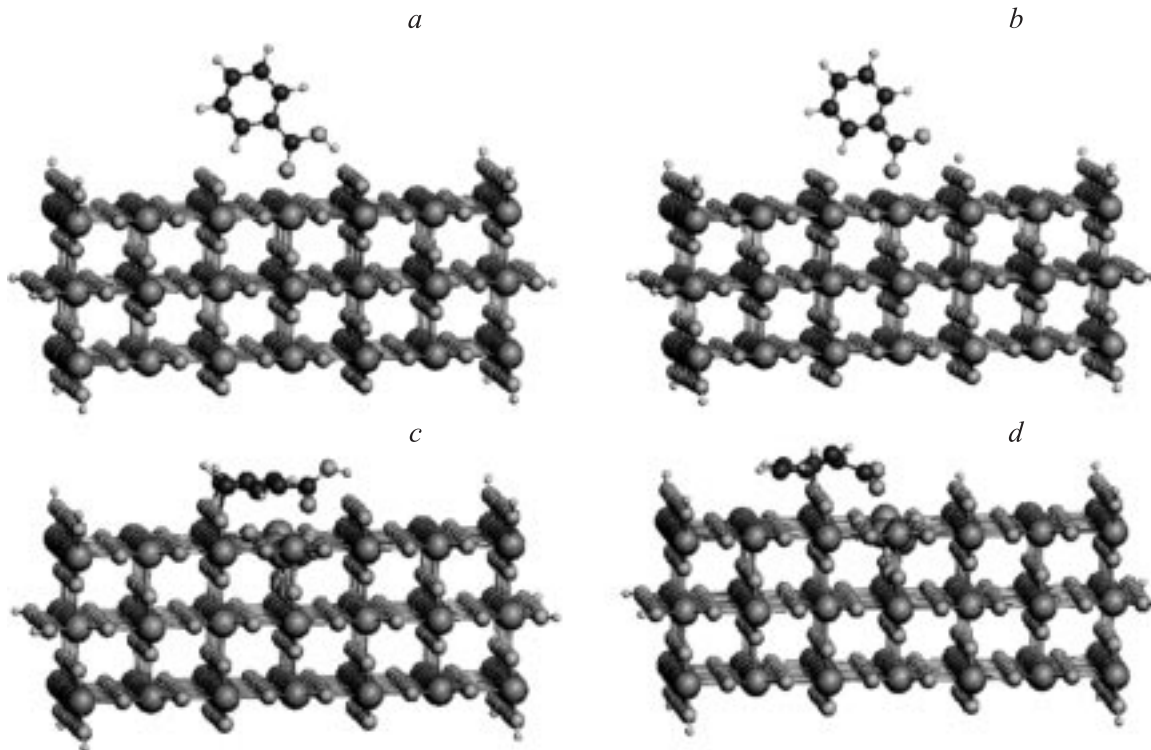
6) The optimization procedure includes the adsorbate molecule as well as a set of selected surface atoms responsible for the selected relaxation mode while other atoms of the cluster, which simulates the considered surface, are kept fixed.

Taking into account the above factors results in a rather massive bulk of the job to be performed. The list of candidates for calculations contains a few tens of clusters, which simulate ad-complexes related to two-mode adsorption on the rutile and anatase surfaces of different defectness. The overwhelming majority of the clusters, each of which is about of 400 atoms, have been studied. Common features and governing tendencies were highlighted that made it possible to decrease the number of studied clusters within each family. Below these findings, having an integrating character, will be presented and illustrated by typical examples.

### 3. Benzoic acid adsorption on rutile (110) and anatase (101) surfaces

Analysis of the ESDIAD/LEED study of the BZA adsorption on the (110)(1 × 1) rutile surface at room temperature [5] has resulted in a dissociative adsorption of the species with two oxygen atoms bridge-bonded to two Ti(5) atoms. The ESDIAD H<sup>+</sup> pattern was interpreted as an upright benzoate molecule with an upright phenyl ring [6]. In accordance with the observation, starting configurations of the ad-complexes involve an upright position of the molecule with respect to the surface (see Fig. 3, *a, b*<sup>1</sup>) in both adsorption modes, with the only difference that the molecule was located normal to the Ti(5) row. This made sense since the distance between two Ti(5) atoms

<sup>1</sup> Hereinafter atomic structures of the studied clusters are shown in atomic radii instead of commonly used ionic. This manner is more suitable for presentation of adsorption complexes.



**Figure 3.** Associative (*a, c*) and dissociative (*b, d*) adsorption of the benzoic acid on the (110) surface of rutile. Starting (*a, b*) and equilibrated (*c, d*) configurations, respectively. The surface is subjected to the one-center relaxation [10].

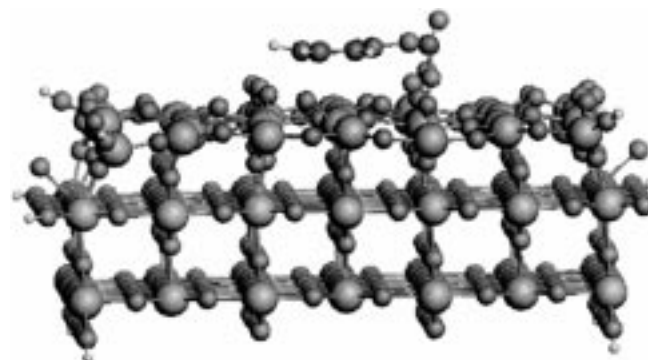
(3.63 Å) exceeds significantly the O–O distance (2.23 Å) in the molecule so that the orientation of the molecular plane parallel to Ti(5) atom row does not seem to be reasonable. Anyway, since the molecule is allowed to take the most profitable position and has enough degree of freedom to rotate along the vertical axis in due course of the geometry optimization, the starting position is not so crucial. Thus determined initial position of the BZA molecule has been subjected to a complete optimization alongside with a partial optimization of the underneath substrate in accordance with the selected regime of the surface relaxation.

Fig. 3, *c, d* corresponds to the one-center regime of surface relaxation [10]. As seen from the figure, the geometry optimization yields to a drastic change in the starting molecule orientation, tilting it towards the surface on almost 90°. The changing concerns both associative and dissociative adsorption modes. The result severely contradicts to the mentioned conclusion made on the basis of experimental data [5,6] although seems to be quite reasonable from physical viewpoint. The matter is that the contribution of the van-der-Waals interaction of any adsorbate with the surface is always significant whichever kind of adsorption takes place (physical or chemical). That means that the optimization of the adsorbate accommodation over surface must maximize the number of atom-atom contacts thus strengthening the interaction. In case of the benzene ring incorporating molecule, the molecule tilting toward the

surface obviously becomes inevitable and observed in many cases, indeed.

General pattern of the adsorbed molecule position occurred to be practically non-dependent on the surface relaxation regime. Fig. 4 shows equilibrated position of the studied ad-complex related to the dissociative adsorption of the molecule under the top-layer relaxation of the surface.

The main characteristics obtained for the studied ad-complexes are given in Table 2. As seen from the table, the adsorption is strong at both modes while the dissociative mode is considerably stronger. Both adsorption modes are accompanied by the formation of chemical bonds between the molecule and surface. But instead of expected O–Ti<sub>lattice</sub>



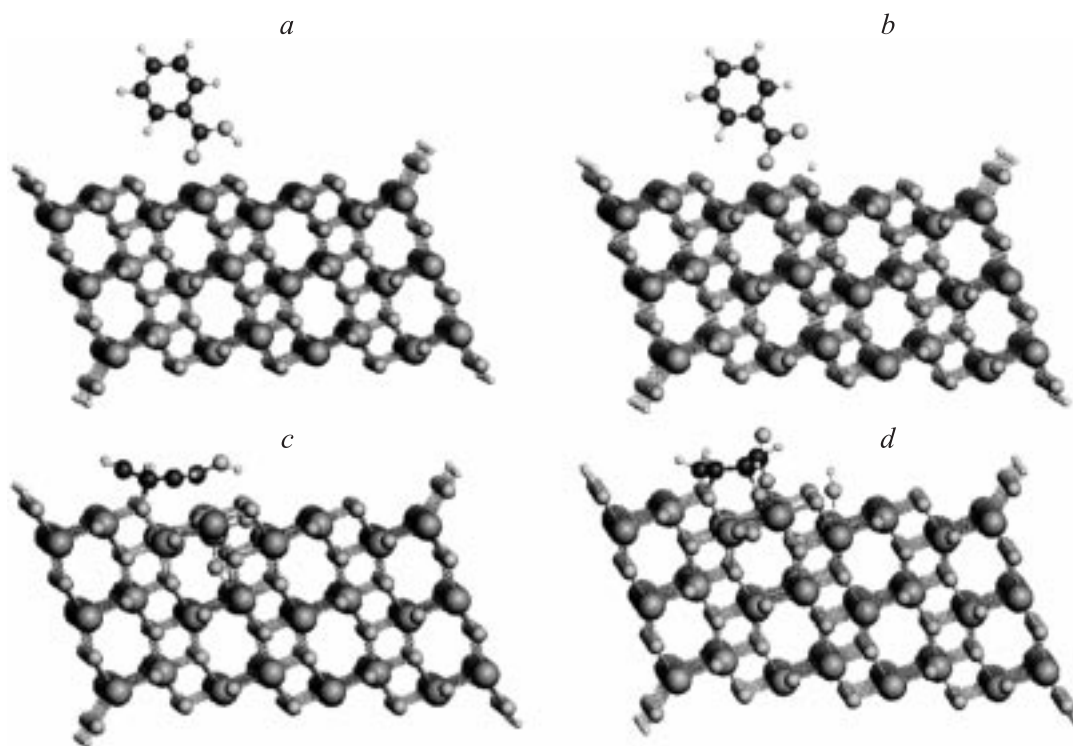
**Figure 4.** Dissociative adsorption of the benzoic acid on the top-layer-relaxed (110) surface of rutile.

**Table 2.** Characteristics of the TiO<sub>2</sub>-based adsorption complexes

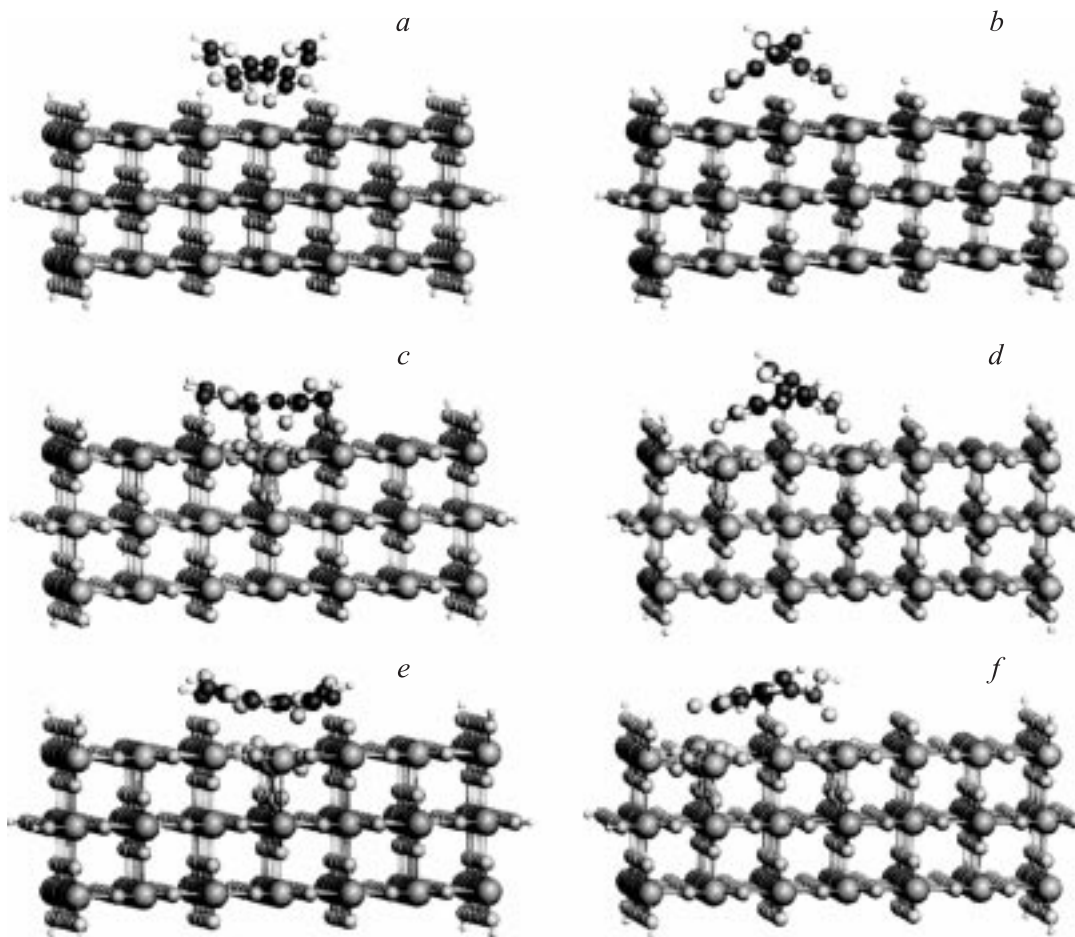
Complexes/adsorption mode <sup>1</sup>	Shortest interatomic distances between substrate and adsorbate, Å			$E_{\text{ads}}^2$ , kcal/mol
	O <sub>benzoate</sub> –Ti <sub>lattice</sub>	C <sub>benzoate</sub> –O <sub>lattice</sub>	H <sub>benzoate</sub> –O <sub>lattice</sub>	
	Rutile (110)			
Cluster 3r/BZA (one-center relxn.)/as	2.24	1.47; 1.55	–	–307.33
Cluster 3r/BZA (one-center relxn.)/ds	2.23	1.45; 1.50; 2.20	0.97	–520.19
Cluster 6r/BZA (top-layer relxn.)/ds	1.84	3.36	0.94	–708.49
Cluster 4r/BNA (two-centers on one line relxn.)/as	2.27	1.46; 1.49	–	–484.81
Cluster 4r/BNA (two-centers on one line relxn.)/ds	1.87; 2.17	1.44; 1.44; 1.47; 1.57	0.97; 0.97	–1017.76
Cluster 5r/BNA (two-centers on different lines relxn.)/as	2.23	1.46; 1.47	–	–437.95
Cluster 5r/BNA (two-centers on different lines relxn.)/ds	1.82; 2.25	1.57	0.96; 0.97	–871.01
Cluster 6r/BNA (top-layer relxn.)/ds	1.81; 1.80	2.17; 2.24; 2.27; 2.29	0.94; 0.94	–1289.85
Cluster 4r/Fe-dye (two-centers on one line relxn.)/ds	2.16	1.46; 1.50; 1.52; 1.58	0.97; 0.99	–1642.11
Cluster 6r/Fe-dye (top-layer relxn.)/ds	1.82	1.43; 1.51; 2.25	0.96; 0.97	–1774.72
	Anatase (101)			
Cluster 3a/BZA (one-center relxn.)/as	3.20	1.44; 1.49	–	–338.94
Cluster 3a/BZA (one-center relxn.)/ds	1.81	1.44; 1.45; 1.52	0.93	–535.95
Cluster 5a/BNA (two-centers on different lines relxn.)/as	3.22	1.41; 2.16; 2.25	–	–362.74
Cluster 5a/BNA (two-centers on different lines relxn.)/ds	1.83; 2.29	2.25; 2.29	0.91; 0.90	–602.89

<sup>1</sup> as and ds mark associative and dissociative adsorption modes.

<sup>2</sup>  $E_{\text{ads}} = \Delta H_{\text{ad-empl}} - \Delta H_{\text{surf}} - \Delta H_{\text{mol}}$ , where  $\Delta H_{\text{ad-empl}}$  and  $\Delta H_{\text{surf}}$  present the heat of formation of the ad-complexes and the relevant surface, respectively, while  $\Delta H_{\text{mol}}$  corresponds to the heat of formation of the molecule in either associative or dissociative form (see Fig. 2), depending on the adsorption mode.



**Figure 5.** Associative (*a, c*) and dissociative (*b, d*) adsorption of the benzoic acid on the (101) surface of anatase. Starting (*a, b*) and equilibrated (*c, d*) configurations, respectively. The surface is in the one-center relaxation mode.



**Figure 6.** Dissociative (*c, d*) and associative (*e, f*) adsorption of bi-isonicotinic acid on the (110) two-center relaxed surface of rutile. *a, b* — starting configurations related to a pair of „on-line“ (*a*) and diagonal (*b*) surface centers to be subjected to the relaxation [10].

coupling, two  $C-O_{\text{lattice}}$  bonds are formed in both cases with the participation of carbon atoms of the phenyl ring and the bridged oxygen atoms of the surface. The finding is fully understood since strictly fixed bridged oxygen atoms of the surface prevent from following the carboxylic oxygen of the BZA the drawing Ti(5) atom into the surface depth under relaxation [10]. That evidences a strong dependence of the adsorption event on the surface structure. Actually, the adsorption energy varies quite considerably when the surface relaxation regime is substituted by the top-layer one (see Table 2). The BZA molecule is attached to the surface via  $O-Ti_{\text{lattice}}$  bond. Its benzene ring is situated parallel with the surface but rather distant from the latter.

There is no evidence, either experimental or theoretical, of the BZA adsorption on anatase surface. The carried computational experiment was designed similarly to that of the BZA-rutile complexes. Fig. 5 presents the results related to the BZA adsorption under the one-center regime of the anatase (101) surface relaxation. As seen from the Fig. 5, the general behavior of the adsorbed molecule is quite similar to that one observed on the rutile surface. In the case of the associative adsorption, the similarity concerns

even details. As for the dissociative mode, the difference between the cases involves the formation of the  $O-Ti_{\text{lattice}}$  bond and one extra  $C-O_{\text{lattice}}$  bond on the anatase substrate additionally to one  $C-O_{\text{lattice}}$  in the case of rutile. This is evidently connected with the anatase surface structure pattern that provides Ti(5) atoms to be spatially more accessible.

#### 4. Bi-isonicotinic acid adsorption

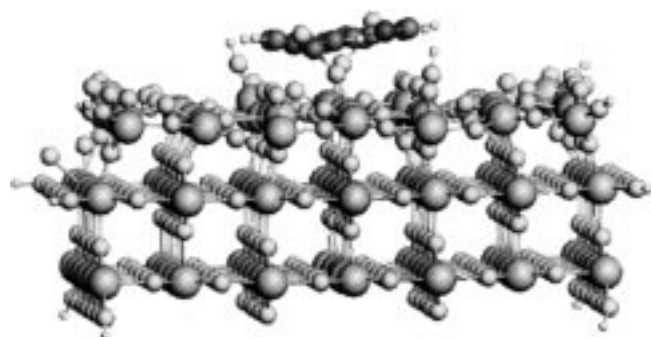
Due to bigger size of the BNA molecule, its adsorption has been studied on clusters with large area of relaxation. Fig. 6 shows results related to the substrate with the two-center relaxation mode of the rutile surface [10]. The two centers were located either along one Ti(5) atom row or across two adjacent rows. Positions of the lowest oxygen atoms in two starting configurations of the BNA in Fig. 6, *a, b*, point to the location of the two centers to be formed later in due course of the geometry optimization. As seen from Fig. 6, *c, d* and Fig. 6, *e, f*, when the optimization is completed, the molecule is seriously reoriented with

respect to the surface in such a way that, at least, one phenyl ring turns out to lay parallel with the surface.

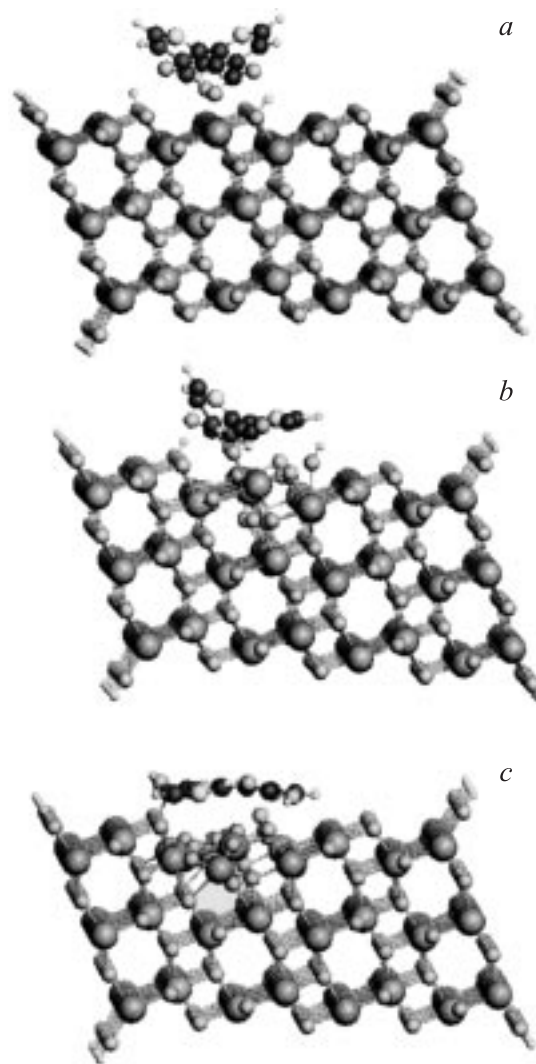
As seen from Table 2, the BNA adsorption complies with the same rules that were observed for the BZA molecule. Thus, the associative events are accompanied by the formation of the  $C-O_{\text{lattice}}$  chemical bonds while the distances  $O-Ti_{\text{lattice}}$  are kept not closer than 2.23 Å. Similarly, the dissociative adsorption is greatly favorable. However, the details, which concern the bond formation under the BNA dissociative adsorption, differ not only from those, observed for the BZA molecule, but also from one relaxation mode in the BNA case to the other. Two latter are similar with respect to the formation of one  $O-Ti_{\text{lattice}}$  bond but differ by the number of the  $C-O_{\text{lattice}}$  bonds formed. These features clearly exhibit the effect of the surface structure on the adsorption events.

The said above is further supported by shown in Fig. 7, which presents the BNA dissociative adsorption on the top-layer relaxed surface of rutile. As seen from the figure, the main spatial feature of the ad-complex is similar to shown in Fig. 6 in the case of the two-center-on-line relaxation mode. It may be formulated as a vivid molecule flattening in planes parallel with the surface caused by the intermolecular interaction. At the same time, more regular surface structure causes a clearly seen bidentant coupling of the BNA molecule with the surface via two  $O-Ti_{\text{lattice}}$  bonds while benzene rings of the molecules are parallel with the surface but rather distant, so that no  $C-O_{\text{lattice}}$  bonds are formed. The configuration shown in Fig. 7 should be regarded as one of the main configurations occurred in practice. It drastically differ from that presented in [7]. The discrepancy can be caused by two factors. Firstly, the calculations in [7] were performed without taking into account the optimization of both the BNA and rutile surface structures while shown above convincingly exhibits a tremendous importance of the latter. Secondly, erroneous interpretation of experimental results provoked authors of [7] to make a non-correct conclusion concerning the availability of the COOH units in the adsorbed molecules.

The BNA adsorption on anatase occurs to be similar to that one for the BNA-rutile family. As previously, the molecule is flattened (see Fig. 8), fully or partially, and the



**Figure 7.** Bi-isonicotinic acid dissociative adsorption on the top-layer relaxed (110) surface of rutile.



**Figure 8.** Associative (*c*) and dissociative (*b*) adsorption of the bi-isonicotinic acid on the (101) two-center relaxed surface of anatase. *a*: starting configuration.

dissociative adsorption is under privilege. Table 2 presents details concerning chemical bond formation in the case.

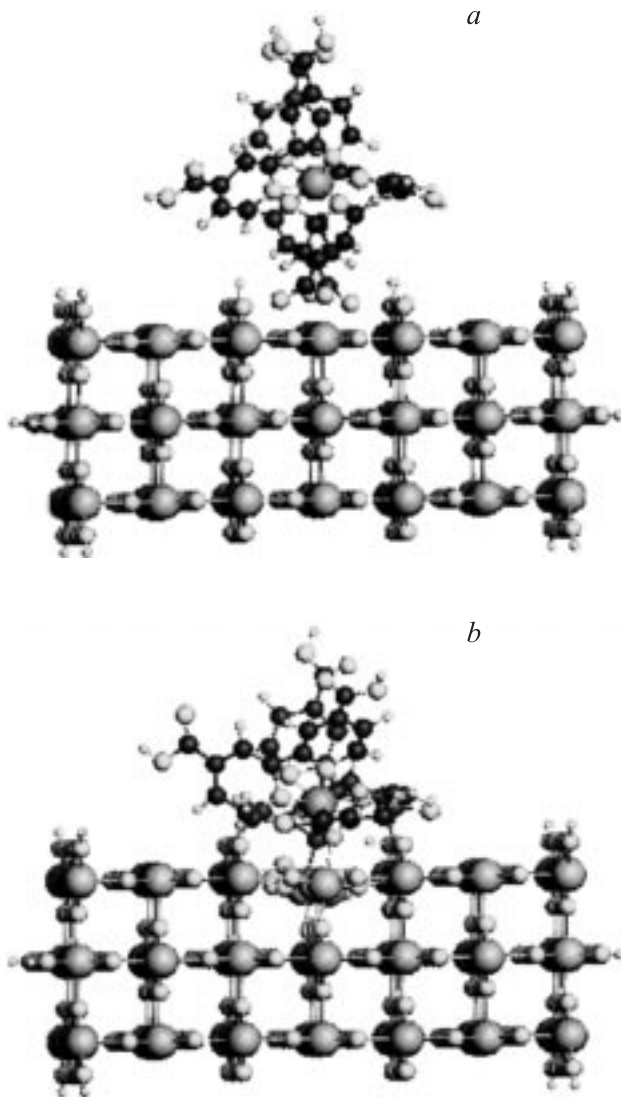
Analyzing the carboxylic acid adsorption, presented in the last two Sections, one can conclude that the acid adsorption on both rutile and anatase surfaces is chemical by nature and is accompanied by the formation of chemical bonds between the acids and surfaces regardless to which of associative or dissociative adsorption mode occurs. Dissociative adsorption is always preferable. The character of the bond formed greatly depends on the details of the substrate structure in the adsorption area.

## 5. Fe-dye adsorption

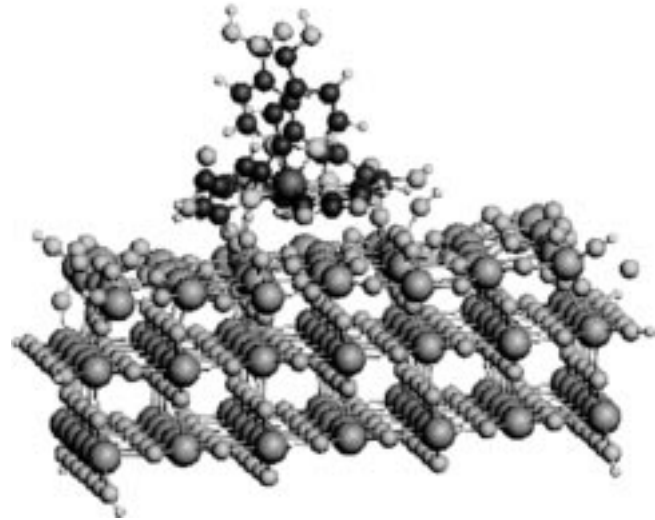
Further complication of the adsorbate structure does not change the common tendency in the adsorbed molecule accommodation. Shown in Fig. 9 is related to the dissociative

adsorption of the Fe-dye on the (110) surface of rutile in the two-center-on-line relaxation regime. Placing over the surface in such a way to provide a bidentant anchoring with the surface, the molecule rejects the predicted manner and is transformed to an „open flower“, with the bottom side contacted with the surface. The contact area is of  $\sim 144 \text{ \AA}^2$  that is rather close to  $150 \text{ \AA}^2$  estimated basing on experimental data for ruthenium dye [3]. Comparing the case with a similar one for the BNA molecule (Fig. 6, *c*), a lot of features occurred to be common (see Table 2). However, a pronounced complication of the molecule structure causes a decreasing in the number of the formed  $\text{O}-\text{Ti}_{\text{lattice}}$  bonds to one in comparison with two bonds in the case of the BNA molecule.

Proceeding with further development of the surface relaxation changes the dye adsorption considerably, as can be seen in Fig. 10. A general tendency is evidently



**Figure 9.** Dissociative adsorption of the tris-(2, 2'-dcbipyridine) Fe(II) complex on the (110) two-center relaxed surface of rutile. Starting (*a*) and equilibrated (*b*) configurations.



**Figure 10.** Tris-(2, 2'-dcbipyridine) Fe(II) complex dissociative adsorption on top-layer relaxed (110) surface of rutile.

proven toward facilitating the  $\text{O}-\text{Ti}_{\text{lattice}}$  bond formation when the surface is more orderly distorted. However, as seen from Table 2, structural details noticeably differentiate the behavior of the Fe-dye ligand from that of the BNA molecule. So that the behavior of a free ligand (BNA) differs from that of a bonded one, which is incorporated in a complex molecular structure (Fe-dye). Similar conclusions follow from the analysis of the data obtained for the Fe-dye adsorption on the (101) anatase surface.

## 6. Conclusions

Presented results clearly show how complicated are adsorption events on the surface of titania nanoparticles in practice. Due to both extreme defectness of the surface and high sensitivity of the ad-complexes' structure and properties to structural parameters within the contact area, there is no possibility to describe the adsorption events in a unique way either experimentally, or computationally. As for the latter, every particular case, the number of which is practically non-countable, should be individually studied that makes the construction of a reliable and detailed computational picture of the phenomenon under study hardly feasible. However, as shown in the paper, each individually considered case exhibits common tendencies to a bigger or smaller degree. Summarizing obtained results, the following general conclusions can be suggested.

1) The coupling of carboxylic species with the (110)(1 × 1) rutile and (101)(1 × 1) anatase surfaces is strong for both associative and dissociative adsorption modes and can be attributed to the chemical type. The intermolecular interaction between the adsorbate and the substrate is accompanied by the chemical bonds formation that bound the complex components tightly together.



2) In all cases, the dissociative adsorption prevails over associative one and gaining in the adsorption energy is about 200-250 kcal/mol per each benzoic unit attached to the surface. Beside of the bond formation, both constituents of the ad-complexes are subjected to a strong structural alteration due to a particular feedback that may cause a considerable contribution to the adsorption energy, which is difficult to estimate so far. As a result, a thorough interpretation of the adsorption energy values is complicated.

3) The carboxylic dyes of the ruthenium (II)-type complexes with carboxylated didentate, tridentate, and tetradentate ligands will be attached to the titania surface via one ligand in all cases due to close-to-round shape of the molecule. As a result, the „open flower“-like adsorption configuration should be common for them all.

4) As for the one-dentate mode of the adsorbed molecule attachment, the benzoic acid family study has clearly highlighted that not a carboxylic group itself, but the molecule as a whole participates in the adsorption process. Close to parallel accommodation of the phenyl ring with the surface not only provides a considerable contribution of the van-der-Waals contacts in the intermolecular interaction but also promotes the formation of chemical bonds between the ring carbon atoms and bridged oxygen atoms of the surface. In many cases the ring contribution dominates in the adsorption process.

5) Similarly, a simplified bi-dentate model of adsorption of either bi-isonicotinic acid or higher dentate dyes does not occur in the „pure“ way and neighboring phenyl rings are actively involved in the adsorption, sometimes dominating.

6) In general, the chemical adsorption of carboxylic species is accompanied by the formation of a rather large spectrum of chemical bonds formed contrary to a common suggestion about a key role of the O–Ti<sub>lattice</sub> bonds only [5–8]. Obviously, the surface loosening caused by the surface structure relaxation strengthens this tendency.

7) Complicated by nature, the titania-carboxylic species interface is a very difficult object for simulation. The experience gained in the current study shows that none of individual results obtained in due course of a single model consideration is able to provide a real picture of the phenomenon under study. No simplified models are promising as well.

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