



Adsorption of phenylphosphonic acid on rutile TiO₂(110)

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ABSTRACT

Binding of functionalized organic molecules to oxide surfaces is an important step in the rational design of molecular devices. In the present investigation, we used synchrotron radiation photoelectron spectroscopy and near-edge X-ray absorption fine structure spectroscopy to determine the binding mode, electronic structure and adsorption geometry of phenylphosphonic acid (PPA) on TiO₂(110)-(1 × 1). We found that PPA multilayers desorb below 380 K leaving a compact PPA monolayer adsorbed on the surface, which remains stable up to 780 K. In the 380–520 K temperature range, molecules are anchored to the surface via a single P–O–Ti covalent bond (monodentate configuration). Furthermore, the phenyl ring is tilted ~45° with respect to the surface plane and it either forms 45° or is randomly oriented with respect to [001] crystallographic direction. Raising the temperature above 520 K partially transforms the monodentate configuration to a mixed one- and twofold deprotonated bidentate binding mode, presumably after surface hydroxyl groups leave the surface as water molecules. This change in molecular binding does not alter the molecular electronic structure nor the adsorption geometry, which remain essentially unchanged.

1. Introduction

The design of new materials with applications in devices used for the generation or storage of renewable energy is a central part of current scientific research [1–3]. Many devices, such as photoelectrochemical and dye-sensitized solar cells are based on the interaction of organic molecules with oxide surfaces. In many cases, the organic molecule adsorption properties, such as bonding and molecular geometry, influence device performance. Thus, a fundamental understanding of the adsorption of organic molecules on oxide surfaces is required.

Organic molecules are tethered on oxide surfaces using various anchoring groups such as carboxylic acids (–COOH), phosphonic acids (–PO(OH)₂) and amide groups (–NH–(C=O)–), among others [4]. Although carboxylic acids are the most commonly used anchoring groups [5], phosphonic acids show better chemical resistance and form more stable and stronger bonds to oxide surfaces [4,5]. Therefore, there has been new interest in the study of the adsorption of phosphonic acid-functionalized molecules on oxide surfaces.

Recently, experimental and computational work was performed to determine the adsorption configuration of phosphonic acid on TiO₂ surfaces. Phosphonic acids can bind via one to three bonds to a substrate, thus monodentate, bidentate or tridentate binding modes are

observed or calculated. For example, computational simulations show that perylene derivatives adsorb on TiO₂(110) substrates via a monodentate bond [6]. On the other hand, a bidentate binding mode was calculated for phosphonic acid molecules on the same substrate [7–9]. These differences can be understood, since the results are largely dependent on the slab size and, in addition, since the binding energies for different binding modes are quite similar [6]. Calculations combined with ¹⁷O NMR and FTIR measurements determined that phenylphosphonic acid molecules adsorb on anatase TiO₂ support via a tridentate bond [10]. The same binding configuration resulted from DRIFTS and ³¹P solid state MAS NMR measurements on phenylphosphonic acid adsorbed on titania particles [11]. Other research groups could not determine unequivocally the binding mode of the phosphonic acid-functionalized molecules [12,13]. IR methods are challenging for titania substrates, since the relevant peaks overlap with substrate peaks [1,14]. ³¹P solid NMR may also not be suitable, since important intermediates cannot be resolved from each other [10,14]. Although ¹⁷O NMR has shown to be suitable to perform qualitative and quantitative studies on the adsorption of molecular species, single crystal surfaces cannot be investigated applying this technique. On the contrary, X-ray photoelectron spectroscopy (XPS) was found to be suitable to determine the binding mode of phosphonic acid groups [1,15,16]. Wagstaffe et al. [15] used synchrotron radiation XPS to study the adsorption of

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phenylphosphonic acid on anatase TiO₂(101). From O 1s XP spectra they propose a bidentate binding mode for low coverages (0.15 ML), and mixed bidentate/monodentate binding modes for higher coverages (0.85 ML).

The discrepancies highlighted above could be resolved taking into account two important parameters, which largely influence the adsorption mode, that is, the molecular coverage [14–17] and the temperature [18]. Thus, in this work we studied the binding mode and adsorption geometry of a monolayer of phenylphosphonic acid on TiO₂(110) using synchrotron radiation XPS, UV photoelectron spectroscopy (UPS) and near edge X-ray absorption fine structure (NEXAFS) as a function of temperature. Our results shed new light on the understanding of the binding modes of phosphonic acid functional groups with oxide surfaces.

2. Experimental

All measurements were performed at the Materials Science beamline (MSB) at Elettra-Sincrotrone in Trieste, Italy. The end-station has a base pressure of 2×10^{-10} mbar and is equipped with a SPECS PHOIBOS 150 hemispherical energy analyzer. The crystal temperature was measured with a K-type thermocouple attached to the sample plate and not directly touching the crystal. Therefore, the measured values during heating overestimate the actual sample temperature. However, the given temperature values were reproducible during all the measurements and were corrected using a reference measurement, with thermocouples glued directly to the crystal that we performed in a follow-up beamtime. The corrections applied assume a linear deviation over the whole temperature range, yielding an estimated uncertainty of 50 K at the highest temperature of 780 K. Prior to each experiment, the TiO₂(110) crystal (CrysTec GmbH Kristalltechnologie) was cleaned by several cycles of sputtering (Ar⁺, 1 kV, 2×10^{-6} mbar) and annealing (800–850 K). After removing from the UHV chamber, the sample had a light blue color. The expected (1 × 1) structure after vacuum annealing was confirmed by LEED. Phenylphosphonic acid was deposited onto a TiO₂(110) single crystal by evaporation in ultrahigh vacuum (UHV) using a Knudsen cell ($T_{\text{evap}} = 130\text{--}140$ °C), while the sample was kept at room temperature.

The intensity of the photoelectron spectra was normalized to the incident photon flux. The spectra were measured with photon energies (energy resolutions in brackets) of 43 eV (0.19 eV) for the valence band, 230 eV (0.39 eV) for the P 2p region, 380 eV (0.50 eV) for the C 1s region, 650 eV (0.50 eV) for the O 1s region and 650 eV (0.80 eV) for the Ti 2p region. All peaks were aligned to lab-source x-ray photoelectron spectroscopy measurements (Al K_α) performed at the MSB; this resulted in the main carbon peak at 285.1 eV. We rule out significant beam damage as successive measurements of the same spot did not show any changes. The NEXAFS spectra at the C K-edge were taken using C KLL Auger yield and while the NEXAFS spectra at the P L_{2,3}-edge were taken using P LMM Auger yield. The polarization of light from the bending magnet beamline has not been measured but is believed to be 90% linear. The energy resolution was estimated to be 0.23 eV for the C K-edge and 0.15 eV for the P L_{2,3}-edge. The usual normalization to the photocurrent provided by the gold mesh was not valid for carbon absorption spectra due to the contamination of the X-ray optical elements of the beamline. Therefore, the C K-edge spectrum was normalized by the intensity of the Ti 3p peak of the TiO₂(110) surface taken at the same photon energy range. This method is sensitive to photoemission features travelling through the regions of the Auger lines and we corrected for this using a clean-up procedure described elsewhere [19].

3. Results and discussion

Fig. 1 shows C 1s, Ti 2p and P 2p XP spectra obtained after depositing a phenylphosphonic acid (PPA) multilayer (~2.7 monolayers)

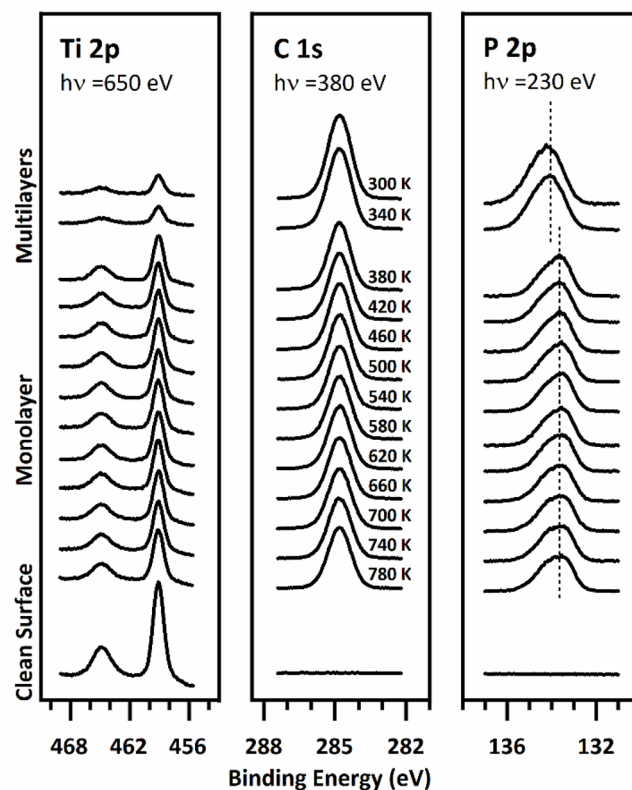


Fig. 1. Ti 2p, C 1s and P 2p XP spectra of phenylphosphonic acid deposited on a freshly prepared TiO₂(110)-(1 × 1) followed by incremental annealing steps. Clean surface spectra are shown for comparison. The excitation energy was 650 eV for Ti 2p, 380 eV for C 1s, and 230 eV for P 2p.

on a freshly prepared TiO₂(110)-(1 × 1) surface at room temperature, followed by incremental annealing steps. Annealing of the PPA multilayer from 340 to 380 K results in an increase of the Ti 2p signal (459.3 eV), while the C 1s (285.1 eV) and P 2p (133.6 eV) signals decrease, indicating multilayer desorption; notably, the P 2p signal shifts to lower binding energy by 0.4 eV. The remaining coverage is assigned to one monolayer, which corresponds to the saturated first layer of adsorbed molecules. Subsequent annealing to higher temperatures does not significantly modify the peak intensities and binding energy positions. This indicates that the monolayer film is stable up to 780 K.

The left panel of Fig. 2 shows the corresponding high-resolution O 1s XP spectra, which can be used to obtain information regarding the binding mode of the molecule to the surface. Spectra were measured using a photon energy of 650 eV, which corresponds to 120 eV kinetic energy, enabling highly surface sensitive measurements.

As we will discuss in detail below, the O 1s spectra are composed of a low binding energy peak at 530.4 eV, due to the substrate oxygen atoms, and three higher binding energy peaks at 531.6, 532.7 and 533.8 eV, arising from the different binding configurations. Annealing at 400 K for 1 min results in a decrease of the high binding energy components and simultaneous increase of the substrate component, which is attributed to multilayer desorption. In line with the temperature-dependent behavior of the C 1s, Ti 2p and P 2p spectra shown in Fig. 1, the total intensity of the O 1s spectra remains constant with further annealing steps. However, changes in the relative intensities of the high binding energy components are observed. As we will see below, they are due to changes in the binding mode with temperature.

It is useful to rationalize the relationship between the binding mode and the XPS intensities of the different O 1s spectral components before discussing the changes observed in Fig. 2. Phosphonic acids can be covalently attached to oxide surfaces in different configurations as

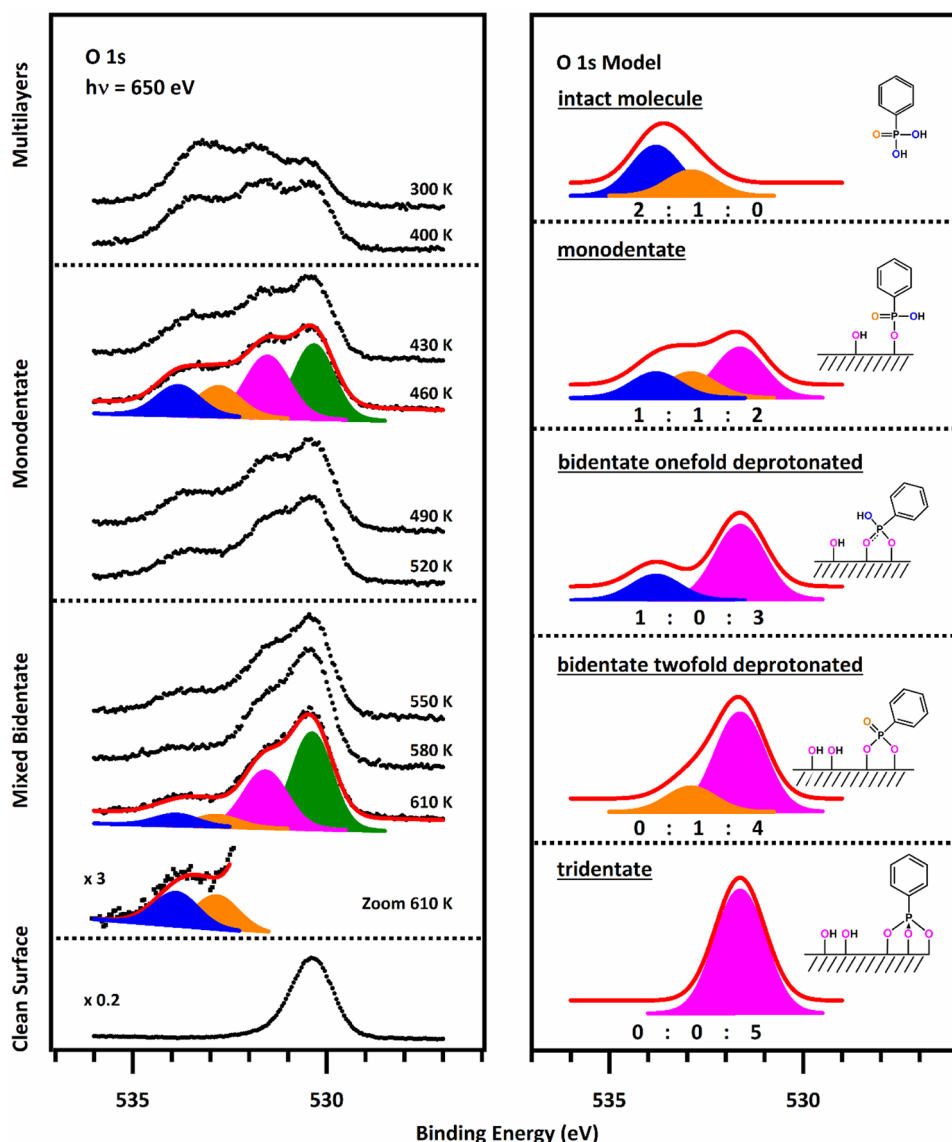


Fig. 2. Left panel: High resolution O 1s XPS spectra of phenylphosphonic acid deposited on TiO₂(110)-(1 × 1), followed by incremental annealing steps using a photon energy of 650 eV. Right panel: Schematic sketch of the different binding configurations of phosphonic acids to oxide surfaces with the corresponding schematic XP spectra.

illustrated in the scheme of the right panel of Fig. 2 [4,16]. Monodentate configurations imply the formation of one P–O–Ti bond to the surface, after deprotonation of a P–OH group and the formation of a Ti–OH surface group. In the onefold deprotonated bidentate configuration, an additional P–O–Ti bond is formed from the P=O group, resulting in two P–O–Ti bonds and one Ti–OH group. In the twofold deprotonated bidentate configuration, both P–OH groups are deprotonated resulting in two P–O–Ti and two Ti–OH bonds, with the P=O bond still intact. Finally, in the tridentate configuration three P–O–Ti bonds and two Ti–OH surface groups are formed.

According to literature, these different oxygen-containing species/groups have different O 1s XPS binding energy positions. Overall, apart from uniform shifts, the observed values are in good agreement (± 0.2 eV) with the values observed for various phosphonic acid-containing compounds on different oxide surfaces. [15,16,20–24] Notably, the peaks observed by Wagstaffe et al. [15] on anatase TiO₂(101) show the same separation but all are observed at 0.5 eV lower binding energy. From this agreement in peak separation, we make the following assignment: the peak at 533.8 eV corresponds to P–OH, the one at 532.7 eV to P=O, and the peak at 531.6 eV to the overlapping signals

of P–O–Ti and Ti–OH. Noteworthy, in an earlier study using a lab-source only three peaks could be resolved [25], which we attribute to a lower energy resolution. The different binding configurations have different relative O 1s XPS component intensities, as illustrated in the schematic spectra in the right panel of Fig. 2. From high to low binding energy, the intensity ratios of the O 1s components are 1:1:2 for monodentate, 1:0:3 for onefold deprotonated bidentate, 0:1:4 for twofold deprotonated bidentate, and 0:0:5 for tridentate.

After these considerations, we can put the focus again on the monolayer O 1s XP spectra in the temperature range from 430 to 610 K in Fig. 2, and Table 1. The spectra in the 430–520 K range are identical and can be fitted with the three components shown in the right panel of Fig. 2, in addition to the substrate component at 530.4 eV [26]. The fit in left panel of Fig. 2 results in a 1.0:1.0:2.1 intensity ratio for the P–OH : P=O : (P–O–Ti + Ti–OH) components, indicating that the binding mode of the phenylphosphonic acid monolayer in the 430–520 K range is dominated by the monodentate configuration.

Annealing to 580 to 610 K changes the intensity of the different components in the O 1s spectra. Overall, the high binding energy shoulder (P–OH + P=O) decreases, while the P–O–Ti/Ti–OH peak

Table 1

O 1s peak positions of substrate and adsorbate signals (with an error of ± 0.1 eV), and their relative contributions to the total signal.

	P-OH	P=O	Ti-OH / P-O-Ti	TiO ₂
Binding Energy	533.8 eV	532.7 eV	531.6 eV	530.4 eV
FWHM	1.19 eV	1.19 eV	1.19 eV	1.18 eV
Contribution to O 1s signal:				
430–520 K	15%	15%	31%	39%
580–610 K	7%	5.5%	32%	55.5%

remains constant and the substrate intensity increases. Despite decreasing, the relative contributions of P-OH and P=O remain very similar, yielding a ratio of 1.3:1.0:5.8 for the P-OH : P=O : (P-O-Ti + Ti-OH) components. There are two possible explanations for this behavior. (1) Considering an equal mixture of onefold and twofold deprotonated bidentate species, would give a ratio of 1:1:7, which roughly agrees with the observed ratio. (2) Alternatively, an equal mixture of monodentate and tridentate species would also yield a ratio of 1:1:7. The intensity ratio of 1.3:1.0:5.8 can thus be rationalized as follows: It is known from literature that in this temperature range, -OH groups present at defect sites on the surface form water and desorb from the surface [27–29]. This would result in a decrease of the Ti-OH contribution to the O 1s spectra. Furthermore, the substrate signal is expected to increase as -OH groups leave the surface, which is indeed observed. Hence, this could free surface sites and thus be the driving force for the formation of bidentate species or in general species with a higher binding order. Thus, for both processes, some surface hydroxyl groups desorb as water, freeing up required surface sites and reducing the ratio from the expected 1:1:7 to the value observed (1.3:1.0:5.8). We favor the assignment as mixed bidentate layer, as will be outlined below.

The bidentate binding modes have already been proposed for similar molecules on TiO₂(110) [8,9]. Pang et al. [8] deposited methyl phosphonate onto TiO₂(110). From DFT calculations, they propose that the monodentate and the onefold deprotonated bidentate species relax towards a twofold deprotonated bidentate species. Skibinski et al. [9] investigated phenylphosphonic acid on TiO₂(110) by DFT calculations and reported a bridged twofold deprotonated bidentate species. The phenyl ring of this species is tilted with respect to the surface.

The formation of a tridentate species cannot be fully ruled out from our data, but is considered less likely: Theoretical calculations by Luschtinetz et al. show that phosphonic acids do not prefer to bind in a tridentate configuration on ideal rutile TiO₂(110) surfaces [7]. This is attributed to the fact that this configuration three oxygen atoms in the phosphonic acid group bind to three different surface Ti atoms. On the ideal surface, the rows of Ti atoms are separated by elevated O atoms rows which sterically hinder the formation of the third bond [7]. Notably, the situation could be different at defect sites on the surface. On the other hand, the authors also claim that both bidentate species are energetically favoured, and have similar stability, which supports the approximate 1:1 ratio of both species.

In the above discussion, we showed that the binding of phosphonic acid monolayers to TiO₂(110) changes with temperature. Between 430 and 520 K, we observe a monodentate species. Annealing to higher temperatures transforms the monodentate species into a mixed bidentate species, possibly as surface hydroxyl groups partially desorb as water freeing up the required surface sites. To determine how the molecular electronic structure is affected by these changes, we measured valence band photoemission spectra with 43 eV photon energy. Fig. 3 shows data for the clean substrate, the phenylphosphonic acid multilayer (300 K), the monolayer of monodentate species (380–460 K) and the mixed bidentate (or monodentate plus tridentate) species (540–780 K). The bottom spectrum of clean TiO₂(110)-(1 × 1) shows a broad O 2p band from 3 to 9 eV and a peak at ~1 eV, which has been identified as defect state (for a detailed discussion see literature)

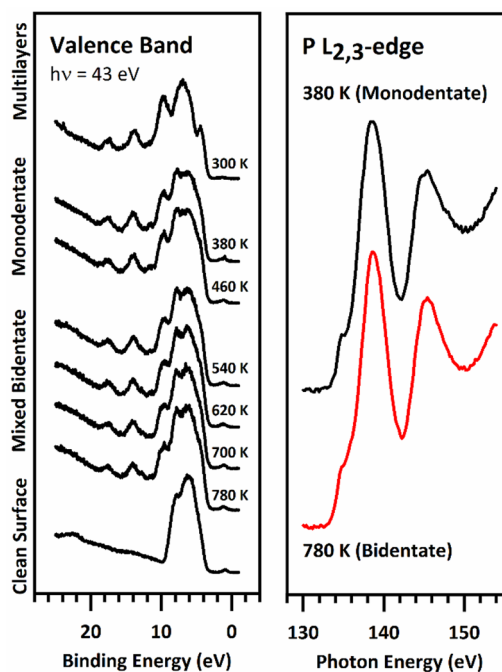


Fig. 3. The left panel shows valence band spectra of TiO₂(110) and a monolayer of PPA prepared on TiO₂(110) followed by incremental annealing steps. In the right panel NEXAFS P L_{2,3}-edge spectra of a monolayer of PPA annealed at 380 and 780 K.

[30–34]. The multilayer spectrum shows distinct molecular states at 17.5, 13.9, 9.7 and 4.5 eV, with the O 2p band of the substrate strongly being damped. A detailed assignment of these peaks cannot be provided without calculations, in particular, since each of the peaks is composed of several molecular levels. The spectra corresponding to the monodentate and mixed bidentate (or mono- and tridentate) monolayer are very similar. The molecular states at 17.5, 13.9 and 9.7 eV are well pronounced, and the much less damped O 2p band broadens towards low binding energy due to its overlap with the molecular state at 4.5 eV. Finally, the defect state at ~1 eV is still present in the monolayer spectra but with a lower relative intensity.

The right panel of Fig. 3 shows the NEXAFS P L_{2,3}-edge spectra of a monolayer of PPA annealed at 380 and 780 K. The spectra are nearly identical to the spectra measured after the adsorption of phosphonic acid functionalized porphyrin molecules on rutile TiO₂(110) surfaces [16]. However, it shows small differences with the reference spectra of pure phenylphosphonic acid [35]. This indicates that the electronic environment of the P atom changes upon adsorption on the TiO₂(110) surface in line with the formation of a covalent bond discussed above.

The VB spectra discussed above provide information regarding the occupied electronic states, whereas the unoccupied electronic states can be assessed using NEXAFS data. Fig. 4 shows the C K-edge NEXAFS spectra of PPA on TiO₂(110) annealed to 380 K for 1 min, which forms a monodentate monolayer as discussed above. Measurements were performed using two different azimuthal angles, 0° and 90°, with respect to the [001] crystallographic direction and five different polar angles, with respect to the surface normal. Note that a polar angle of 0° implies normal photon incidence (electric field vector parallel to the surface) and a polar angle of 80° implies grazing photon incidence (electric field vector close to perpendicular to the surface). The NEXAFS spectra in Fig. 4 show five well-defined peaks due to electronic transitions from the C 1s core level to different unoccupied molecular orbitals. The low photon energy peak at 284.9 eV (a) is assigned to a π^* resonance. The peak at 288.6 eV (c) is due to a mixture of Rydberg and -CH σ^* transitions [15], whereas the peaks at 290.7 (d) and 293.2 eV (e) are due to σ^* resonances. The small feature present at 286.9 eV (b) in all

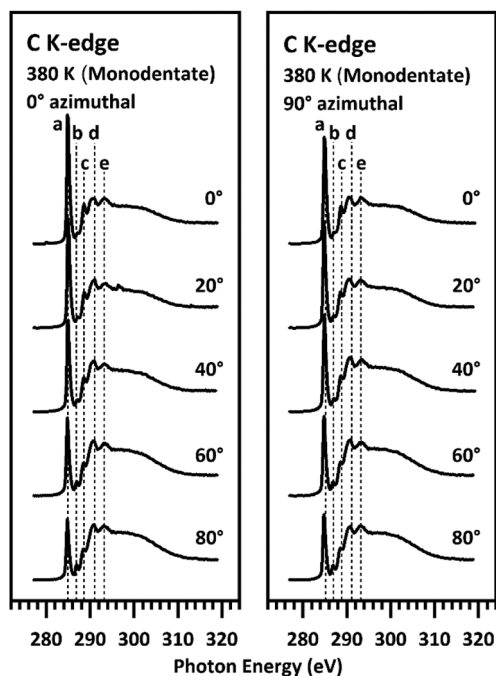


Fig. 4. NEXAFS C K-edge spectra of a PPA monolayer annealed to 380 K for different polar angles and for two different azimuthal angles of the incoming radiation. Normal incidence corresponds to 0° incidence angle and grazing incidence to 80°. The left panel shows the spectra for 0° azimuthal and the right panel for 90° azimuthal with respect to the [001] direction.

the spectra has been previously observed after the adsorption of phenylphosphonic acid on rutile surfaces and was assumed to be substrate-related [15]. Here, we should mention that the above spectra display the same transitions as those observed when PPA is adsorbed on anatase TiO₂ surfaces [15].

C K-edge NEXAFS measurements were also carried out after annealing to 650 or 780 K, for a mixed bidentate monolayer; see Fig. 5. Overall, the spectra are very similar to that of the monodentate monolayer in Fig. 4. This is in complete agreement with the VB data and shows that the changes in the binding mode do not have a significant influence on the unoccupied electronic structure.

The angular dependence of the π^* resonance intensity gives information regarding the molecular orientation of the phenyl ring. Maximum intensity is observed when the electric field of the radiation is perpendicular to the phenyl ring; on the other hand no intensity is observed, when the electric field is parallel to the ring [36]. Fig. 6 shows the area of the π^* transition as a function of polar incidence angle for both azimuthal angles, for a monolayer of monodentate (380 K) and mixed bidentate (spectra at 650 and 780 K). After normalizing to the edge jump, the data was fitted using the π^* intensity dependence on polar angle for twofold symmetry substrates considering the four molecular domains arising from the two possible azimuthal angles and polar tilt angles of the phenyl ring [16,37]. Fitting yields a polar tilt angle of 45° with an azimuthal angle of 42° for the monodentate monolayer (380 K) and a polar tilt angle of 44° with an azimuthal angle of 45° for the mixed bidentate (or mono- and tridentate) monolayer (650–780 K). The fitting procedure was performed following the procedure from Ref. [37] In line with the unchanged electronic structure, the molecular orientation does not change (within the margin of error) when a monodentate monolayer of phenylphosphonic acid is annealed to form a mixed bidentate layer. Notably, for the onefold deprotonated bidentate, a polar tilt angle of ~40° is estimated from Fig. 8 in Ref. [9]. For comparison, we note that 0.85 ML of phenylphosphonic acid adsorbs on anatase TiO₂(101) surfaces at room temperature with a phenyl ring tilted 65° with respect to the surface plane

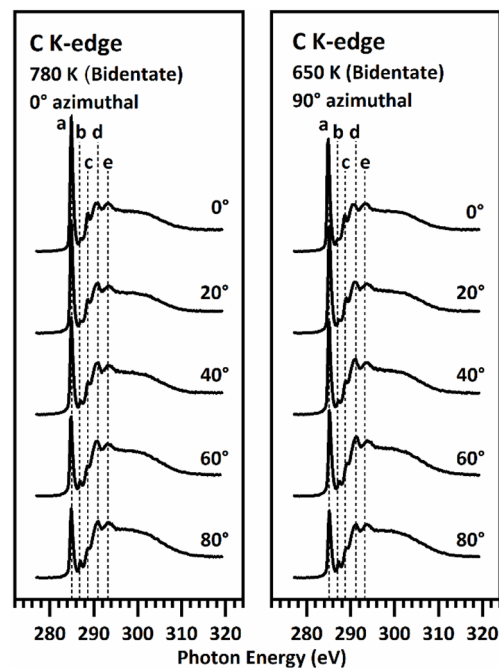


Fig. 5. NEXAFS C K-edge spectra of a PPA monolayer annealed to 780 or 650 K for different polar angles and for the different azimuthal angles of the incoming radiation respectively. Normal incidence corresponds to 0° incidence angle and grazing incidence to 80°. The left panel shows the spectra for 0° azimuthal and the right panel for 90° azimuthal with respect to the [001] direction.

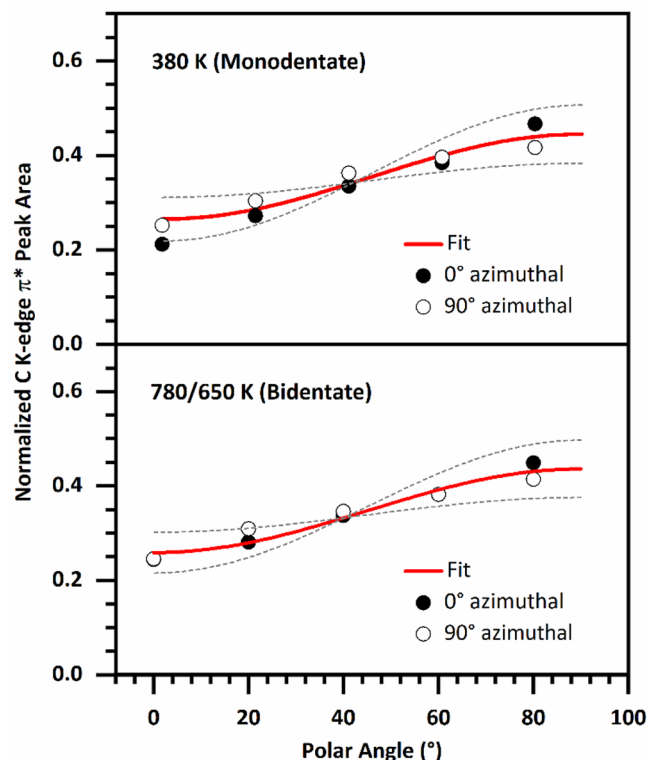


Fig. 6. Intensity of the π^* transition as a function of incidence polar angle for PPA monolayers annealed to 380 and 780/650 K and two azimuthal angles. Data was taken from Figs. 4 and 5. Full lines are fittings using the equation for twofold substrates taking into account four possible molecules domains. The dashed lines are additional fit curves with a polar angle of $\pm 5^\circ$ in comparison to the red fit curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[15]. Thus, similar to the present study, the molecules are neither flat lying nor fully standing up, but slightly tilted. Finally, we should mention that a 45° azimuthal angle on twofold symmetry substrates could indicate that either the molecules form 45° with respect to the [001] crystallographic direct or that the azimuthal orientation of the molecules is random. This latter case could be due to the rotation of the phenyl ring with respect to the phosphorous atom.

4. Conclusions

Phenylphosphonic acid multilayers desorb from rutile TiO₂(110) surfaces at around 380 K leaving a compact monolayer film that remains stable up to 780 K. Two different binding configurations are observed as a function of temperature. In the 430–520 K temperature range, molecules are attached to the surface via a single P–O–Ti chemical bond (monodentate configuration). Increasing the temperature results in the formation of two coexisting bidentate species, which are presumably formed when surface sites become available after the desorption of hydroxyl groups as water and after sufficient thermal energy is provided to overcome the activation barrier. Both monolayers possess essentially the same electronic structure with molecules tilted 45° with respect to the surface and with either a random azimuthal orientation or a 45° one. Our results indicate that phosphonic acid functional groups bind to TiO₂(110) surfaces forming strongly bond bidentate configurations.

Author contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declaration of Competing Interest

There are no conflicts to declare.

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References

- [1] G. Guerrero, J.G. Alauzun, M. Granier, D. Laurencin, P.H. Mutin, Phosphonate coupling molecules for the control of surface/interface properties and the synthesis of nanomaterials, *Dalton Trans.* 42 (2013) 12569–12585.
- [2] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films, *Nature* 353 (1991) 737–740.
- [3] M. Grätzel, Dye-sensitized solar cells, *J. Photochem. Photobiol.* 4 (2003) 145–153.
- [4] R. Boissezon, J. Muller, V. Beaugeard, S. Monge, J.-J. Robin, Organophosphonates as anchoring agents onto metal oxide-based materials: synthesis and applications, *RSC Adv.* 4 (2014).
- [5] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Dye-Sensitized Solar Cells, *Chem. Rev.* 110 (2010) 6595–6663.
- [6] M. Nilsing, P. Persson, S. Lunell, L. Ojama, Dye-Sensitization of the TiO₂ Rutile (110) Surface by Perylene Dyes: quantum-Chemical Periodic B3LYP Computations, *J. Phys. Chem. C* 111 (2007) 12116–12123.
- [7] R. Lushtinetz, J. Frenzel, T. Milek, G. Seifert, Adsorption of Phosphonic Acid at the TiO₂ Anatase (101) and Rutile (110) Surfaces, *J. Phys. Chem. C* 113 (2009) 5730–5740.
- [8] C.L. Pang, M. Watkins, G. Cabailh, S. Ferrero, L.T. Ngo, Q. Chen, D.S. Humphrey, A.L. Shluger, G. Thornton, Bonding of Methyl Phosphonate to TiO₂(110), *J. Phys. Chem. C* 114 (2010) 16983–16988.
- [9] E.S. Skibinski, W.J.I. DeBenedetti, M.A. Hines, Solution Deposition of Phenylphosphonic Acid Leads to Highly Ordered, Covalently Bound Monolayers on TiO₂(110) Without Annealing, *J. Phys. Chem. C* 121 (2017) 14213–14221.
- [10] V. Lafond, C. Gervais, J. Maquet, D. Prochnow, F. Babonneau, P.H. Mutin, ¹⁷O MAS NMR study of the bonding mode of phosphonate coupling molecules in a titanium oxo-alkoxy-phosphonate and in titania-based hybrid materials, *Chem. Mater.* 15 (2003) 4098–4103.
- [11] G. Guerrero, P.H. Mutin, A. Vioux, Anchoring of phosphonate and phosphinate coupling molecules on titania particle, *Chem. Mater.* 13 (2001) 4367–4373.
- [12] S. Pawsey, K. Yach, L. Reven, Self-assembly of carboxyalkylphosphonic acids on metal oxide powders, *Langmuir* 18 (2002) 5205–5212.
- [13] F. Brodard-Severac, G. Guerrero, J. Maquet, P. Florian, C. Gervais, P.H. Mutin, High-Field 17O MAS NMR Investigation of Phosphonic Acid Monolayers on Titania, *Chem. Mater.* 20 (2008) 5191–5196.
- [14] D. Geldof, M. Tassi, R. Carleer, P. Adriaensens, A. Roevens, V. Meynen, F. Blockhuys, Binding modes of phosphonic acid derivatives adsorbed on TiO₂ surfaces: assignments of experimental IR and NMR spectra based on DFT/PBC calculations, *Surf. Sci.* 655 (2017) 31–38.
- [15] M. Wagstaffe, A.G. Thomas, M.J. Jackman, M. Torres-Molina, K.L. Syres, K. Handrup, An Experimental Investigation of the Adsorption of a Phosphonic Acid on the Anatase TiO₂(101) Surface, *The Journal of Physical Chemistry C* 120 (2016) 1693–1700.
- [16] C.C. Fernández, D. Wechsler, T.C.R. Rocha, H.-P. Steinrück, O. Lytken, F.J. Williams, Adsorption of phosphonic-acid-functionalized porphyrin molecules on TiO₂(110), *J. Phys. Chem. C* 123 (2019) 10974–10980.
- [17] C. Di Valentin, D. Costa, Anatase TiO₂ surface functionalization by alkylphosphonic acid: a DFT + D Study, *J. Phys. Chem. C* 116 (2012) 2819–2828.
- [18] E.S. Gawalt, M.J. Avaltroni, N. Koch, J. Schwartz, Self-assembly and bonding of alkanephosphonic acids on the native oxide surface of titanium, *Langmuir* 17 (2001) 5736–5738.
- [19] O. Lytken, D. Wechsler, H.-P. Steinrück, Removing photoemission features from Auger-yield NEXAFS spectra, *J. Electron Spectrosc. Relat. Phenomena* 218 (2017) 35–39.
- [20] E.S. Gawalt, G. Lu, S.L. Bernasek, J. Schwartz, Enhanced Bonding of alkanephosphonic acids to oxidized titanium using surface-bound alkoxyzirconium complex interfaces, *Langmuir* 15 (1999) 8929–8933.
- [21] M. Gnauck, E. Jaehne, T. Blaettler, S. Tosatti, M. Textor, H.-J.P. Adler, Carboxy-terminated oligo(ethylene glycol)-alkane phosphate: synthesis and self-assembly on titanium oxide surfaces, *Langmuir* 23 (2007) 377–381.
- [22] N. Tsud, M. Yoshitake, Vacuum vapour deposition of phenylphosphonic acid on amorphous alumina, *Surf. Sci.* 601 (2007) 3060–3066.
- [23] N. Adden, L.J. Gamble, D.G. Castner, A. Hoffmann, G. Gross, M. Henning, Phosphonic acid monolayers for binding of bioactive molecules to titanium surfaces, *Langmuir* 22 (2006) 8197–8204.
- [24] S. Tosatti, R. Michel, M. Textor, N.D. Spencer, Self-Assembled monolayers of dodecyl and hydroxy-dodecyl phosphates on both smooth and rough titanium and titanium oxide surfaces, *Langmuir* 18 (2002) 3537–3548.
- [25] C. Viorneri, Y. Chevolot, D. Le'onard, B.-O. Aronsson, P. Péchy, H.J. Mathieu, P. Descouts, M. Grätzel, Surface modification of titanium with phosphonic acid to improve bone bonding: characterization by XPS and ToF-SIMS, *Langmuir* 18 (2002) 2582–2589.
- [26] U. Diebold, T.E. Madey, TiO₂ by XPS, *Surface Sci. Spectra* 4 (1996) 227–231.
- [27] Y. Du, N.G. Petrik, N.A. Deskins, Z. Wang, M.A. Henderson, G.A. Kimmel, I. Lyubinsky, Hydrogen reactivity on highly-hydroxylated TiO₂(110) surfaces prepared via carboxylic acid adsorption and photolysis, *Phys. Chem. Chem. Phys.* 14 (2012) 3066–3074.
- [28] J.M. White, J. Szanyi, M.A. Henderson, The Photon-Driven Hydrophilicity of titania: a model study using TiO₂(110) and Adsorbed Trimethyl Acetate, *J. Phys. Chem. B* 107 (2003) 9029–9033.
- [29] M.B. Hugenschmidt, L. Gamble, C.T. Campbell, The interaction of H₂O with a TiO₂(110) surface, *Surf. Sci.* 302 (1994) 329–340.
- [30] U. Diebold, The surface science of titanium dioxide, *Surf. Sci. Rep.* 48 (2003) 53–229.
- [31] A.G. Thomas, W.R. Flavell, A.K. Mallick, A.R. Kumarasinghe, D. Tsoutsou, N. Khan, C. Chatwin, S. Rayner, G.C. Smith, R.L. Stockbauer, S. Warren, T.K. Johal, S. Patel, D. Holland, A. Taleb, F. Wiame, Comparison of the electronic structure of anatase and rutile TiO₂ single-crystal surfaces using resonant photoemission and x-ray absorption spectroscopy, *Phys. Rev. B* 75 (2007) 035105.
- [32] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J.Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, The role of interstitial sites in the Ti3d defect state in the band gap of titania, *Science* 320 (2008) 1755–1759.
- [33] Z. Zhang, S.P. Jeng, V.E. Henrich, Cation-ligand hybridization for stoichiometric and reduced TiO₂(110) surfaces determined by resonant photoemission, *Phys. Rev. B Condens. Matter* 43 (1991) 12004–12011.
- [34] C.M. Yim, C.L. Pang, G. Thornton, Oxygen vacancy origin of the surface band-gap state of TiO₂(110), *Phys. Rev. Lett.* 104 (2010) 036806.
- [35] J. Kruse, P. Leinweber, K.U. Eckhardt, F. Godlinski, Y. Hu, L. Zuin, Phosphorus L (2,3)-edge XANES: overview of reference compounds, *J. Synchrotron Radiat.* 16 (2009) 247–259.
- [36] J. Stöhr, NEXAFS Spectroscopy, Springer Science & Business Media, Germany, 1992.
- [37] C.C. Fernández, D. Wechsler, T.C.R. Rocha, H.-P. Steinrück, O. Lytken, F.J. Williams, Adsorption geometry of carboxylic acid functionalized porphyrin molecules on TiO₂(110), *Surf. Sci.* 689 (2019) 121462.