Adsorption of carboxyl groups and phosphate groups on the surface of titanium dioxide

Bachelor Thesis

Mathias Poline

October 20, 2016

Table of contents

Contents

1	Bac	ckground	3
	1.1	Applications for dye-sensitized solar cells	3
	1.2	Titanium dioxide	4
	1.3	Adsorption principle	4
	1.4	Acetic acid	5
	1.5	Methylphosphonic acid	5
2	Mo	del and method	6
	2.1	Bulk structures	6
	2.2	Anatase (101) surface \ldots	7
	2.3	Slab thickness	8
		2.3.1 Structural relaxation	8
		2.3.2 Surface formation energy	8
		2.3.3 Adsorption energy	8
	2.4	Computational details	9
		2.4.1 Born-Oppenheimer approximation	9
		2.4.2 Density Functional Methods	9
		2.4.3 Kohn-Sham theory	9
		2.4.4 Generalized Gradient Approximation	9
3	\mathbf{Res}	sults	10
	3.1	Structural relaxation	10
	3.2	Surface formation energy	11
	3.3	Adsorption of acetic acid	12
	3.4	Combination of adsorption modes	14
	3.5	Adsorption of Methylphosphonic acid	16
	3.6	Comparison	18
4	Con	nclusion	18
5	Ref	rences	19



Stockholm University, Department of Physics

Abstract

Acetic acid and methylphosphonic acid are two simple molecules which can be used as anchoring groups in dye-sensitized solar cells. Their behavior in proximity of the anatase (101) surface has been studied by means of first principle density functional theory using a slab geometry with the same computational setup to enable direct comparison. The slab thickness was first determined to five layers after investigation of the structural relaxation and surface formation energy. The most stable adsorption geometry for both molecules was found to be a molecular monodentate inter configuration. Further investigation by combination of different adsorption modes for acetic acid supported these results. The adsorption of methylphosphonic acid was found to be stronger than acetic acid.

Acknowledgements

This project was conducted at the Chemical Physics department of Stockholm University. I would like to thank my supervisor Michael Odelius who provided expertise that greatly assisted my research. I would also like to thank my friend Dany Gerstenberg for his support and help in the layout of the manuscript.

Motivation

A lot of research has been done the past years in the field of dye-sensitized solar cells. One of the fundamental part in the development is the investigation of an appropriate chemical substituent which can enable the adsorption of dyes on the titanium dioxide surface and effectively transfer electrons. The objective is to minimize energy losses included in the adsorption process, and thus maximize the efficiency of the transformation of solar energy into electrical energy. The stability and durability of this chemical substituent are also important in order to have long term viable solar cells. This project consists of examining how carboxyl and phosphonate groups binds to the anatase (101) surface. This includes analyzing the number of attachment points the molecules have on the surface, their orientation relative to the surface's directions, and the energy gain obtained from the adsorption.

Previous studies have shown that different adsorption modes affect the properties of dye-sensitized solar cells. Consequently, the adsorption energies of these modes have been investigated and results have differed in some cases. The objective of this study is to make a consistent comparison of the adsorption of RCOOH and RPO_3H_2 within the same computational framework and relate to previous studies. Hopefully, this study might add some clarity and provide valuable results.

1 Background

This section presents the context of the project. It is introduced by a description of the applications for dye-sensitized solar cells and the principle of operation, followed by a description of the material used in dye-sensitized solar cells and its properties, and an explanation of the adsorption phenomenon. Lastly, the chemical substituents are presented, with a description of the different possible adsorption modes.



Figure 1: Principle of operation of a dye-sensitized solar cell

1.1 Applications for dye-sensitized solar cells

Dye-sensitized are the latest class of advanced solar cell, and use a process which is similar to photosynthesis, by using a molecular absorber to convert light to electrical power.

In a standard photovoltaic cell, light absorption and current generation are both performed by a photoactive material by means of electron-hole pair creation. However, this involves using expansive high purity materials. Another disadvantage is the inefficiency at low light intensities due to charge recombination by impurities. [1]

In dye-sensitized cells, these two processes are separated.

Dye molecules adsorbed to TiO_2 nanoparticles and emerged in an electrolyte, absorb incoming photons and reach the excited states, step (1) in figure 1. The excited electrons are then injected through oxidation, to the conduction bands of the TiO_2 electrodes (2).

The electron diffuses between nanoparticles until it reaches the conduction anode (3). This transition occurs via energetically disordered sites, a process different from standard electron conduction. This eventually causes a voltage in the circuit, corresponding to the difference between the electron's Fermi level and the potential of the electrolyte. The electrolyte, usually an organic solvent, is reduced at the end of the counter electrode, and quickly restores the dye's original state before charge recombination can occur.

One important part of the process is the immobilization of the dye molecules onto the titanium dioxide surface. This is usually achieved by adding an "anchoring group", that is, a chemical substituent which can adsorb the dye molecule onto the surface.

Common molecules used for this process are carboxylic acids and organosilanes. In this study, the adsorption of carboxyl and phosphonic acids on the surface of titanium dioxide is investigated and compared.

¹Picture obtained from research article from Hsu *et al.* [2]

1.2 Titanium dioxide

Titanium dioxide, is a naturally occurring metal oxide with chemical formula TiO_2 . The stochiometry is described by one atom of titanium and two atoms of oxygen.

There are three natural mineral forms of titanium dioxide: Anatase, rutile and brookite. The structure, energetics and reactivity of their surfaces have been analyzed and compared in various studies. Rutile was found to be the most stable and abundant form. It has various properties which makes it useful for different applications. It is for instance commonly used as white pigments in paints due to its efficient scattering of white light and chemical stability. [3]

Anatase is a metastable polymorph of TiO₂, and eventually transforms to rutile phase upon heating to high temperatures (above 600°C). However, it was found to be more efficient than rutile for photocatalysis. [4] Other experimental observations have showed that anatase is the most stable form for smaller nanoparticles up to 14 nanometers. [5]. This is particularly of interest since nanoparticles have a large surface area suitable for adsorption.

There are various stable crystal structures of TiO_2 with different oxygen/titanium ratios. As a result, reduction (loss of oxygen atoms) can occur easily. These bulk defects result in a high conductivity in the material, and makes it suitable as a n-typed semiconductor. [6]. The material is also rather inexpansive. These properties altogether, make titanium dioxide, and more specifically anatase, an ideal material for dye-sensitized solar cells applications.



Figure 2: Potential energy as function of distance z

1.3 Adsorption principle

When a molecule reaches a surface, it can behave in different ways.[7]

- Elastic scattering: The molecule bounces back off the surface without any energy exchange,
- Inelastic scattering: The molecule bounces back off the surface and loses or gains some energy in the process.
- Physisorption: The molecule is fastened to the surface by weak van der Waals forces.
- Chemisorption: The molecule forms chemical bonds with the surface.

Strong chemical bonds are expected in this research, since the oxygen atoms can form bonds with the titanium and hydrogen ions by exchange and sharing of electrons. The atoms on the surface are also unsaturated and therefore react easily with other chemical compounds. The energy for this type of adsorption tends to be in the range of 40 to 1000 kJ/mol and have high stability. There is also two ways in which the molecule can form these bonds.

- Non-dissociative chemisorption: The molecule first reaches a brief physisorption state and then go over to chemisorption by passing a small energy barrier. See figure 2.
- Dissociative chemisorption: The molecule undergoes the same process finds a channel to pass the second energy barrier as well and breaks into two fragments, which are adsorbed to the surface.

Both are expected under these calculations, since both groups can dissociate by giving up an hydrogen ion to an oxygen atom on the surface. For the two molecules considered, acetid acid and methylsphonic acid, the adsorption modes are presented and discussed in next section.

Acetic acid 1.4

Acetic acid is a molecule with chemical formula CH_3OOH which belongs to the group of carboxylic acids. A schematic of the molecule follows here.



Acetic acid molecule

The adsorbate can bind to the titanium dioxide surface in several different ways. The two principal adsorption modes are monodentate and bidentate, depending on the number of oxygen atoms or ions which coordinate with the titanium atoms. When different bonds are considered, the adsorption modes are distinguished by their geometries. Those are denoted inter or intra, depending on the alignment of the atoms relative to the surface (explained later in the results section). The principal modes are schematically presented here.

Methylphosphonic acid 1.5

Methylphosphonic acid is a molecule with chemical formula CH₃PO₃H₂which belongs to the group of phosphonic acids, and is schematically represented as:



Methylphosphonic acid molecule

The molecule has three phosphate-oxygen bonds and therefore multiple anchoring possibilities. A tridentate adsorption can be considered (binding with three surface oxygen atoms), but also monodentate and bidentate adsorptions can occur with different oxygen atoms and different number of hydrogen bonds. The three principal adsorption modes are displayed in the following figures. Different combinations for each mode are also possible.



The molecules can also adsorb to the surface by means of dissociation, as discussed in previous section. In that case, the dissociated protons attach to another oxygen atom. For methylphosphonic acid, both protons can also dissociate. The modes are presented schematically as follows:



2 Model and method

2.1 Bulk structures

To describe the initial geometry of the crystal structure, some concepts of crystallography and space groups theory are required. To define a crystalline arrangement, it is common to use Bravais lattices. A Bravais lattice is defined as an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed [8]. It can be described by position vectors \mathbf{R} of the form:

$$\mathbf{R} = n_1 \mathbf{a_1} + n_2 \mathbf{a_2} + n_3 \mathbf{a_3} \tag{1}$$

where $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ are three primitive vectors which spans the lattice.

These Bravais lattices are classified into space groups (also known as symmetry groups), which can be denoted by the Hermann–Mauguin notation. [9]

The atomic positions, cell parameters and space groups have been obtained by previous experiments using neutron and X-ray diffraction. Table 1 and 2 show results from experiments conducted at room temperature. [10]

From Table 1, we find that Rutile and Anatase belong to the space groups $P4_2/mnm$ and $I4_1/amd$. The first letter gives us information about the centering of the Bravais Lattice. For example P stands for primitive and I stands for Body-centered (from the German "Innenzentriert"). The numbers denote the screw axis and and the small letters contain information about glide planes and mirroring.

From this, the unit cells of anatase and rutile were constructed using the computer program GNU Octave. Figure 3 and 4 shows a balls and sticks representation for the unit cell of rutile and anatase, modelled with Molden, a visualization program of molecular structure.

Atoms present on the edges of a unit cell are shared by more than one unit cell. For example, an atom on a corner is shared by eight unit cells. Thus, only one eighth of an atom can be assigned to each of the unit cells.

Thus we find that the rutile bulk structure is composed of two titaniums atoms forming a body centered cell. Two entire oxygen atoms plus four half oxygen atoms surround the central atom in a octahedral-like configuration. The second titanium atom form the corners of the cell.

Anatase has a similar bulk structure with its center also being composed of a distorted octahedral structure of oxygens atoms surrounding titanium atoms. The central octahedral form chains with other four other octahedra coordinated to the edges of the cell, making a total of four titanium atoms and eight oxygen atoms.



Figure 3: Rutile unit cell



Figure 4: Anatase unit cell

	Rutile	Anatase
Space group	$P4_2/mnm$	$I4_1/amd$
Cell constant a	4.59308 Å	$3.78479 \ { m \AA}$
Cell constant c	$2.95889 { m \ \AA}$	$9.51237~{ m \AA}$

 Table 1: Structure Refinement

The cell constants a and b are equal.

	Rutile			Anatase		
Atom	х	У	\mathbf{Z}	х	У	\mathbf{Z}
Ti	0	0	0	0	0.09375	0.375
0	0.30476	0.30476	0	0	0.041715	0.16686

Table 2: Atomic positions in internal crystal units

2.2 Anatase (101) surface

By repeating the unit cell of anatase in all three directions, a bulk lattice can be constructed. From this, we can theoretically create any surface by cutting the crystal along any plane. In reality, only a few specific planes holds a stable structure. Crystals have a tendency to split along these planes under a phenomenon called cleavage.

Experimental observations have showed that the most stable surface for anatase is the (101) surface. It is hence the most exposed surface, and constitutes more than 94 percent of the crystal surface. [11]

The notation arises from Miller indices, which are used to describe planes in crystal Bravais lattices. Our cell can be described by three primitive vectors $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ which point in the x, y, z directions and have lengths a,b and c respectively. The Miller indices (h,k,l) denotes a plane which is normal to the reciprocal lattice vector

$$\mathbf{G} = h\mathbf{b_1} + k\mathbf{b_2} + l\mathbf{b_3} \tag{2}$$

For a orthorhombic lattice, the reciprocal lattice vector is parallel to the primitive vectors and so a plane denoted by (101) has the normal $a\hat{x} + c\hat{z}$.

To obtain the anatase (101) slab, a larger structure was constructed and the given plane was marked, as seen in figure 5.

The characteristics of the sought slab are a periodicity along the given plane, and a number of oxygens atoms twice the number of titanium atoms. After investigation, a unit cell holding these characteristics was determined, see figure 6.

This Anatase (101) cell is composed of four titanium atoms and eight oxygen atoms, in a very distinctive sawtooth form. The cell constants for this unit cell are a'=10.23766 Å, b'=c'=3.78479 Å. From this unit cell, the surface of anatase (101) can now be simulated using a chosen amount of atomic layers repeated in any direction in the plane dimensions.



Figure 5: Anatase crystal with (101) plane



Figure 6: Anatase (101) unit cell

2.3 Slab thickness

When modeling an open surface, it is crucial to determine a suitable slab thickness to work with. The slab thickness is the amount of atomic layers which constitute the surface, that is, the amount of times the unit cell is repeated in any directions. To obtain a realistic representation of a surface, we need to select a slab which reaches a certain convergence upon structural relaxation. To do that, the atomic displacements upon relaxation for different slab thickness are calculated. These are displayed in the Results section. Ideally we would use an infinitely thick slab. This would give us a realistic model since surfaces have a very large number of layers but we have to limit ourselves due to restrictions in computational time and capacity.

2.3.1 Structural relaxation

When cutting a solid, the resulting surface is never perfect in the sense that it does not match the structure of the material in the bulk. Additional surface energy is produced by cutting bonds, during the creation of the surface. In order to minimize this surface energy and limit the number of dangling bonds, atoms in a crystal may assemble in a new different configuration, by means of reconstruction and/or relaxation. For Anatase (101), only the latter has been observed to occur. [12]

This relaxation can be important and usually manifest by a slight displacement of the atoms perpendicular to the surface. It can be can either be positive (increased distance) or negative (decreased distance), depending on the material.

To determine these displacements, a geometrical optimization is performed for a slab and for a bulk model.

See the "Computational details" section on the next page, for further information about the calculations.

2.3.2 Surface formation energy

The energy required to separate a crystal and form an unit area of surface can be computed as:

$$E_S = \frac{E_{\rm slab} - E_{\rm bulk}}{2A} \tag{3}$$

where E_{slab} and E_{bulk} are the energies of given slab respectively bulk structures. A is the unit surface area and a factor 2 to take account for the fact that we form two surfaces in our slab model.

The surface energy can also be computed in a different way, to reduce the error due to varying bulk energy. Then the formula is:

$$E_S = \frac{E_{\text{slab}} - n \cdot E_{\text{bulk}*}}{2A} \tag{4}$$

where $E_{\text{bulk}*}$ is the energy of the bulk per formula unit for an infinite system, and n is the number of formula units in the slab. [13]. The average energy per formula unit of different sized bulk is used.

This energy gives us information about the stability of the surface. The more energy per area required to cleave the surface, the less stable the slab is expected to be.

2.3.3 Adsorption energy

Using different initial adsorption geometries, geometrical optimization are performed on the adopted slab model.

The adsorption energies are calculated by taking the difference between the system's total energy and the energy of the anatase surface plus the adsorbate molecule's energy.

$$E_{\rm ads} = E_{\rm tot} - (E_{\rm surf} + E_{\rm mol}) \tag{5}$$

All values are presented in the Results section.

2.4 Computational details

The calculations are performed using CP2K [14], a suit of open source programs including methods based on density functional theory and molecular dynamics simulations. Electronic structure methods are used, which require the Born-Oppenheimer approximation.

2.4.1 Born-Oppenheimer approximation

The total Hamilton operator in the Schrödinger equation, is the sum of the kinetic and electrostatic interactions:

$$\mathbf{H}_{\text{tot}} = \mathbf{T}_{\mathbf{N}} + \mathbf{T}_{\mathbf{e}} + \mathbf{V}_{\text{NN}} + \mathbf{V}_{\text{Ne}} + \mathbf{V}_{\text{ee}} \qquad (6)$$

Molecules consist of a number of electrons encircling a set of positively charged particles. Since electrons move a lot faster than nuclei, they can be considered to move on a time scale of fixed nuclei positions. As a consequence, we can separate the wave function into a nuclear and electronic part.

$$\Psi(X,x) = \Psi_N(X)\Psi_e(X,x) \tag{7}$$

This way we can solve the Schrödinger equations separately for the electrons, and map a potential energy surface. The nuclei, being heavy particles, can be approximated as classical particles, else defining a clear molecular structure would be difficult. Quantum tunneling and Heisenberg's principle would make it problematic to determine precise atomic positions, as we would only be able to define a probability density to find the nucleus within a certain volume.

The construction of a complete potential energy surface for larger systems would be very laborious and therefore the calculations are often restricted to finding useful information, as the lowest energy path from one minimum to another. [15]

The Born-Oppenheimer approximation is therefore a useful tool for describing molecular motion, but can break down in some special cases when the solutions to the electronic Schrödinger equation are close energetically and couple strongly.

2.4.2 Density Functional Methods

The DFT methods are built upon the proof by Hohenberg and Kohn[16] that a correspondence between the electron density of a system and its energy exists. They consist of functions connecting the electron density with the energy [17].

For a fixed geometry, under the Born-Oppenheimer approximation, the nuclear-nuclear repulsion $\mathbf{V}_{\mathbf{NN}}$ is constant. The total kinetic energy can be expressed as one single term $T(\rho)$, and the electron-electron interaction can be divided into a Coulomb and an exchange part.

To obtain an accurate representation of the kinetic energy, the theory of molecular orbitals is used. This is known as Kohn-Sham theory, which the majority of the applications with CP2K is based on.

2.4.3 Kohn-Sham theory

Ì

The solutions of the Schrödinger equations can be computed as Slater determinants of molecular orbitals ϕ_i . If we neglect electron interaction, then the exact solution to the kinetic energy can be found as:

$$T_S = \sum_{i=1}^{N_{\rm el}} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle \tag{8}$$

The density can be related to this set of auxiliary one-electron orbitals as:

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_{\rm el}} |\phi_i(\mathbf{r})|^2 \tag{9}$$

A general energy expression can then be written with an exchange correlation term in the total energy, which takes into account all the errors we have due to our approximations.

$$E_{\rm DFT} = T_S[\rho] + E_{Ne}[\rho] + J[\rho] + E_{xc}[\rho]$$
(10)

The main task behind KS theory is thus to find a good approximation to the exchange-correlation energy functional, so that we can solve the KS equation for KS one electron orbitals.

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}[\rho] + J[\rho] + V_{xc}\right]\phi(r) = \epsilon_i\phi(r) \quad (11)$$

In CP2K, these can be solved using the Generalized Gradient Approximation of the energy functional.

2.4.4 Generalized Gradient Approximation

The Local Density Approximation is the assumption that the electron density varies slowly and can be described as an uniform electron gas. Unfortunately, this is not really accurate, as the electron density in molecules is not uniform. An improvement to this, is the introduction of the gradients of the density. The exchange-correlation term is then described as a function of the density and its gradient.

$$E_{xc} = E_{xc}(\rho(r), \nabla \rho(r)) \tag{12}$$

Different versions of this approximation exist, for these calculations, the BLYP[18][19] functional is used, where the letters stand for Becke who introduced the exchange part and Lee, Yang and Parr the correlation part. The method is reasonably accurate in determining geometries and interaction energies and used regularly in the fields of chemical physics and solid states physics.

3 Results

This section starts with a presentation of the structural relaxation with pictures and a table. Following these results, the slab thickness is determined to five layers. Next, the results for the adsorption energies of acetic acid and methylphosphonic acid are presented and compared. The adsorption of multiple acetic acid molecules is investigated.

3.1 Structural relaxation

The slabs are repeated periodically and separated by a vacuum region of 9 Ångström to reduce any interaction between the slabs. The ions displacements in the direction perpendicular to the surface, were computed for different slab thickness, and are displayed in table 3. Since the slabs have identical top and bottom surfaces, the bond displacements are symmetrical, and only the top layers are considered.

The surface atoms are labeled according to figure 7. The structures are denoted as UxVxW where U, V and W denote the number of repetition of the anatase (101) unit cell in any of the three directions in our new coordinate system. Figure 7 show how these layers are denoted, and as an example, images of the 1x3x3 structure prior to, and after relaxation are shown.

As we see, sixfold and fivefold coordinated titanium atoms occur on the surface, which are denoted as Ti1 and Ti2 respectively. Twofold and threefoldcoordinated oxygens are also present, which have unsaturated bonding. The surface expands upon relaxation, as most atoms on the surface move outwards.

The atoms denoted O4 and Ti1 on the surface are the most affected as more layers are added. From figure 8, one can see that the oxygen atom O4 elevates above the titanium atom Ti2 upon relaxation. The titanium atoms move in contrary directions, and approach an horizontal alignment. This can of course influence the adsorption geometries and therefore it is relevant to chose an sufficiently thick slab.

As we reach five layers, the atoms in the middle layer have minor displacements upon relaxation. The displacements of the outer atoms reach a certain convergence.

Structure		01	O2	O3	O4	Ti1	Ti2
1x3x1	1	-0.20	0.09	-0.09	0.20	0.28	-0.28
1x3x2	1	-0.21	0.12	0.02	0.03	0.22	-0.18
1x3x3	1	-0.23	0.09	0.03	0.06	0.18	-0.13
	2	-0.04	0.04	-0.04	0.04	0.12	-0.12
1x3x4	1	-0.23	0.09	0.03	0.07	0.17	-0.12
	2	-0.05	0.03	-0.03	0.05	0.09	-0.09
1x3x5	1	-0.23	0.09	0.03	0.07	0.16	-0.12
	2	-0.05	0.03	-0.03	0.04	0.08	-0.07
	3	-0.04	0.02	-0.02	0.04	0.06	-0.06
1x3x6	1	-0.23	0.09	0.04	0.05	0.16	-0.12
	2	-0.02	0.02	-0.03	0.02	0.07	-0.06
	3	-0.05	0.01	-0.02	0.06	0.02	-0.02
1x3x7	1	-0.23	0.09	0.04	0.05	0.16	-0.11
	2	-0.04	0.02	-0.04	0.05	0.06	-0.05
	3	-0.05	0.01	-0.02	0.04	0.03	-0.02
	4	-0.05	0.01	-0.01	0.05	0.01	-0.01

Table 3: Atomic displacements [Å] in the (101) direction Numbers 1-4 denote layer position



Figure 7: Atoms label at the surface



Figure 8.a: Atomic structure of the 1x3x3 surface before optimization



Figure 8.b: Atomic structure of the 1x3x3 surface after optimization

3.2 Surface formation energy

Table 4 show the calculated energy per area for different slab thickness, using formulas (3) and (4) from section 2.3.2. When using equation (3), it can be noted that the energy is found to be lower for even numbers of layers. While equation (4) tends to give less variation, but no special pattern. Regardless of the formula used, a convergence of the results wasn't found.

In an attempt to understand the cause, a further investigation was done. Figure 9 show the energy for different sized slab and bulk models, divided by the amount of layers n. It appears that the bulk energy varies when using equation (3), which could explain the disparity of the calculated surface energies in table 4. When using equation (4), the average energy per formula unit of different sized bulk is used as the bulk energy $E_b ulk*$, it is therefore constant, and shown as the red line on the graph. We expected that it would improve the results but it didn't give us any convergence either.

According to Sorescu et al. [20], who used PBE DFT methods, at least five layers are required to achieve a converged surface energy of $0.95 J/m^2$. Our results were rather close to this value but none of the methods used provided satisfying results. The variety of DFT calculations methods lead to different results, and the method used (BLYP, see Computational details section), is known to be less accurate for calculations of surface energies. [21]

Considering previous studies results, and the results from the previous section, we chose to use an anatase structure with five layers for our adsorption calculations. The 1x3x5 structure has satisfying results for the atom displacements upon relaxation and for its surface energy.

Structure Atoms Energy (3) Energy	(4	4)	
---	----	---	---	--

		00 ()	0, ()
1x3x2	72	0.89	0.84
1x3x3	108	0.93	0.89
1x3x4	144	0.83	0.90
1x3x5	180	0.91	0.85
1x3x6	216	0.84	0.88
1x3x7	252	0.90	0.89



Figure 9: Energy of different sized slab and bulk models using equation (3) (blue), and (4) (red)

3.3 Adsorption of acetic acid

The bond distances between the molecule's atoms and the surface atoms are presented in table 5. Table 6 show the calculated adsorption energies for acetic acid, using equation (5), for the three different modes displayed in figure 10-12.

The results seem to agree with Spreafico *et al.*[23], who computed similar values for the same slab thickness as this study. They used Hybrid DFT methods, which are quiet similar to ours but more accurate. In their study, the importance of the slab thickness is reviewed and it is found that the difference in adsorption energy between different modes decreases as more layers are added.

Our results seem to point out a monodentate inter geometry as being the favoured mode, where the molecule form an hydrogen bond with an oxygen atom crosswise on the surface.

This is contrary to results obtained by Chan *et al.*, who found the bidentate adsorption to be the most energetically favourable. on the other hand, a thinner slab was used for their calculations. Their calculations were made using DFT methods with PBE functionals. The difference in the methods used might explain the difference in order of magnitude of the computed energies. An agreement can at least be made about the adsorption mode Monodentate intra, which yields lowest adsorption energy for these two studies and ours.

To extend our analysis, we investigate the adsorption of multiple molecules with different modes to see if the interaction between the molecules impact the favoured state.

Structure	O1-Ti	O2-Ti	H1-O
Monodentate inter	-	$2.12, (2.26)^1$	$1.58 \ (1.62)^1$
Monodentate intra	-	$2.18 \ (2.26)^1$	$1.64 \ (1.62)^1$
Dissociative bidentate	$2.07 \ (2.22)^1$	$2.08 \ (2.22)^1$	0.97

Structure	Ti-O bonds	H-O bonds	This study	Spreafico et al. [23]	Chan $et al.$ [24]
Monodentate inter	1	1	128.79	125.0	150.52
Monodentate intra	1	1	119.84	114.6	144.72
Dissociative bidentate	2	1*	127.86	119.5	164.99

Table 5: Bond distances (Å)

Table 6: Adsorption energies and number of atomic bounds for acetic acid [kJ/mol]

 $^{^1\}mathrm{Refer}$ to results obtained by Manzhos et~al.[22]

Graphics of the adsorption modes of acetic acid



Figure 10.a: Monodentate inter: Side view



Figure 11.a: Monodentate intra: Side view



Figure 12.a: Dissociative Bidentate: Side view



Figure 10.b; Monodentate inter: Top view



Figure 11.b: Monodentate intra: Top view



Figure 12.b: Dissociative Bidentate: Top view

3.4 Combination of adsorption modes

The favorability of the combination of adsorption modes can be evaluated by calculating the energy difference between the individual adsorption modes and the combination of two.

$$\Delta E = E_{M1+M2} - (E_{M1} + E_{M2}) \tag{13}$$

A positive value means a favorable adsorption mode combination. Table 7 show the calculated adsorption energy differences for the adsorption modes shown in figure 13-18.

Here again we find that the system gains energy by having molecules placed in a monodentate crosswise position. This is contrary to experimental results (Grinter *et al.*[27]), who observed dissociative bidentate binding geometry on the anatase surface at room temperature. Several factors can account for this inconsistency. Spreafico *et al.*[23] mention and discuss the state of the dissociated proton. They found that the proton can migrate to a different position through a low energy pathway, and reach a subsurface position. In our study, the proton is assumed to have a definite position on the surface, and may therefore interact with the molecules counter-productively It was also found that the solvent used plays a underlying role in the detachment of the molecule and the proton's migration. It can be noted that the presence of oxygen vacancy defects on natural TiO₂ surfaces can also affect the adsorption geometries. Further investigation would be required to explain the results.

System	Energy difference ΔE
Monodentate inter + Monodentate inter	4.58
Monodentate inter + Monodentate intra	3.45
Monodentate inter + Bidentate dissociative	-2.09
Monodentate intra + Monodentate intra	-2.81
Monodentate intra + Bidentate dissociative	-3.72
Bidentate dissociative + Bidentate dissociative	-8.93

Table 7: Adsorption energy differences [kJ/mol]

Graphics of the combination of adsorption modes of acetic acid



Figure 13: M-inter+M-inter top view



Figure 15: M-inter+B-dissociative top view



Figure 17: M-intra+B-dissociative top view



Figure 14: M-inter+M-intra top view



Figure 16: M-intra+M-intra top view



Figure 18: B-dissociative+B-dissociative top view

3.5 Adsorption of Methylphosphonic acid

The bond distances between the molecule's atoms and the surface atoms are presented in table 7. Table 8 show the calculated adsorption energies for methylphosphonic acid, for the give different modes displayed in figure 19-23. Two studies are used for comparison, one using tight-binding DFT method[26], and another using hybrid-functional (B3LYP) DFT method[25]. Both studies concern the adsorption of phosphonic acid, which is the same molecule without a methyl group. The order of magnitude may therefore differ, but the adsorption modes of the molecule are similar. Our results seem to agree

well with Nilsing *et al.*, who also found monodentate inter to be the most beneficial adsorption mode. The computed bond distances in our study are somehow larger for the absorption modes Monodentate inter 1 and Monodentate intra, but otherwise mostly in agreement. Here again the results differ depending on the method used. Luschtinetz *et al.* found the dissociative bidentate mode to be the most stable, in agreement with previous experimental results ([28]). The hydrogen bond interactions in the surface and the role of the solvent can also be discussed in this case. No stable tridentate geometry could be found, which seems to be in agreement with previous studies.

Structure	O1-Ti	O2-Ti	H1-O	H2-O
Monodentate inter 1	-	$2.06 \ (2.07)^2$	$1.86 \ (1.69)^2$	$1.66 \ (1.63)^2$
Monodentate inter 2	-	$2.00 \ (2.06)^2$	$1.58 \ (1.57)^2$	$1.57 \ (1.56)^2$
Monodentate intra	-	$2.51 \ (2.26)^2$	$1.77 \ (1.58)^2$	$1.98 \ (1.92)^2$
Dissociative bidentate 1	$2.00 \ (2.08)^2$	$2.01 \ (2.01)^2$	$1.64 \ (1.62)^2$	$0.97 \ (0.97)^2$
Dissociative bidentate 2	$1.95 \ (1.96)^2$	$1.95 \ (1.98)^2$	$1.01 \ (1.02)^2$	$1.01 \ (1.03)^2$

Table 8: Bond distances (Å)

Structure	Ti-O bonds	H-O bonds	This study	Nilsing et al.[25]	Luschtinetz et al.[26]
Monodentate inter 1	1	2	205.83	180.75	-
Monodentate inter 2	1	2	227.07	197.07	189.372
Monodentate intra	1	2	143.43	115.06	-
Dissociative bidentate 1	2	$1^{*},1$	218.85	184.51	260.028
Dissociative bidentate 2	2	2^{*}	211.50	168.62	272.946

Table 9: Adsorption energies and number of atomic bounds for methylphosphonic acid [kJ/mol]

²Refers to results obtained by Nilsing et al.[25]

Graphics of the adsorption modes of methylphosphonic acid



Figure 19.a: Monodentate inter 1: Side view



Figure 20.a: Monodentate inter 2: Side view



Figure 21.a: Monodentate intra: Side view



Figure 19.b: Monodentate inter 1: Top view



Figure 20.b: Monodentate inter 2: Top view



Figure 21.b: Monodentate intra: Top view



Figure 22.a: Dissociative bidentate 1: Side view



Figure 23.a: Dissociative bidentate 2: Side view



Figure 22.b: Dissociative bidentate 1: Top view



Figure 23.b: Dissociative bidentate 2: Top view

3.6 Comparison

The investigated adsorption modes are very similar for both molecules and comparable in their geometry. In both cases we find that the molecules favor a monodentate inter geometrical adsorption mode. The difference being that methylphosphonic acid have two hydrogen-oxygen bonds instead of one for acetic acid. Monodentate intra is found to be rather unstable for both molecules, specially for the second, with an adsorption energy 50-70 kJ/mol lower than for other modes. Comparing the results, we find that the adsorption energies of methylphosphonic acid to be approximately 60% higher than for acetic acid. The bond distances seem also to be shorter on average. These results suggest that this molecule is more strongly attached to the surface.

4 Conclusion

A set of adsorption geometries for acetic acid and methylphosphonic acid on clean TiO_2 anatase (101) surfaces have been investigated using the BLYP-DFT method. Bond lengths and adsorption energies were calculated and compared to previous studies. We found that several adsorption modes, of both monodentate and bidentate types, result in high adsorption energies. Consequently, both molecules can be used as anchoring groups to bind molecules to titanium dioxide surfaces. The strongest adsorption mode we calculated was in both cases, a monodentate inter geometry. This agrees with some previous results obtained by Spreafico *et al.*[23] and Nilsing *et al.* but not with experimental finding of the presence of bidentate modes. Different factors were found to influence the results and are discussed in the results section. The adsorption energy of methylphosphonic was found to be significantly stronger (60 %) than for acetic acid, which makes it a more strongly bound anchor group for dye-sensitized solar cells applications.

5 References

- Environmental Physics: Sustainable Energy and Climate Change, Egbert Boeker, Rienk van Grondelle. *Third Edition, Wiley* (2011)
- [2] Solid-state dye-sensitized solar cells based on spirofluorene and arylamines as hole transporting materials Chih-Yu Hsu, Yung-Chung Chen, Ryan Yeh-Yung Lin, Kuo-Chuan Ho and Jiann T. Lin Phys. Chem. Chem. Phys., 14, 14099-14109 (2012)
- [3] Comparison of Dye-Sensitized Rutile- and Anatase-Based TiO₂ Solar Cells
 N.-G. Park, J. van de Lagemaat, and A. J. Frank. J. Phys. Chem. B, 104, 8989-8994 (2000)
- [4] Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results
 A. L. Linsebigler, G. Lu, and J. T. Yates. *Chem. Rev.*, 95, 735-738 (1995)
- [5] Thermodynamic analysis of phase stability of nanocrystalline titania Hengzhong Zhang and Jillian F. Banfield J. Mater. Chem., 8, 2073-2076 (1998)
- [6] The Influence of the Bulk Reduction State on the Surface Structure and Morphology of Rutile TiO₂(110) Single Crystals.
 M. Li, W. Hebenstreit, U. Diebold, A.M Tyryshkin, M.K. Bowman, G.G.Dunham, M.A. Henderson.

J. Phys. Chem. B, 104 (20), 4944-4950 (2000)

- [7] Surface ChemistryElaine M.McCash. First Edition, OUP Oxford (2001)
- [8] Solid States Physics Neil W. Ashcrof, N. David Mermin. First Edition, Cornell University (1976)
- [9] International Tables for Crystallography Mois Ilia Aroyo, Theo Hahn. Sixth edition, Volume A: Space Group Symmetry
- [10] Structural-Electronic Relationships in Inorganic Solids: Powder Neutron Diffraction Studies of the Rutile and Anatase Polymorphs of Titanium Dioxide at 15 and 295 K
 Jeremy K. Burdett, Timothy Hughbanks, Gordon J. Miller, James W. Richardson, Jr, and Joseph V. Smith. J. Am. Chem. Soc., 109, 3639-3646 (1987)
- [11] Structure and energetics of stoichiometric TiO₂ anatase surfaces
 Michele Lazzeri, Andrea Vittadini, and Annabella Selloni. *Phys. Rev.*, B65, 119901 (2002)
- [12] Surface science : An introductionOura, K., Lifshits, V.G., Saranin, A., Zotov, A.V., Katayama, M. Springer (1941)
- [13] CO2 adsorption on TiO₂(101) anatase: A dispersion-corrected DFT study
 Dan C. Sorescu , Wissam A. Al-Saidi, Kenneth D. Jordan J. Chem. Phys., 135, 124701 (2011)
- [14] CP2K: atomistic simulations of condensed matter systems
 WIREs Comput Mol Sci 2014, 4:15–25. doi: 10.1002/wcms.1159
- [15] Introduction to computational chemistry Frank Jensen. Second edition, Wiley (2007)
- [16] Inhomogeneous Electron GasP. Hohenberg and W. Kohn. *Phys. Rev.*, 136, B864 (1964)
- [17] A Chemist's Guide to Density Functional Theory Wolfram Koch, Max C. Holthausen. Second Edition, Wiley (2001)
- [18] Density-functional exchange-energy approximation with correct asymptotic behavior A. D. Becke. *Phys. Rev.*, A38, 3098 (1988)

- [19] Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density C. Lee, W. Yang, and R. G. Parr *Phys. Rev. B 37*, 785 (1988)
- [20] CO2 adsorption on TiO₂(101) anatase: A dispersion-corrected DFT study
 Dan C. Sorescu, Wissam A. Al-Saidi, Kenneth D. Jordan. J. Chem. Phys., 135, 124701 (2011)
- [21] Molecular and Solid-State Tests of Density Functional Approximations: LSD, GGAs, and Meta-GGAs Stefan Kurth, John P. Perdew, Peter Blahah. ISSN, Vol. 75, 889
- [22] A Density Functional Tight Binding Study of Acetic Acid Adsorption on Crystalline and Amorphous Surfaces of Titania Sergei Manzhos, Giacomo Giorgi, and Koichi Yamashita. *Molecules*, 20, 3371-3388 (2005)
- [23] Structure and Mobility of Acetic Acid at the Anatase (101) Acetonitrile Interface Clecia Spreafico, Florian Schiffman, and Joost VandeVondele. J. Phys. Chem. C, 118, 6251-6260 (2014)
- [24] Anharmonic vibrations of the carboxyl group in acetic acid on TiO₂: implications for adsorption mode assignment in dye-sensitized solar cells
 Matthew Chan, Tucker Carrington Jr, and Sergei Manzhos.
 Phys. Chem. Chem. Phys., 15, 10028-10034 (2013)
- [25] Phosphonic acid adsorption at the TiO_2 anatase (101) surface investigated by periodic hybrid HF-DFT computations

Mattias Nilsing, Sten Lunell, Petter Persson, Lars Ojamäe. Surface Science 582, 49-60 (2005)

- [26] Adsorption of Phosphonic Acid at the TiO₂ Anatase (101) and Rutile (110) Surfaces Regina Luschtinetz, Johannes Frenzel, Theodor Milek, and Gotthard Seifert J. Phys. Chem. C, 113, 5730–5740 (2009)
- [27] Acetic Acid Adsorption on Anatase TiO₂(101)
 David C. Grinter, Marco Nicotra, and Geoff Thornton. J. Phys. Chem. C, 116, 11643-11651 (2012)
- [28] 1H Fast MAS NMR Studies of Hydrogen-Bonding Interactions in Self-Assembled Monolayers Pawsey, S. McCormick, M.; Paul, S. D.; Graf, R.; Lee, Y. S.; Reven, L.; Spiess, H. W. J. Am. Chem. Soc., 125, 4174 (2003)