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# Binding modes of phosphonic acid derivatives adsorbed on $TiO_2$ surfaces: Assignments of experimental IR and NMR spectra based on DFT/PBC calculations

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## ABSTRACT

A DFT study on the adsorption of a series of phosphonic acids (PAs) on the $TiO_2$ anatase (101) and (001) surfaces was performed. The adsorption energies and geometries of the most stable binding modes were compared to literature data and the effect of the inclusion of dispersion forces in the energy calculations was gauged. As the (101) surface is the most exposed surface of $TiO_2$ anatase, the calculated chemical shifts and vibrational frequencies of PAs adsorbed on this surface were compared to experimental $^{31}P$ and $^{17}O$ NMR and IR data in order to assign the two possible binding modes (mono- and bidentate) to peaks and bands in these spectra; due to the corrugated nature of anatase (101) tridentate binding is not possible on this surface. Analysis of the calculated and experimental $^{31}P$ chemical shifts indicates that both monodentate and bidentate binding modes are present. For the reactive (001) surface, the results of the calculations indicate that both bi- and tridentate binding modes result in stable systems. Due to the particular sensitivity of $^{17}O$ chemical shifts to hydrogen bonding and solvent effects, the model used is insufficient to assign these spectra at present. Comparison of calculated and experimental IR spectra leads to the conclusion that IR spectroscopy is not suitable for the characterization of the different binding modes of the adsorption complexes.

## 1. Introduction

Modification of a metal oxide surface with organic components combines the stability of the inorganic material with the versatility of the organic functional groups on the surface. The resulting materials have been widely studied and have led to numerous advanced applications such as organic-inorganic membranes [1], implant biomaterials [2,3], and (dye-sensitized) solar cells [4–6]. The main issue with creating organic-inorganic materials is the interaction between the two components. Several anchor groups (thiols, carboxylic acids, alkoxysilanes, sulfonic acids, phosphonic acids, *etc.*) have been used to covalently bind the organic component to the inorganic phase; a more comprehensive list of the possible anchor groups and their interactions with metal oxide surfaces can be found in a recent review article of Pujari *et al.* [7]. The most common of these anchor groups are silanes, carboxylates and organophosphonic acids, but since organosilylated metal oxides are very susceptible to hydrolysis [8] and the bonding of carboxylates to a metal oxide surface is weak compared to other adsorbents, thereby jeopardizing their stability [9], attention has recently been shifted towards functionalization of $TiO_2$ surfaces with phosphonic acid derivatives (PAs) as anchor groups. The strength of P–O–Ti bonds [10–12] and the fact that PAs are easily prepared and that PA modification of the $TiO_2$ surface is possible in both water and organic solvents, have been cited as the main advantages.

The two most powerful experimental techniques to characterize the covalent grafting of PAs on $TiO_2$ are $^{31}P$ solid-state nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. However, the interpretation of the $^{31}P$ chemical shifts to distinguish mono-, bi- or tridentate binding modes [13,14] is not straightforward, because the binding mode is not the only parameter influencing the $^{31}P$ chemical shifts [15]. Even though IR spectra clearly indicate the presence of PAs on the surface due to the disappearance of P–O–H and P=O bands in favor of P–O–Ti bands, further characterization of the binding mode using IR spectroscopy is severly hampered by the overlap of the P–O stretching region and the bands in the native $TiO_2$ spectrum [13,14]. Recently, also $^{17}O$ NMR spectroscopy was applied to study the binding modes of PAs adsorbed on anatase [15]: this technique was able to distinguish P=O, P–O–H and P–O–Ti bonds, which led to the conclusion that multiple binding modes are possible, but that the tridentate binding mode is the most dominant. However, due to the

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requirement of $^{17}$O-enriched PAs this technique is difficult to use on a routine basis.

A number of computational studies were published on the energetics of PA-grafting onto $TiO_2$, performed to complement experimental measurements. These indicated that the most stable binding modes on the anatase (101) and rutile (110) surfaces are mono- and bidentate [16–18]. In addition, both bi- and tridentate binding modes were found to be stable on anatase (001) [17]. The latter is a minority facet [7% (001) compared to 90% (101)] but its surface is more reactive than anatase (101) [19]; in addition, it has recently been shown that uniform anatase crystals with more than 80% of (001) can be prepared [20,21]. Despite this, its properties with respect to PA grafting have not been fully investigated.

Despite the large body of experimental and computational work performed on these systems, the precise nature of the binding modes of PAs on the surface and the associated assignments of important peaks in both NMR and IR spectra remain unclear. The main reason for this may be that up to now computational and experimental work has been carried out separately and very little attention has been paid to linking both. In this work, the binding modes of PAs on the anatase (101) and (001) surfaces will be investigated and directly linked to experimental vibrational frequencies and $^{31}$P and $^{17}$O NMR chemical shifts measured in the solid state in order to obtain a benchmark by which experimental spectra can be unambiguously assigned.

## 2. Experimental

### 2.1. Computational details

All calculations were performed under Periodic Boundary Conditions (PBC) with the Quantum Espresso (QE) software package [22] using plane waves as basis sets. The Wu and Cohen functional (WC) – a modification of the PBE functional – allows for a high-quality description of solid-state materials and was, therefore, used throughout this work [23]. Treatment of the core electrons is based on the projector augmented wave (PAW) method [24] using the Troullier-Martins form [25]. The 1s electrons are treated as core electrons for C and O atoms, whereas P and Ti atoms are treated with the valence configurations $3s^23p^3$ and $3s^23p^64s^23d^2$, respectively. The influence of the k-point grid and cutoff was analyzed with reference to the total energy of bulk and surface anatase: a cutoff of 800 eV and a k-grid of 6×6×3 were chosen. The geometry of the bulk structure was optimized until the residual forces were below 0.0002 Ry/au. The optimized bulk lattice parameters of anatase were $a$=3.785 Å and $c$=9.545 Å, which is in good agreement with experimental results ($a$=3.789 Å and $c$=9.522 Å) [26] and other calculations [27,28].

The anatase (001) and (101) surfaces were constructed using the cif2cell program [29] with a 15 Å vacuum width to avoid interactions between the slab and its image; after introduction of the PA molecules the surface coverage amounts to about 0.9 groups/nm$^2$. Based on previous studies concerning the surface properties of $TiO_2$ in function of the number of layers, 3- and 4-layer slabs were constructed for the (101) and (001) surfaces, respectively [30–32]. A cutoff of 600 eV and a 3×3×1 k-grid was chosen for the clean surfaces and adsorption complexes. The atoms in the lowest layer of the slab were constrained to their initial bulk positions, while all other layers were allowed to relax. The geometry of the clean surface and adsorption complexes was optimized until the residual forces were below 0.001 Ry/au. The geometrical parameters of the relaxed top layer of the (101) and (001) slabs are given in Table 1 with atom labels in Fig. 1, and are in complete agreement with previous studies [33–35].

Calculations of the chemical shifts were performed using the Gauge-Independent Projector Augmented Waves (GIPAW) method [36], as implemented in the QE software package; for more background on the calculation of NMR parameters of solids see refs. 37 and 38. The isotropic chemical shift $\delta_{iso}$ is defined as $\delta_{iso}=-(\sigma-\sigma_{ref})$, but in order to compare experimental and calculated chemical shifts, the isotropic shielding of the reference needs to be carefully selected. For the $^{31}$P spectra, berlinite ($AlPO_4$) with $\delta_{iso}(^{31}P)=-24.5$ ppm [39] referenced to $H_3PO_4$ was chosen to define $\sigma_{ref,calc}(^{31}P)$. For the $^{17}$O spectra, $\sigma_{ref,calc}(^{17}O)$ was obtained from a fit between experimental data and the calculated values for a set of $SiO_2$ polymorphs, a method applied in a computational study of the chemical shifts of phenylphosphonic acid which resulted in a very good agreement with the experimental data [40]. Vibrational frequencies of both the isolated molecules and the adsorption complexes were calculated at the gamma point using density functional perturbation theory, as implemented in the phonon package of the QE software package. Dispersion interactions were taken into account by adding an additional term to the DFT total energy based on the DFT-D2 method by Grimme [41,42].

**Table 1**
Selected geometrical parameters (bond lengths in Å and angles in degrees) of the relaxed top layers of the anatase (101) and (001) surfaces. Atom labels refer to Fig. 1.

| **Anatase (101)** | **This work** | **Ref.** [a] [32] | **Ref.** [b] [33] |
|---|---|---|---|
| Ti1-O1 | 1.855 | 1.845 | 1.866 |
| Ti2-O1 | 1.818 | 1.830 | 1.823 |
| Ti2-O2 | 1.779 | 1.779 | 1.786 |
| Ti2-O3 | 1.972 | 1.981 | 1.975 |
| Ti2-O4 | 2.038 | 2.068 | 2.078 |
| **Anatase (001)** | **This work** | **Ref.** [a] [32] | **Ref.** [c] [34] |
| Ti1-O1 | 2.210 | 2.202 | 2.207 |
| O1-Ti2 | 1.755 | 1.758 | 1.738 |
| Ti1–O1–Ti2 | 145.4 | 146.0 | 146.7 |

[a] DFT/PBE, plane waves, pseudopotential, six O-Ti-O layers.
[b] DFT/GGA, plane waves, pseudopotential, three O-Ti-O layers.
[c] DFT/B3LYP, Gaussian basis set, pseudopotential, four O-Ti-O layers.

### 2.2. Experimental details

$TiO_2$/MPA, $TiO_2$/EPA, $TiO_2$/BPA and $TiO_2$/PPA were prepared by dispersing 1 g of P25 Degussa $TiO_2$ in 20 ml of a 0.1 M solution of the relevant phosphonic acid in water. After stirring the reaction mixture for 24 h at 20 °C the solids were recovered by membrane filtration (VitraPOR Borosilicate 3.3) and washed with 200 ml of water in order to remove any remaining free MPA. Finally, the material was dried at 120 °C under vacuum for 24 h. $TiO_2$/OPA was prepared by dispersing 1 g of P25 Degussa $TiO_2$ in 20 ml of a 0.1 M solution of OPA in toluene. After stirring the reaction mixture for 24 h at 20 °C the solids were recovered by membrane filtration (VitraPOR Borosilicate 3.3) and washed with 200 ml of toluene in order to remove any remaining free OPA. Finally, the material was dried at 120 °C under vacuum for 24 h.

Solid-state $^{31}$P CP/MAS (cross-polarization magic angle spinning) NMR spectra were acquired at ambient temperature on an Agilent VNMRS DirectDrive 400 MHz spectrometer (9.4 T wide bore magnet) equipped with a T3HX 3.2 mm probe dedicated for small sample volumes and high decoupling powers. Magic angle spinning (MAS) was performed at 10 kHz using ceramic zirconia rotors of 3.2 mm in diameter (22 µl rotors) and with TOSS (total suppression of spinning side bands). Orthophosphoric acid ($H_3PO_4$) was used to calibrate the phosphorus chemical shift scale (0 ppm). The applied acquisition parameters were: a spectral width of 50 kHz, a 90° pulse of 2.5 µs, a spin-lock field for cross polarization (CP) of 100 kHz, a contact time for CP of 1700 µs, an acquisition time of 20 ms, a recycle decay of 20 s and between 500 and 3000 accumulations. High-power proton dipolar decoupling during the acquisition time was set to 100 kHz. The Hartmann-Hahn condition for CP was calibrated accurately on the samples themselves.