Binding mechanism of arsenate on rutile (110) and (001) planes studied using grazing-incidence EXAFS measurement and DFT calculation

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Abstract: Characterization of contaminant molecules on different exposed crystal planes is required to conclusively describe its behavior on mineral surfaces. Here, the structural properties and relative stability of arsenate adsorbed on rutile TiO$_2$ (110) and (001) surfaces were investigated using grazing-incidence extended X-ray absorption fine structure (GI-EXAFS) spectra and periodic density functional theory (DFT) calculation. The combined results indicated that arsenate mainly formed inner-sphere bidentate binuclear (BB) and monodentate mononuclear (MM) complexes on both surfaces, but the orientational polar angles of arsenate on the (110) surface were commonly smaller than that on the (001) surface for the two adsorption modes. The DFT calculation showed that the (110) plane had a higher affinity toward arsenate than the (001) plane, suggesting that, for a given adsorption mode (i.e., MM or BB structure), a small polar angle was more favorable for arsenate stabilized on the rutile surfaces.

Keywords: surface complex; molecular orientation; adsorption stability; GI-EXAFS; density functional theory
1. Introduction

Arsenic contamination in drinking water and groundwater resources has been a serious environmental problem due to its toxic impact on human health (Oremland and Stolz, 2003). Solid-water interfacial behaviors control arsenic mobility, toxicity and bioavailability (Liu and Aydil, 2009; Singer et al., 2013). It is therefore important to determine the adsorption geometries and bonding interactions that hold the arsenic species to the surface, which is directly related to the reversibility, lability and surface reactivity, and is essential to predict their fate in the environment (Makov and Payne, 1995).

Atomic-level understanding of the structure of contaminant molecules on mineral surfaces is growing through the application of spectroscopic and computational techniques, such as extended X-ray absorption fine structure (EXAFS) spectroscopy and density functional theory (DFT) calculation (Sherman and Randall, 2003; Zhang et al., 2005; He et al., 2009; Shimizu et al., 2011; Li et al., 2012). Over the last decades, EXAFS spectroscopy was successfully applied to determine the structure of adsorbates at water-mineral interfaces, and has been one of the most important techniques for structural analysis (Waychunas et al., 1993; Makov and Payne, 1995; Arai et al., 2001). However, standard EXAFS experiment are carried out using powder samples, where different types of crystal planes of the mineral are mixed. Multiple surface terminations and extensive defects of mineral powder produce a large number of different sites where adsorbates may adsorb (Catalano et al., 2005). Therefore, the structural data obtained from standard powder EXAFS spectra are therefore an average for various crystal planes.

These problems can be overcome by using grazing-incidence EXAFS (GI-EXAFS) spectroscopy. GI-EXAFS uses well-characterized single-crystal sample and polarized X-ray, which enables it to offer more structural information (interatomic distance, coordination number and polar angle) toward
the oriented absorbates than standard powder EXAFS (Waychunas et al., 2005). These advantages may trigger wide applications of GI-EXAFS in geosciences, chemistry and environmental sciences as synchrotron facilities are improving (Roscioni et al., 2013). Density functional theory (DFT) calculation can provide a detailed description of adsorbed molecules at solid surfaces, including aspects of structure, bonding, and energy (He et al., 2011; Li et al., 2012). Therefore, the combination of GI-EXAFS and DFT calculation is able to identify the structural properties and relative stability of arsenic on specific crystal planes.

Rutile, the most abundant polymorph of TiO₂, is one of the most common and technologically important metal oxides for modern science and technology (Wang et al., 1997; Liu and Aydil, 2009), and shows a high affinity to arsenic (Pena et al., 2005; Luo et al., 2010). The (110) surface is the predominantly exposed plane of natural rutile (60%), and the (001) surface is studied intensively in surface science due to its large-coordinate unsaturation (Ramamoorthy et al., 1994; Ahmed et al., 2011).

Here we apply GI-EXAFS spectroscopy and periodic DFT calculation to study the binding mechanism of arsenate on rutile (110) and (001) surfaces. In the GI-EXAFS measurement, two directions of the X-ray electric vector, parallel and perpendicular to the substrate, were used to determine the structure of the adsorbed arsenate on both surfaces. Periodic DFT calculation was carried out to describe the bonding and energetic properties of arsenate on rutile TiO₂ surfaces.

2. Experimental and theoretical methods

2.1. Sample preparation

Highly polished 10×10×0.5 mm³ rutile TiO₂ (110) and (001) single crystals were obtained
commercially from Shanghai Daheng Optics and Fine Mechanics Co., Ltd, China. The orientations were
checked using high accuracy X-ray single crystal orientation instrument (DX-4A, Dandong, China) and
were found to be perfectly oriented to the resolution limits of the equipment (~2 Å). The roughness was
assessed with AFM (Veeco Dimension 3100) and was found to be ≤5 Å rms. Prior to initial use, the
crystals were washed in 10⁻⁴ M nitric acid and ethanol followed by multiple rinses with MilliQ (18 MΩ)
water. The crystals were then equilibrated with 0.1 M Na₂HAsO₄ solution at pH 6.8 for 2h to achieve a
sufficient adsorption density and hence adequate signal-to-noise ratio for GI-EXAFS data collection. A
constant ionic strength was maintained by use of 0.01 M NaNO₃. All chemicals used for solution
preparation were of reagent grade quality.

2.2. GI-EXAFS data collection

Grazing-incidence EXAFS data were collected on beamline BL14W1 at the Shanghai Synchrotron
Radiation Facility (SSRF) using a purposely build apparatus (Fig. 1). The instrument consists of a
carriage that holds the sample stage (KOHZU multi-dimensional sample stage), with motor drives for
positioning the sample over 5 degrees of freedom (Waychunas et al., 2005). Then, a wet arsenate-loaded
crystal sample was prepared on the sample stage for GI-EXAFS measurements. The carriage can be
rotated around the incident X-ray beam to set the angle of the X-ray electric vector polarization plane
with respect to the sample surface. Ionization chamber detectors were mounted on both sides of the
sample for transmission absorption data collection, and a 4-channel Si drift detector (SDD, Canberra
Industries, Inc.) was used to collect fluorescence signals.
Fig. 1. Apparatus used in the GI-EXAFS data collection (SSRF, BL14W1). $I_0$ and $I_1$ are gas ionization chambers for measuring the intensities of the incident beam and the reflected beam from the sample surface, respectively.

The angle of the incident X-rays (beam diameter of ~30 μm) to the single-crystal surfaces was set to 0.15°, which is less than the critical angle of rutile TiO$_2$ at the energy position of As K-edge (Klockenkämper, 1997). The experimental uncertainty on the incident angle of X-rays is ≤ 0.01°. The GI-EXAFS experiments were carried out using two scan modes with the electric vector parallel and perpendicular to the single-crystal substrate. Samples were mounted in a Teflon cell and sealed with Mylar film during the GI-EXAFS measurements. The cell was continuously purged with a constant flow of water-saturated ultrapure N$_2$ to keep the crystals moist. An average of 3 scans was performed to achieve suitable single/noise, and no obvious change in spectral data was observed during the 3 scans.

2.3. GI-EXAFS data analysis

The spectral data were processed following the standard procedures of background absorption removal, normalization, k-space conversion, and Fourier transformation, and then the structural information was extracted using WinXAS 3.1 software package with Fourier filtering and shell fitting (Ressler, 1998). A linear function fit for the pre-edge region and a second-order polynomial fit in the
post-edge region were used to yield the normalized and background-corrected spectra. Subsequently, the normalized spectra were converted to frequency \((k)\) space using a cubic spline and weighted by \(k^3\). The \(k^3\chi(k)\) spectra, from 2.2 to 12.0 Å\(^{-1}\), were Fourier-transformed (FT) to \(R\) space using a Bessel window function with smoothing parameter of 4. The theoretical phase shift and amplitude functions for single- and multiple-scattering paths were calculated by ab initio Feff 9.0 code (Ankudinov et al., 1998) using the cluster of scorodite (FeAsO\(_4\)·2H\(_2\)O) with the Fe atom replaced by Ti atom. This method has been successfully used in the study of arsenate adsorption on Ti- and Al-(hydr)oxide surfaces (Arai et al., 2001; Pena et al., 2006). An amplitude reduction factor \((S_0^2)\) of 0.9 was used in data-fitting procedure (Jing et al., 2005; Grafe et al., 2008). The coordination number \((CN)\) of As-O shell and two As-Ti subshells were initially fixed at 4, 2, and 1, respectively, to obtain estimated values for interatomic distances \((R)\), DW factors \(\sigma^2\), and \(\Delta E_0\) (within \(\pm\)6.0 eV). Then the \(R, \sigma^2, \text{ and } \Delta E_0\) were fixed to obtain the estimated \(CN\) for each shell. The estimated values of \(CN, R, \sigma^2, \text{ and } \Delta E_0\) were then used for a sequential fitting that recorded the reduction of the residual until the best fit was obtained. Finally, all the parameters \((CN, R, \sigma^2, \text{ and } \Delta E_0)\) for each backscattering paths were allowed to vary. All the residuals were less than 11\%, indicating the good quality of the final data fitting. The experimental spectra were also fitted using the As-As scattering path and As-O-O-As multiple scattering path (see Supplementary data), and no significant improvement was found by adding the As(V)-bearing solid phase and multiple scattering effects to the fitting.

2.4. Computational settings

All calculations were performed using the density functional theory (DFT) code DMol3 module in Materials Studio software (Accelrys Software Inc.) under periodic boundary conditions (PBC) (Delley, 1995). In the spin-restricted DFT calculations, the exchange-correlation interaction was treated with the
generalized gradient approximation (GGA) parameterized by Perdew, Burke and Enzerhof (PBE) (Perdew et al., 1996). A double numerical plus polarization (DNP) basis set (including a polarized d-function for all non-hydrogen atoms and p-function for all hydrogen atoms) (Delley, 2000) and a global orbital cutoff of 5.2 Å were employed. The size of the DNP basis set is comparable to Gaussian 6-31G (d, p), but the DNP is more accurate than a Gaussian basis set of the same size (Inada and Orita, 2008). The core electrons were treated with effective core potentials (ECP) (Hay and Wadt, 1985). The conductor-like screening model (COSMO) was applied to simulate the water solvent environment (Klamt and Schuurmann, 1993). The fine quality mesh size for the numerical integration was chosen. The Brillouin zone was sampled using the Monkhorst-Pack special k-point scheme with a 4×4×1 mesh for structural optimization. To improve sampling convergence, a Fermi smearing of 0.005 hartree (1 hartree = 27.2114 eV = 2625.5 kJ mol\(^{-1}\)) was used (Delley, 1995). The geometry optimization convergence tolerances of the energy, gradient, and displacement were 1×10\(^{-5}\) Hartree, 2×10\(^{-3}\) Hartree Å\(^{-1}\), and 5×10\(^{-3}\) Å, respectively.

2.5. Computational model

The unit cell of rutile TiO\(_2\) was firstly optimized, and the obtained lattice constant (\(a = 4.646\) Å, \(c = 2.988\) Å) agreed favorably with the experimental values (\(a = 4.594\) Å, \(c = 2.959\) Å) (Baur and Khan, 1971) and other theoretical works (Perron et al., 2007). The supercell expansions and lattice parameters used to construct each surface slab are listed in Table 1. The rutile (110) surface model was constructed by a 2×1 surface supercell of 5.92 Å×6.50 Å. The surface model consisted of four O-Ti-O tri-layers (i.e., twelve atomic planes) with the thickness of 13.70 Å (Fig. 2a). During the DFT calculations, the arsenate and the top two TiO\(_2\) layers (i.e., six atomic planes) were allowed to relax, and the bottom two TiO\(_2\) layers were fixed at equilibrium crystal lattice sites to simulate bulk
conditions (Ojamäe et al., 2006; Huang et al., 2011). A 3D supercell consisted of $2 \times 2$ non-primitive surface unit cells was created to model the (001) surface. Eight atomic planes were included in this model, which resulted in the spatial dimensions of 9.19 Å $\times$ 9.19 Å $\times$ 11.84 Å (Fig. 2b). During the geometrical optimization, the positions of arsenate and the top four atomic planes were allowed to relax, and the bottom four atomic planes were fixed at the bulk crystal lattice sites. Hydroxylation of rutile TiO$_2$ surfaces would occur in the solution, and the specific protonation states of the Ti-O is controlled by pH. It has been determined that the protonation constants of rutile surfaces were 5.9 and 4.9 for the terminal ($pK_{H1}$, TiOH$^-$ + H$^+ = $ TiOH$_2$) and bridging ($pK_{H2}$, Ti$_2$O$^-$ + H$^+ = $ Ti$_2$OH) oxygen sites, respectively (Machesky et al., 2008). According to the protonation constants, the TiOH$^-$ (terminal sites) and Ti$_2$O$^-$ (bridging sites) groups should be the dominant species on rutile surfaces under the GI-EXAFS experimental pH 6.8 condition. Therefore, the rutile surfaces were terminated by protonated terminal oxygens and unprotonated bridging oxygens in the calculation of arsenate surface complexation (see Fig. 2 and 4), corresponding to the pH condition in our GI-EXAFS experiment. These models were separated from their periodic images normal to the surface by a vacuum gap of 15 Å to eliminate spurious interactions between the adsorbate and the periodic image of the bottom layer of the slabs (Huang et al., 2011; Roscioni et al., 2013). A counter positive charge was automatically added by DMol3 package during the calculations in order to keep the neutrality of the whole model to avoid divergence in the electrostatic energy (Makov and Payne, 1995). 

9
Fig. 2. Rutile TiO$_2$ (110) and (001) surface models used in the DFT calculation. Gray, red, big purple and yellow balls represent titanium, oxygen in rutile bulk, surface hydroxyl oxygen and hydrogen atoms, respectively.

Table 1. Supercell expansions and lattice parameters used to construct rutile (110) and (001) surface models

<table>
<thead>
<tr>
<th>surface</th>
<th>expansion</th>
<th>$U$(Å)</th>
<th>$\nu$(Å)</th>
<th>area(Å$^2$)</th>
<th>$n_{TiO_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>2×1</td>
<td>5.98</td>
<td>6.57</td>
<td>38.45</td>
<td>30</td>
</tr>
<tr>
<td>(001)</td>
<td>2×2</td>
<td>9.29</td>
<td>9.29</td>
<td>84.42</td>
<td>42</td>
</tr>
</tbody>
</table>

The selection of parameters and models was justified by performing test calculations (see Table S1 and Fig. S4 in Supplementary data). Increasing $k$-points from 4×4×1 to 5×5×3 and orbital cutoff from 5.2 to 6.0 had almost no effect on adsorption geometry and energy. Similarly, no obvious difference was found in the adsorption structure when the relaxed O-Ti-O tri-layers increased from 2 to 3, and the corresponding change in binding energies was less than 4 kJ mol$^{-1}$. This result indicated that the structure and relative energy of arsenate adsorption were converged when the relaxed O-Ti-O tri-layers increased to 2, which were in line with the DFT results for other adsorbates in literatures (Ojamäe et al., 2006; Zhang et al., 2006; Huang et al., 2011). Addition of four explicit H$_2$O molecules to the model was
carried out to test the effects of outer-sphere H$_2$O molecules on the surface complexation of arsenate. The results showed that the outer-sphere H$_2$O molecules do not strongly affect the geometry of adsorbed arsenate (As-O distances shifted by <0.02 Å, As-Ti distances shifted by <0.01 Å, polar angles deviated by less than 1°, and the difference in binding energies was less than 8 kJ/mol). These tests verified that the present parameters and models were reliable for describing the properties of arsenate on rutile surfaces.

3. Results and discussion

3.1. GI-EXAFS analysis

The $k^2$-weighted and Fourier transform spectra of As K-edge GI-EXAFS for the adsorption samples of arsenate on rutile (110) and (001) single-crystal surfaces are shown in Fig. 3. The fitting data are presented in Table 2. Based on our fitting results, we estimated the accuracies of the As–O shell to be ±0.005 Å for interatomic distance ($R$) and ±5% for coordination number ($CN_{\text{As-O}}$). The estimated errors were ±0.02 Å, ±0.03 Å and ±20% for $R$ of As–Ti first subshell, $R$ of As–Ti second subshell and $CN_{\text{As-Ti}}$, respectively. The fitting results showed that the first coordination shell of the arsenic atom consisted of four oxygen atoms at a distance of ~1.71 Å, which agreed with the literature (Pena et al., 2006). As a result of the high symmetry of AsO$_4$ tetrahedron (H$_2$AsO$_4^-$ belongs to $C_{2v}$ point-group symmetry), no obvious difference in $CN_{\text{As-O}}$ (Table 2) was observed between both polarized scans (electric vector parallel and perpendicular to the substrate).

GI-EXAFS fitting results showed that the second peak (at 2.3-3.4 Å) of the Fourier transform spectra was dominated by two titanium subshells (Table 2). The experimentally measured As-Ti distances [3.27±0.02 Å and 3.58±0.03 Å on (110) plane, 3.31±0.02 Å and 3.56±0.03 Å on (001) plane]
were consistent with the DFT calculated values of bidentate binuclear (BB) [3.26 Å for (110) surface, 3.36 Å for (001) surface] and monodentate mononuclear (MM) [3.63 Å for (110) surface, 3.60 Å for (001) surface] complexes, respectively (see Table 3). The As-Ti shells were also fitted using one single As-Ti scattering path. The residuals of single-shell fits were commonly larger than that of two-subshell fits (see Supplementary data), which confirmed the multiple coordination structures (i.e., the mixture of BB and MM adsorption) of arsenate on rutile surfaces.

Fig. 3. (a) \(k^3\)-weighted and (b) Fourier transform As K-edge GI-EXAFS spectra of arsenate adsorption on rutile (110) and (001) planes measured using two scan modes (electric vector parallel and perpendicular to the substrate). The solid lines are the experimental spectra, while the dashed lines are fitting curves. The peak positions are uncorrected for phase shifts.

An obvious difference in \(CN_{\text{As-Ti}}\) was observed from the same sample between the two scan modes (Table 2), resulting from the polarization dependence of As-Ti bonds. Different to the \(CN_{\text{iso}}\) determined by standard powder EXAFS, the polarized coordination number (\(CN_{\text{pol}}\)) obtained from GI-EXAFS varies with the angle between the incident electric vector and the bond (Waychunas et al., 2005). The polarization dependence allows a maximum of \(CN_{\text{pol}}\) when the bond parallel to the
direction of electric vector, and a near-zero value would appear when the bond normal to the electric vector in the GI-EXAFS measurement. For instance, Fitts et al. presented that the $CN_{pol}$ of Cu-Si bond on SiO$_2$ (0001) surface in monodentate complex was 0.3 when the electric vector parallel to the substrate (Fitts et al., 1999). It was also reported that a zero $CN_{pol}$ value of Co-O bond occurred in an on-top complex of Co(II) adsorbed on α-Al$_2$O$_3$ (0001) surface when the bond was absolutely normal to the E-vector (Shirai et al., 1992; Shirai et al., 1994). The difference of $CN_{As-Ti}$ between both polarized scans can be used to deduce the polar angle ($\phi$, angle between the As-Ti vector and the substrate normal), and to determine the stereostructure of each surface complex. For the two scan modes (electric vector parallel and perpendicular to the support plane), the relationships between the coordination numbers of a polarized EXAFS measurement ($CN_{pol}$) and that of isotropic EXAFS ($CN_{iso}$) are $CN_{pol}^\perp = CN_{iso} \times 3 \cos^2 \phi$ and $CN_{pol}^{\parallel} = \frac{3}{2} CN_{iso} \times \sin^2 \phi$, respectively (Manceau et al., 2002; Waychunas et al., 2005). Based on the two equations, the polar angles ($\phi$) of BB complex obtained from GI-EXAFS fitting were 31°±8° on (110) surface and 43°±5° on (001) surface, while the experimental $\phi$ of MM complex on (110) and (001) surfaces were 15°±6° and 18°±9°, respectively.

Table 2. GI-EXAFS measured structural parameters of arsenate adsorption on rutile (110) and (001) single-crystal planes$^a$

<table>
<thead>
<tr>
<th>Shell</th>
<th>R(Å)</th>
<th>$CN_{pol}$</th>
<th>Type of neighbor</th>
<th>DW(σ$^2$)</th>
<th>$\Delta E_0$</th>
<th>Residual$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(110) surface E-vector$^b$ parallel to surface</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First</td>
<td>1.73 ± 0.005</td>
<td>4.0 ± 0.2</td>
<td>O</td>
<td>0.004 ±0.002</td>
<td>-1.566 ±0.161</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.27 ± 0.02</td>
<td>0.7 ± 0.1</td>
<td>Ti</td>
<td>0.006 ±0.003</td>
<td>3.621 ±0.073</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>3.57 ± 0.03</td>
<td>0.2 ± 0.1</td>
<td>Ti</td>
<td>0.007 ±0.002</td>
<td>4.814 ±0.051</td>
<td></td>
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<tr>
<td>Second</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td><strong>(110) surface E-vector normal</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First</td>
<td>1.73 ± 0.005</td>
<td>4.0 ± 0.2</td>
<td>O</td>
<td>0.004 ±0.001</td>
<td>-1.429 ±0.019</td>
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<tr>
<td></td>
<td>3.28 ± 0.02</td>
<td>4.4 ± 0.8</td>
<td>Ti</td>
<td>0.005 ±0.002</td>
<td>4.013 ±0.017</td>
<td>6.5</td>
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<td>3.59 ± 0.03</td>
<td>2.8 ± 0.6</td>
<td>Ti</td>
<td>0.007 ±0.003</td>
<td>-5.580 ±0.012</td>
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(001) surface E-vector parallel to surface

<table>
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<tr>
<td></td>
<td>1.70 ± 0.005</td>
<td>4.0 ± 0.2</td>
<td>O</td>
<td>0.005 ±0.002</td>
<td>0.541 ±0.015</td>
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<tr>
<td></td>
<td>3.30 ± 0.02</td>
<td>1.6 ± 0.3</td>
<td>Ti</td>
<td>0.008 ±0.002</td>
<td>-3.986 ±0.650</td>
<td>10.7</td>
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<tr>
<td></td>
<td>3.55 ± 0.03</td>
<td>0.3 ± 0.1</td>
<td>Ti</td>
<td>0.007 ±0.003</td>
<td>-5.683 ±1.107</td>
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(001) surface E-vector normal

<table>
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<tbody>
<tr>
<td></td>
<td>1.70 ± 0.005</td>
<td>4.0 ± 0.2</td>
<td>O</td>
<td>0.003 ±0.001</td>
<td>-1.487 ±0.007</td>
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</tr>
<tr>
<td></td>
<td>3.33 ± 0.02</td>
<td>3.2 ± 0.6</td>
<td>Ti</td>
<td>0.006 ±0.002</td>
<td>3.365 ±0.002</td>
<td>5.1</td>
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<tr>
<td></td>
<td>3.56 ± 0.03</td>
<td>2.7 ± 0.5</td>
<td>Ti</td>
<td>0.006 ±0.003</td>
<td>5.705 ±0.009</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The listed parameters (CN, coordination number; R, interatomic distance; \(\sigma^2\), Debye-Waller factor) reflected the final best fit.

\(^b\) E-vector, electric vector.

\(^c\) Residual gives a measure of the agreement between experimental and theoretical FT curves. All Residuals are < 11%, indicating reliable fits.

3.2. Periodic DFT calculation

\(\text{H}_2\text{AsO}_4^-\) is the predominant species of \(\text{H}_n\text{AsO}_4^{3-n}\) (pKa\(_1\)=2.2, pKa\(_2\)=7.0) (Ladeira et al., 2001) under the GI-EXAFS experimental pH 6.8 condition, and hence was used in the DFT calculation as the arsenate species. Calculated structures of arsenate on rutile (110) and (001) surfaces are shown in Fig. 4. DFT results showed that the average As-O bond lengths of arsenate tetrahedron in different adsorption states were about 1.73 Å (Table 3), which were generally slightly longer than the experimentally measured As-O distances (1.70-1.73 Å). This phenomenon was also observed in the adsorption of arsenite on Fe-(hydr)oxides (Zhang et al., 2005). This difference between experimental and theoretical values may be due to the theoretical underestimation of solvent effect from COSMO model (Costentin et al., 2004; Tossell, 2005). However, we expect that this artifact does not affect the relative stability of the adsorption modes and their complexation properties. DFT-calculated polar angles (\(\phi\), angle between the As-Ti vector and the substrate normal) of the BB and MM complexes on the rutile (110) surface were 27° and 6°, respectively. On the rutile (001) surface, the calculated \(\phi\) were respectively 42° and 19° for the BB and MM complexes (Table 3). The discrepancies between experimental and DFT-calculated polar angles were less than 10°, indicating that a good estimation of the polar angles
Bidentate mononuclear (BM) complex was the potential adsorption mode at the bridging oxygen sites on (110) surface (see Fig. S4 in Supplementary data). Our DFT results indicated that BM adsorption mode would yield an As-Ti distance of 2.88 Å, much smaller than the distance obtained from experimental GI-EXAFS measurement (3.30 ± 0.02 Å and 3.57 ± 0.03 Å), which confirmed the fact that the twofold bridging oxygen is less active than the high coordination-unsaturated terminal oxygen at the rutile (110) surface (Ojamäe et al., 2006; Li et al., 2012). Our previous DFT study showed that the forming of outer-sphere H-bonded complexes were more thermodynamically unfavorable than inner-sphere adsorption of arsenate on anatase TiO$_2$ surfaces (He et al., 2009). Moreover, the As-Ti distances would be ~5 Å in outer-sphere Ti-AsO$_4$ complexes, however, no effective signals were observed more than 4 Å away from the As atom in the GI-EXAFS spectra (see Fig. 3b). Therefore, in order to directly compare the calculated results with experimental data, complexation at the bridging oxygen sites on (110) surface and outer-sphere adsorption was not included in the analysis and discussion here.
**Fig. 4.** DFT-calculated structures of arsenate adsorbed on rutile TiO$_2$ surfaces: (a) BB complex on (110) plane; (b) MM complex on (110) plane; (c) BB complex on (001) plane; (d) MM complex on (001) plane. Gray and red circles denote the Ti and O atoms in the TiO$_2$, respectively. Purple and green circles denote As and O atoms in the AsO$_4$ tetrahedron, respectively. Yellow circles represent the H atoms.

**Table 3.** DFT-calculated interatomic distances, polar angles and binding energies ($\Delta E$) of arsenate adsorbed on rutile surfaces

<table>
<thead>
<tr>
<th>Bond</th>
<th>Interatomic distances (Å)</th>
<th>Polar angle (°)</th>
<th>$\Delta E$ (kJ mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>As-O</td>
<td>As-OH</td>
<td>Average</td>
</tr>
<tr>
<td>BB-110</td>
<td>1.69</td>
<td>1.70</td>
<td>1.77</td>
</tr>
<tr>
<td>MM-110</td>
<td>1.69</td>
<td>1.74</td>
<td>1.73</td>
</tr>
<tr>
<td>BB-001</td>
<td>1.68</td>
<td>1.75</td>
<td>1.79</td>
</tr>
<tr>
<td>MM-001</td>
<td>1.67</td>
<td>1.70</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Polar angle is the angle between the surface normal and the interatomic As-Ti vector direction. $\Delta E$ were calculated as $\Delta E = E_{\text{tot}}(\text{Ti-AsO}_4) - [E_{\text{tot}}(\text{arsenate}) + E_{\text{tot}}(\text{TiO}_2)]$, where $E_{\text{tot}}(\text{Ti-AsO}_4)$ was the total energy of Ti-AsO$_4$ adsorption complex, $E_{\text{tot}}(\text{arsenate})$ and $E_{\text{tot}}(\text{TiO}_2)$ were the total energy of arsenate molecule and TiO$_2$ cluster, respectively. The structure of non-adsorbed arsenate were optimized in a periodic box with a side length of 10 Å (Ojamäe et al., 2006).

Based on the spectral and computational results, the polar angles of monodentate and bidentate complexes on the (110) surface were both smaller than that on the (001) surface (see Table 3). DFT-calculated energies showed that adsorptions on the (110) plane (-261.4 kJ mol$^{-1}$ for BB complex and -265.9 kJ mol$^{-1}$ for MM complex) were generally energetically more favorable than that on the (001) plane (-245.5 kJ mol$^{-1}$ for BB complex and -161.4 kJ mol$^{-1}$ for MM complex), indicating that the (110) plane had a higher affinity toward arsenate.

**4. Conclusions**

The spectral and computational results showed that arsenate primarily bonded as bidentate binuclear (BB) and monodentate mononuclear (MM) inner sphere complexes on both (110) and (001)
surfaces of rutile TiO\textsubscript{2}, but the spatial orientations of adsorbed arsenate were different on the two crystal planes (i.e., crystal-face-dependent). The orientational polar angles on the (110) surface were commonly smaller than that on the (001) surface for both monodentate and bidentate complexes. The DFT calculation showed that the (110) plane displayed a higher affinity toward arsenate, suggesting that, for a given adsorption mode (i.e., MM or BB structure), a small polar angle was more favorable for arsenate stabilized on rutile surfaces.

**Acknowledgements**

The study was supported by the NNSF of China (21377003, 21207151), and the special fund of State Key Joint Laboratory of Environment Simulation and Pollution Control (12L02ESPC). We thank SSRF for providing the beam time and Dr. Xiangjun Wei for help in GI-EXAFS data collection and data analysis. We thank the Supercomputing Center of the Chinese Academy of Sciences for providing access to the Materials Studio software.

**Appendix A. Supplementary data**

Details on EXAFS fitting based on different path functions/models, and discussion on the validation of computational settings. Supplementary data associated with this article can be found in the online version, at

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