AUTHOR QUERY FORM

ELSEVIER	Journal: COMMAT Article Number: 5585	Please e-mail or fax your responses and any corrections to: E-mail: corrections.esch@elsevier.sps.co.in Fax: +31 2048 52799

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. Note: if you opt to annotate the file with software other than Adobe Reader then please also highlight the appropriate place in the PDF file. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult http://www.elsevier.com/artworkinstructions.

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof. Click on the 'Q' link to go to the location in the proof.

Location in article	Query / Remark: click on the Q link to go Please insert your reply or correction at the corresponding line in the proof
Q1	Please confirm that given name(s) and surname(s) have been identified correctly.
Q2	Please check the placement of Fig. 4, and correct if necessary.

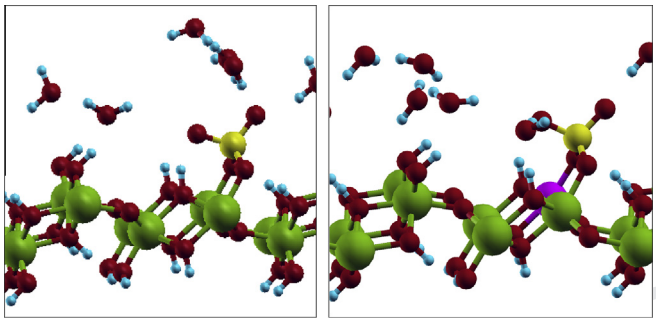
Please check this box if you have no corrections to make to the PDF file ☐

Thank you for your assistance.

Graphical abstract

Phosphate adsorption on goethite and Al-rich goethite **pp xxx–xxx**

Patricia G. Belelli *, Silvia A. Fuente, Norberto J. Castellani



BBH0 on (110) goethite BBH0 on (110) Al-goethite

Highlights

• Vibrational spectra for phosphate/goethite(1 1 0) were considered. • Monoprotonated bidentate mononuclear species dominates at low pH. • Bidentate binuclear species dominates at intermediate and high pH. • P/Al-doped–goethite modes on Al show specific shifts. • H-bonding affects P/Al-doped–goethite spectra significantly.

Computational Materials Science xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Phosphate adsorption on goethite and Al-rich goethite

Q1 Patricia G. Belelli*, Silvia A. Fuente, Norberto J. Castellani

IFISUR, Grupo de Materiales y Sistemas Catalíticos, Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, Bahía Blanca B8000CP, Argentina

ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 10 December 2013
Accepted 14 December 2013
Available online xxxx

Keywords:
Phosphate adsorption
Goethite
Al-goethite
Periodic DFT

ABSTRACT

The adsorption of phosphate complexes on pure and Al-rich goethite surfaces was studied by using density functional theory (DFT) and a periodic slab model. Several phosphate complexes are evaluated on these surfaces, which were not studied in other earlier theoretical works. The following complexes have been considered: bidentate binuclear (BB), bidentate mononuclear (BM), monodentate mononuclear (MM) and monodentate binuclear (MB), with their respective mono-protonated and non-protonated species. Our calculations indicate that the formation of all these species is possible on both goethite surfaces. Particularly, the direct correlation between calculated vibrational frequencies of phosphate complexes on pure goethite and experimental results indicates that some specific species are formed at certain pH values. For these cases we are able to provide an alternative interpretation to the experimental bands. On the other hand, the obtained vibrational frequencies of phosphate adsorbed on Al-goethite can be useful for the forthcoming experimental results. We noticed that the band shifts are extremely dependent on the kind of pretreated samples; for this reason the surface model used in calculations establishes restrictions on the IR experimental results to be compared.

1. Introduction

Phosphate is one of the main nutrients for plants and, therefore, constitutes a fundamental component of fertilizers used with agricultural purpose in crop and fields. The indiscriminate use of these agrochemicals is object of special preoccupation in environmental chemistry, since phosphate is largely responsible for the eutrophication arising in nearby water bodies [1,2].

However, the transport and bio-compatibility of these nutrients can be controlled by the retaining ability of certain mineral surfaces. The most studied systems are iron (Fe) oxides and oxo-hydroxides found in soils and sediments. The presence of phosphate complexes in these minerals was evidenced using different experimental techniques, such as potentiometry [3,4] and X-ray absorption [5]. Goethite is the Fe oxo-hydroxide most studied, due to its crystallinity and stability in natural ambient. The phosphate adsorption on goethite is so strong that it can be produce even though the solid surface is negatively charged [6,7]. Phosphates are known by their capacity to form strongly bonded complexes with the goethite surface in a wide pH range [8–12].

The FTIR spectra of phosphate adsorbed on goethite was studied only by a limited number of authors [9–11]. As the bands originated from the O—H stretch vibrations of hydrated goethite surface are broad and overlap with the O—H stretch modes of protonated phosphate complexes, the frequencies commonly analyzed in experiments are in the interval 1200–850 cm^{-1}. Other structural goethite bands appear also below 950 cm^{-1}.

Tejedor-Tejedor and Anderson [9] deduced, based on experimental vibrational frequencies, that the spectra are modified when increasing pH values are applied and when the phosphate surface coverage changes, indicative that different coordination of phosphate with the goethite surface ions are present. The phosphate complexes formed on goethite at different coverages are non-protonated monodentate and bidentate for a wide pH range of 3–8 [9]. At pH = 6 these species can co-exist, where the predominant surface species would be the non-protonated bidentate binuclear. Analogous species were supposed to be present on TiO_2 [13].

On the other hand, the assigned bands previously mentioned were questioned by other authors [10,14]. Persson et al. [10] reported that the IR spectra for phosphate adsorbed on goethite changes according to the pH; at lower pH values the bands are located at 1178 and 1001 cm^{-1}, while as the pH is raised, other two bands appear at 1122 and 1049 cm^{-1}. At the highest pH value studied, the spectrum showed only two new bands at 1057 and 966 cm^{-1}. In order to explain the changes of band positions as a function of pH, these authors considered the molecular symmetry of implied phosphate complexes. During the period of pH increasing, the C_{3v}, C_{2v} and C_{3v} symmetries were assigned to the same mono-coordinated phosphate with different protonation degree: di-, mono-, and non-protonated complexes. However, these authors performed IR spectra on dried goethite samples and significant shifts in bands positions could be generated by different water contents.

* Corresponding author. Tel.: +54 291 4595141; fax: +54 291 4595142.
E-mail address: patricia.belelli@uns.edu.ar (P.G. Belelli).

0927-0256/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.commatsci.2013.12.030

Arai and Sparks [14] performed ATR-FTIR spectroscopic investigations for the phosphate adsorption on ferrihydrite surface. The results were interpreted as an evidence for the formation of non-protonated bidentate binuclear phosphate complexes at pH ⩾ 7.5, in co-existing with other surface species as monodentate mononuclear. These authors showed that when the phosphates establish hydrogen bonding with hydroxyl groups, the different surface complexes exhibit low symmetries. Moreover they reported that at pH < 7.5, the protonated monodentate mononuclear and/or protonated bidentate binuclear complexes could not be elucidated.

In order to solve the controversy about the phosphate frequency assignment on goethite, Kwon and Kubicki [15] studied theoretically different adsorption modes with a cluster model. The latter consists of two edge-sharing iron octahedral clusters and does not represent any specific goethite plane. Their calculated frequencies were contrasted with the experimental values extracted from Persson studies on dried goethite [10]. They proposed the presence of di-protonated bidentate complex ($\equiv Fe_2O_2P(OH)_2$) at low pH, and the formation of mono-protonated monodentate ($\equiv FeOPO_2(OH)$) or non-protonated bidentante complex ($\equiv Fe_2O_2PO_2$) at neutral pH.

On the other hand, Rahnemaie et al. [16] evaluated the PO_4^{3-} adsorption on goethite surface using an interfacial charge distribution (CD) approach based on ion adsorption and interfacial water ordering. The charge distribution values showed the relevance presence of a non-protonated bidentate surface complex at high pH values and the presence of a mono-protonated monodentate complex at low pH.

In a recent work, the characterization of phosphate and sulfate adsorptions on Fe-(hydr)oxide surface was carried out. The reactivity, pH effect, free energies and hydrogen bonds were evaluated through the topological analysis of the electron density (Laplacian) [17]. They indicated the existence of positive cooperative effects that bring additional stabilization to the studied systems.

In this work, the phosphate adsorption on the (1 1 0) goethite surface and on Al-goethite, substituted by 12.5%/mol of Al is evaluated theoretically. The Al content was considered taking into account the highest amount of Al substitution found in synthetic goethites. All the calculations were performed using a periodic method. It is important to emphasize this point because scarce works related to this issue were found in the open literature [18].

2. Surface models and computational details

The calculation corresponding to phosphate adsorption on goethite and Al-goethite surfaces were performed in the framework of spin-polarized DFT, using the *Vienna Ab-Initio Simulation Package* (VASP) [19–21]. In this package the interaction between core states and valence electrons is described by the projector-augmented wave method (PAW) [22,23].

In a previous work, two different approximations were considered to treat exchange and correlation: (1) the LDA + U and (2) GGA + U, following the approach of Dudarev for different values of U [24]. The results indicated that best structural and energetic description of both goethite and Al-goethite were obtained using GGA + U with U = 6 eV [25]. The Kohn–Sham valence states were expanded in a plane-waves basis set with a kinetic energy cutoff of 450 eV.

Both goethite and Al-goethite surfaces were represented by slab models. The (1 1 0) goethite surface is one of the its most usual crystal faces of this mineral [26]. This surface can be constructed by a stoichiometric truncation of bulk goethite, where three Fe—O and three hydrogen bonds need to be broken per unit cell. For the surface model construction the cell optimized parameters of bulk goethite (a = 4.601 Å, b = 9.994 Å and c = 3.035 Å) were taken from our previous results [25]. In our slab model the bidimensional 1 × 2 cell has 8 (FeOOH) units, i.e. its contain 4 Fe layers. Afterwards, this surface was fully hydroxylated in such a way that all Fe ions preserve their octahedral coordination to cancel any spurious charge. Hence, the corresponding unit cell is formed by 8 (FeOOH) units plus $2H_2O$ molecules (Fig. 1a). Earlier calculations showed that due to the small relaxations with respect to the bulk (lower than 1%), it is possible to use this relatively thin slab [27]. A vacuum gap of approximately 14 Å was used in normal direction to avoid the interaction between slabs. The optimized slab geometry was obtained relaxing all the superficial OH groups and the Fe atoms. The reciprocal space was described with a Monkhorst–Pack mesh of 2 × 4 × 1 k-points for both goethite and Al-goethite surfaces. All the geometries were optimized until the calculated forces on the atoms are lower than 0.01 eV/Å.

Based on our previous work and taking into account the most stable magnetic arrangement in the bulk, the initial magnetic configuration for the goethite slab was considered anti-ferromagnetic (AFM) [25]. This magnetic phase presents the AFM + - + - sequence, which corresponds to alternated magnetic moments of Fe atoms along the b-vector axis. These results are compatible with experiments [28] and previous calculations reported using the PBE (Perdew–Burke–Enzerhof) functional [27].

In case of the (1 1 0) Al-goethite surface, a 1 × 2 cell was constructed where one of the Fe atoms was isomorphously replaced by one Al atom, giving an Al-substitution of 12.5 mol%. The bulk optimized parameters with U_{eff} = 6 eV are a = 4.572 Å b = 9.919 Å and c = 6.045 Å. The Al-goethite surface was also fully hydroxylated (Fig. 1b). The magnetic configuration of Fe atoms was liberated, considering for the initial configuration the same as that in bulk Al-goethite with Al-substitution of 25 mol% [25]. In this case, the position of up and down iron spin projections is alternated, as it was observed for pure goethite. Hence, the most stable magnetic arrangement has the same spin projection for the two Fe atoms surrounding the Al atom.

The reaction energy of these systems was obtained taking into account the phosphate adsorbed on the goethite surface, as the

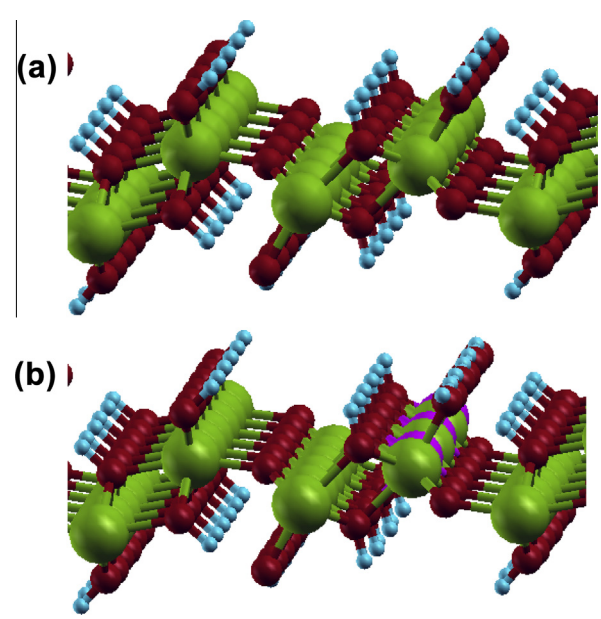


Fig. 1. (a) Hydroxylated (1 1 0) surface of goethite and (b) hydroxylated (1 1 0) surface of Al-goethite. Green, red, purple and cyan are the corresponding colors of Fe, O, Al and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

final state, and the isolated phosphoric acid and goethite, as reactants:

$$E_{reacc} = E_{phosphate/goethite} - E_{goethite} - E_{H_3PO_4} \quad (1)$$

E_{H3PO4} corresponds to the optimization of a phosphoric acid plus three water molecules that establish H-bonds with the acid. On the one hand, $E_{goethite}$ gives the energy for the optimized bare surface of goethite. On the other hand, the optimization of phosphate species adsorbed on goethite surface ($E_{phosphate/goethite}$) includes five water molecules, three of them taken into account as in the isolated molecule of phosphoric acid, and other two water molecules generated from the surface reaction between the phosphoric acid and clean goethite. In this sense, the inclusion of explicit water molecules tries to mimic the solvation effect on the reaction energies [29]. The presence up to 10 water molecules was evaluated; the results indicated that no significant modifications are produced on the geometrical structures, reaction energies and vibrational frequency values, with respect to the results obtained with five explicit water molecules. The reaction energies obtained from Eq. (1) can be used to predict which species would be more favorable thermodynamically. Negative values indicate an exothermic reaction.

It was observed that the reaction energies are practically unchanged if the dipole correction is included in the calculation of electronic energies. This correction was evaluated for different phosphate/goethite systems and the more significant E_{reacc} difference obtained was of 0.05 eV. This difference is negligible taking into account the magnitude of the calculated reaction energies, as it will be shown in Section 3.

The numerical calculation of second derivatives in the potential energy surface with the harmonic approach provided the vibrational frequencies and the corresponding normal modes. A geometrical displacement of 0.02 Å was used for the derivative computations. Frequencies were scaled by a factor of 1.066 to correct for systematic errors, such as neglect of anharmonicity [30]. Vibrational mode assignments were made by visual inspection of atomic displacements created during the frequency calculation [31].

3. Results and discussion

3.1. (1 1 0) goethite surface

Different coordination modes of adsorbed phosphate species were examined considering two surface complexes: protonated (H_1) and non-protonated (H_0), which are the most common species found under experimental conditions [9]. Specifically, four coordination modes have been evaluated: bidentate binuclear (BB), bidentate mononuclear (BM), monodentate mononuclear (MM) and monodentate binuclear (MB), with their respective protonated and non-protonated species. Concerning earlier theoretical works, the bidentate binuclear and monodentate mononuclear complexes with the respective protonated species were the most studied structures [12,29]. Here, all the phosphate anchoring possibilities have been considered. In Fig. 2 the optimized geometries corresponding to these phosphate complexes are shown.

In Table 1 the geometrical parameters and reaction energies for the different coordination modes above mentioned are summarized. Notice that the P=O distances are unchanged for almost all the phosphate complexes formed on the goethite surface, but they present a lengthening with respect to the isolated phosphoric acid ($d_{(P-OH)}$ = 1.47 Å). The MMH0 species has three different P=O distances, being one of them nearly 0.1 Å longer than the corresponding bond in phosphoric acid. Besides, the P—O_H bonds also change

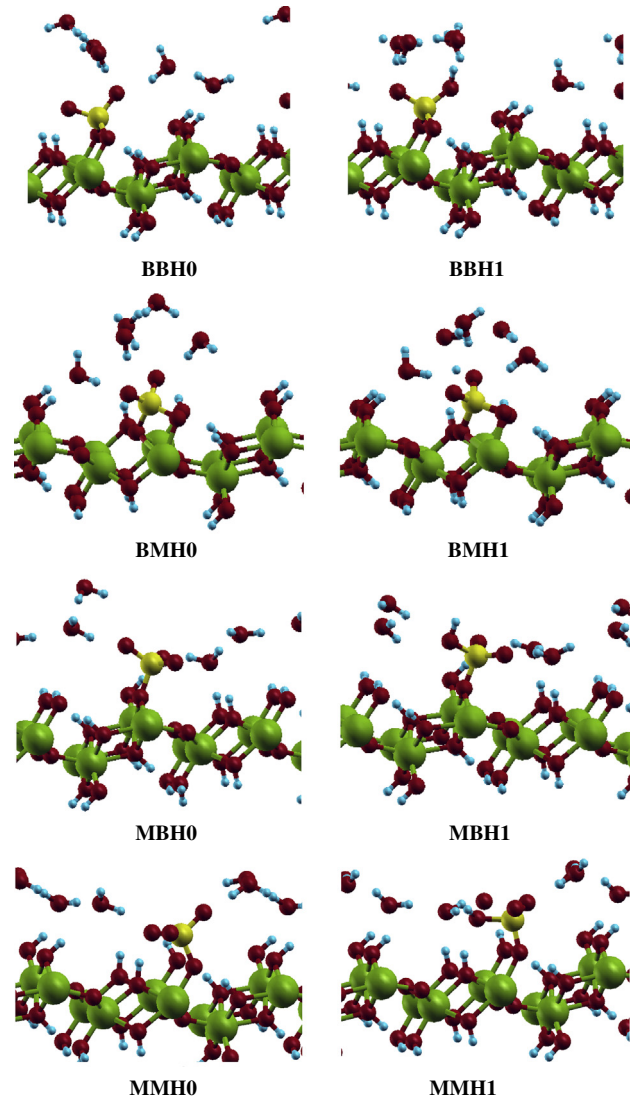


Fig. 2. Optimized geometries of all phosphate complexes formed on (1 1 0) goethite surface.

with respect to the phosphoric acid ($d(P-O_H)$ = 1.51 Å), becoming shorter for bidentate complexes, BBH1 and BMH1, and longer for monodentate complexes, MBH1 and MMH1. The P—O_H bond lengthening in monodentate species could be associated with the hydrogen bonds formed between the phosphate O atom and the H atom pertaining to surface OH groups or to the explicitly water molecule added for the solvation effect. On the other hand, the bidentate complexes also form a hydrogen bond between the H atom of OH group in phosphate species and the O atom of water molecules. The presence of this hydrogen bond is corroborated by the O—H bond elongation in phosphate bidentate complexes (approximately 1.05 Å with respect to the value of 0.98 Å for monodentate complexes).

We also observe that the length of P—O_s bonds, which are the phosphate links with the surface, could be associated with the E_{reacc} values (see Table 1). When the P—O_s bond is shortened, the phosphate complex formed on the goethite surface becomes more stable. Regarding the Fe—O bonds, their lengths are dependent on the type of phosphate anchoring on the goethite surface. The Fe—O distances are longer for the bidentate phosphate complexes than for the monodentate ones; particularly, when the phosphate forms the strained bidentate mononuclear complexes.

Table 1
Reaction energies (E_{reac} in eV), geometrical parameters (in Å), and parameters of correlation between experimental[a] and calculated frequencies of phosphate complexes formed on (1 1 0) goethite surface.

PO_4 complex	E_{reac}	d(P=O)	d(P—O_H)	d(O_s—P)	d(O_s—Fe)	s	$r^{2,b}$
BBH0	−3.43	1.53/1.55	–	1.59	1.98/2.00	1.01	1.00[iii]
BBH1	−3.11	1.54	1.57	1.57/1.58	2.00	1.00	1.00[ii]
BMH0	−2.81	1.53	–	1.58/1.65	2.02/2.08	1.01	0.97[iii]
BMH1	−1.96	1.52	1.59	1.58/1.62	2.05/2.12	0.99	0.99[i]
MBH0	−1.48	1.53	–	1.67	1.97/1.98	1.03	0.99[iii]
MBH1	−3.36	1.52	1.63	1.59	2.04	1.01	0.94[ii]
MMH0	−3.17	1.52/1.55/1.56	–	1.60	1.91	1.01	0.90[iii]
MMH1	−3.44	1.51/1.53	1.67	1.56	1.99	0.98	0.99[i]
						1.01	0.97[ii]

Free H_3PO_4: d(P=O) = 1.47 Å; d(P—O_H) = 1.61 Å.
[a] Experimental data extracted from Persson Ref. [10].
[b] pH that the correlations are performed:
[i] pH = 3.1.
[ii] pH = 4.2.
[iii] pH = 12.8.

Our optimized values for the BBH0, BBH1, MMH0 and MMH1 geometrical parameters can be compared with previous results reported by Rahnemaie et al. [16], performed using a DFT approach and a cluster model. In general, the tendency observed was the same, except that our P=O and P—O_s distances are slightly lower, for both bidentate and monodentate complexes, than the respective values obtained by these authors; nevertheless, but they are in agreement with the experimental value of 1.54 Å for the mean distance in PO_4 minerals (ICSD) [16].

In almost all the cases, the E_{reacc} values, around 3 eV, for the phosphate complexes formed on the goethite surface are indicative of a strong interaction. The most stable complexes show hydrogen bonding between the phosphate O atoms and the H atoms of surface hydroxyl groups. Thus, this situation can be one of the reasons for the significant reaction energies attained in calculations. Besides, another hydrogen bonding develops with the H atoms of the explicitly included water molecules. From these results, we can highlight that the phosphate species most probably formed on our hydroxylated goethite surface are the BBH0 and MMH1.

The net charges for the adsorbed phosphate complexes were computed according to the atoms in molecules approach of Bader [32] (Table 2). Notice that the amount of negative charge for the phosphate complex depends on the type of anchoring with the surface. The corresponding values for the bidentate complexes decrease in the following order: BMH0 > BBH0 > BMH1 > BBH1. As it was expected, the non-protonated species have higher negative charges, nearly −2.0*e*, than the mono-protonotated ones, nearly −1.5*e*. This fact can be related with the presence of PO_4^{3-} and PO_4H^{2-} phosphate ions, respectively. For the monodentate complexes, the amounts of negative charges decrease in this ordering: MMH0 > MBH0 > MMH1 > MBH1. On the other hand, though the magnetic moments of goethite Fe atoms do not change after adsorption of phosphate species, some smaller modifications were observed for the O atoms surrounding the Fe atoms where phosphate is adsorbed.

In Table 3 the theoretical vibrational frequency values for different phosphate complexes adsorbed on goethite, obtained with our slab models, have been summarized. Experimental IR spectra characterizing these systems are composed by a relatively small number of bands. Their position and broadening are very dependent on the H bonding established between phosphate and surface hydroxyl groups. Therefore, the results of Persson et al. [10], obtained from previously dehydrated goethite, provided different vibrational information than those reported by Tejedor-Tejedor–Anderson [9] and by Arai–Sparks [14], on ferryhidrate. Although the dehydration or the hydration degree of each goethite surface is unknown, our surface model is hydroxylated and, hence it could be considered somewhat hydrated, compared with a fully bare goethite surface, but not at the high level proposed by Ghose et al. [33] in their work, with up to two water layers were included. After a first inspection of IR spectra obtained in previously mentioned works [9,10], we can outline that the measured frequencies for certain adsorbed complexes show similarities to those calculated in the present work, pointing out that our surface model is more comparable to a partially dehydrated goethite than to a completely dehydrated one.

In the past, the assignation of experimental phosphate IR bands was accomplished mostly on base to symmetry arguments for the

Table 2
Bader charges (q in *e*) for the phosphate complexes formed on (1 1 0) goethite and on (1 1 0) Al-goethite surface.

PO_4 complex	Goethite $q(PO_4H_x)$[a]	Al-goethite $q(PO_4H_x)$[a]
BBH0	−1.82	−1.90
BBH1	−1.51	−1.67
BMH0	−1.95	−2.09
BMH0 (Al)	–	−2.14
BMH1	−1.53	−1.62
BMH1 (Al)	–	−1.75
MBH0	−1.60	−1.67
MBH1	−1.21	−1.26
MMH0	−1.66	−1.67
MMH0 (Al)	–	−1.89
MMH1	−1.23	−1.23
MMH1 (Al)	–	−1.33

[a] *x*: corresponds to the number of H atom in the phosphate complex, 0 or 1 values.

Table 3
Vibrational frequency assignments for phosphate complexes adsorbed on (1 1 0) goethite surface (in cm^{-1}).

PO_4 complex	ν(P=O)[a]	ν(P—O_H)	ν(O_s—P)[a]	ν(O—H)[a]
BBH0 (C_{2v})	1066_a-974_s	–	830_a-817_s	–
BBH1 (C_1)	1122	1049	985_a-930_s	2447
BMH0 (C_{2v})	1091_a-1080_s	–	908_a-771_s	–
BMH1 (C_1)	1150	1007	843_a-610_s	1555
MBH0 (C_{3v})	1101_I-1097_{II}-1003_{III}	–	806	–
MBH1 (C_1)	1120_a-1095_s	856	591	3848
MMH0 (C_{3v})	1092_I-997_{II}-956_{III}	–	872	–
MMH1 (C_1)	1142_a-1085_s	765	1001	3931

[a] a: asymmetric stretch; s: symmetric stretch; I and II: symmetric stretches of two P=O and other one asymmetric; III: symmetric stretch of three P=O.

adsorbed complex. This procedure has limitations, such as the phosphate bidentate $(FeO)_2PO_2$ complex cannot be distinguished from the monodentate monoprotonated $(FeO)(OH)PO_2$ because both satisfy the same C_{2v} symmetry. An adsorbed phosphate, due to its coordination with the surface and its interaction with surface hydroxyls, generally shows less symmetry compared to the free species. Therefore, taking into account our theoretical frequencies for the different adsorbed phosphate complexes studied, we achieve to an alternative description of experimental spectra.

Making a direct comparison between our theoretical frequencies and the results of Persson et al. [10] we arrived to several correlations. At low pH values the bands at 1178 and 1001 cm^{-1} can be assigned to P=O and P—O_H stretching bonds of BMH1 species, respectively (see Table 3). For the first band our theoretical value is 1150 cm^{-1}, which shows a small red shift 20 cm^{-1}, related possibly to the high sensibility of band position to the water content in goethite samples and to the influence of H bonding between complexes and water molecules [10]. This inference arises from considering the difference in band positions in Tejedor-Tejedor and Persson spectra, obtained from goethite samples pretreated in a different way [9,10]. The band position can undergo important shifts if a significant number of water molecules are taken into account in the frequency computation [29,34]. In our approach, the increase of this number from 5 to 10 molecules did not modify appreciably the frequency values. This observation is in agreement with previous results obtained by Kubicki et al. [29] for carbonates adsorbed on a goethite cluster.

Between pH = 4.2 and pH = 7.9, several experimental peaks and non-well resolved bands are observed, due likely to the coexistence of at least two species [10]. At pH = 5.2 two well resolved bands began to appear at 1122 and 1047 cm^{-1}, whose signals are intensified at pH = 5.7. These peaks could be assigned to the stretching of P=O and P—O_H bonds of our modeled BBH1 species. Hence, in this pH range two species, BMH1 and BBH1, coexist. At pH = 7.9, the BMH1 band disappear whereas that corresponding to BBH1 persists with low intensity. At high values, pH = 12.8, the bands at 1057 and 966 cm^{-1} can be assigned to the asymmetric and symmetric modes of P=O bonds for the BBH0 species, respectively. The corresponding computed frequencies are at 1066 and 970 cm^{-1}. The agreement is enough satisfactory, taking into account that some discrepancy could be expected owing to anharmonic effects [35].

In addition to the specific analysis of each phosphate band, a correlation between calculated and experimental frequencies was performed in order to corroborate the assignations accomplished before. In Table 1 the corresponding parameters for a linear correlation are summarized. For that purpose, only those theoretical frequencies with values close to the resolved experimental bands were compared in the correlation. In Fig. 3, schematic views for the phosphate complexes with better correlation are shown. At pH = 3.1, the experimental bands at 1178 and 1001 cm^{-1} exhibit better correlation with the BMH1 species rather than with the MMH1 one. The experimental bands measured at pH = 4.2, appearing at 1122 and 1049 cm^{-1}, could be attributed to BBH1, MBH1 or MMH1 species. The linear correlation results indicate that the phosphate complex giving the best band description is the BBH1 species. On the other hand, the bands registered at pH = 12.8, appearing at 1058 and 966 cm^{-1}, could be attributed to BBH0, BMH0, MBH0 or MMH0 species. In this case, the correlation indicates that the BBH0 species is the closest to the experiments. Finally, in the pH interval form 4.2 to 7.9, we have the BBH1 species.

These assignations differ noticeably form those proposed by Persson et al. [10]. From low to high pH values, these authors suggest that, based on symmetry arguments, the experimental bands above commented are due to MMH2, MMH1 and MMH0 monodentate species. The bands appearing at 1178 and 1001 cm^{-1} are

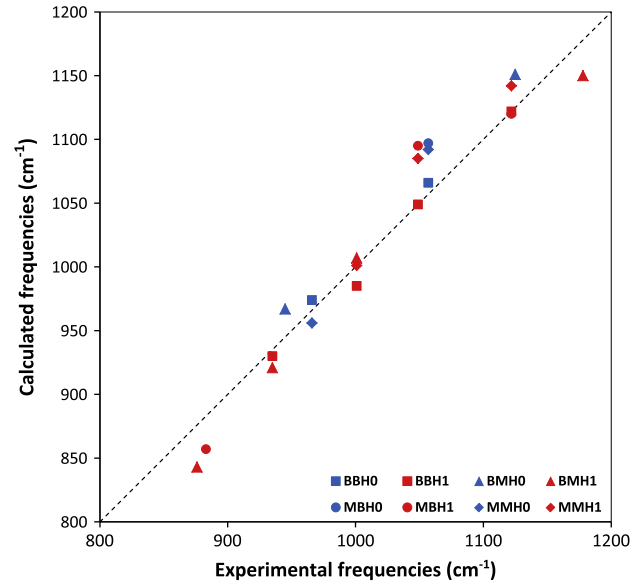


Fig. 3. Correlation between experimental and calculated frequencies of our models of phosphate surface complexes.

attributed only to species with C_{3v} symmetry. Consequently, they assume that the phosphate tetrahedron of MMH2 species would present negligible distortions, i.e., from a symmetry point of view, the O—Fe ligand would be equivalent to the other two O—H ligands. Notice that three of the four computed frequencies for modeled BMH1 species, appearing at 1150, 1007 and 843 cm^{-1}, are placed in the range of measured frequencies. Therefore they could be attributed erroneously to a phosphate species with C_{3v} symmetry, which that also present three bands. We underline that this species has not been theoretically studies before. An analogous reasoning was applied by these authors for the assignation of bands at higher pH values to the MMH0 species, also with C_{3v} symmetry. Nevertheless, we want to emphasize that surface phosphate complexes decrease their symmetry compared to the free species.

Our phosphate band assignations also differ from those made by Kwon and Kubicki, based on a goethite cluster constructed by two edge-sharing iron octahedral units [15,29]. They assigned the measured bands at pH = 4–6, 7.5–7.9 and 12.8, to the BBH2, MMH1 and MMH0 species, respectively. More specifically, according to these authors, the bands at pH = 4.2 appearing at 1178, 1122, 1049, 1001 and 876 cm^{-1} would be originated only from the BBH2 species, whilst a careful examination of results obtained by Persson et al. [10] indicates that at pH = 3.1 the bands appearing at 1178, 1001 and 876 cm^{-1} are already present. Hence, it can be argued that at pH = 4.2 two species coexist, one giving the latter frequencies and another giving the other two, at 1122 and 1049 cm^{-1}. Our results clearly consider the presence of two phosphate species coexisting at pH values equal or higher than 4.2: BMH1, starting from pH = 3.1 and BBH1, starting from pH = 4.2. These two species should continue to coexist in equivalent contributions until pH = 5.7. At pH = 7.9 only the BBH1 species is preserved, and at higher pH, the new BBH0 species dominates IR spectrum, with only an insignificant contribution from BBH1. Finally, the BBH0 species is the unique present at the highest pH value, 12.8 (see Fig. 4). Q2

In another theoretical work by Rahnemaie et al. [16], the IR spectra of Tejedor-Tejedor and Anderson [9] have been also interpreted. These authors deduced, by means of an interfacial change distribution approach, that at low pH values the most probable species would be MMH1, whereas for higher pH values they suggest the BBH0 species. These results are not in complete agreement with the proposals by Tejedor-Tejedor and Anderson [9], because

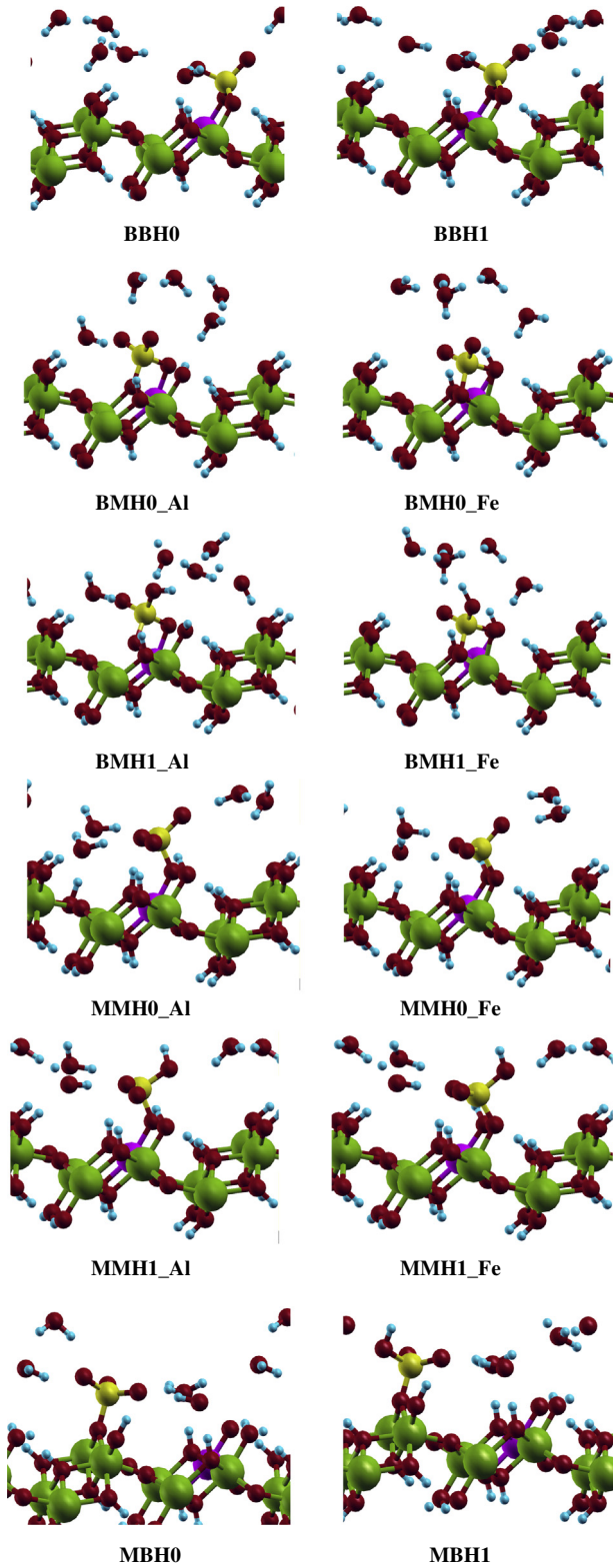


Fig. 4. Optimized geometries of all phosphate complexes formed on (110) Al-goethite surface.

at low pH values the IR bands were attributed to the BBH1 species and not to the MMH1 one.

It is outstanding to take into account that the results obtained in the present work are concerned with all the possible reactions of phosphate with goethite exposing only the (110) face, whilst the experimental data are obtained from synthetic goethite samples, where more than one crystallographic plane are exposed. Recently, FTIR spectra were performed for phosphate adsorbed on microgoethite and nanogoethite samples [12]. The authors showed that the changes observed in band positions could be attributed, at least in part, to the variations in different exposing facets between samples.

3.2. (110) Al-goethite surface

All the results obtained with our model for the phosphate complexes adsorbed on Al-goethite surface are summarized in Table 4. On this surface, some phosphate complexes can be formed on sites including only an atom of Al instead of Fe. This is the situation for the BMH0, BMH1, MMH0 and MMH1 mononuclear species. For all these cases, the reaction energies on both Fe and Al atoms were calculated (see Table 4).

The P=O bonds of these phosphate species have practically the same distances than the corresponding complexes on pure goethite. For MMH0 adsorbed on Fe, P=O distances have a difference of 0.03 Å with respect to goethite, but this difference increases at 0.06 Å when it is adsorbed on the Al atom. As it was observed on pure goethite, the P—O_H bonds are shorter for bidentate complexes, BBH1 and BMH1, and slightly longer for monodentate complexes, MBH1 and MMH1, than for phosphoric acid.

Usually, the O_s—Al bonds of bidentate phosphates are shorter than the O_s—Fe bonds and both distances are longer in bidentate phosphates than the corresponding distances in monodentate phosphates. Notice that, for almost all phosphate complexes formed on both goethite and Al-goethite, the P—O_s bonds show opposite behavior, with the exception of the BM species bonded to the Al atom of Al-goethite. In latter cases, the O_s—Al distances are lower, ~0.1 Å, compared to the same species formed on the Fe atom. For the BM species, the P—O_s bond linking to the goethite O atom is longer than the P—O_s bond linking to the O atom of the surface hydroxyl group. Furthermore, these complexes have lower stability, compared to the BB species due to their extremely constrained geometries.

In general, the bidentate complexes formed on Al-goethite surface are more stable than the corresponding phosphate species formed on pure goethite, with the exception of the BMH0 species, whose reaction energies are 0.5–0.7 eV smaller than the corresponding species on goethite. Instead, the monodentate complexes are less stable on Al-goethite than on goethite. The mononuclear complexes formed on the Al atom have always lower reaction energies than the complexes formed on the Fe atom on Al-goethite.

We observed that the P—O_s bonds of phosphate complexes could be associated with their reaction energies, as it was also previously found on pure goethite. When the P—O_s bond is shortened, the phosphate complex formed on this surface becomes more stable. The most stable phosphate species formed on Al-goethite are: BBH0, BBH1, MBH1 and MMH1. We note that neither previous experimental data nor theoretical investigations related with the phosphate species adsorbed on Al-goethite, was found in the open literature to be compared with our studies.

The Bader charges of phosphate species on Al-goethite are also summarized in Table 2. The amount of negative charges for the bidentate complexes decrease in the following order: BMH0 > BBH0 > BMH1 > BBH1, whereas the values of monodentate complexes decrease in the order: MMH0 > MBH0 > MMH1 > MBH1. In both cases, the mononuclear species anchoring present more negative values than the binuclear species anchoring. The PO_4H_x charges are nearly −2.0*e* for non-protonated bidentate species and nearly −1.5*e* for mono-protonated bidentate species. Instead, the net charges of PO_4H_x complexes are approximately −1.7*e* for non-protonated monodentate species and −1.2*e* for protonated monodentate species. The complexes formed on the Al atom have

Table 4
Reaction energies (E_{reac} in eV) and geometrical parameters (in Å) of phosphate complexes formed on (1 1 0) Al-goethite surface.

PO_4 complex*	E_{reac}	d(P=O)	d(P—O_H)	d(P—O_s)	d(O_s—Fe)	d(O_s—Al)
BBH0	−3.86	1.53/1.55	–	1.58	2.02	1.91
BBH1	−3.42	1.53	1.57	1.58	2.03	1.93
BMH0	−2.38	1.52	–	1.60/1.66	2.05/2.22	–
BMH0 (Al)	−2.08	1.52		1.59/1.64	–	1.92/2.16
BMH1	−2.20	1.52	1.55	1.58/1.63	2.05/2.27	–
BMH1 (Al)	−2.23	1.53	1.56	1.58/1.62	–	1.92/2.19
MBH0	−1.44	1.53	–	1.66	1.99	–
MBH1	−3.26	1.52	1.64	1.60	2.04	–
MMH0	−2.64	1.53/1.56	–	1.59	1.95	–
MMH0 (Al)	−2.46	1.51/1.57	–	1.59	–	1.85
MMH1	−3.62	1.54	1.61	1.56	2.00	–
MMH1 (Al)	−3.42	1.54	1.62	1.55	–	1.89

* In parenthesis the Al atom where the phosphate complex is linked.

more negative charge than those formed on the Fe atom. As it was found on pure goethite, the charge values are dependent on the anchoring type with the surface and on the protonation degree. All these values are slightly more negative when the phosphate complexes are linked on Al-goethite surface than when they are on pure goethite.

As it was observed on pure goethite, the adsorbed phosphate species does not modify significantly the ion magnetic moments in Al-goethite. Besides, the magnetic moments of O atoms surrounding Fe and Al atoms where the phosphate is adsorbed, undergo only slight changes.

Vibrational frequencies for phosphate complexes adsorbed on Al-goethite surface are summarized in Table 5. Unfortunate there are no experimental results for comparison with our calculations; notwithstanding, we analyzed the obtained vibrational frequencies and then, they were compared with the corresponding values for phosphate species on pure goethite. For BMH0 species, significant differences in the frequency positions were observed, depending on which site the phosphate is linked. The BMH0 mode for pure goethite at 1176 cm^{-1} is displaced toward 1135 cm^{-1} when this species is adsorbed on the Al atom. This peak corresponds to the P=O asymmetric stretching, whereas the symmetric stretching remains unchanged. Besides, the O_s—P stretching vibrations are blue shifted by more than 50 cm^{-1}. In case of the MMH0 species linked to the Al atom, the band corresponding to the symmetric stretching of two P=O combined with another one asymmetric, shifts to a higher value in comparison with the linking to the Fe atom. On the other hand, the second stretching frequency mode for this system shifts to a lower value than MMH0 on the Fe atom. Taking into account that the frequency range where phosphate complexes are measured and the species lightly present at high pH values, we expect that both the BBH0 and MMH0 species could hardly be distinguished from each other, with the exception of using high resolution spectra. The experimental spectra showed broadbands [9–12]; nevertheless, if such high quality spectra could be acquired, the MMH0 on Al atom would be distinguishable with respect to the others two non-protonated species. The remaining non-protonated complexes show some frequency shifts that allow the assignation of correct species without difficulty.

On the other hand, at low pH values the most expected species should be the protonated ones. The phosphate complexes, which can be linked to the Fe or Al atom, present bands with little differences between them. Therefore, both BMH1 and MMH1 species could not be distinguishable by the site where they are formed. As it was mentioned above, the IR spectrum must be obtained with high resolution to be able to assign on which atom the mono-protonated species is formed: on Fe or Al. On the other hand, the remaining protonated species are clearly identified.

In general, we note that a slight shift of ±20 cm^{-1} can be observed in many phosphate frequencies. These changes can be related to very small variations of the adsorption geometries generated by the substitution of Fe atom by Al atom (see Tables 1 and 4). However, other more relevant changes take place in case of BMH0 and MMH1 complexes. Despite that the respective geometrical modifications are similar to those commented above, stronger interactions are involved for the latter complexes, yielding to greater frequency changes. They can be associated to the H bonding between O atom of phosphate P=O and H atom of Al-goethite surface, which are not observed on pure goethite surface. From these results, it can be notice that the phosphate-goethite interaction is highly depended of the surface hydration degree. The H bonding established between phosphate and surface hydroxyls affects markedly the phosphate vibrational frequencies, with significant shift of ±50 cm^{-1}. Fitted ATR-FTIR data for phosphate adsorbed on dried microgoethite and nanogoethite surfaces showed that some bands changed their positions or disappeared in comparison with those of wet microgoethite and nanogoethite samples [12].

Table 5
Vibrational frequency assignments for phosphate complexes adsorbed on (110) Al-goethite surface (in cm^{-1}).

PO_4 complex	ν(P=O)*	ν(P—O_H)	ν(O_s—P)*	ν(O—H)*
BBH0 (C_{2v})	1057_a-1013_s	–	950_a-902_s	–
BBH1 (C_1)	1144	1042	962_a-919_s	2404
BMH0	1176_a-1061_s	–	861_a-769_s	–
BMH0 (Al)	1135_a-1064_s	–	919_a -840_s	–
BMH1	1145	1097	933_a-842_s	1602
BMH1 (Al)	1162	1052	949_a-857_s	3103
MBH0 (C_{3v})	1084_I-1048_{II}-998_{III}	–	829	–
MBH1 (C_{2v})	1138_a-1078_s	828	918	4054
MMH0	1054_I-996_{II}-964_{III}	–	892	–
MMH0 (Al)	1097_I-966_{II}-942_{III}	–	921	–
MMH1	1064_a-1048_s	1018	950	4097
MMH1 (Al)	1073_a-1059_s	1016	1010	4113

* a: asymmetric stretch; s: symmetric stretch; I and II: symmetric stretches of two P=O and other one asymmetric; III: symmetric stretch of three P=O.

4. Conclusions

In this work the phosphate adsorption on pure goethite and on Al-rich goethite surfaces was evaluated. The ensemble of cases here considered for adsorbed phosphate complexes on pure goethite is larger than in earlier theoretical papers because all the possibilities were included. Taking into account that our surface model corresponds to a hydroxylated goethite surface, not highly hydrated, the results were compared with specific experimental results [10]. The most satisfactory correlation was obtained by assigning the BMH1, BBH0 and BBH1 species to the experimental

bands observed at pH = 3.1, pH = 4.2–7.9 and at pH = 12.8, respectively. The results reported here give a new interpretation to experimental bands found in open literature for phosphate on goethite.

On the other hand, the vibrational frequencies of phosphate complexes adsorbed on Al-rich goethite were also calculated. These results are useful because they will allow the assignation by experimentalists to the bands obtained in FTIR spectra for phosphate complexes adsorbed on Al-rich goethite at 12%/mol content. The hydration degree of both goethite and Al-goethite surfaces is an extremely important factor for defining the phosphate band shifts, because in this situation other interactions arise between phosphate complexes and surface H atoms. For this reason, another surface model is probably necessary to explain the Tejedor-Tejedor and Anderson [9] spectra, where pre-adsorbed water molecules are included.

Acknowledgements

The authors thank the financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the Agencia de Promoción Científica y Tecnológica (ANPCyT) and the Universidad Nacional del Sur (UNS).

References

[1] H. Klapper, Control of Eutrophication in Inland Water, Ellis Horwood, Chichester, 1991.
[2] Q. Zhou, C.E. Gibson, Y. Zhu, Chemosphere 42 (2001) 221–225.
[3] N. Nilsson, L. Lövgren, S. Sjöberg, Chem. Spec. Bioavail. 4 (1992) 121–130.
[4] L. Sigg, W. Stumm, Colloids Surf. 2 (1981) 101–117.
[5] N. Khare, D. Hesterberg, S. Beauchemin, S.-L. Wang, Soil. Sci. Soc. Am. J. 68 (2004) 460–469.
[6] T. Hiemstra, W.H. Van Riemsdijk, J. Colloid Interface Sci. 179 (1996) 488–508.
[7] R. Strauss, G.W. Brümmer, N.J. Barrow, Eur. J. Soil Sci. 48 (1997) 101–114.
[8] Y. Kim, R.J. Kirkpatrick, Eur. J. Soil Sci. 55 (2004) 243–251.
[9] M.I. Tejedor-Tejedor, M.A. Anderson, Langmuir 6 (1990) 602–611.
[10] P. Persson, N. Nilsson, S. Sjöberg, J. Colloid Interface Sci. 177 (1995) 263–275.
[11] C. Luengo, M. Brigante, J. Antelo, M. Avena, J. Colloid Interface Sci. 300 (2006) 511–518.
[12] J.D. Kubicki, K.W. Paul, L. Kabalan, Q. Zhu, M.K. Mrozik, M. Aryanpour, Langmuir 28 (2012) 14573–14587.
[13] P.A. Connor, A.J. McQuillan, Langmuir 15 (1999) 2916–2921.
[14] Y. Arai, D.L. Sparks, J. Colloid Interface Sci. 241 (2001) 317–326.
[15] K.D. Kwon, J.D. Kubicki, Langmuir 20 (2004) 9249–9254.
[16] R. Rahnemaie, T. Hiemstra, W.H. van Riemsdijk, Langmuir 23 (2007) 3680–3689.
[17] N.Y. Acelas, S.M. Mejia, F. Mondragón, E. Flórez, Comp. Theor. Chem. 1005 (2013) 16–24.
[18] K.W. Paul, J.D. Kubicki, D.L. Sparks, Eur. J. Soil Sci. 58 (2007) 978–988.
[19] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558–561.
[20] G. Kresse, J. Hafner, Phys. Rev. B 48 (1993) 13115–13118.
[21] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
[22] P. Blöchl, Phys. Rev. B 50 (1994) 17953–17979.
[23] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758–1775.
[24] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Phys. Rev. B 57 (1998) 1505–1509.
[25] S.A. Fuente, P.G. Belelli, N.J. Castellani, M. Avena, Mater. Chem. Phys. 137 (2013) 1012–1020.
[26] J.R. Rustad, A.R. Felmy, B.P. Hay, Geochim. Cosmochim. Acta 60 (1996) 1563–1576.
[27] B. Russell, M. Payne, L. Colombi, Phys. Rev. B 79 (2009) 165101–165114.
[28] J.B. Forsyth, I.G. Hedleys, C.E. Johnson, J. Phys. C (Proc. Phys. Soc.) 1 (1968) 179–188.
[29] J.D. Kukicki, K.D. Kwon, K.W. Paul, D.L. Sparks, Eur. J. Soil Sci. 58 (2007) 932–944.
[30] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502–16513.
[31] P. Canepa, R.M. Hanson, P. Ugliengo, M. Alfredsson, J. Appl. Cryst. 44 (2011) 225–229.
[32] R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Oxford Science, Oxford, UK, 1990.
[33] S.K. Ghose, G.A. Waychunas, T.P. Trainor, P.J. Eng, Geochim. Cosmochim. Acta 74 (2010) 1943–1953.
[34] J.R. Bargar, J.D. Kukicki, R. Reitmeyer, J.A. Davis, Geochim. Cosmochim. Acta 69 (2005) 1527–1542.
[35] J.D. Kubicki, K.W. Paul, D.L. Sparks, Geochem. Trans. 9 (2008) 4–16.