Revision 3

Competitive adsorption geometries for the arsenate As(V) and phosphate P(V) oxyanions on magnetite surfaces: Experiments and theory

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ABSTRACT

In the present study, the competitive adsorption geometries for arsenate and phosphate on magnetite surfaces over a pH range of 4-9 was investigated using *in situ* attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) and two-dimensional correlation analysis (2D-COS). The adsorption energies and infrared vibrational frequencies of these surface complexes were also calculated by first principles simulations. Arsenate and phosphate have different preferences for the magnetite surface in the presence of aqueous solvent at both acid and alkaline pH. For the adsorption of phosphate, mono-protonated monodentate mononuclear (MMM) complexes dominated at acid pH, while non-protonated bidentate binuclear (NBB) complexes were dominant at alkaline pH. Arsenate mainly formed bidentate binuclear (BB) complexes with some outer-sphere species, both of which were more prevalent at acid pH. The pre-absorbed inner-sphere arsenate species were scarcely affected by the introduction of phosphate. However, the pre-absorbed phosphate oxyanions, especially the MMM complexes, were significantly substituted by BB arsenate at the magnetite surfaces. The adsorption affinity of phosphate and arsenate species for magnetite surface was found to increase in the following order: MMM phosphate complex < NBB phosphate complex < BB arsenate complex, which was consistent with the calculated adsorption energies. The simulated infrared vibrational frequencies for the most favored adsorption modes of each oxyanion display distinctive patterns, in which trends are in excellent agreement with experimental data.

The effects of pH, adsorption sequence and mineral species on the competitive adsorption between arsenate and phosphate oxyanions are also discussed, and their different competing ability and stability on the magnetite surfaces were ascribed to the variations in adsorption geometry and strength of binding. To the best of our knowledge, this is the first study aiming to distinguish the stability of the different phosphate and arsenate complexes on magnetite by employing a highly suitable combination of powerful *in situ* spectroscopy and DFT simulations.

This study provides molecular-level insight into the geometries and relative stabilities of the adsorption of phosphate and arsenate on magnetite surfaces, which is useful for the interpretation of the mobility and bioavailability of these anions.

Keywords: Phosphate; Arsenate; Competitive adsorption; Adsorption geometry; ATR-FTIR; First-principles simulations

INTRODUCTION

Contamination of soil and aquatic systems by arsenic (As) and phosphorus (P) is of global environmental concern. Arsenic is often found at elevated concentrations in freshwater, attributed to a variety of natural (e.g., geothermal processes and mineral weathering) and anthropogenic (e.g., mining industry and agriculture) processes (Kocourkova-Vikova et al., 2015; Kunhikrishnan et al., 2017). Owing to its biotoxicity and carcinogenic risk, the presence of arsenic in drinking water ranks among the greatest threat to public health (Antelo et al., 2015), which has led the World Health Organization to propose a limit of 10 μg L^{-1} (WHO, 2011). However, in ~~the~~ arsenic contaminated water, the As concentration can reach several ppm (Chakraborti et al., 2002; Sprague and Vermaire, 2018; Winkel et al., 2011). Arsenic exists in several oxidation states (-III, 0, III and V), with arsenate (AsO_4^{3-}) being the most common form found in natural aqueous systems (Choppala et al., 2016). Phosphorous (P) is an essential nutrient for plant growth. But the input of excess P from agricultural land runoff or over-fertilization may lead to levels above the limit of 0.1 mg L^{-1} recommended by the United States Environmental Protection Agency (USEPA), causing severe environmental problems including eutrophication (Neupane et al., 2014). P occurs naturally only in the pentavalent state, forming ortho-phosphates, pyrophosphates, longer-chain polyphosphates and several types of organic phosphates (Correll, 1998).

After their release from natural and anthropogenic sources, As and P undergo a series of geochemical reactions, e.g., adsorption, reduction/oxidation, precipitation (Zhang

et al., 2017b), and sequestration by soil and sediments (Grossl et al., 1997). The adsorption in the mineral/water interface is vital for their mobility. Iron (hydr)oxides are ubiquitous in soils and aquatic sediments (Pedersen et al., 2005), with high adsorption affinity towards arsenate and phosphate. The surface complexation is the dominant adsorption mechanism reported for arsenate and phosphate species, as verified in macroscopic batch experiments (Swedlund et al., 2014), model calculations (Tiberg et al., 2013) and microscopic studies (Johnston and Chrysochoou, 2014). Bidentate-binuclear (BB), monodentate-mononuclear (MM) and bidentate-mononuclear (BM) complexes are the prevalent surface binding configurations of arsenate and phosphate on iron oxides (Fendorf et al., 1997; Liu et al., 2015), with distribution dependent on pH, ionic strength, and surface coverage (Krumina et al., 2016). Generally, the ability to form bridging bidentate surface complexes is dependent upon the proximity of terminal Fe-O sites on the surface (Livi et al., 2017; Villalobos et al., 2009).

P and As belong to group 5A of the periodic table and form species with comparable chemical properties. Both arsenate and phosphate oxyanions have a tetrahedral geometry with close thermochemical radii, i.e., 2.48 and 2.38 Å (Silva and Fraustoda, 2001), respectively, and very similar proton affinities, e.g., 2.2, 7.0 and 11.5 for pKa_1, pKa_2 and pKa_3 of arsenate and 2.2, 7.2 and 12.3 for pKa_1, pKa_2 and pKa_3 of phosphate (Elzinga and Sparks, 2007; Mohan and Pittman, 2007). Thus, they display analogous adsorption characteristics in the aspects of kinetics, pH dependence, and effect of ionic strength. As arsenate and phosphate oxyanions frequently occur together in

surface environments, their competitive adsorption onto mineral surfaces explicitly determines their bioavailability and leachability, which is crucial for the prediction of potential risk of environmental contamination. However, the current knowledge on this hypothesis is scattered and fragmented, even regarding the adverse effect of phosphate on arsenate adsorption. For example, arsenate is found preferentially adsorbed on iron oxide at a low pH, whereas phosphate shows the opposite trend (Han and Ro, 2018). But in soil stabilized by iron oxide, phosphate can replace the adsorbed arsenate when the concentration of the former is larger than the latter (So et al., 2012). This is contrary to the results reported by Hashem et al., where arsenate was found bonded to iron oxide more strongly than phosphate (Hashem et al., 2015). Moreover, contradictory information is also found in the literature concerning the adsorption geometry. For arsenate, BB complexes were considered ~~as~~ the predominant adsorption configuration on iron oxide surfaces (Carabante et al., 2010). MM coordination is also found for arsenate binding on some iron oxides, as verified by combined EXAFS and IR analyses (Antelo et al., 2015; Loring et al., 2009). Although BM configuration has also been assigned under certain conditions (Neupane et al., 2014), these have been excluded by Sherman et al., as the EXAFS signal attributed to the BM complex was simply due to multiple scattering (Sherman and Randall, 2003). For phosphate, the IR analysis indicates that protonated BB complexes are the predominant species on iron oxides at pH between 3 and 6, whereas the non-protonated BB complexes are dominant at pH > 7.5 (Carabante et al., 2010). On the contrary, ~~the~~ surface complexation modeling (SCM) predicts that deprotonated BB

phosphate and deprotonated MM phosphate dominate at lower pH and higher pH values, respectively, while the contribution of protonated BB is very small (Kanematsu et al., 2010). This shows ~~that~~ great divergence in the competitiveness ~~exists~~ not only within the individual adsorption geometries of phosphate and arsenate, but also during their co-adsorption.

To date, the competitive adsorption of arsenate and phosphate on calcite (So et al., 2012), clay minerals (Violante and Pigna, 2002), and certain iron oxides, e.g., ferrihydrite (Antelo et al., 2015) and goethite (Zhao and Stanforth, 2001), has been investigated intensively. In comparison, their competitive adsorption on magnetite, which is a common constituent of soil and sediment, is poorly understood. Magnetite exists in anoxic sediments and soils (Guo and Barnard, 2013), and is formed naturally via several pathways, including ferrous iron oxidation and iron metal corrosion, as well as chemical and biological reduction of ferric oxides (Gorski et al., 2010). Additionally, the remediation of contaminated groundwater and soil is increasingly carried out using an emerging technology based on zero-valent iron (ZVI) nanoparticles, where magnetite is the major corrosion product formed as the outer layer of ZVI (Filip et al., 2014). With the inverse spinel structure, magnetite has several features that make its reaction properties interesting; specifically, (i) electron donor Fe^{2+} ions on octahedral sites, which are active for the reduction of certain oxyanions, e.g., CrO_4^{2-} and UO_3^{-}; and (ii) octahedral Fe^{2+} and Fe^{3+} cations which can oxidize and reduce reversibly during the reaction with adsorbed oxyanions, while keeping the spinel structure unaffected. In previous studies, magnetite is shown to be

efficient at scavenging metal oxyanions in natural and engineered aquatic systems, including chromate (Zhang et al., 2017a), arsenate (Zhang et al., 2011), and uranyl (Scott et al., 2005). These properties and behavior highlight the important role of magnetite in the transport of arsenate and phosphate in soil and aqueous systems. Due to the low specific surface area or surface site density of magnetite (<50 m^2 g^{-1}, 1–2 sites nm^{-2}) (Sun et al., 1998; Tamura et al., 1993), relative to ferrihydrite (>200 m^2 g^{-1}, 2.5–3 sites nm^{-2}) (Hiemstra, 2013) and goethite (<50 m^2 g^{-1}, 2.5–3.5 sites nm^{-2}) (Ona-Nguema et al., 2005; Zhao and Stanforth, 2001), the resulting low surface coverage of arsenate and phosphate on magnetite makes it difficult to analyze spectroscopically. Extended X-ray absorption fine structure (EXAFS) spectroscopy is the most widespread technique used to investigate the geometry of surface complexes (Ona-Nguema et al., 2005), which has shown the formation of BB arsenate complexes on the surfaces of ferrihydrite, hematite, goethite and lepidocrocite (Sherman and Randall, 2003). However, it is difficult to analyze light elements such as P using soft X-rays, due to their poor signal-to-noise ratios. *In situ* attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy is a reliable method that is capable of tracing the coordination environment and protonation state of most oxyanions at mineral-water interfaces without interference of signals from the liquid phase (Brechbuhl et al., 2012). Although the in individual and competitive coordination structure of phosphate and arsenate on ferrihydrite, geothite and hematite has been previously investigated using ATR-FTIR, the analysis of the relatively broad vibrational bands led to inconclusive interpretation (Gao et al., 2013). Recently,

two-dimensional correlation spectroscopy (2D-COS) has been successfully applied in ATR-FTIR analysis by resolving overlapped peaks and enhancing the spectral resolution (Yan et al., 2016). Despite the advances achieved using ATR-FTIR in the understanding of the adsorption mechanism and geometries of phosphate and arsenate complexes, it is still unclear what are the factors that drive their competition under complex and realistic conditions. This uncertainty may be resolved by employing periodic density functional theory (DFT) calculations and comparing the simulated geometries, vibrational modes, and/or relative adsorption energies to experimental results, which will provide a better understanding from a thermodynamic point of view of the competition between arsenate and phosphate (He et al., 2009).

In this study, the competitive adsorption of arsenate and phosphate species on the surface of chromium-doped magnetite was investigated by *in situ* ATR-FTIR spectroscopy and complemented by DFT calculations. An interesting feature of natural magnetite is the substitution of iron by other metals, while maintaining the spinel structure. Cr is the a common impurity element in natural magnetite as trace element (less than 0.1%), minor element (0.1%-1%) and major element (more than 1%), forming solid solution series between magnetite (Fe_3O_4) and chromite ($FeCr_2O_4$) (Dupuis and Beaudoin, 2011). Moreover, the substitution of Cr^{3+} for Fe^{3+} is known to enhance the adsorption capacity of magnetite (Liang et al., 2012), and thus increase the signals and accuracy of *in situ* ATR-FTIR experiments. The competitive adsorption was carried out under different addition subsequences. A discussion and comparison between our results and previous investigations was also conducted and a

comprehensive atomic-level understanding on the adsorption of phosphate and arsenate on magnetite is used to better interpret their geochemical behaviors in the earth surface and their effects on nucleation, growth, and phase transformation of the mineral phases.

MATERIALS AND METHODS

Preparation of Cr-substituted magnetite

Magnetite with Cr substitution was synthesized by the precipitation-oxidation method described in Text A.1. The obtained sample had the spinel structure (Figure. A.1) and X-ray absorption fine structure (XAFS) spectra illustrated that chromium in the valence state of +3 mainly occupies the octahedral sites. The detailed discussion of XAFS results has been presented elsewhere (Liang et al., 2013). The high surface area (112 m^2 g^{-1}) and surface site density (3.6 sites nm^{-2}) of the magnetite particles (Table A.1) increased the likelihood of obtaining good contact and allowed us to probe large quantities of adsorbed species (Liang et al., 2017). During the adsorption, the concentration of leaching Cr and Fe was below the detection limit of the instrument.

In situ ATR-FTIR and 2D-COS analyses

In situ ATR-FTIR analysis of phosphate and arsenate adsorption on magnetite was conducted using a Bruker Vertex 70 FTIR spectrometer equipped with a liquid N_2-cooled MCT detector and a horizontal ATR accessory made of ZnSe crystal. Before the IR analysis, the magnetite particle layer was prepared on the ZnSe crystal.

1 mL of magnetite suspension (5 g L^{-1}) was dropped onto the crystal surface and dried overnight at room temperature. The film was then rinsed with deionized (DI) water to remove the loosely deposited particles, which stabilized the deposited layer (Hug, 1997). At the end of adsorption experiment, the magnetite film was inspected for signs of film erosion, which were not observed.

Before adsorption, a NaCl background electrolyte solution (0.01 mol L^{-1}) at the designated pH was flowed through the cell with magnetite deposition layer at a rate of 1 mL min^{-1} until no further change in spectra was seen. A background spectrum comprising the absorbance of the ZnSe crystal and the deposited adsorbent was then collected, followed by the injection of solutions containing 100 μmol L^{-1} of arsenate or phosphate, and 0.01 mol L^{-1} of NaCl to start the adsorption reaction. IR spectra were recorded as a function of time until the adsorption reached equilibrium without any signal variation. NaCl was selected as the background electrolyte, because it was inert or non-adsorbed on solid surfaces. All liquid samples were purged with N_2 during spectrum collection. The pH was adjusted within the range of 4.0–9.0 using NaOH (0.1 mol L^{-1}) and HCl (0.1 mol L^{-1}). Desorption experiments were conducted by introducing NaCl solution (0.01 mol L^{-1}) into the ZnSe cell when the adsorption of oxyanions reached equilibrium. The comparative adsorption was carried out through the reversible substitution of arsenate solution (100 μmol L^{-1} at pH 4.0 and 7.0, and 500μmol L^{-1} at pH 9.0) with phosphate solution of the same concentration. It is necessary to emphasize that the arsenate concentrations used in this study, i.e., 100 and 500 ppm are at the low end of the range of concentrations examined in past

233 experimental studies (molecular-scale studies: 5 to 10000 μmol L^{-1}, macroscopic
234 studies: 0.7 to 30000 μmol L^{-1}), as indicated by Catalano, et al. (Catalano et al., 2008).
235 The IR spectra were processed and analyzed with the OPUS software. Curve-fitting
236 analysis of the peaks was conducted using the Gaussian line shape. To obtain an
237 accurate assignment of the IR peaks for the surface complexes, the spectra were
238 analyzed using the 2D-COS technique (Text A.2).
239
240 **Computational methods**
241 To simulate the interaction between the Fe_3O_4(001) surface and phosphate/arsenate
242 oxyanions in aqueous solution, the periodic plane-wave density functional theory
243 (DFT) method within the Vienna *ab-initio* simulation package (VASP) was employed
244 (Kresse and Furthmuller, 1996a; Kresse and Furthmuller, 1996b; Kresse and Hafner,
245 1993; Kresse and Hafner, 1994). The Perdew, Burke and Ernzerhof (PBE) semi-local
246 functional approximation was used to calculate the exchange-correlation energy
247 (Perdew et al., 1996; Perdew et al., 1997). The projector augmented wave (PAW)
248 method was used to model the atomic frozen core states and their interaction with the
249 valence levels (Fe: 4*d*5*s*, O: 2*s*2*p*, H: 1*s*, P: 3*s*3*p* and As: 4*s*4*p*) (Blochl, 1994; Kresse
250 and Joubert, 1999). The expansion of the Kohn-Sham (KS) valence states was
251 calculated with a kinetic energy cut-off of 400 eV. We have tested larger cut-off values,
252 but these led to negligible energy differences with respect to a reference, such as the
253 adsorption energies reported in our previous studies (Santos-Carballal et al., 2018;
254 Santos-Carballal et al., 2014). The electronic partial occupancies were determined

during geometry optimizations using the Gaussian smearing method with the width set at 0.02 eV (Mermin, 1965). Furthermore, the tetrahedron method with Blöchl corrections was used in static simulations to obtain accurate total energies as well as all the electronic and magnetic properties. Long-range dispersion interactions were modeled using the D2 semi-empirical method of Grimme (Grimme, 2006). The optimization of the structures was conducted *via* the conjugate-gradients method, which stopped when the forces on all atoms were smaller than 0.01 $eV \cdot Å^{-1}$. The Dudarev *et al.* (Dudarev et al., 1998) approach was used within the DFT+*U* methodology (Anisimov et al., 1992) to improve the description of the localized and strongly correlated Fe *d* states, which were corrected by applying the value of U_{eff} = 3.7 eV (Santos-Carballal et al., 2018; Santos-Carballal et al., 2014). All calculations were spin-polarised and the initial magnetic moments were set following a high-spin ferrimagnetic structure, *i.e.* with opposite spins in the tetrahedral and octahedral sites (Neel, 1948; Shull et al., 1951). These criteria allowed convergence of the total electronic energy within 10^{-4} eV per atom. We decided to only model the magnetite (001) surface as this is the thermodynamically most stable facet, with the lowest relaxed surface energy and the most prominent plane in the calculated crystal morphology (Santos-Carballal et al., 2014), which is in agreement with the observations made by Zhao *et al.* at pH ≤ 13 (Zhao et al., 2008). Moreover, Jönsson and Sherman found that the bidentate interaction of the inner-sphere As(V) complexes is only possible at the rows of exposed Fe_B ions formed in the [011] direction of the magnetite (001) surface (Jonsson and Sherman, 2008), which is in line with its largest

density of exposed Fe cations (Santos-Carballal et al., 2014). However, similar to goethite, we cannot rule out that that arsenate and phosphate may have different affinities for other less stable and less prominent magnetite surfaces, which may saturate with a small fraction of the total number of adsorbed oxyanions (Kubicki et al., 2012), thus providing a minor contribution to the observed infrared spectra. For the inner-sphere complexes, the adsorption of the phosphate and arsenate species on the $Fe_3O_4(001)$ surface was simulated under both acid and alkaline conditions. Different initial binding geometries, including MM, BM, BB and tridentate trinuclear (TT), were taken into account. All possible binding sites were also inspected, including the protruding Fe_A atom and the Fe_B ion as well as their possible combinations. Thus, we are confident that we have considered all possible adsorption geometries for the oxyanion complexes. However, given the large positional degree of freedom of the water molecules, there may be some uncertainty in their location, but this lies beyond the scope of this work. Further details of the computational methods used, including surface models, inner- and outer-sphere complex models, approach used for the simulation of acid and alkaline conditions, calculation of adsorption energy, Bader charges and vibrational frequencies are presented in Text A.3 and Figure A.2.

296 # RESULTS AND DISCUSSION

297 ## Individual molecular adsorption

298 Arsenate adsorption on magnetite

299 The intensity of characteristic bands obtained by *in situ* ATR-FTIR was
300 proportional to the level of adsorption; as pH decreased, the arsenate adsorption was
301 obviously enhanced (Figure A.3). Given the point of zero charge (PZC) of magnetite
302 at 6.8 (Table A.1), the surface of this mineral gradually changed from negative charge
303 at alkaline pH to positive charge under acid conditions, improving the adsorption of
304 arsenate oxyanions. Besides band intensity, the spectrum profile also showed
305 significant changes with pH. At high pH, the spectra displayed a broad but
306 asymmetrical band at 855 cm^{-1}, with a shoulder peak at 820 cm^{-1}. As the pH decreases,
307 the band at 855 cm^{-1} became more symmetrical and sharpened, which was also
308 characteristic of aqueous $HAsO_4^{2-}$ (Figure. A.4). Thus, outer-sphere (OS) $HAsO_4^{2-}$
309 complexes were formed on magnetite at acidic pH, which was verified in desorption
310 experiments at pH = 4.0 (Figure. A.5). Once the arsenate solution was replaced by
311 NaCl solution, the intensity of the band at 855 cm^{-1} quickly decreased in 10 min, and
312 then slowly declined in the following 140 min, suggesting the coexistence of both OS
313 and inner-sphere (IS) arsenate complexes, as OS species have faster desorption rates
314 than IS species (Catalano et al., 2008). According to previous work, neither As(III)
315 oxidation nor As(V) reduction occurs on the magnetite surface (Jonsson and Sherman,
316 2008).

317 According to the 2D-COS analysis results (Text A.5), the band at 855 cm^{-1} and those

318 at 870, 830 and 805 cm^{-1} are attributed to different adsorption complexes of arsenate.
319 The band at 855 cm^{-1} was identical to that of aqueous $HAsO_4^{2-}$ (Figure A.4),
320 supporting the formation of these OS complexes. The contribution at 870 cm^{-1} was
321 assigned to the asymmetric stretching (ν_3) of As-O, while those at 830 and 805 cm^{-1}
322 were assigned to the asymmetric and symmetric stretchings (ν_3) of As-OFe,
323 respectively (Brechbuhl et al., 2012; Hu et al., 2015). The presence of three ν_3 bands
324 indicated the C_{2v} or lower symmetry for the IS arsenate complexes. The above
325 characteristic bands are consistent with the observations of arsenate adsorption on
326 ferrihydrite, hematite and rutile (Brechbuhl et al., 2012; Hu et al., 2015). Gao et al.
327 attributed the IR bands at 830 and 804 cm^{-1} to the arsenate adsorbed in the BB
328 geometry on the ferrihydrite surfaces at high pH (Gao et al., 2013). The BB
329 complexes are also the dominant geometry of arsenate adsorbed on most iron
330 (hydr)oxides, as verified by EXAFS (Jonsson and Sherman, 2008; Sherman and
331 Randall, 2003). Thus, in this study, the IS arsenate complexes on magnetite were also
332 assigned to the BB geometry.
333 The ATR-FTIR spectra were deconvoluted to gain additional insight into the arsenate
334 adsorption geometries (Figure. 1a). The relative amounts of adsorbed OS and IS
335 species and their contributions to the total adsorption (based on the sub-spectral area)
336 varied with pH (Figure. 2a). At pH > 7, almost no OS complexes were formed,
337 ascribed to the electrostatic repulsive force between the arsenate oxyanions and the
338 negatively charged magnetite surface. The IS complexes with BB geometry are the
339 main species at high pH (Eq. (1)). As the pH decreased, the magnetite surface became

positively charged, leading to the rapid increase in both the adsorption and contribution of OS complexes (Eq. (2)). Once the OS complexes were formed, the Coulombic attraction between the magnetite surface and arsenate oxyanions further improved the formation of IS complexes with BB geometry by ligand exchange. These findings explain why the IS species dominate over the OS complexes throughout the studied pH range.

$$2{\equiv}FeOH + HAsO_4^{2-} \rightarrow ({\equiv}FeO)_2(AsO)OH + 2OH^- \quad (1)$$

$${\equiv}FeOH_2^+ + H_2AsO_4^- \rightarrow {\equiv}FeOH_2^{+}\cdots HAsO_4^{2-} + H^+ \quad (2)$$

Phosphate adsorption on magnetite

The adsorption of phosphate on magnetite was also affected by pH (Figure. A.7). When pH decreased from 9.0 to 4.0, the IR spectra increased in intensity, and displayed variations in shape. Specifically, a blue-shift of the highest peak from 1028 (pH = 9.0) to 1050 cm^{-1} (pH = 4.0) was seen, alongside the appearance of two shoulder peaks at 1000 and 1100 cm^{-1}. The IR spectra of the adsorbed phosphate were clearly different from the aqueous phosphate oxyanions at identical pH (Figure. A.8), suggesting the formation of IS complexes. This is also confirmed in the desorption experiment at pH = 4.0 (Figure. A.9), where the IR intensity only decreased slightly after desorption for 180 min.

Based on the 2D-COS analysis (Text A.5), the IR bands of phosphate at 1075, 1028 and 965 cm^{-1} and those at 1108, 1050, 1000 and 870 cm^{-1} were assigned to different IS complexes of phosphate. Both complexes had three ν_3 vibrations, indicating a C_{2v}

362 symmetry or lower. Through the deconvolution of the spectra (Figure. 1b) and the
363 calculation of its sub-spectral area (Figure. 2b), the contribution of each predominant
364 adsorbed phosphate complex was calculated at acid and alkaline pH (Figure. 2b).
365 Based on the very close IR signals at high pH, a complex with similar coordination
366 environment and protonation degree to 1075, 1028 and 965 cm^{-1} was reported for the
367 adsorption of phosphate onto ferrihydrite (1070, 1025 and 940 cm^{-1}) (Arai and Sparks,
368 2001; Carabante et al., 2010). These complexes were in a non-protonated form, as
369 confirmed through the comparison of spectra obtained in D_2O and H_2O medium (Arai
370 and Sparks, 2001). Considering their C_{2v} or C_1 symmetry and the alkaline pH range of
371 stability, these non-protonated species were affiliated to BB complexes (Eq. (3)) (Arai
372 and Sparks, 2001; Kubicki et al., 2012), which were also reported in the adsorption of
373 phosphate on goethite (1089, 1044 and 945 cm^{-1}) (Kubicki et al., 2012) and hematite
374 (1085, 1035, and 966 cm^{-1}) (Elzinga and Sparks, 2007). The bands at 1075 and 1028
375 cm^{-1} were attributed to the stretching of the PO_2 bond, while the 965 cm^{-1} peak
376 belonged to Fe-O-P bending.

377 $$2{\equiv}FeOH + HPO_4^{2-} \rightarrow (FeO)_2PO_2^- + H_2O{+}OH^- \quad (3)$$

378 The dominant complexes at acid pH were the protonated species. In previous studies,
379 the characterization of their coordination environments and protonation degree were
380 controversial (Arai and Sparks, 2001; Elzinga and Sparks, 2007; Luengo et al., 2006;
381 Tejedortejedor and Anderson, 1990), as the formations of $(XO_3)PO$ and $(XO_2)PO_2$
382 (X=Fe or H) were suggested. Protonated $(XO_3)PO$ species, including monoprotonated
383 BB complexes ($(\equiv FeO)_2(OH)PO$, MBB) and di-protonated MM complexes

384 (≡$FeO(OH)_2PO$, DMM), were reported for the adsorption on ferrihydrite (1124, 1035
385 and 998 cm^{-1}) (Carabante et al., 2010), goethite (1123, 1006 and 982 cm^{-1}) (Luengo et
386 al., 2006; Tejedortejedor and Anderson, 1990), and hematite (1120, 1010 and 970 cm^{-1})
387 (Elzinga and Sparks, 2007). The bands at high frequency (≥ 1120 cm^{-1}) were
388 attributed to the P=O stretching of the $(XO_3)PO$ species (Arai and Sparks, 2001;
389 Elzinga and Sparks, 2007). The adsorption geometry of protonated $(XO_2)PO_2$, i.e.,
390 monoprotonated MM (≡$(FeO)(OH)PO_2$), was identified on ferrihydrite (1100, 1028
391 and 920 cm^{-1}) (Arai and Sparks, 2001) and hematite (1115, 1006 and 970 cm^{-1})
392 (Elzinga and Sparks, 2007). For these complexes, bands at ~1100 and ~1115 cm^{-1}
393 were assigned to the PO_2 group since its frequencies were between $\upsilon_{P=O}$ (1120 cm^{-1})
394 and $\upsilon_{P\text{-}OFe}$ (1000 cm^{-1}) (Tejedortejedor and Anderson, 1990). In the present study, the
395 phosphate complexes (1108, 1050 and 1000 cm^{-1}) that predominated at acid pH were
396 monoprotonated MM complexes (MMM) (Eq. (4)), as the band with the highest
397 frequency (1108 cm^{-1}) was too low to be assigned to the P=O stretching. The bands at
398 1108 and 1050 cm^{-1} were attributed to the stretching of the PO_2 bond, while those at
399 1000 and 870 cm^{-1} belonged to the Fe-O-P and P-OH bending, respectively. The
400 formation of the $FeOPO_3$ (C_{3v}) complexes were excluded, as they have a molecular
401 symmetry higher than the lowest C_{2v} allowed.

402 $$\equiv FeOH + H_2PO_4^- \rightarrow \equiv FeO(PO_2)OH^- + H_2O \quad (4)$$

403

Competitive molecular adsorption

Substitution of phosphate by arsenate

At pH = 4, the MMM complexes are the dominant phosphate species followed by the NBB complexes (Figure. 2b). When the phosphate solution was substituted by an arsenate solution of equal molar concentration, the bands of phosphate (1200–870 cm^{-1}) immediately decreased in intensity, suggesting their desorption from the magnetite surface (upper panel of Figure. 3a). Simultaneously, the bands assigned to the adsorbed arsenate in the region of 900–800 cm^{-1} appeared and their intensity increased with the adsorption time. This became more obvious upon subtracting the equilibrium spectrum for the adsorbed arsenate recorded at 270 min, from the signals recorded at 135 min, i.e., immediately before the introduction of arsenate. This subtraction highlighted only the bands for which intensity decreased (positive bands) or increased (negative bands) (lower panel of Figure. 3a). Based on the spectral integration, 32% of adsorbed phosphate was replaced by arsenate. The proportion of phosphate substituted by arsenate was close to the replacement found in previous studies using ferrihydrite and goethite (O'Reilly et al., 2001). For example, Carabante et al. reported that 35% of phosphate was desorbed from the ferrihydrite surface by arsenate using D_2O as solvent at pD = 4 (Carabante et al., 2010), while Liu et al. and Neupane et al. found that between 26%-28% of the absorbed phosphate on goethite and ferrihydrite surfaces was replaced by arsenate (Liu et al., 2001; Neupane et al., 2014). In order to determine the coordination environments, the positive bands in the range 1200-870 cm^{-1} were deconvoluted into three contributions at 1108, 1050 and

426 1000 cm^{-1}, which were assigned to MMM phosphate complexes. Moreover, the
427 negative bands at 870, 827 and 801 cm^{-1} were attributed to arsenate BB complexes
428 (Figure. 3a).
429 Similar competitive experiments were also conducted under neutral (pH = 7, Figure.
430 3b) and alkaline conditions (pH = 9, Figure. 3c), where partial substitution of
431 phosphate by arsenate was also observed. At pH = 7.0, the amount of phosphate
432 adsorbed as MMM and NBB complexes were comparable (Figure. 2b). However, the
433 integral spectrum of the NBB complexes (1075, 1026 and 960 cm^{-1}) was much lower
434 than for the MMM complexes (1100, 1050, 1000cm^{-1}, Figure. 3b). The differences
435 between the integrals of these bands indicates that the desorption of the MMM
436 complexes was more significant than for the NBB, which was also found in the
437 desorption of phosphate from ferrihydrite (Carabante et al., 2010).
438 To enhance the IR signal of the IS species at alkaline pH (Figure. 2), the
439 concentrations of both phosphate and arsenate were increased from 100 μmol L^{-1} to
440 500 μmol L^{-1} (Figure. 3c). The desorption of phosphate (~15%) was lower under
441 alkaline conditions than at acid pH (~32%) (Figure. 3a), where the removal of both
442 MMM and NBB complexes was comparable. Based on the integral area of the
443 difference spectrum, the proportion of desorbed NBB complexes was below 15% of
444 the total adsorbed phosphate. Moreover, the NBB complexes required 350 min to
445 achieve desorption equilibrium, which was much slower than the removal of MMM at
446 acid and neutral pH (135 min).
447

448 Substitution of arsenate by phosphate

449 At pH = 4, the adsorbed arsenate was mainly forming BB complexes, with a low
450 proportion of OS species (Figure. 2a). After the introduction of phosphate solution of
451 equal molar concentration, the bands in the region of 1200–900 cm^{-1} corresponding to
452 phosphate appeared immediately and increased in intensity with time (Figure. 4a),
453 illustrating adsorption on magnetite surfaces. However, the IR intensity of arsenate
454 initially decreased slightly (~10%), but then stabilized, which suggests that the
455 phosphate oxyanions can only substitute partially the pre-adsorbed arsenate. After
456 subtracting the spectrum recorded just before the addition of phosphate and after its
457 adsorption had reached equilibrium, at 135 min and 270 min, respectively, the
458 positive bands related to adsorbed phosphate were located at 1108, 1050 and 1000
459 cm^{-1}. As mentioned above, these bands were associated with the MMM phosphate
460 complexes prevalent at acid pH. The negative bands that appeared at 852 and 798
461 cm^{-1} were attributed to the As-O asymmetrical stretching (υ_3) and the As-OH vibration
462 of the arsenate OS species (Hu et al., 2015).

463 Similarly to the competitive adsorption at pH = 4, phosphate could not substitute the
464 pre-adsorbed arsenate at neutral pH (Figure. 4b). The introduction of phosphate did
465 not lead to a decrease in the IR intensity of arsenate. Although the individually
466 absorbed phosphate species in neutral conditions were in equal proportions in both
467 MMM and NBB geometries (Figure. 2b), only the former configuration was stable
468 upon introduction of arsenate, as indicated by the phosphate bands at 1106, 1049, 994
469 and 896 cm^{-1}. Meanwhile, the difference spectrum did not show evidence of signals

from the desorbed arsenate, which confirms that the arsenate BB complexes are the dominant adsorption configuration, with a higher binding affinity than both the MMM and NBB phosphate complexes.

At alkaline pH, the amount of arsenate that adsorbed onto magnetite was low, resulting in a poor signal-to-noise ratio for the spectra. Thus, competitive adsorption under alkaline conditions was not analyzed in this study.

DFT calculations

Outer-sphere complexes

The outer-sphere (OS) complexes comprising the solute surrounded by water molecules are displayed in Figure. A.11. P-based anions are consistently smaller than their As-containing counterparts, as the intramolecular mean distance from the central atom to the oxygen ions differs by ~0.17 Å (Table 1). The degree of protonation of the solute does not noticeably affect the single and double bond distances (Table 1). As expected, the Bader charges of the solute ions are underestimated by ~17% with respect to their formal charges, which increases to ~23% with the pH value (Table 2). For the outer-sphere complexes under alkaline conditions, a charge of approximately -0.66 e^- was calculated for the OH groups (Table 2), which prefer to coordinate the protruding Fe_A ion at 1.92 and 1.95 Å for $HAsO_4^{2-}$ and HPO_4^{2-}, respectively (Figure. A.11).

Figure A.11 displays the radial distribution functions for $H_2PO_4^-$, HPO_4^{2-}, $H_2AsO_4^-$, and $HAsO_4^{2-}$, where the radii are measured from the central atom of the P or As solute

492 to the O of the water molecules. The main hydration shells for these oxyanions lie
493 between 3.5 and 6.0 Å, which is in excellent agreement with the molecular dynamics
494 (MD) simulations of Pathak and Bandyopadhyay (2016) for AsO_4^{3-} and supports the
495 suitability of the size of our water simulation box (Pathak and Bandyopadhyay, 2016).
496 Under acid conditions, the di-protonated arsenate ($H_2AsO_4^-$) and phosphate ($H_2PO_4^-$)
497 ions are the dominant species with C_{2v} symmetry and 15 fundamental vibrational
498 modes. Alkaline pH values lead to the deprotonation of the outer-sphere complexes,
499 thus increasing their symmetry to the C_{3v} molecular point group, with a reduction to 3
500 singly degenerate vibrations for the H atom. Generally, most of the fundamental
501 vibrational modes for As-containing anions are red-shifted with respect to their
502 phosphate counterparts, in excellent agreement with the ATR-FTIR experiments
503 (Table 3). The only exceptions are the stretching ν(PO−H) and bending δ(POH) mode
504 for HPO_4^{2-} and $H_2PO_4^-$, respectively, which appear at higher wavenumbers than for
505 the iso-structural As-based molecules. However, taking into account that the bending
506 δ(POH) is 1245 cm^{-1} for $H_2PO_4^-$ at acid pH (Table 3), which compares closely with
507 the experimental value of 1240 cm^{-1} (Figure. A.8), we are confident of the predictive
508 accuracy and consistency of our approximate vibrational modes. More details about
509 the DFT results of outer-sphere complexes are described in Text. A.4.
510
511 Arsenate adsorption on the Fe_3O_4(001) surface
512 The dissociative adsorption process of the $H_2AsO_4^-$ solute onto the Fe_3O_4 (001)
513 surface at acid pH can be represented as Eq. (5):

514 $$Fe_{24}O_{32}(001)(s) + H_2AsO_4(aq) = Fe_{24}O_{31}(001).OH.HAsO_4(s). \quad (5)$$

515 $HAsO_4^{2-}$ in the BB configuration is the most thermodynamically stable inner-sphere
516 complex calculated for arsenate (Figure. 5a), with the largest adsorption energy of
517 -2.19 eV per molecule (Table 2). The surface Fe_B ions coordinate the adsorbate O
518 atoms at 2.06 Å, which reduces their electronic density and induces an elongation of
519 the As=O bond distances by 0.03 Å with respect to the outer-sphere complexes. The
520 O−As=O and particularly the O=As=O bond angles become narrower after adsorption,
521 but the latter still remains wider than the former (Table 1). The dissociated proton
522 binds a neighboring surface O atom at 1.02 Å, which is a slightly larger bond distance
523 than in any of the other discussed solutes. The computed As-O bond length and As-Fe
524 distance of the BB arsenate complex are ca. 1.71 and 3.20 Å, respectively, which is
525 consistent with the values (1.69 and 3.42 Å) obtained from EXAFS analysis (Jonsson
526 and Sherman, 2008).
527 The acid proton has a typical charge of 0.67 e^-, while the inner-sphere complexes gain
528 0.60 e^- compared to the di-protonated molecule in solution. Consistent with the
529 presence of two types of H atoms, *i.e.,* in the inner-sphere complexes and directly
530 attached to the surface, six singly degenerate vibrational modes associated with these
531 atoms are found (Table 3). The stretching ν(AsO−H) and bending δ(AsOH) in the
532 adsorbed molecule are red-shifted with regard to the outer-sphere complexes, in line
533 with their different chemical environments. The stretching modes involving the
534 central As atom have the typical pattern of BB complexes. For instance, the largest
535 wavenumber of 816 cm^{-1} is assigned to the As=O bond, whereas the intermediate

vibrations between 751 and 786 cm^{-1} are calculated for the symmetric and asymmetric ν(As−OFe). In agreement with its largest distance, the softer mode is computed for the single bond between the central atom and the protonated oxygen.

Unlike the outer-sphere $H_2AsO_4^-$ complexes, which adsorb dissociatively in acid environment, the $HAsO_4^{2-}$ anion does not change its stoichiometry after binding to the Fe_3O_4(001) surface at alkaline pH (Eq. (6)):

$$Fe_{24}O_{32}(001).OH(s) + HAsO_4(aq) = Fe_{24}O_{32}(001).OH.HAsO_4(s). \quad (6)$$

The mono-protonated adsorbed As-containing molecule interacts with two Fe_B surface ions, forming a bidentate (BB) configuration that resembles the inner-sphere complexes of arsenate at acid pH (Figure. 5b).

However, the presence of an adsorbed OH^- group rather than H^+ causes noticeable energetic and structural changes in the adsorbate. The adsorption energy increases by 1.35 eV per $HAsO_4^{2-}$ molecule when the pH changes from acid to alkaline, becoming comparable to the experimental value reported by Sabur and coworkers for arsenate at neutral pH conditions (Sabur et al., 2015). The Fe_B−O bonds between the molecule and surface are 0.07 Å shorter at high than at low pH. The bond distance from the central As atom to the hydroxy group is stretched from 1.76 to 1.86 Å following the increase in pH. After adsorption, the adsorbed OH group moves 0.08 Å away from the surface and leans towards a nearby surface O atom to form a hydrogen bond. Table 1 shows that the relative order ∠(O−As=O) < ∠(O=As=O) is restored for the bond angles upon the formation of the inner-sphere complexes. Despite the same stoichiometry, the Bader charge analysis reveals that the adsorbate loses 0.14 e^- after

558 adsorption, but the charge of the OH^- remains almost unaffected at -0.68 e^-.

559 Owing to the similar adsorption configuration for $HAsO_4^{2-}$ at both acid and alkaline
560 pH, the number and type of fundamental vibrational modes in these two conditions
561 are the same. However, all vibrations shift for $HAsO_4^{2-}$ as a result of the change in pH
562 (Table 3). For example, the wavenumber for ν(As−OH) increases greatly to 3007 cm^{-1},
563 whereas ω(AsOH) is red-shifted to 830 cm^{-1}. The increase in pH has a strong impact
564 on the stretching mode of the elongated As−OH bond of the surface-immobilized
565 $HAsO_4^{2-}$species. Moreover, the formation of the inner-sphere arsenate complexes and
566 FeOH···H hydrogen bond have a major effect on the ν(FeO−H) and ω(FeOH) modes.
567 Our DFT predicted vibrational frequencies for the hardest modes ν(As=O) and
568 ν(As=OFe) of the inner-sphere $HAsO_4^{2-}$ complex under both acid and alkaline
569 conditions are under-estimated by ~60 cm^{-1} with respect to the experimental values.
570 However, the deviation between the ATR-FTIR spectra and the simulated frequency is
571 90 and 190 cm^{-1} under acid and alkaline conditions, respectively, for the softer mode
572 ν(As−OH).

573

574 Phosphate adsorption on the Fe_3O_4(001) surface

575 Among the various possible binding geometries of phosphate onto magnetite, the
576 mono-protonated monodentate mononuclear (MMM) mode is the most stable
577 adsorption configuration at acid pH, wherein the HPO_4^{2-} anion binds the Fe_B surface
578 cation and releases 1.89 eV per molecule (Table 2 and Figure. 6a). The dissociative
579 adsorption of $H_2PO_4^-$ on the Fe_3O_4(001) surface at acid conditions can be represented

by Eq. (7):

$$Fe_{24}O_{32}(001)(s) + H_2PO_4(aq) = Fe_{24}O_{31}(001)OH.HPO_4(s) \quad (7)$$

As shown in Figure. 6a, the dissociated proton prefers to interact at 0.98 Å with a nearby surface oxygen atom to form acid $Fe_{24}O_{31}(001)$.OH groups rather than H_3O^+ cations in solution. The strong chemisorption is characterized by the adsorbate-surface PO−Fe_B interatomic bond distance of 2.08 Å, which is only 0.02 Å larger than the O−Fe_B distance in the bulk of Fe_3O_4 (Table 1). The average P=O distances for the outer- and inner-sphere P-containing complexes are very close at acid pH. Compared to $H_2PO_4^-$ in solution, the P−O bond stretches, whereas the PO−H bond distance decreases by approximately 0.05 Å for the adsorbed HPO_4^{2-}. The O−P=O bond angle experiences the largest change, from 109.06° to 105.01°, given that the adsorbate loses half of its single bonded O atoms during the dissociative adsorption of $H_2PO_4^-$. The charge of the dissociated H is 0.65 e^-, while the adsorbed anion becomes 0.66 e^- more negative than its parent ion in solution (Table 2).

Dissociative adsorption of $H_2PO_4^-$ in the MMM configuration causes its molecular point group to reduce to C_s and to 12 the total number of fundamental vibrational modes. After binding to the surface, the POH wagging is not detected above 600 cm^{-1}, while the PO−H stretching is shifted to 3625 cm^{-1} and the POH bending is red-shifted by approximately 200 cm^{-1} (Table 3). In line with the new symmetry, the two largest stretching modes are assigned to $P=O_2$, whereas 942 cm^{-1} corresponds to P−OFe and the lowest wavenumber is calculated for the protonated O atom. For the dissociated proton, the FeO−H stretching as well as the FeOH bending and wagging were

602 obtained at the usual position for OH groups. The calculated vibrational frequencies
603 were also underestimated for the inner-sphere phosphate complexes in acid conditions,
604 with the largest discrepancy observed for the modes with the smallest wavenumber.
605 For example, the simulated values for the hardest *v*(P=O) modes were just 5 and
606 20cm^{-1} below the experimental frequencies; while the difference for the softer (softest)
607 *v*(P=OFe) [*v*(P−OH)] mode was 60 (104) cm^{-1}.
608 Under alkaline conditions, HPO_4^{2-} prefers to adsorb dissociatively onto the Fe_3O_4(001)
609 surface, forming the non-protonated bidentate binuclear (NBB) inner-sphere complex
610 and liquid water as follows:

611 $$Fe_{24}O_{32}(001).OH(s) + HPO_4(aq) = Fe_{24}O_{32}(001).PO_4(s) + H_2O(l). \quad (8)$$

612 This process releases 0.69 eV per molecule, which is the weakest adsorption energy
613 reported in this study (Table 2). Two O atoms from the anion coordinate the surface
614 Fe_A and Fe_B ions at 1.91 and 1.95 Å, respectively (Table 1 and Figure. 6b). A small
615 stretch in the P=O bond from the average value of 1.56 Å is also observed in those
616 atoms directly interacting with the surface, whereas the bond angles remain perfectly
617 tetrahedral at 109.44°. The Bader charge for the inner-sphere PO_4^{3-} complex is −2.13
618 e^-, which is the largest reported in this paper. The charge of the fully deprotonated
619 phosphate ion explains its small adsorption energy, caused by the strong Coulombic
620 repulsion at the negatively charged Fe_3O_4(001) surface. The PZC of magnetite at 6.8
621 suggests that at alkaline pH, the Fe_3O_4 surfaces become negative due to adsorbed OH^-
622 groups.
623 Despite its C_s point group, the adsorbed NBB PO_4^{3-} species has the simplest set of

624 vibrational frequencies with only 4 measurable fundamental modes (Table 3). The
625 largest frequencies are for the asymmetric and symmetric P=O modes, at 1111.64 and
626 948.85 cm^{-1}, respectively. The longest and weakest P−OFe bonds are characterized by
627 the smallest frequencies, which were calculated at 909 and 884 cm^{-1} for the
628 asymmetric and symmetric modes, respectively.
629 Although phosphate OS complexes are smaller than their arsenate counterparts (Table
630 1), the three solvation shells found are formed roughly at the same distance from the
631 central atom for the two different oxyanions, which essentially remain tetrahedral.
632 However, when the phosphate and arsenate molecules approach the Fe_3O_4(001)
633 surface, they form IS complexes of different geometries and number of interactions
634 with the exposed Fe ions. The adsorption energies show that under both acid and
635 alkaline conditions arsenate prefers to form MBB complexes with two neighboring
636 Fe_B ions from the Fe_3O_4(001) surface. However, phosphate forms an NBB complex
637 with the exposed Fe_A and Fe_B ions at alkaline pH, while HPO_3^{2-} coordinates a single
638 Fe_B ion as an MMM species under acid conditions (Figures. 6 and 7). On
639 thermodynamic grounds, arsenate species bind more strongly to the Fe_3O_4(001)
640 surface than the phosphate complexes under acid and alkaline conditions (Table 2),
641 which explains the stronger adsorption affinity of arsenate over phosphate. The
642 oxyanions release the largest adsorption energies under acid conditions and the
643 calculated Bader charges explain the trends found for the adsorption energies.
644 Adsorption reduces the molecular point group of the oxyanions, which impacts the
645 frequency of the four stretching modes involving the central atom and the oxygen

atoms (Table 3). The shift of the vibrational modes for the adsorbed oxyanions with respect to the OS complexes offers an unambiguous route to characterize the geometry and coordination number of the IS species.

Effect of pH on individual and comparative adsorption

During individual molecular adsorption of equal amounts of arsenate and phosphate, their adsorption edges have very similar curve profiles, in agreement with previous works (Arai and Sparks, 2001; Jia et al., 2007; Luengo et al., 2006). In this study, the arsenate and phosphate adsorption increased gradually on magnetite as the pH decreased (Figures. A.3 and A.6), ascribed to the positive charge of the mineral surface. Such variations have also been observed in the individual adsorption of arsenate and phosphate onto goethite, which is the most studied mineral adsorbent (Hingston et al., 1971; Liu et al., 2001; Manning and Goldberg, 1996). As reported by Liu et al., the surface coverage of phosphate and arsenate on goethite was 112 and 109 mol kg^{-1} at pH = 8, respectively, which values increased to 193 and 197 mol kg^{-1} at pH = 3. Although the individual arsenate and phosphate adsorption showed similar dependence on the pH, the binding efficiency was greatly affected by pH during competitive adsorption. In this study, when pre-adsorbed on magnetite, 32% of phosphate was desorbed in the presence of arsenate at pH = 4 (Figure. 5), while only 15% was desorbed at pH = 9 (Figure. 7). The phosphate adsorption strength increased with pH, which was also observed during adsorption onto goethite and ferrihydrite. Liu et al. found that, in the presence of arsenate, the efficiency of phosphate

668 adsorption on goethite increased from 50% (pH = 3) to 70% (pH = 8) and was not
669 significantly influenced at alkaline pH, i.e., 69% (pH = 7), 70% (pH = 8) and 72%
670 (pH = 9) (Liu et al., 2001). In order to evaluate the ability of phosphate (or arsenate)
671 to depress the adsorption of arsenate (or phosphate) during competitive adsorption,
672 the competition efficiency (%) of phosphate η_P was calculated as $\eta_P = 100$
673 $\times(1-N_{arsenate}/N^o_{arsenate})$, where $N_{arsenate}$ was the amount of arsenate adsorbed in the
674 presence of phosphate and $N^o_{arsenate}$ was the amount of arsenate individually adsorbed
675 (Liu et al., 2001). The obtained results show that, independently of pH, the
676 competition efficiency of arsenate over phosphate ranged from 70 to 74%. In contrast,
677 phosphate was more stable under alkaline than acid conditions.
678 The pH effect on the competitive adsorption efficiency between phosphate and
679 arsenate has been observed in previous studies. For example, in soils, the inhibitory
680 effect of phosphate toward arsenate adsorption is stronger than the other way round
681 when the pH is higher than 6 (Melamed et al., 1995; Peryea, 1991). Gao and Mucci
682 reported that the phosphate introduction obviously restrained the arsenate adsorption
683 on goethite at alkaline pH. The arsenate addition, even in excess, led to only slight
684 decrease in the amount of phosphate adsorbed (Gao and Mucci, 2001). These findings
685 are different from ours, where the individual arsenate and phosphate adsorptions were
686 found to be comparable at alkaline pH. However, the affinity towards goethite is
687 stronger for arsenate than for phosphate at acid pH (Carabante et al., 2009; Violante
688 and Pigna, 2002; Zhao and Stanforth, 2001), which becomes comparable under
689 neutral conditions (Manning and Goldberg, 1996). Therefore, pH plays a vital role in

690 the competitive adsorption between arsenate and phosphate.

691

692 Effect of adsorption sequence on individual and comparative adsorption

693 The simultaneous or successive addition of oxyanions is important in the context of
694 competitive adsorption (Carabante et al., 2010; Liu et al., 2001). In nature,
695 environmental substances are more commonly adsorbed onto minerals sequentially
696 than simultaneously. When pre-adsorbed arsenate was replaced by phosphate on
697 goethite, the competition efficiency of arsenate and phosphate remained constant at
698 70–74% and 20%, respectively, independent of pH (Liu et al., 2001). However,
699 substitution of pre-adsorbed phosphate by arsenate led to an increase of the
700 competition efficiency of phosphate from 50% (acid pH) to 65% (alkaline pH), while
701 arsenate decreased from 30% (acid pH) to 10% (neutral pH). For the simultaneous
702 addition of the adsorbates, the efficiency of arsenate and phosphate was 50% and 40%,
703 respectively. Although the competitive adsorption experiment was carried out using
704 different adsorption sequences, arsenate was always adsorbed more strongly than
705 phosphate, indicating that arsenate has the highest affinity towards the goethite
706 surfaces. This was also found during the competitive arsenate and phosphate
707 adsorption onto magnetite and ferrihydrite (Carabante et al., 2010). For example, as
708 reported in this study, the amount of phosphate adsorbed decreased by 32% after the
709 introduction of arsenate at equal concentration under acid conditions. Conversely, the
710 subsequent addition of phosphate only resulted in about 10% arsenate desorption.
711 This is consistent with the results from the DFT calculations, where it was found that

712 arsenate has stronger adsorption affinity to magnetite than phosphate.

713

714 Effect of mineral species on individual and comparative adsorption

715 Diverse competitive adsorption trends appear for phosphate and arsenate during
716 interaction with different mineral phases in soils. In general, the competitive ability
717 towards iron (hydr)oxides is stronger for arsenate than for phosphate. As mentioned
718 above, during the adsorption on ferrihydrite and goethite, the restraining effect of
719 arsenate on phosphate is obviously the strongest. A similar phenomenon is also seen
720 in this study, where arsenate has higher affinity for and stability on magnetite than
721 phosphate. However, the opposite was found when aluminum (hydr)oxides were the
722 mineral phases. Manning et al. investigated competitive adsorption of arsenate and
723 phosphate on goethite and gibbsite (Manning and Goldberg, 1996). On both mineral
724 phases, phosphate induced the desorption of *ca.* 15mmol kg^{-1} of arsenate. However,
725 the arsenate addition only decreased the phosphate adsorption by 8mmol kg^{-1} on
726 gibbsite, which indicates a preference for phosphate rather than arsenate. ~~The~~
727 Arsenate and phosphate also display similar competitive adsorption on calcite ~~and~~
728 ~~aluminum (hydr)oxides~~. The arsenate adsorption is significantly inhibited by
729 phosphate, while the phosphate adsorption is barely affected by arsenate (So et al.,
730 2012).

731 In addition to the chemical formula of the mineral phases, the competitive adsorption
732 properties of arsenate and phosphate are also affected by the crystallinity of the
733 material. Xu et al. studied the effect of arsenate addition on the phosphate desorption

734 kinetics from crystalline and amorphous hydrargillite (Xu et al., 2008). Phosphate was
735 easily replaced by arsenate, which had the largest affinity for amorphous rather than
736 for crystalline hydrargillite, because of difference in the density of surface active sites.
737
738 Competitive adsorption mechanism
739 Despite the similar individual adsorption behavior, the mechanism for the competitive
740 adsorption between arsenate and phosphate onto the iron (hydr)oxide surfaces is still a
741 topic of debate. Phosphate with its smaller thermochemical radius is expected to have
742 the strongest affinity for these mineral phases, yet arsenate displays the strongest
743 preference, especially at acid pH.
744 During arsenate and phosphate adsorption onto iron (hydr)oxides, these oxyanions
745 adopt diverse geometries with different binding strengths. For example, phosphate
746 adsorbed on ferrihydrite displays two adsorption geometries, i.e., protonated BB and
747 non-protonated BB, as observed by *in situ* ATR-FTIR (Carabante et al., 2010).
748 Arsenate is mainly adsorbed in the BM and BB geometries, as determined by *in situ*
749 ATR-FTIR and XAFS (Carabante et al., 2010; Neupane et al., 2014). However, these
750 adsorption complexes display different affinities towards mineral surfaces. For
751 example, phosphate induces the desorption of the BM arsenate complexes, while the
752 BB arsenate complexes are less affected (Neupane et al., 2014), which indicates that
753 the stability is higher for the BB than for the BM arsenate species.
754 In this study, *in situ* ATR-FTIR and DFT calculations have revealed that phosphate
755 was individually adsorbed onto magnetite in the NBB and MMM geometries, while

arsenate mainly formed BB complexes with few OS species. However, under competitive adsorption conditions, the BB arsenate complexes obviously substituted both the MMM and to a lesser extent the NBB phosphate complexes. These findings illustrate that NBB phosphate complexes are more stable than MMM complexes, and also that their binding strength is weaker than for the BB arsenate complexes. The competitive adsorption of phosphate and arsenate can be explained by variations in adsorption geometries with pH. Under acid conditions, the dominant MMM phosphate species had the smallest adsorption energies (E_{ads} = -0.69 eV, Table 2) and were easily replaced by arsenate (E_{ads} = -0.84 eV). As pH increased, NBB became the main phosphate species, displaying enhanced stability (E_{ads} = -1.89 eV), which resulted in decreasing desorption by arsenate. Throughout the studied pH range, the adsorbed arsenate remained in the BB geometry with higher stability than phosphate. Thus, the competitive efficiency for phosphate increased with pH, while for arsenate it remained almost stable. These results for magnetite are in excellent agreement with the findings on goethite (Liu et al., 2001).

Besides the adsorption geometry, the Coulombic interaction between the positively charged magnetite surfaces and negatively charged adsorbates is another important factor controlling the competitive adsorption between arsenate and phosphate. Given the magnetite PZC at 6.8, the electrostatic attraction with phosphate and arsenate oxyanions increases as pH decreases. This improves the adsorption onto the magnetite surface and thus, decreases the proportion of hydroxyl groups covering adsorption sites. The adsorption geometry of phosphate species changes from NBB to MMM

778 complexes, which contain fewer protons. A similar variation in adsorption
779 complexation from binuclear to mononuclear is also observed during the adsorption
780 of arsenate onto ferrihydrite (Neupane et al., 2014). To form BB complexes with
781 higher stability than MM configurations, the oxyanions should be bound to two
782 adjacent protonated oxygen sites. However, only mononuclear complexes are formed
783 if the protonated oxygen site is far away from the adsorbate. Based on the shorter
784 intramolecular O···O distance in phosphate compared to arsenate (2.45 and 2.6–2.8 Å,
785 respectively), the latter is more likely to form BB complexes than the former (So et al.,
786 2012). Lumsdon et al. found that the interaction with hydroxyl sites was stronger for
787 arsenate than for phosphate, because of the different molecular sizes of the adsorbates
788 (Lumsdon et al., 1984). Thus, arsenate bidentate binuclear complexes dominate in
789 areas of high surface coverage, whereas monodentate species are only found in areas
790 of low surface coverage (Fendorf et al., 1997). In contrast, the large surface coverage
791 of phosphate species prefers the formation of monodentate complexes (Liu et al.,
792 2001), which was also found under the acidic condition in this study.
793 Compared to other iron oxides, the formation of abundant monodentate mononuclear
794 phosphate complexes on magnetite alongside a low proportion of arsenate OS species
795 is unique for this combination of substrate and adsorbates. The PZC value for
796 magnetite (~6.8) is lower than for goethite (~9.1), ferrihydrite (~7.6-8.1) or hematite
797 (~11), which leads to Fe_3O_4 displaying a lower degree of protonation than other iron
798 oxides at the same pH. Protonated surface sites facilitate IS surface complexation
799 because water is more easily displaced than hydroxyl groups (Johnston and

Chrysochoou, 2012). Thus, the decrease of protonation on the magnetite surface results in the formation of more MM complexes of phosphate with fewer hydroxyl groups, as well as OS species of arsenate. Similar variations have appeared in sulfate adsorption, where IS complexes are exclusively found on hematite with the highest PZC (Hug, 1997), and both OS and IS complexes are formed on ferrihydrite (Johnston and Chrysochoou, 2014).

IMPLICATIONS

This study provides a molecular-level insight into the competitive adsorption between arsenate and phosphate on magnetite surfaces. Magnetite has a widespread occurrence in surface environment and is found coating the zero-valent iron nanoparticles increasingly used for environmental engineering, especially for As removal. Thus, our new results would be beneficial for assessing the environmental fate of arsenate and phosphate, as well as for other ions that may compete for or otherwise react with the magnetite surface sites.

Owing to the low surface site density of magnetite, its adsorption towards oxyanions has seldom been surveyed by *in situ* techniques. In this study, with the aid of 2D-COS analysis, we have resolved better the peaks of *in situ* ATR-FTIR spectra, which greatly facilitates the identification of adsorption species and geometries of both oxyanions. For phosphate, MMM complexes dominated at acid pH, while NBB complexes were dominant at alkaline conditions. Arsenate mainly formed BB complexes with some outer-sphere species, both of which were more prevalent at acid

than at alkaline pH. This is somewhat different from the cases on other iron oxides, e.g., ferrihydrite and goethite, ascribed to the lower surface site density of magnetite. The competitive adsorption of these adsorption species was further investigated by ATR-FTIR for different substitution sequences, providing spectroscopic evidence for their adsorption affinity towards magnetite surface. The adsorption strength was also thermodynamically confirmed for the first time through DFT calculations. Therefore, this study offers an important step forward in understanding the adsorption of oxyanions in complex systems, which is more environmentally realistic.

The adsorption affinity of the geometries as observed increased in the following order: MMM phosphate complex < NBB phosphate complex < BB arsenate complex. The high stability of adsorbed arsenate suggests the vital role of magnetite in the transfer and transformation of arsenic in surface environment. Meanwhile, magnetite could be used as an arsenic scavenger for *in situ* remediation of phosphate-rich groundwater and soil.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version, at XXX.

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1144 # TABLES

1145 **TABLE 1.** Adsorption sites, mean interatomic distances (*d*) and bond angles (∠) for the energetically preferred outer- (OS) and inner-sphere (IS)

1146 complexes of arsenate and phosphate at the Fe_3O_4 (001) surface in both acid and alkaline conditions.

Solute	pH	Adsorption site	[a]*d*(*X*−O)	*d*(*X*=O)	*d*(*X*O−H)	*d*(*X*O−Fe)	*d*(Fe−OH)	*d*(FeO−H)	∠(O−*X*−O)	∠(O−*X*=O)	∠(O=*X*=O)	∠(*X*OH)
			(Å)						(°)			
$H_2AsO_4^-$	acid	–	1.77	1.69	1.04	–	–	–	104.72	108.90	116.03	108.08
$HAsO_4$		Fe_B, Fe_B	1.76	1.72	1.05	2.06		1.02	–	107.31	111.54	112.97
$HAsO_4^{2-}$	alkaline	–	1.76	1.72	1.01	–	1.92	0.99	–	109.81	109.06	109.42
$HAsO_4$		Fe_B, Fe_B	1.82	1.71	1.01	2.00	2.00	0.99	–	104.45	114.00	106.64
$H_2PO_4^-$	acid	–	1.60	1.53	1.02	–	–	–	105.88	109.06	114.38	114.21
HPO_4		Fe_B	1.65	1.54	0.98	2.08	–	0.98	–	105.01	113.55	114.25
HPO_4^{2-}	alkaline	–	1.60	1.54	1.03	–	1.95	0.97	–	106.99	111.87	120.38
PO_4		Fe_A, Fe_B	–	1.56	–	1.93	–	–	–	–	109.44	–

1147 [a]: *X* represents the central atom (P or As) of adsorbate.

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1148 **TABLE 2.** Adsorption sites, adsorption energies (E_{ads}) and charges (q) for the energetically preferred outer- (OS) and inner-sphere (IS)

1149 complexes of arsenate and phosphate at the Fe_3O_4 (001) surface in both acid and alkaline conditions.

Solute	pH	Adsorption site	E_{ads} (eV per molecule)	[a]$q(H_mXO_4)$ (e^-)	q(OH)	q(H)
$H_2AsO_4^-$	acid	–	–	−0.82	–	–
$HAsO_4$		Fe_B, Fe_B	−2.19	−1.42	–	0.67
$HAsO_4^{2-}$	alkaline	–	–	−1.52	−0.66	–
$HAsO_4$		Fe_B, Fe_B	−0.84	−1.38	−0.68	–
$H_2PO_4^-$	acid	–	–	−0.84	–	–
HPO_4		Fe_B	−1.89	−1.50	–	0.65
HPO_4^{2-}	alkaline	–	–	−1.54	−0.65	–
PO_4		Fe_A, Fe_B	−0.69	−2.13	–	–

1150 [a]: *X* represents the central atom (P or As) of adsorbate. *m* indicates the degree of protonation of the solute, which can take integer values from 0 to 3.

1151

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1153 outer- (OS) and inner-sphere (IS) complexes of arsenate and phosphate at the Fe_3O_4 (001) surface in both acid and alkaline conditions. The
1154 presented vibrational frequencies are stretching (ν), bending (δ) and wagging (ω).

Solute	pH	Sym	Adsorption site	ν(FeO−H)	[a]ν(*X*O−H)	δ(*X*OH)	ω(*X*OH)	ν(*X*=O)	ν(*X*−OH)	ν(*X*=OFe)	δ(FeOH)	ω(FeOH)
				(cm^{-1})								
$H_2AsO_4^-$	acid	C_{2v}	OS	−	3066	1372	1028	870	735	−	−	−
					2266	1268	756	817	666			
$HAsO_4^{2-}$		C_s	Fe_B, Fe_B	2875	2429	1291	1037	816	721	786	1042	1035
										751		
$HAsO_4^{2-}$	alkaline	C_{3v}	OS	3365	3120	1190	776	830	728	−	1060	721
								790				
								756				
$HAsO_4^{2-}$		C_s	Fe_B, Fe_B	3458	3007	1278	830	792	624	810	928	797
										782		
$H_2PO_4^-$	acid	C_{2v}	OS	−	2826	1269	938	1096	904	−	−	−
					2742	1221	920	1012	839			
HPO_4^{2-}		C_s	Fe_B	3350	3625	1018	−	1088	766	942	1170	706
								1045				
HPO_4^{2-}	alkaline	C_{3v}	OS	3739	2626	1271	947	1045	867	−	718	616
								1003				
								926				
PO_4^{3-}		C_s	Fe_A, Fe_B	−	−	−	−	1112	−	909	−	−
								949		884		

1155 [a]: *X* represents the central atom (P or As) of adsorbate.

FIGURE CAPTIONS

FIGURE 1. Infrared spectra for the individual adsorption of arsenate (a) and phosphate (b) on magnetite surface at acid, neutral and alkaline conditions, as well as the spectral fitting with different adsorption species (arsenate: inner-sphere (green line) and outer-sphere (red line) species; phosphate: monoprotonated monodentate-mononuclear (green line) and non-protonated bidentate-binuclear complexes (red line)). The total fit is represented by the blue line.

FIGURE 2. Integrated absorbance (IA) of the bands assigned to the adsorbed arsenate (a) and phosphate (b) plotted vs. pH, and the relative percentage of different adsorption species (arsenate: inner-sphere and outer-sphere species; phosphate: monoprotonated monodentate-mononuclear (MMM) and non-protonated bidentate-binuclear (NBB) complexes).

FIGURE 3. Infrared spectra of phosphate adsorbed onto magnetite at pH = 4 (a), pH = 7 (b) and pH = 9 (c). After 135 (a and b) or 350 (c) min, arsenate was added at an equal (molar) concentration and the spectral change was monitored for another 135 (a and b) or 350 (c) min.

FIGURE 4. Infrared spectra of arsenate adsorbed onto magnetite at pH = 4 (a) and pH = 7 (b). After 135 min, a phosphate solution at an equal (molar) concentration was added and the spectral change was monitored for another 135 (a and b) min.

FIGURE 5. Top and side view of the aqueous inner-sphere species $HAsO_4^{2-}$ in (a) acid and (b) alkaline conditions. Tetrahedral Fe_A atoms are in orange, octahedral Fe_B atoms are in violet, O atoms are in red, As atoms are in green and H atoms are in pink. Surface atoms are represented as (top panels) balls and (bottom panels) sticks, water solvent molecules are represented as wireframe and the solute molecules are represented as balls-and-sticks. Light and dark dashed lines mark hydrogen bonds and the limits of the computational cell, respectively. The double arrows indicate interatomic distances in Å.

FIGURE 6. Top and side view of the aqueous inner-sphere species (a) HPO_4^{2-} and (b) PO_4^{3-} in acid and alkaline conditions, respectively. Tetrahedral Fe_A atoms are in orange, octahedral Fe_B atoms are in violet, O atoms are in red, P atoms are in blue and H atoms are in pink. Surface atoms are represented as (top panels) balls and (bottom panels) sticks, water solvent molecules are represented as wireframe and the solute molecules are represented as balls-and-sticks. Light and dark dashed lines mark hydrogen bonds and the limits of the computational cell, respectively. The double arrows indicate interatomic distances in Å.

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1144 # TABLES

1145 **TABLE 1.** Adsorption sites, mean interatomic distances (*d*) and bond angles (∠) for the energetically preferred outer- (OS) and inner-sphere (IS)

1146 complexes of arsenate and phosphate at the Fe_3O_4 (001) surface in both acid and alkaline conditions.

Solute	pH	Adsorption site	[a]*d*(*X*−O)	*d*(*X*=O)	*d*(*X*O−H)	*d*(*X*O−Fe)	*d*(Fe−OH)	*d*(FeO−H)	∠(O−*X*−O)	∠(O−*X*=O)	∠(O=*X*=O)	∠(*X*OH)
			(Å)						(°)			
$H_2AsO_4^-$	acid	−	1.77	1.69	1.04	−	−	−	104.72	108.90	116.03	108.08
$HAsO_4$		Fe_B, Fe_B	1.76	1.72	1.05	2.06		1.02	−	107.31	111.54	112.97
$HAsO_4^{2-}$	alkaline	−	1.76	1.72	1.01	−	1.92	0.99	−	109.81	109.06	109.42
$HAsO_4$		Fe_B, Fe_B	1.82	1.71	1.01	2.00	2.00	0.99	−	104.45	114.00	106.64
$H_2PO_4^-$	acid	−	1.60	1.53	1.02	−	−	−	105.88	109.06	114.38	114.21
HPO_4		Fe_B	1.65	1.54	0.98	2.08	−	0.98	−	105.01	113.55	114.25
HPO_4^{2-}	alkaline	−	1.60	1.54	1.03	−	1.95	0.97	−	106.99	111.87	120.38
PO_4		Fe_A, Fe_B	−	1.56	−	1.93	−	−	−	−	109.44	−

1147 [a]: *X* represents the central atom (P or As) of adsorbate.

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1148 **TABLE 2.** Adsorption sites, adsorption energies (E_{ads}) and charges (q) for the energetically preferred outer- (OS) and inner-sphere (IS)

1149 complexes of arsenate and phosphate at the Fe_3O_4 (001) surface in both acid and alkaline conditions.

Solute	pH	Adsorption site	E_{ads} (eV per molecule)	[a]$q(H_mXO_4)$ (e^-)	q(OH)	q(H)
$H_2AsO_4^-$	acid	–	–	−0.82	–	–
$HAsO_4$		Fe_B, Fe_B	−2.19	−1.42	–	0.67
$HAsO_4^{2-}$	alkaline	–	–	−1.52	−0.66	–
$HAsO_4$		Fe_B, Fe_B	−0.84	−1.38	−0.68	–
$H_2PO_4^-$	acid	–	–	−0.84	–	–
HPO_4		Fe_B	−1.89	−1.50	–	0.65
HPO_4^{2-}	alkaline	–	–	−1.54	−0.65	–
PO_4		Fe_A, Fe_B	−0.69	−2.13	–	–

1150 [a]: *X* represents the central atom (P or As) of adsorbate. *m* indicates the degree of protonation of the solute, which can take integer values from 0 to 3.

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1154 presented vibrational frequencies are stretching (ν), bending (δ) and wagging (ω).

Solute	pH	Sym	Adsorption site	ν(FeO−H)	[a]ν(*X*O−H)	δ(*X*OH)	ω(*X*OH)	ν(*X*=O)	ν(*X*−OH)	ν(*X*=OFe)	δ(FeOH)	ω(FeOH)
				(cm^{-1})								
$H_2AsO_4^-$	acid	C_{2v}	OS	−	3066	1372	1028	870	735	−	−	−
					2266	1268	756	817	666			
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										751		
$HAsO_4^{2-}$	alkaline	C_{3v}	OS	3365	3120	1190	776	830	728	−	1060	721
								790				
								756				
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								1045				
HPO_4^{2-}	alkaline	C_{3v}	OS	3739	2626	1271	947	1045	867	−	718	616
								1003				
								926				
PO_4^{3-}		C_s	Fe_A, Fe_B	−	−	−	−	1112	−	909	−	−
								949		884		

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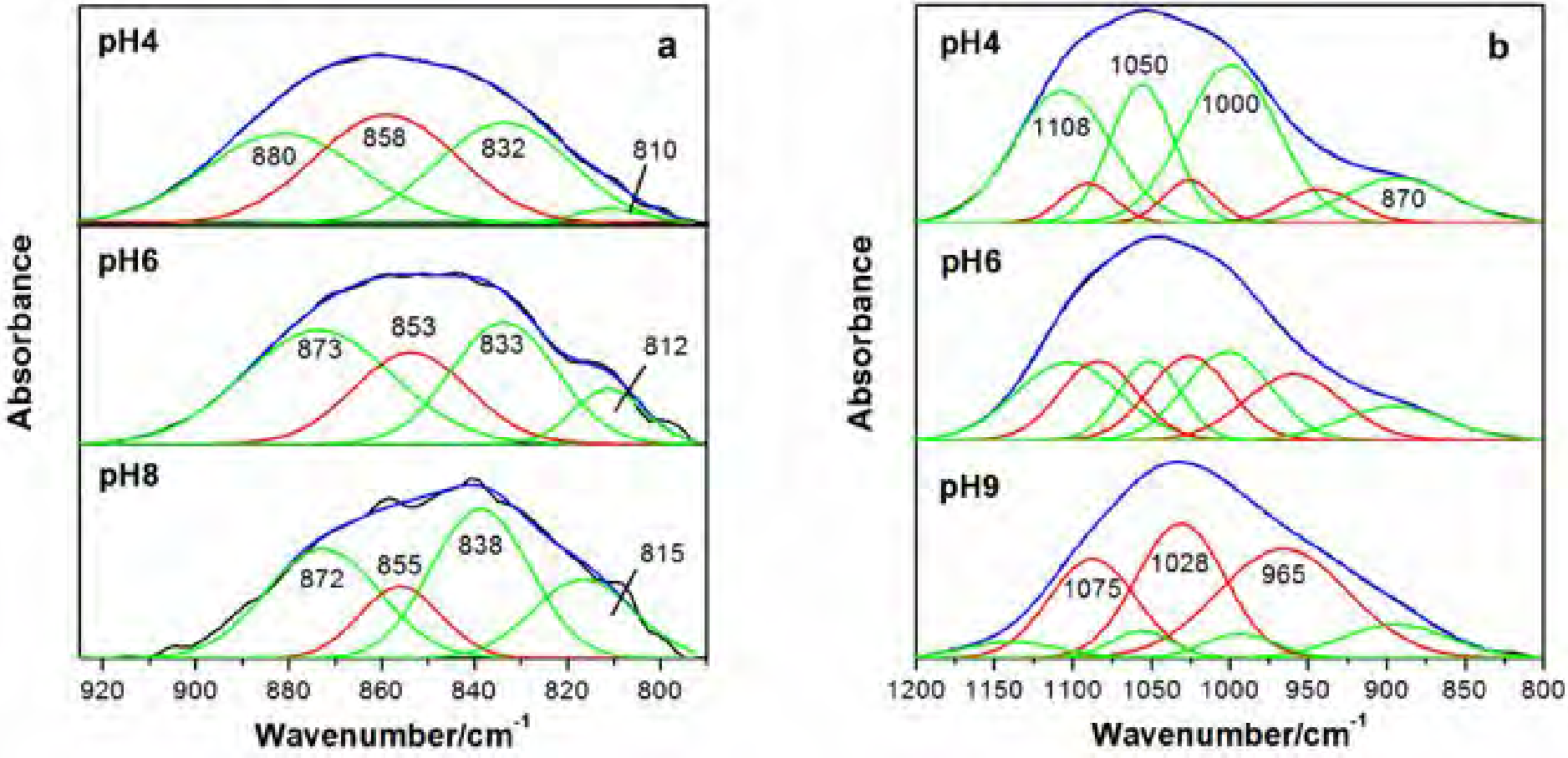
Figure.1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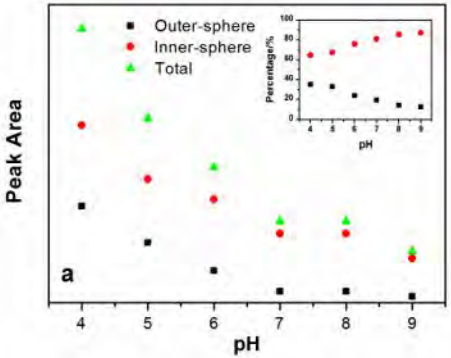
858
832
810
pH6
873
853
833
812
pH8
872
855
838
815
Absorbance
920
900
880
860
840
820
800
Wavenumber/cm-1
pH4
b
1108
1050
1000
870
pH6
pH9
1075
1028
965
Absorbance
1200
1150
1100
1050
1000
950
900
850
800
Wavenumber/cm-1

Figure.2


Outer-sphere
Inner-sphere
Total
Peak Area
pH
a
Percentage/%
pH

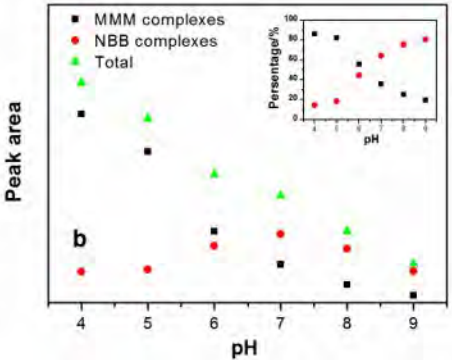
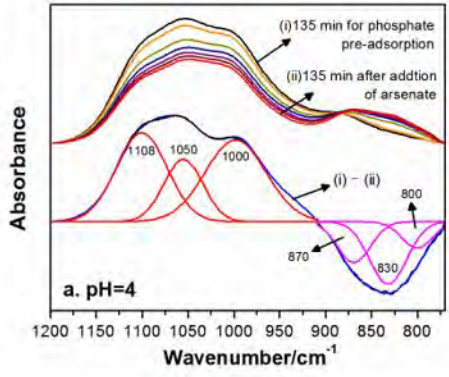
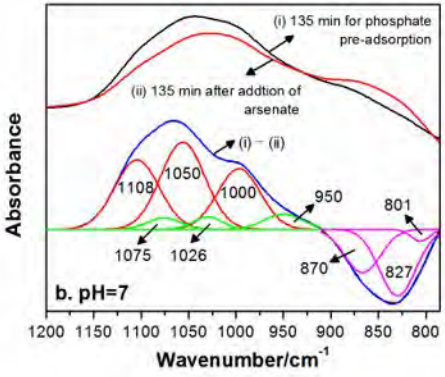

MMM complexes
NBB complexes
Total
Peak area
pH
b
Persentage/%
pH

Figure.3


(i)135 min for phosphate pre-adsorption
(ii)135 min after addtion of arsenate
1108
1050
1000
(i) − (ii)
800
870
830
a. pH=4
Absorbance
1200 1150 1100 1050 1000 950 900 850 800
Wavenumber/cm-1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(ii) 135 min after addtion of arsenate
(i) − (ii)
1108
1050
1000
950
801
1075
1026
870
827
b. pH=7
Absorbance
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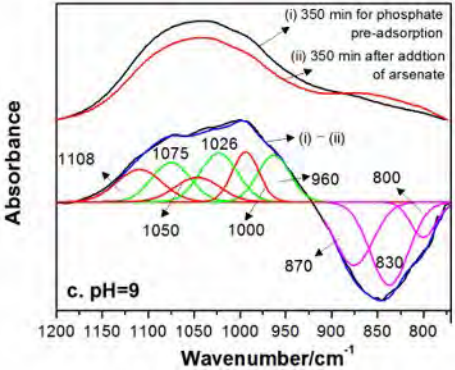
Wavenumber/cm-1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1075
1026
(i) − (ii)
960
800
1050
1000
870
830
c. pH=9
Absorbance
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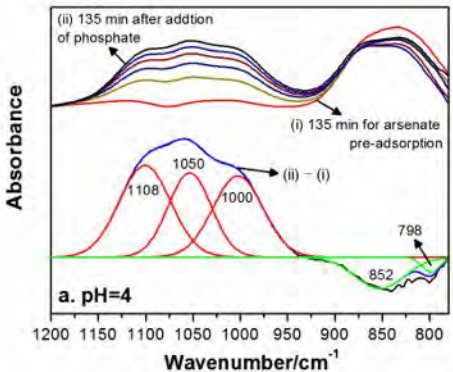
Wavenumber/cm-1

Figure.4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(i) 135 min for arsenate pre-adsorption
(ii) − (i)
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1050
1000
798
852
a. pH=4
Absorbance
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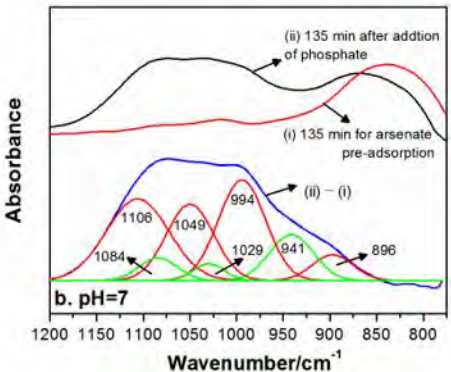
Wavenumber/cm-1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(i) 135 min for arsenate pre-adsorption
(ii) − (i)
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1084
1049
1029
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941
896
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Absorbance
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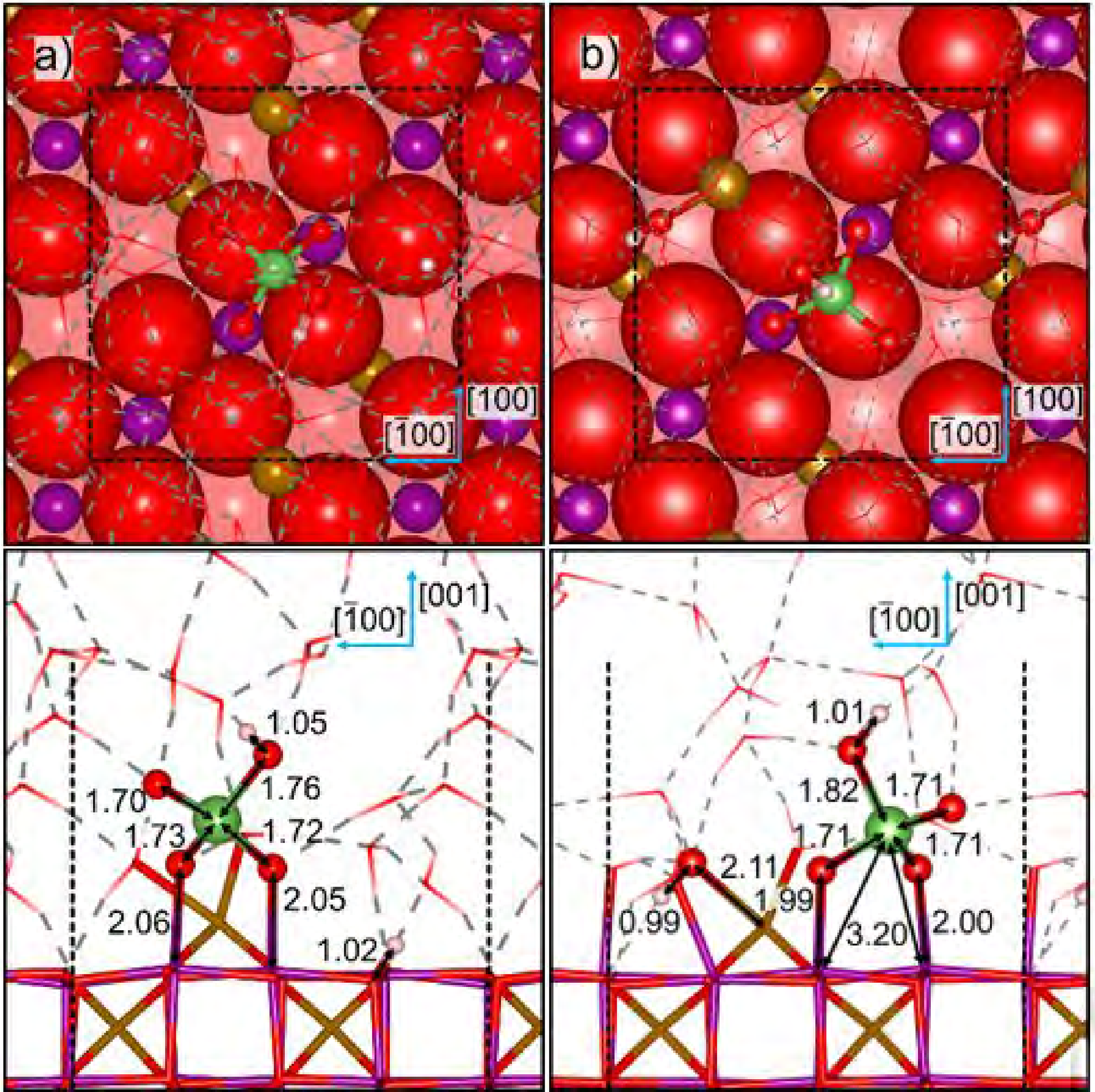
Wavenumber/cm-1

Figure.5.


a)
b)
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[001]
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1.73
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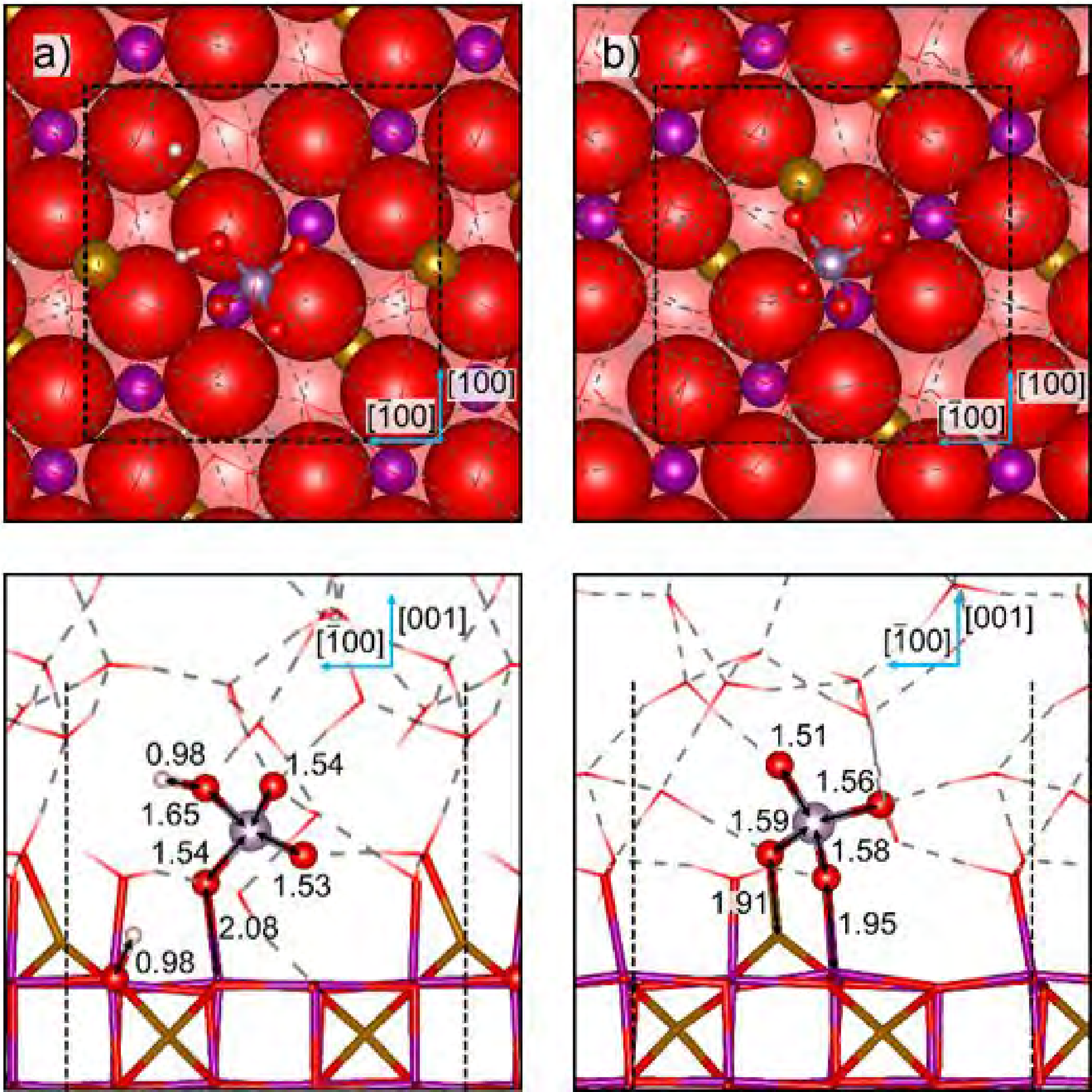
2.11
1.99
0.99
3.20
2.00

Figure.6


a)
[1̄00]
[100]
b)
[1̄00]
[100]
[1̄00]
[001]
0.98
1.54
1.65
1.54
1.53
2.08
0.98
[1̄00]
[001]
1.51
1.56
1.59
1.58
1.91
1.95