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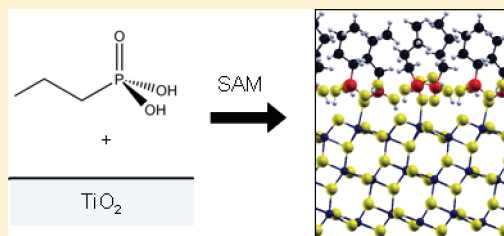
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Anatase TiO₂ Surface Functionalization by Alkylphosphonic Acid: A DFT+D StudyCristiana Di Valentin^{*,†} and Dominique Costa^{*,‡}[†]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, via Cozzi 53, 20125 Milano, Italy[‡]Laboratoire de Physico-Chimie des Surfaces, UMR CNRS-ENSCP 7045, Ecole Nationale Supérieure de Chimie de Paris, Chimie-Paristech 11, rue Pierre et Marie Curie, 75005 Paris, France

S Supporting Information

ABSTRACT: We report on a DFT study of the adsorption of *n*-butylphosphonic acid [CH₃(CH₂)₃PO(OH)₂] on the anatase (101) TiO₂ model surface. The pure GGA (PBE and rPBE) approach is compared to a hybrid functional (B3LYP). Dispersion forces are taken into account in the Grimme framework correcting both energies and gradients. The surface coverage is varied from 0.25 ML (one phosphonic unit every four surface Ti_{5c}) to 1 ML (one phosphonic unit/Ti_{5c}). The overall picture resulting from these three approaches is qualitatively the same, although quantitative details are different. At low coverage, the alkylphosphonic acid adsorbs in a monodissociated bidentate mode, forming two P=O–Ti_{5c} bonds with one additional OH–O_s bond, where Ti_{5c} and O_s refer to surface titanium and oxygen atoms. At full coverage, the molecules adsorb in a monodentate mode and reorient in order to minimize lateral repulsion and maximize H-bonds. The contribution of dispersion forces to the adsorption energy increases with the coverage. The 0.75 and 1 ML coverages, which are the most favored, correspond nicely to the reported experimental coverages. The results suggest that for entropic reasons the surface could be rather disordered, with coexisting domains of different coverages 0.75 and 1 ML. No additional states in the band gap of the semiconductors are formed for this hybrid organic–inorganic system. The workfunction decreases by 0.7 eV when a full self-assembled monolayer is supported on the surface.



1. INTRODUCTION

A biomaterial is defined as any natural or man-made material that constitutes part of a living structure or a biomedical device performing a natural function. Such materials are essentially used in medical applications. The biocompatibility of a material is defined independently of where and how the material is to be used. The “ideal” biomaterial should induce little or no immune response in a given organism and should be able to integrate with a particular cell type or tissue. Also, it should be resistant to corrosion, nontoxic, nor induce rejection or allergies. Ti and Ti alloys are typical biomaterials used for hip joints, bone plates, and dental implants, as these materials present most of the characteristics listed above and, additionally, have a high mechanical strength.¹

However, Ti, in the same way as gold, is biologically inactive. In order to achieve the desired functionality *in vivo*, surface treatments of metallic materials have been proposed. In particular, self-assembled monolayers (SAMs) are used to functionalize metal surfaces. SAMs are single-layered organic coatings that are deposited on metal or metal oxide surfaces by the adsorption of organic molecules from a solution. A further step for biomedical applications is the attachment to the supported SAMs of a variety of biomolecules, involving proteins, peptides, DNA, carbohydrates, antibodies, and therapeutics. As a possible application on Ti, arginine-glycine-aspartic acid (RGD) peptides were attached to phosphonic acid

SAMs to enhance the cell attachment to Ti surfaces.² Crucial issues in the biomedical context are the stability of SAMs under physiological and sterilizing conditions. Note that Ti and Ti alloys exposed to ambient conditions and physiological media are covered with a thin native TiO₂ oxide film.^{3–6} This film (whose structure is not known) is largely hydroxylated.^{3,4,6}

There is an increasing number of experimental studies of phosphonic acid SAMs on Ti/TiO₂ (see refs 2 and 7–18 for a nonexhaustive list). Helmy and Fadeev have investigated octadecylphosphonic acid (C₁₈H₃₇PO₃H₂) SAMs formation on anatase TiO₂ and found that the SAM order gradually improves with coverage and that highly ordered SAMs are obtained only for high surface coverages, the monolayer density being 4.3–4.8 groups/nm².¹⁵ Gawalt et al. showed by means of diffuse reflectance infrared spectroscopy (DRIFT) that octadecylphosphonic acid (ODPA) forms ordered monolayers on native titanium dioxide surfaces.² The degree of monolayer ordering was reported to increase with increasing chain length.¹¹ Pawsey et al., Guerrero et al., and Mutin et al. proposed that bond of the organophosphonic acids to the surface is usually bi- or tridentate.^{16–18} The stability of SAMs on TiO₂ mainly depends on the type of head groups and on their

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affinity toward the metal oxide surface. It has been reported that dodecylphosphonic acid $[\text{CH}_3(\text{CH}_2)_{11}\text{P}(\text{O})(\text{OH})_2]$ SAMs on Ti are stable in ambient air¹¹ and in water.^{8,19}

Besides applications for biomaterials, organic molecules adsorption and self-organization on TiO_2 surfaces, especially phosphonic acid, are also of interest in the field of dye-sensitized solar cell systems,²⁰ catalysis,²¹ photoelectrochemistry,²² and optoelectronic.²³

DFT approaches have been robustly used by the physicists' and chemists' communities during the last 2 decades and are nowadays successfully applied to model the reactivity of complex and large surfaces for applications in, for example, catalysis,²⁴ nanoelectronics,²⁵ geology,²⁶ or biomedicine.^{27,28} Theoretical works concerning the interaction of metal/alloy surfaces with organic molecules are found in the literature, where the partners building the interface (surfaces, organic molecules) are considered both when separated and when in contact (organic molecules adsorbed at inorganic surfaces). Numerous ab initio studies have been devoted to bulk and surface properties of metals and metal oxides. TiO_2 anatase and rutile (the two most common polymorphs) surfaces have been deeply investigated during the past few years.^{29,30} Particular attention has been focused on the details of the electronic structure of reduced and hydroxylated surface of TiO_2 .³¹ Such defects on the substrate surface behave as preferential adsorption sites for molecular adsorption.

Due to their well-ordered, oriented, and dense structure, SAMs offer excellent model systems for atomic scale theoretical studies of adsorption of organic compounds. Recent papers have been published on SAMs at gold surfaces (refs 32–35 and references therein). Theoretical studies have confirmed that the intermolecular van der Waals and H bonds interactions between the methylene chains of molecules are responsible for the ordered, close-packed structure of monolayer, whereas the headgroup of the molecule is responsible for the strong metal–molecule interaction that is usually chemisorption, and the tail functional group determines the physical and chemical properties of the modified surface.

The study of the interaction of organic molecules with oxide surfaces is also increasingly performed by means of ab initio tools.^{20,36–47} Some computational investigations on the adsorption of phosphonic,^{20,42} alkyl phosphonic,⁴³ octylphosphonic,⁴⁴ methyl phosphonic,⁴⁵ and dimethyl methylphosphonic⁴⁶ acids on inorganic surfaces and, in particular, also on TiO_2 anatase surface exist in the literature. Nilsing et al. found at the B3LYP level a strong adsorption energy for HPO_3H_2 phosphonic acid on (101) anatase TiO_2 of 180 kJ/mol (1.9 eV), in a monodentate nondissociated adsorption mode.²⁰ In contrast, Luschtinetz et al., exploring a great amount of possible conformations, found, with the DFT-B method, that the most stable configuration of HPO_3H_2 (with a surface coverage of 0.5 ML) was a bidentate monodissociative one with an energy of adsorption of 255 kJ/mol (2.6 eV).⁴² Methylphosphonic acid adsorption on (110) rutile was studied by means of STM and DFT.⁴⁵ As the coverage of adsorbates approaches 0.5 ML, STM images show an ordered 2×1 overlayer consistent with LEEDS results. According to DFT, at this coverage the molecule adsorbs dissociatively in the bidentate mode, with a strong adsorption energy of 2.5 eV.⁴⁵ Finally, the adsorption of dimethyl methylphosphonate on (101) anatase TiO_2 was calculated at the B3LYP level and the methyl groups were found to be bidentate dissociative with an energy of adsorption of 25 kcal/mol (1.1 eV).⁴⁶ Thus, it appears that alkylphos-

phonic acids have a strong interaction with TiO_2 surfaces and could be able to form ordered, high density SAMs.

Phosphonic acid is an interesting case where the head of the molecule has a significant size, being composed of two O(H) moieties. In this case, on the one side, the formation of strong interactions with the surface, through e.g. multipoint anchoring, is expected, whereas on the other side, the self-organization of the adsorbed layer may be limited by the steric hindrance of the head function. Therefore, it is interesting to study which of the present factors (Ti surface density, head size, or chain stacking properties) or which combination of factors determines the SAMs density (and the resulting properties).

In the present paper we propose a DFT study of the adsorption of an alkylphosphonic acid $[\text{CH}_3(\text{CH}_2)_3\text{PO}(\text{OH})_2]$ on the anatase (101) TiO_2 model surface. In this acid the alkyl chain is sufficiently long to allow for some chain–chain interactions. A pure GGA approach (PBE^{48,49} or rPBE^{50,51}) is compared to the use of a hybrid functional (B3LYP^{52,53}). We expect that rPBE corrects for PBE overbinding,⁵⁰ while B3LYP reduces the self-interaction problem.³¹ Moreover, GGA calculations are definitively computationally less expensive, which allows one to investigate a larger number of configurations. In this study, we also consider the correction for dispersion forces to the total energy and gradients. Recently, few works appeared in the literature that take dispersion forces into account in a DFT approach when studying organic molecules adsorbed on inorganic surfaces.^{54–57} The reader may be interested in a review of the present advantages and limits of each method, available in refs 56 and 57. Here, we used the dispersion contribution estimation recently proposed by Grimme et al. in the DFT-D scheme.⁵⁷

2. COMPUTATIONAL METHODS

2.1. VASP Calculations. The periodic calculations were performed using the DFT method based on the GGA approximation employing the PBE^{48,49} and rPBE^{50,51} exchange–correlation functionals. These methods were used as implemented in the plane-wave program VASP.^{58,59} The projector-augmented wave (PAW) potentials^{60,61} were used for the core electron representation with a PAW core radius of 1.52 Å for oxygen. With plane wave methods, the quality of the basis set is determined by a single parameter, the energy cutoff (E_{cut}). We used a converged value of $E_{\text{cut}} = 400$ eV. The integration in reciprocal space was performed with a Monkhorst–Pack grid.⁶² The k -points grid is $4 \times 4 \times 2$ for the bulk. The bulk cell parameters were calculated as $a_{\text{calc}} = 3.864$ Å, $c_{\text{calc}} = 9.707$ Å (rPBE) [respectively $a_{\text{calc}} = 3.871$ and $c_{\text{calc}} = 9.724$ (PBE)], a value in agreement with experimental ($a_{\text{exp}} = 3.776$ Å and $c_{\text{exp}} = 9.486$ Å)⁶³ and other theoretical data with the same method.⁶⁴

The anatase (101) surface was modeled with a periodically repeated slab. We considered a surface supercell containing 72 atoms in three triatomic layers, of dimension 1×2 in the $[10\bar{1}]$ and $[010]$ directions, respectively, corresponding to a surface area of 10.45×7.73 Å². The surface slab exhibits four 5-fold coordinated Ti (Ti_{sc}) surface atoms. Such a large cell allows us to study increasing surface coverage, from one to four phosphonic acids/unit cell, as well as different configurations at a given coverage. The Ti and O atoms of the bottom layer were fixed to the bulk positions, the cell size was kept fixed to the PBE (respectively rPBE) optimized bulk lattice parameters, and the other atoms were free to relax. Details of the surface are shown in Figure 1a. A vacuum layer of 30 Å along the z

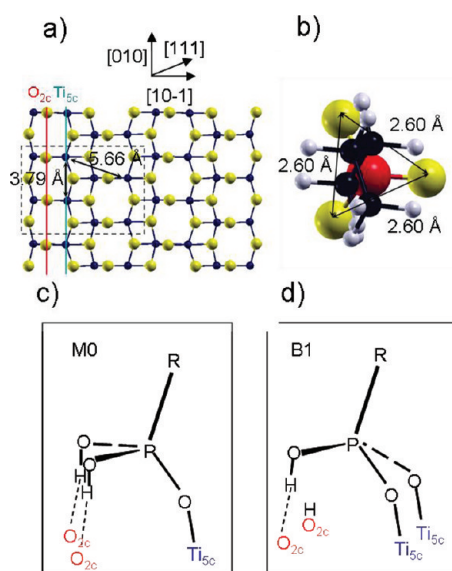


Figure 1. (a) Top view of the anatase (101) TiO_2 surface. Ti and O atoms are dark and light spheres, respectively. Lattice parameters are B3LYP data. Rows of O_{2c} and Ti_{5c} are represented by red and green, respectively. The repeated supercell is shown with dashed lines. (b) Top view of one *n*-butylphosphonic acid. (c, d) Schematic view of the M0 and B1 modes of adsorption.

direction perpendicular to the surface (x and y being parallel to the surface) was employed to prevent interactions between the repeated slabs. A k -point mesh of $2 \times 2 \times 1$ was used. A dipolar correction was introduced along the z axis perpendicular to the surface to take into account the spurious polarity induced by the nonequivalence of the top and bottom surfaces. A convergence criterion of forces on relaxed atoms $<10^{-3}$ eV \AA^{-1} (0.02×10^{-3} au) was applied.

In order to test our approach, water adsorption has been investigated and compared with other theoretical and experimental data, e.g., those reported in refs 65 and 66. Isolated molecular water adsorption on a Ti_{5c} atom was found to be exothermic by 0.61 eV (PBE) and 0.49 eV (rPBE). These values are in the range of previous values of 0.60^{67,68} and 0.75 eV found with the same code and PW91 functional.⁶⁹ Other works also report an adsorption energy of 0.72 eV.^{70,71} The B3LYP binding energy (see next section for details) is 0.60 eV, in good agreement with the PBE value here and with data from the literature.^{36,67,69,70} Further tests have shown that the differences between the adsorption energies obtained are due to the functional, but also, for a given functional, to the choice of plane-waves potentials, especially for describing the O valence electrons, and the choice of the cutoff energy. Our final choice for the plane waves was motivated by the aim to correctly describe the balance between ionocovalent and H-bonds. It is indeed well-known that the PW91 and PBE functionals overestimate H-bonds.⁷² This drawback can be partly corrected in using high-quality PAW potentials with a large cutoff for the O atom.⁷³

When dispersion forces are included (the D2 scheme approach with a scaling parameter of $s = 0.75$ is used in VASP), we obtained a value of 0.87 eV (PBE-D) and 0.68 eV (rPBE-D) for water adsorption on anatase (101). These values are compatible with the range of experimental value of 48–67 kJ/mol (0.5–0.7 eV) for water adsorption obtained exper-

imentally.^{66,74} Table 1 of the Supporting Information summarizes all those data.

2.2. CRYSTAL09 Calculations. The anatase (101) surface was modeled with the same periodically repeated slab as described above. However, periodic boundary conditions are in two dimensions (2D calculations). The optimized bulk lattice parameters are taken from previous studies,⁷⁵ in which the same approximations as in this work were used. As above, the atoms in the bottom layer were fixed to their bulk positions during geometry optimizations, in order to simulate the presence of the bulk underneath. The gradients with respect to atomic coordinates are evaluated analytically. The equilibrium structure is determined by using a quasi-Newton algorithm with a BFGS Hessian updating scheme.⁷⁶ Convergence in the geometry optimization process is tested on the root-mean-square (rms) and the absolute value of the largest component of both the gradients and nuclear displacements. For all atoms, the thresholds for the maximum and the rms forces have been set to 0.000 45 and 0.000 30 au and those for the maximum and the rms atomic displacements to 0.001 80 and 0.001 20 au, respectively.

Calculations were performed using the hybrid B3LYP^{52,53} functional with the Kohn–Sham orbitals expanded in Gaussian-type orbitals (GTO), as implemented in the CRYSTAL09 code⁷⁷ [Ti 86411(d41), slab O 8411(d1), O8411(d11), C6311(d11), H 511(p1), P 8521(d1) all-electron basis-sets]. The basis set superposition error (BSSE) was evaluated in one sample case by using the counterpoise correction method (see Table 1).⁷⁸ The percentage of exact Hartree–Fock (HF) exchange in the B3LYP functional is 20%.

Table 1. Calculated Energies of Adsorption (ΔE_{ads} , in eV) of *n*-Butylphosphonic Acid on Anatase TiO_2 (101) Surface, Using the PBE, rPBE and B3LYP Functionals without and with Dispersion Corrections Included at the Respective Optimized Geometries, and Energy Differences between the M0 and B1 Structures

| method coverage and configuration | PBE | PBE-D | rPBE | rPBE-D | B3LYP ^a | B3LYP-D ^a |
|--|-------|-------|-------|--------|--------------------|----------------------|
| 0.25 ML M0 | 1.57 | 2.00 | 1.20 | 1.55 | 1.59 | 2.28 |
| 0.25 ML B1 | 1.44 | 2.03 | 1.08 | 1.66 | 1.62 | 2.50 |
| 0.5 ML M0 | 1.59 | 2.17 | 1.15 | 1.56 | 1.36 | 2.26 |
| 0.5 ML B1 | 1.54 | 2.23 | 0.98 | 1.59 | 1.70 | 2.69 |
| 0.75 ML M0 | — | — | 0.54 | 1.18 | 0.96 | 2.00 |
| 0.75 ML M0/M1/B1 | 1.16 | 1.98 | 0.56 | 1.27 | — | 2.43 |
| 1 ML M0/M1 | 0.73 | 1.83 | 0.05 | 0.88 | 0.66 | 1.48 |
| $\Delta E(\text{B1-M0})$ (eV) ^b | | | | | | |
| 0.25 ML | −0.13 | 0.03 | −0.12 | 0.11 | 0.03 | 0.22 |
| 0.5 ML | −0.05 | 0.06 | −0.17 | 0.03 | 0.34 | 0.43 |

^aThe BSSE was computed for the M0/0.25 ML case to be 0.26 eV. For all the other cases we estimate a BSSE in the range between 0.20 and 0.26 eV per adsorbed molecule. ^bA positive value indicates that the B1 structure is the most stable.

A shrinking factor of 2 was used for the k -points mesh sampling the irreducible Brillouin zone. The densities of states (DOS) were computed using a 10 k -points mesh.

In order to evaluate the relevance of the dispersive forces in the alkylphosphonic acid–anatase TiO_2 surface interaction, calculations were performed also with B3LYP-D, which includes an empirical correction first suggested by Grimme.⁵⁷

In the variant adopted here, B3LYP-D, the covalent radii have been properly rescaled (scaling factor 1.05) to improve the dispersive contribution, as proposed by Civalleri et al.⁷⁹ Two different approaches have been adopted to account for dispersive interactions: (i) a full B3LYP-D optimization only for the adsorbed alkyl phosphonic acid molecules (D_{PA}) and (ii) a full B3LYP-D optimization for both the anatase (101) slab and for the adsorbed alkylphosphonic acid molecules (D).

The calculation of the adsorption energy of a molecule from the gas phase on the surface was described in previous papers.⁴¹ The adsorption energy is the difference between the total energy of the molecule-surface system and the energies of the molecule and the surface separately optimized: $\Delta E_{ads} = -[E_{total}(molecule-surface) - E_{opt-isol}(molecule) - E_{opt-isol}(surface)]$. For n adsorbed molecules, we evaluate the adsorption energy per molecule as $\Delta E_{ads} = -1/n[E_{total}(molecule-surface) - nE_{opt-isol}(molecule) - E_{opt-isol}(surface)]$. ΔE_{ads} (DFT), ΔE_{ads} (D), and ΔE_{ads} (DFT-D) are calculated at the DFT, D, and DFT-D levels, respectively. Positive ΔE_{ads} energies indicate exothermic adsorption.

For some cases we have also evaluated the contribution of dispersion forces to the cohesion (ΔE_{coh}) and the interaction (ΔE_i) energies per molecule, defined as the cohesion in the adsorbed layer $\{\Delta E_{coh} = -1/n[E_{geom-ads}(SAM) - nE_{opt-isol}(molecule)]\}$ and the interaction between the layer and the surface $\{\Delta E_i = -1/n[E_{total}(molecule/s\ surface) - E_{geom-ads}(SAM) - E_{geom-ads}(surf)]\}$. The D contributions are obtained with the following formulas: $\Delta E_{coh}(D) = \Delta E_{ads}(B3LYP-D_{PA}) - \Delta E_{ads}(B3LYP)$; $\Delta E_i(D) = \Delta E_{ads}(B3LYP-D) - \Delta E_{ads}(B3LYP-D_{PA})$.

3. RESULTS AND DISCUSSION

In the following, we present a study of the n -butylphosphonic acid adsorption on anatase (101) TiO_2 surface at several coverages. We define one monolayer as the ratio of one molecule per Ti_{5c} atom. In section 3.1 we focus the attention on the comparison of different adsorption modes at low coverage (0.25 ML) and at 0.5 ML. Then, in section 3.2, increasing coverages of 0.75 and 1 ML are presented. Then, in section 3.3, results obtained with the different functionals and the dispersion forces contributions are analyzed. Finally, in section 3.4 the electronic structure of these hybrid organic/inorganic systems is briefly presented.

3.1. Monodentate vs Bidentate Adsorption Mode. **3.1.1. Adsorption at Low Coverage 0.25 ML ($\theta = 1.25$ molecule/nm²).** Earlier theoretical works have proposed that the phosphonic acid may adsorb either in a monodentate or a bidentate mode on (101) anatase TiO_2 surfaces (Figure 1c,d).^{42,46} Lufschinetz et al., in a study using DFT-B, concluded that bidentate adsorption of phosphonic acid, at a coverage of 0.5 ML, is far more stable than a monodentate one.⁴² In contrast, in their B3LYP study, Nilsing et al. concluded that the most stable state for the coverage 0.25 ML is a monodentate molecular configuration with an energy of adsorption of 1.9 eV; however, the bidentate, dissociated configuration is only slightly less stable, 1.7 eV.²⁰ Comparison is not easy, as both the coverages and the methods used are different. In order to disentangle this question in the present case of the n -butylphosphonic acid, we report a detailed comparison of both configurations at 0.25 and 0.5 ML by using several methods. It is relevant to note that the acidity of n -butylphosphonic acid is expected to be different to that of phosphonic acid. Here, we compare the monodentate and

bidentate modes of adsorption as well as the degree of dissociation of the molecule (non-, mono-, and bidissociated). In a first step, we verified that the two structures mentioned here are the most stable among the monodentate and bidentate configurations (see Supporting Information, section S2). For the purpose of clarity, we refer to the structures as Mn/Bn , where M/B stands for mono or bidentate and n stands for the dissociation degree (or the number of protons adsorbed on the surface, $n = 0-2$). Table 1 reports the results obtained for the most stable configurations. The results described in this section for different possible configurations were obtained at the PBE and rPBE levels, including dispersion or not. Since the picture which comes out is coherent for all the approaches, we do not specify the method used. All geometric details are given in the Supporting Information, section S3. When not specified, in the text and in the Figures 2–5, we refer to geometrical details calculated at the B3LYP-D level.

Starting from bidissociated and monodissociated modes M2 and M1, the structures evolve spontaneously toward the undissociated mode M0 (Figure 2). This means that the surface

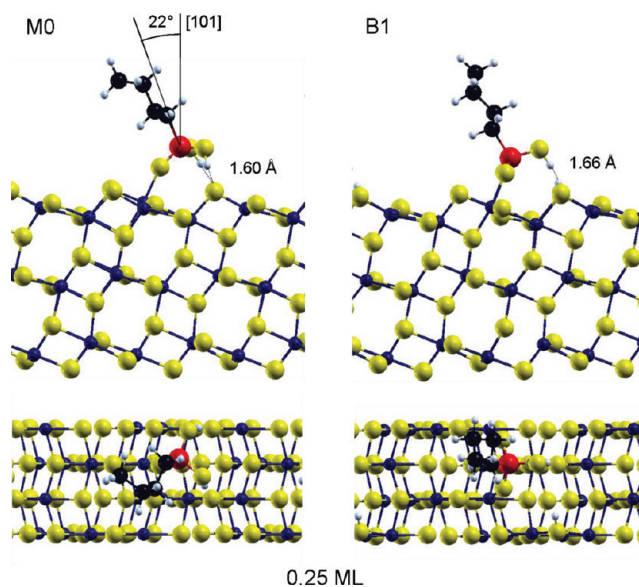


Figure 2. B3LYP-D ball and stick representation (side and top views) of M0 and B1 modes of adsorption for one n -butylphosphonic acid molecule adsorbed on the $TiO_2(101)$ surface at 0.25 ML coverage. Ti, O, C, H, and P atoms are dark, light, black, small light, and large dark spheres, respectively.

oxygen atoms are not basic enough to attract a proton from the phosphonic acid. We verified that the structures where the proton was placed too far to recombine during the geometry optimization were less stable than the M0 structure. In the same way, the B2 structure spontaneously evolves to B1 (Figure 2).

We notice that in both configurations the $P=O-Ti_s$ bond is in the same direction as the bulk $Ti-O$ bond, thus imposing an epitaxial-like relationship to the phosphonic acid. The bent orientation of the head function is further stabilized by the formation of $OH-O_s$ bonds (Figure 2). The aliphatic chain is consequently tilted by 22° from the normal to the surface.

The PBE and rPBE $Ti-O$ bond lengths between the surface Ti and O atom from the phosphonate molecule as well as the $H-O_s$ bond lengths are reported in section S3 of the Supporting Information. We notice that the rPBE bond lengths

are slightly larger than the PBE ones, in agreement with the correction factor introduced in rPBE. We note that the relaxation introduced by the dispersion forces induces some variations to the bond lengths, regardless of the functional used: as an example, with B3LYP, the PO–Ti_s in the M0 configuration shortens from 2.043 to 2.024 Å and the POH–O_s bonds also shorten from 1.64 to 1.60 Å.

In Table 1 the M0 and B1 configurations are compared in the framework of the different methods used. Discrimination between the two configurations is not straightforward, the differences in energy being most of the times very small. The main trend observed is that the pure PBE and rPBE functionals give the M0 and B1 modes as isoenergetic, both without and with dispersion forces included. In contrast, at the B3LYP level, the B1 mode is the most stable even without dispersion, and this trend is reinforced when van der Waals forces are included. The reason for this may be that the dissociative state implies electrostatic interactions between the anionic phosphonate and the surface, which are better described by the hybrid functional.

We notice that the energies of adsorption are systematically higher when calculated with PBE or B3LYP than with rPBE, due to the corrective factor added in the rPBE to compensate the overestimation of covalent binding energies. We must note that B3LYP values are affected by BSSE, which was computed to be 0.26 eV for M0 and is estimated to be about the same for B1. In the B3LYP framework, at 0.25 ML, the difference in energy between M0 and B1 is weak, confirming previous results by Nilsing et al.²⁰ for phosphonic acid. From the whole set of calculations, we may conclude that the PA molecule adsorbs strongly at the surface at 0.25 ML coverage, with an energy of adsorption in the range 1.7–2 eV (rPBE-D and B3LYP-D without BSSE, respectively), in a bidentate monodissociated mode B1.

3.1.2. Half-Monolayer 0.50 ML ($\theta = 2.5$ molecule/nm²).

The modes of adsorption M and B are also compared at 0.5 ML. In the B mode of adsorption, there is only one possible configuration, as all Ti_{5c} atoms are engaged in a Ti–O bond with the adsorbate. In contrast, in the M adsorption mode, only half of the surface Ti_{5c} atoms are bonded to a phosphonic O. We studied several possibilities of rows formation. On the (101) anatase, rows can be formed along the [11 $\bar{1}$] and [010] directions while zigzag rows formed along the [10 $\bar{1}$] direction. Note that Ti_{5c} atoms are distant from 5.61 Å (along the [11 $\bar{1}$] axis) and 3.78 Å (along the [010] axis), respectively; thus, the steric hindrance is expected to be different depending on the rows direction. At this point, it is interesting to compare the Ti_{5c}–Ti_{5c} distances at the surface with the interatomic distances in unsupported SAM layer of 5.3–5.8 Å (calculated with rPBE-D). On the basis of these values, along the [010] direction, some steric hindrance is expected to take place. Indeed, the row along the [010] axis is less stable than rows along [11 $\bar{1}$] and [10 $\bar{1}$] axis (see Supporting Information, section S4). The row along the [11 $\bar{1}$] direction is slightly less stable than a zigzag row along [10 $\bar{1}$] and is also reported in section S4 of the Supporting Information.

Therefore, we compare zigzag rows of phosphonic acid in the Mn adsorption mode along the [10 $\bar{1}$] direction with the B adsorption mode (Figure 3). Again, as at lower coverage, starting from M1 (respectively B2) configuration resulted in M0 (respectively B1) configuration. In the M0 configuration, the PO–Ti_s bond lengths are about 2.09 Å while the POH–O_s bond lengths are all about 1.65 Å, except one which is 2.24 Å (B3LYP). Such a distance suggests a more electrostatic

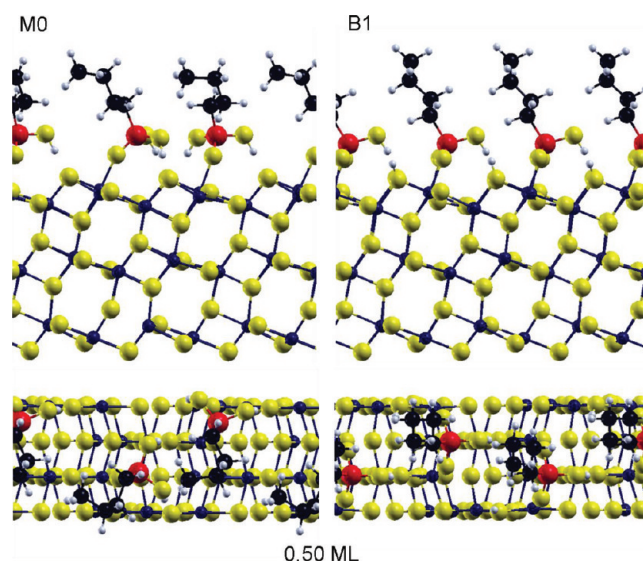


Figure 3. B3LYP-D ball and stick representation (side and top views) of M0 and B1 modes of adsorption for two *n*-butylphosphonic acid molecules adsorbed on the TiO₂ (101) surface in a zigzag row along the [10 $\bar{1}$] direction at 0.5 ML coverage. Ti, O, C, H, and P atoms are dark, light, black, small light, and large dark spheres, respectively.

interaction than a real covalent bond between the Ti_s and the phosphonic O. Dispersion forces induce a slight shortening of the PO–Ti_{5c} bonds to 2.045 and 2.066 Å and of the POH–O_s hydrogen bonds to 1.56 and 2.14 Å for the longer distance (B3LYP-D). In the B1 configuration, the most stable position found for the proton adsorbed was on the oxygen row in between the adsorbed molecules. The two PO–Ti_s distances for the bidentate configuration are all between 2.03 and 2.05 Å with a negligible effect of dispersion forces. The POH–O_s hydrogen bonds are 1.64 and 1.66 Å before and 1.62 and 1.64 Å after the introduction of dispersion forces.

As observed at low coverage, at the pure GGA level (PBE and rPBE), there is no significant difference in the energies of adsorption between both modes of adsorption while the inclusion of dispersive forces weakly stabilizes the B1 mode. The difference between the two configurations is more marked at the B3LYP level, with stabilization of the B1 mode, again reinforced when dispersion forces are included. A significant difference of 0.43 eV per molecule is obtained at the B3LYP-D level in favor of the B1 mode. In order to check that the use of a different approach (localized atomic basis functions vs plane-wave pseudopotentials) has no effect on these energy differences, PBE calculations were performed also with the CRYSTAL09 code and were perfectly coherent with those obtained with the VASP code.

We conclude that the bidentate adsorption mode is favored over the monodentate one, especially at the 0.5 ML coverage. This result reconciles nicely with that previously reported in the literature. At low coverage (0.25 ML), without taking into account dispersion, the M0 and B1 structures are nearly isoenergetic. Indeed, we find a difference of 0.03 eV (B3LYP) in favor of B1, whereas Nilsing et al. found that M0 is more stable by 0.11 eV (B3LYP) for the phosphonic acid. As already stated, inclusion of dispersion induces the B1 to be more stable. At higher coverage, the B1 mode of adsorption becomes more stable. B3LYP-D results are consistent with the DFT-B ones for the phosphonic acid in ref 42. We calculate an energy of adsorption of 2.26 eV for M0 and 2.69 eV for B1 structures of

n-butylphosphonic acid, to be compared with 1.96 eV for the M0 configuration and 2.87 eV for the B1 one in ref 42 for phosphonic acid. These energy values indicate stronger acidic properties of the phosphonic acid with respect to *n*-butylphosphonic acid, as one would expect considering the donor properties of an *n*-alkyl chain.

The difference in trends observed with different methods (GGA vs B3LYP) in Table 1 clearly derives from a different treatment of the forces involved. Indeed, the balance between mono- and bidentate adsorption is a matter of describing the relative basic properties of the phosphonate anion and the surface oxygen, the Ti–O_{PA} bond strength (Ti Lewis character), and the O–H bond strength. The description of the phosphonate group basicity is a delicate issue, as recently shown in a work where MP2 and higher levels of theory⁸⁰ were applied.

Finally, we conclude this section by pointing out that at coverage of 2.5 molecule/nm², a layer of B1 molecules forms involving all the surface Ti_{5c} atoms, with an adsorption energy of 1.6–2.5 eV per molecule, corresponding to 3.2–5 eV/unit cell (rPBE-D and B3LYP-D without BSSE, respectively).

3.2. Increasing Coverages. **3.2.1. 0.75 ML ($\theta = 3.75$ molecule/nm²).** When three of four surface Ti atoms are covered with one phosphonate group, obviously the bidentate adsorption mode (which involves two Ti_{5c} ions per molecule) cannot take place for all molecules. Therefore, the most stable conformation obtained at 0.75 ML (shown in Figure 4) is a

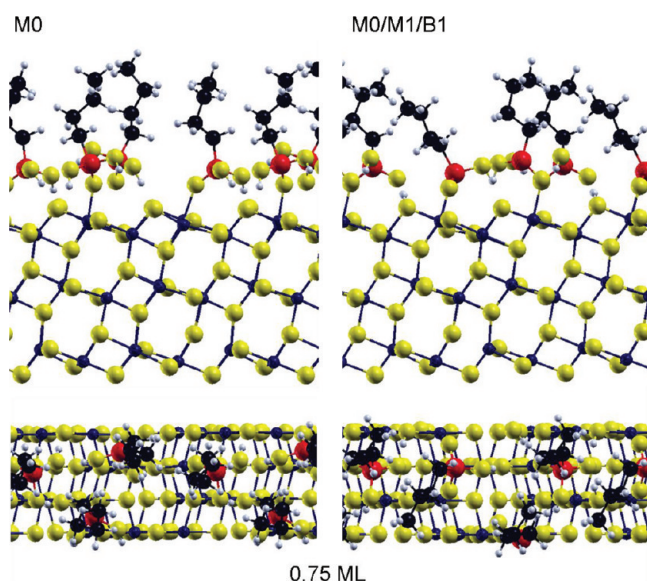


Figure 4. B3LYP-D ball and stick representation (side and top views) of M0 and M0/M1/B1 modes of adsorption for three *n*-butylphosphonic acid molecules adsorbed on the TiO₂ (101) surface at 0.75 ML coverage. Ti, O, C, H, and P atoms are dark, light, black, small light, and large dark spheres, respectively.

mixed configuration with one M0, one M1, and one B1 configuration. Again, energies calculated with B3LYP are more exothermic than those obtained with pure functional, and again, inclusion of dispersive forces stabilizes the adsorption. The calculated adsorption energy is $\Delta E_{\text{ads}}(\text{B3LYP-D}) = 2.43$ eV (around 2.2 without BSSE), a value slightly less exothermic than at lower coverage. Indeed, some Ti–O bonds formed are weaker than at 0.5 and 0.25 ML coverages, as Ti–O = 1.98, 2.03 (B1), 2.17 (M1), and 2.29 (M0) Å (B3LYP-D). This is a

consequence of the formation of a H-bond network between adsorbed molecules. For this reason, the energy of adsorption is not larger than in the 0.5 ML case. In other words, we observe here a competition between the formation of an intermolecular H-bond network and the bonding with the surface. A complementary calculation (see Supporting Information, section S5) has confirmed this trend. We also notice that one M0 molecule is spontaneously dissociated to M1 during the geometry optimization. In this case, the dissociation is assisted by the H-bond network as previously observed for other protic molecules on oxide surfaces, e.g. water/MgO⁸¹ or water/ZnO.⁸² The configuration with three monodentate adsorbed molecules (Figure 4) is less stable by 0.43 eV/molecule, as calculated with B3LYP-D (see Table 1).

Thus, a coverage of 3.75 molecule/nm² (0.75 ML) corresponds to a mixed adsorption mode, with all Ti_{5c} ions covered with phosphonate groups, with a binding energy of 1.3–2.2 eV/molecule or 3.9–6.6 eV per unit cell (rPBE-D and B3LYP-D without BSSE, respectively).

3.2.2. Full Layer ($\theta = 5$ molecule/nm²). The surface Ti_{5c} density being 5 atom/nm², we can estimate that the maximum layer density must be 5 molecule/nm². To obtain a global minimum in the potential energy surface (PES) at this full coverage, a preliminary molecular dynamics (MD) run was performed at 300 K to allow the reorientation of the head groups and of the aliphatic chains. We indeed observed this reorientation of the phosphonic acid moieties to minimize the steric hindrance at the surface. Also, a H bond network was formed (Figure 5). It has been possible to find a stable

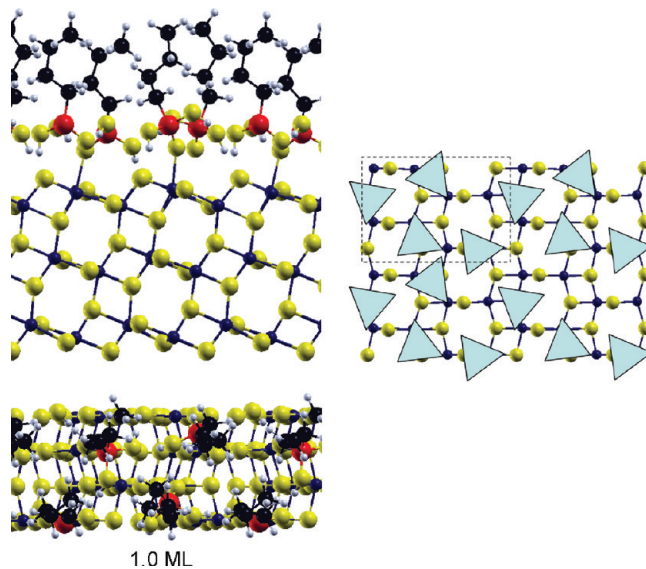


Figure 5. B3LYP-D ball and stick representation (side and top views) of the adsorption of four *n*-butylphosphonic acid molecules adsorbed on the TiO₂ (101) surface at 1 ML coverage. Ti, O, C, H, and P atoms are dark, light, black, small light, and large dark spheres, respectively. On the right is the schematic top view of the phosphonic acid oxygens triangle on the surface. The repeated supercell is shown as dashed lines.

configuration where all the four adsorbed molecules are covalently or electrostatically bound to the surface. The PO–Ti_{5c} distances are between 2.12 and 2.41 Å (B3LYP). However, when the system is relaxed in the presence of dispersion forces, distances are elongated to 2.27, 2.31, 2.60, and 2.89 Å (B3LYP-

D), suggesting more electrostatic than covalent interactions. The POH–O_s distances are in the range between 1.0 and 2.0 Å (B3LYP), which means that in one case a proton has been transferred to the surface (acid dissociation) and in other cases the protons are rather far from the surface with virtually no hydrogen bonding. If dispersion forces are taken into account, no dissociation takes place and the POH–O_s distances are above 1.4 Å.

This significant reorganization of the molecules allows the adsorption to be exothermic by $\Delta E_{\text{ads}} = 0.05$ (rPBE), 0.73 (PBE), and 0.66 (B3LYP) eV, values which are significantly less exothermic than at lower coverages, certainly due to the steric hindrance between phosphonic groups at the surface. Taking into account the dispersion forces, we obtain adsorption energies of $\Delta E_{\text{ads}} = 0.88$ eV (rPBE-D), 1.83 (PBE-D), and 1.48 eV (B3LYP-D). For all methods, the adsorption is strongly stabilized when dispersion forces are included.

At the maximum possible coverage, 5 molecule/nm², the molecules adsorb in the M0 mode, with an energy of 0.9–1.3 eV/molecule or 3.6–5.2 eV/unit cell (rPBE-D and B3LYP-D without BSSE, respectively). We observe that the gain in energy per unit cell (or surface area) is about the same for the two highest coverages, 3.75 and 5 molecule/nm². The trend calculated suggests that the surface could be rather disordered, with coexisting domains of 0.75 and 1 ML coverages. Note that these coverages correspond nicely to the experimental measured coverages of 4.3–4.8 molecule/nm².¹⁵

3.3. Overview of the Results. In Figure 6 the onset of all adsorption energy data per molecule are plotted vs coverage, as a function of the method, without (Figure 6a) and with (Figure 6c) dispersion included in the DFT-D optimized geometry. The dispersive contribution is also shown (Figure 6b). As already stated, the adsorption energy lowers with increasing coverage, both considering DFT and DFT-D levels. From the histogram it appears that PBE and B3LYP adsorption energies are always larger than rPBE ones, both with and without dispersion forces included. The dispersive contributions increase with coverage (Figure 6b), a result of lateral interactions between molecules but also of molecule–surface interactions. Dispersion forces computed for B3LYP calculations are systematically larger than with PBE or rPBE, which might be connected to the different parameters used for the two functionals. For the B3LYP case, there might be some overestimation.⁷⁹

We note that at low coverage (0.25 ML), the molecules being distant by about 10 Å (*x* axis) and 7.5 Å (*y* axis), there is no lateral interaction (either at the DFT or DFT-D level) contribution to the energy of adsorption. The dispersive contribution must be due to the molecule–surface interaction. At 0.5 ML, the dispersive forces are made of lateral interactions and molecule–surface interactions. Along the $[10\bar{1}]$ direction, dispersion forces induce some additional cohesion energy between adsorbed molecules, $\Delta E_{\text{coh}}(\text{D}) = 0.23$ eV per molecule, and some additional interaction energy with the surface, $\Delta E_i(\text{D}) = 0.67$ eV. Upon increasing the coverage to 0.75 ML (three molecules adsorbed on the slab model), the steric effects are predominant, which reflects into a lower binding energy per molecule with respect to the previous coverages. The contribution of dispersion forces to the cohesion energy in the adsorbed layer is of about $\Delta E_{\text{coh}}(\text{D}) = 0.50$ eV, while that to the interaction energy is $\Delta E_i(\text{D}) = 0.55$ eV. For the full monolayer coverage, the cohesion energy [$\Delta E_{\text{coh}}(\text{B3LYP-D}) = 0.75$ eV] and the interaction energy

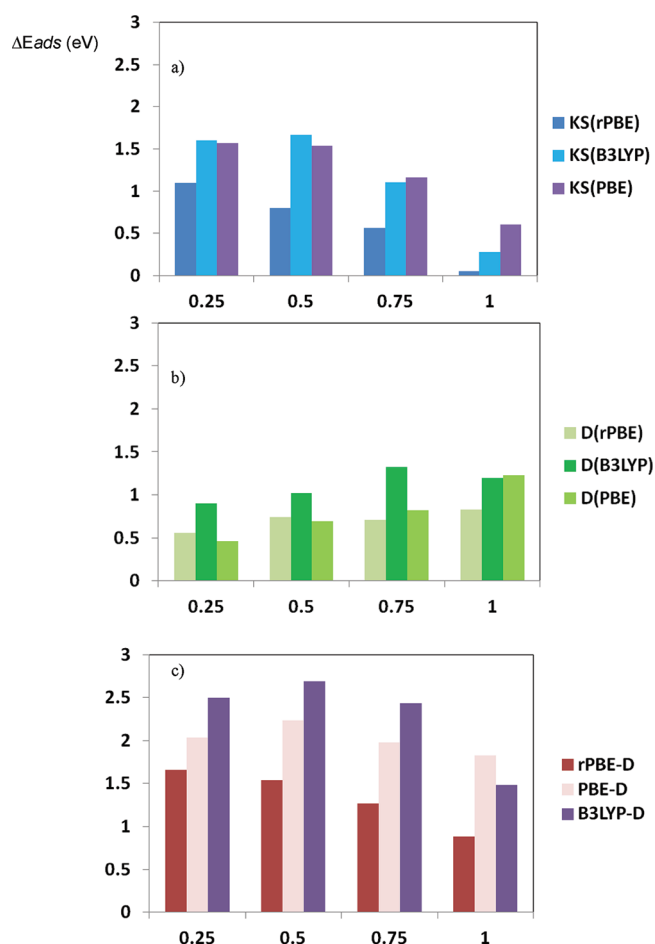


Figure 6. Adsorption energies [ΔE_{ads} (eV)] as a function of the coverage (0.25–1 ML): (a) DFT (Kohn–Sham) contribution, (b) dispersion forces contribution, and (c) total (DFT-D) adsorption energy per molecule.

[$\Delta E_i(\text{B3LYP-D}) = 1.57$ eV] are enhanced by dispersion forces between adsorbed molecules [$\Delta E_{\text{coh}}(\text{D}) = 0.38$ eV] and with the surface [the contribution of dispersion forces to molecule–surface interaction is $\Delta E_i(\text{D}) = 0.44$ eV].

We wish to add a comment related to alkyl phosphonic acid vs water adsorption. The adsorption energy of phosphonic acid on anatase TiO₂(101) surface is larger than that of water (see Supporting Information, section S1) at each coverage (indeed, the energy of adsorption of water is poorly dependent on the surface coverage).⁶⁴ This result suggests that a phosphonic acid layer could replace adsorbed water molecules, which is coherent with the numerous experimental data reporting the formation of a direct Ti–O–P bond.⁸³

3.4. Electronic Structure Analysis. It is interesting to analyze the electronic structure of these systems, and the B3LYP functional provides a better framework given that the band gap of TiO₂ is largely underestimated with standard DFT. The main question is whether the adsorbed molecule induces the formation of new states in the band gap of the material, which could have interesting consequences, for example, for the possibility of absorption in the visible spectrum. However, from the density of states (DOS) reported in Figure 7 for the 0.25 and 1 ML coverages, it is evident that no additional gap states are formed. The molecular states fall in the same energy range of the valence band and higher in energy with respect to the lower part of the conduction band.

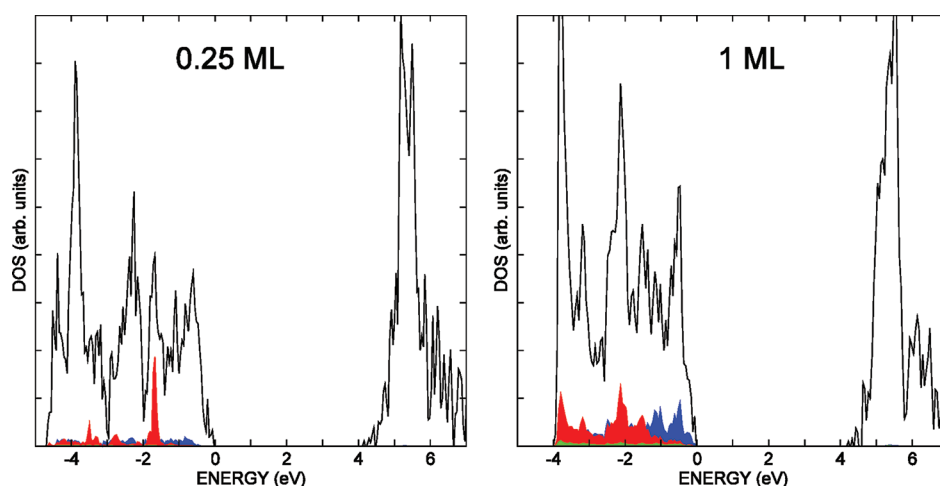


Figure 7. Density of states from B3LYP calculations for 0.25 ML (M0) and 1 ML coverages. Total DOS in black, projections on P atoms in green, on O atoms in blue, and on C atoms in red. The zero for the energy scale is set at the top of the valence band.

When a full monolayer of *n*-butylphosphonic acid molecules is adsorbed on the oxide surface, a work function decrease of 0.7 eV is computed, as a consequence of the resulting surface dipole effect.

4. CONCLUSIONS

In this work, the adsorption of an alkylphosphonic acid [$\text{CH}_3(\text{CH}_2)_3\text{PO}(\text{OH})_2$] at various coverages ranging from 0.25 to 1 ML has been investigated. Different approaches have been used and compared in order to assess the types of interactions that control the adsorption modes and SAM properties of this system. In particular, standard GGA (PBE and rPBE) calculations have been compared with the hybrid functional B3LYP results. The choice is justified by the fact that rPBE corrects for PBE overbinding, while B3LYP reduces the self-interaction problem. Moreover, dispersion forces have been described with the Grimme approach, correcting for the energies and the gradients.

This comprehensive study allows one to draw some relevant conclusions on this prototype system for SAMs on anatase TiO_2 surface based on the phosphonic head anchoring through direct bonding to undercoordinated Ti_{5c} and intermolecular hydrogen bonding with surface bridging oxygens. The size of the tail has been chosen so that chain–chain interactions are beginning to be relevant for SAM formation. The SAM structures as well as the forces responsible for adsorption and cohesion have been investigated as a function of the surface coverage.

At low and intermediate coverages, the acid adsorbs preferentially in the monodissociated bidentate (B1) mode, forming two $\text{P}=\text{O}-\text{Ti}_{5c}$ bonds with one additional $\text{P}-\text{OH}-\text{O}_s$ hydrogen bond. At 0.75 ML, a mixture of M0, M1, and B1 adsorption modes is computed to be the favored configuration. At full coverage, when the B1 mode is not possible for a lack of surface Ti_{5c} sites, the molecules reorient in order to minimize lateral repulsion and maximize H bonds between the OH groups. Evidence of several different binding modes in phosphonic acids monolayers was experimentally obtained by high-field ^{17}O MAS NMR.⁸³

Except for the full monolayer case, adsorption energies per molecule are computed to be between 1.5 and 2.2 eV, according to the functional (DFT-D) used (BSSE correction is included in this estimation for B3LYP data). We consider the

smaller rPBE values to be more realistic because they are corrected for the GGA overbinding problem. However, the B3LYP method is more reliable as regards relative stability of different binding modes, especially when these involve interaction of charged species with the surface. In general, the values here reported are in line with previous DFT studies for adsorbed phosphonic or methylphosphonic acids,^{20,42,45} where binding energies were in the range between 1.9 and 2.5 eV.

The contribution of dispersion forces in the adsorption energy increases with the coverage. The contribution of dispersion forces to the cohesion energy and to the molecules–surface interaction has been disentangled for the various cases, but especially for the full monolayer coverage where SAM properties are most relevant. We find that dispersion contributions to the SAM cohesion and to the SAM/surface interaction are similar (about 0.4 eV).

In order to compare different coverages at equal footing, the energy gain associated with the adsorption per unit cell was evaluated. This is similar for the 0.75 and 1 ML coverages, corresponding to 3.75 and 5 molecule/ nm^2 , and is about 6–7 eV per unit cell. These results suggest that the surface could be rather disordered, with coexisting domains of 0.75 and 1 ML coverages. Such coverages nicely correspond to the experimental measured coverages of 4.3–4.8 molecule/ nm^2 .¹⁵

Finally, the electronic structure of the hybrid organic–inorganic system does not present any additional states inside the band gap of the semiconductor at any coverage, as observed from DOS calculations with B3LYP functional. For the full monolayer we observe a 0.70 eV reduction of the work function resulting from the surface dipole effect.

This work is a first step in the attempt to study Ti functionalization for biomimetic properties. In particular, it will be interesting to investigate coadsorption with water, as well as the role of the tail function nature on both the SAM formation and the layer properties (hydrophobicity, hydrophilicity, anchoring of bioactive species as RGD or collagen), and to reproduce observable quantities such as vibrational frequencies or core level shifts, in order to compare those results with experimental ones (IR and XPS data, respectively).

■ ASSOCIATED CONTENT

■ Supporting Information

Additional adsorption modes and additional information on the structures and the energetics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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