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Modelling the adsorption of uranyl on the surface of goethite

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Abstract—Atomistic simulations have been carried out to study the adsorption of the hydrated uranyl ion on a variety of faces of goethite (α -FeOOH). The relative stabilities of these faces have been assessed by calculation of the corresponding surface energies. We find that adsorption onto dry stable surfaces yields structures of variance with extended X-ray absorption fine structure data, whilst adsorption onto hydrated (110) and (001) surfaces yields structures compatible with these data. Copyright © 2002 Elsevier Science Ltd

1. INTRODUCTION

Understanding the mechanism by which very abundant reactive mineral surfaces interact with environmentally sensitive elements such as uranium is of considerable importance. Fe-oxyhydroxides occur as components of muds in oxidising environments at or near the surface and in the reducing environment just below the surface. Goethite, α -FeOOH, is the commonest form of Fe-oxyhydroxide, and its surface chemistry is particularly important to soil science. The small size of goethite crystals means that their surfaces may account for 50 to 70% of the total surface area of soil (Schwertmann and Taylor, 1989). Sorption onto geological materials has been suggested as a major removal mechanism for trace contaminants in natural waters, with goethite having a particularly high affinity for the sorption of many cations and anions (Cornell and Schwertmann, 1996).

Oxide surfaces in general react through surface complex formation. The sorption of cations at low pH is minimal but increases with increasing pH, whilst this process is reversed for anions. A number of studies have indicated that at high pH, the uptake of Cu(II) is associated with the release of two protons from the mineral surface, leading to Cu(II) forming inner-sphere complexes with the goethite surfaces. Barrón and Torrent (1996) observed singly coordinated OH groups on the (100), (010), (110), and (021) faces of goethite, and it has been suggested that these groups are related to the formation of bidentate surface complexes with phosphates and other anions (Parfitt et al., 1975; Goldberg and Sposito, 1985). Infrared spectroscopy has provided evidence for the formation of a bidentate (FeO)₂POOH bridging surface complex, which is further supported by the slow exchange of the sorption species. Hayes et al. (1987) also suggested that selenium binds to the goethite surface via a bidentate mechanism. A number of studies involving actinides have been reported. Nakayama and Sakamoto (1991) studied the sorption of neptunium onto naturally occurring iron-containing minerals and observed that the uptake by biotite and goethite increased with increasing pH. Combes et al. (1992) predicted an inner-sphere complex for the

binding of Np(V)O₂⁺ on goethite surfaces. Hsi and Langmuir (1985) measured the absorption of uranyl onto ferric oxyhydroxides and found that all the iron oxide material strongly absorbed dissolved uranyl species for pH values above 5 and 6, with an associated loss of between two and three protons per uranyl sorbed. Waite et al. (1994) conducted a study of the adsorption by ferrihydrite of U(VI) over a wide range of concentrations and pHs and by using a surface complexation model, they concluded that an inner-sphere bidentate complex of the type (\equiv FeO₂)UO₂ was formed. The existence of this species was further supported by extended X-ray absorption fine structure (EXAFS) data, which suggested various U–O bonds: two at 1.80 Å, three at 2.35 Å, and two at 2.52 Å. The experimental data suggested an Fe–U nearest-neighbour distance of 3.41 Å, with no evidence of U–U nearest neighbours. Moyes (1998), using EXAFS, found seven U–O distances. Five were at 2.38 Å and two at 1.79 Å, with an Fe–U distance of 3.49 Å calculated.

The bulk goethite structure consists of double rows of edge-sharing Fe-octahedra, which parallel the [001] direction and are two octahedra wide in the [010] direction. Octahedral rows are separated along the [010] and [100] directions by vacant double rows that also run along the [001] direction. The rows are connected to one another by sharing apical oxygen atoms. The structure of goethite is represented in Figure 1.

Goethite has a perfect cleavage on (010) as well as common growth faces on (110), (120), (111), (011), and (101). Rakovan et al. (1999) studied a number of the goethite cleavages. From low-energy electron diffraction results, they found that the (010) surface has long-range atomic ordering, with a symmetry that is consistent with the bulk structure perpendicular to the b-axis, but these experimental results gave no information as to where the surface plane intercepts the b-axis. Rakovan et al. employed ab initio and semiempirical models of the (010) surface to determine through which charge neutral plane cleavage occurred. Their results indicated that it occurred through the hydroxide plane.

In this paper we use atomistic modelling methods to study the interactions of uranyl with goethite surfaces, which necessitates some force field parameterisation. We first model the bulk and surface structure of this mineral, with particular em-

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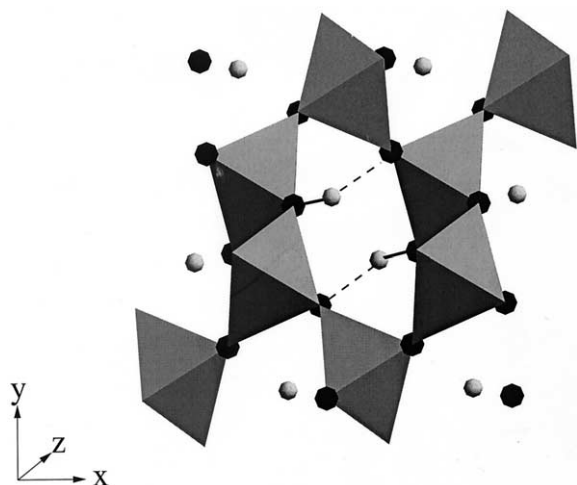


Fig. 1. Polyhedra representation of Fe(III) in octahedral coordination in the bulk goethite structure.

phasis on different cleavage planes, and then model uranyl adsorption onto a number of such surfaces.

2. COMPUTATIONAL DETAILS

2.1. Force Field Parameterisation

We use interatomic potential functions to model the interactions between the atoms and ions within the systems. These potential functions describe the energy of the system in terms of atomic positions and include contributions from ionic, covalent, and van der Waals interactions. For ionic or semi-ionic materials, the dominant contribution to the cohesive energy arises from the Coulombic or electrostatic term. This is evaluated using an Ewald transformation for bulk calculations (Ewald, 1921) and the corresponding two-dimensional version for the simulation of surfaces (Tosi, 1964; Parry, 1975, 1976). As ions are not simple point charges, the short-range repulsive interactions produced by the overlap of nearest-neighbour electron clouds must also be considered. Such short-range, non-bonded interactions are modelled within this study using a Buckingham potential, which has both repulsive ($A\exp[-r/\rho]$) and attractive dispersive (C/r^6) contributions, in common with the Lennard-Jones potential. The corresponding bonded interactions are treated using a Morse function (Saul et al., 1985),

which, unlike a classical harmonic potential, correctly describes dissociation. Extra angular dependent forces were included using a three-body harmonic term. In addition, polarisation of the oxygen ions was included using the shell model (Dick and Overhauser, 1958). Here, the charge cloud of the ion can be polarised by its surrounding ions, allowing it to become nonspherical and creating a dipole on the ion. The minimum energy structures and corresponding energetics of the bulk were accomplished using the General Utility Lattice Program (GULP) (Gale, 1998) code, which implements three-dimensional periodic boundary conditions. The surface calculations were performed using the Minimisation and Relaxation of Vacancies and Interstitials for Neutral Surfaces program (Gay and Rohl, 1994), which considers the crystal to consist of planes of atoms, periodic in the two dimensions parallel to the surface and finite in the direction perpendicular to the surface.

Some parameterisation of the force field to be used was found to be required. The Fe–O, Fe–OH, and H–OH Buckingham A parameters within the goethite structure were refitted to the crystal structure. The values of the ρ parameter, which are largely unaffected by the chemical environment, were taken from a previous study (Lewis et al., 1995). All reparameterisation, designed to improve agreement with experimental bulk constants, was performed within GULP by a least squares fitting procedure. The final force field used is given in Table 1.

A two-body U–O Morse function and a three-body O–U–O bending term for the uranyl (UO_2^{2+}) species were parameterised by fitting to the potential energy surface generated by a number of electronic structure calculations at a range of U–O separations and O–U–O angles. Here, the Moller-Plesset second-order perturbation (MP2) level of theory was used (Hehre et al., 1986), employing a 3–21g basis set on all atoms except uranium, for which an SDD pseudopotential was used. All electronic structure calculations were performed using the Gaussian98 program (Frisch et al., 1998). These calculations gave a U–O bond length of 1.783 Å, which compared well with a number of previous theoretical studies (van Wezenbeek et al., 1991; Pyykkö et al., 1994; Craw et al., 1995; Cornell and Schwertmann, 1996; Spencer et al., 1999) and is in agreement with the accepted experimental value. The force field generated by fitting to the potential energy surface gave a U–O distance of 1.800 Å and predicted UO_2^{2+} to be linear, with calculated harmonic frequencies of 1062, 234, and 1134 cm^{-1} , which correspond to symmetric stretch, bend, and antisymmetric stretch. The corresponding values from Craw et al. (1995) are

Table 1. Interatomic potentials for α -FeOOH.

Two-body short-range potentials			
	A/eV	$\rho/\text{\AA}$	C/eV \AA^6
Buckingham			
Fe ³⁺ – O ²⁻	1204.00	0.3299	0.000
Fe ³⁺ – O ^{-1.426}	870.00	0.3299	0.000
H ^{0.426+} – O ²⁻	280.97	0.2500	0.000
H ^{0.426+} – O ^{1.426-}	311.97	0.2500	0.000
O ^{1.426-} – O ^{1.426-}	19864.00	0.1490	27.880
Morse	D _e /eV	$\beta/\text{\AA}^{-1}$	R _e / \AA
H ^{0.426+} – O ^{1.426-}	7.0525	2.1986	0.9485
Shell model interaction			
	$\gamma/ e $	K/eV \AA^{-2}	
O ²⁻	-2.869	74.9200	

Table 2. Uranyl force field.

Two-body short-range interaction				
Morse	D_0/eV	$\beta/\text{\AA}^{-1}$	$R_0/\text{\AA}$	Cutoff/ \AA
$U^{6+} - O^{2-}$	0.3898	2.19838	1.783	0.00 to 2.00
Buckingham	A/eV	$\rho/\text{\AA}$	$C/eV\text{\AA}^6$	
$U^{6+} - O^{2-}$	3500.00	0.34123	0.00	0.0 to 12.0
$U^{6+} - O^{1.426-}$	2500.00	0.34123	0.00	0.0 to 12.0
$U^{6+} - O^{0.852-}$	1200.00	0.34123	0.00	0.0 to 12.0

1183, 264, and 1254 cm^{-1} for a Hartree-Fock calculation and 933, 154, and 962 cm^{-1} for an MP2 calculation.

The $U-O_{\text{water}}$ Buckingham potential was fitted to $UO_2^{2+} \cdot (H_2O)_x$ clusters optimised at the Hartree-Fock level, for x values of 4, 5 and 6. Up to two of the water ligands were substituted by hydroxyl groups, enabling the derivation of $U-OH$ parameters. The electronic structure calculations gave $U-O_{\text{water}}$ bond lengths for the $UO_2^{2+} \cdot (H_2O)_x$ of 2.40, 2.44, and 2.50 \AA for x values of 4, 5, and 6, respectively. The derived $U-O_{\text{water}}$ and $U-OH$ Buckingham functions reproduced these bond lengths to within 3%. All calculated parameters are given in Table 2. The water parameters used were those of de Leeuw and Parker (1997).

3. MODELLING SORPTION OF URANYL

Experimental data from Waite et al. (1994) and more recently from Moyes (1998) suggest that uranyl ions interact with goethite surfaces as a bidentate ligand, with at least one Fe atom at a distance of 3.5 \AA from the uranium centre. The two axial uranyl oxygens are at 1.8 \AA , and a further four or five oxygen atoms at ~ 2.4 \AA , from the uranium centre. Waite et al. (1994) observed a splitting of five oxygens into three at a distance of 2.35 \AA and two at a distance of 2.52 \AA . In our calculation, the sorption of uranyl ligands was investigated using sites on the (010), (110), and hydroxylated (001) surfaces. For each surface, supercells of an appropriate size were used to prevent the docked ligand from interacting with its periodic image. The number of unit cells required naturally depends upon the particular cleavage plane being studied and varies from two to six. Since it is known that uranyl compounds retain a number of their primary solvation waters when reacting, the actual sorption species modelled was a uranyl ion coordinated to three water molecules. This solvated uranyl species could then be docked along the goethite surfaces in a bidentate manner to two oxygen atoms associated with the goethite surface.

4. COMPUTATIONAL RESULTS

The a , b , and c unit cell parameters of goethite were reproduced to within 6% of the accepted experimental values of 4.596, 9.957, and 3.021 \AA , respectively, by the use of our force field (Table 1). The $Fe-OH$ and $Fe-O$ bond lengths of Forsyth et al. (1968) were also reproduced to within 3%. A measure of the stability of any surface may be obtained from its surface energy γ , which is defined as the work needed to cleave the crystal:

$$\gamma = \frac{U_s - U_b}{A} \quad (1)$$

Here, U_s is the energy of a number of atoms at the surface, U_b is the energy of an equivalent number of atoms in the bulk, and A is the surface area. The surface energies of the (010) perfect cleavage plane and of the abundant growth faces (110), (120), (101), and (111), as well as that of the less abundant (100) and (001) fundamental cleavage planes for both the relaxed and unrelaxed faces, are given in Table 3. A low value indicates a more stable surface.

The most stable surface is the (010) surface, where the surface termination is defined by the hydroxyl groups it divides into two. A schematic picture of the relaxed lowest energy structure is shown in Figure 2. Cutting at this depth produces a relaxed surface 57% more stable than cleavage through the corresponding oxide layer. The same trend was predicted by Rakovan et al. (1999), whose calculations gave surface energies of 1.76 and 2.26 J/m^2 for hydroxide and oxide termination, respectively. These compared to the energies of 1.26 and 3.17 J/m^2 calculated in this study for similar unrelaxed cuts. Figure 3 shows schematic sketches of each relaxed surface studied, with the coordination of the $Fe(III)$ centres at the surface indicated. The majority of the surfaces are composed of four and five coordinate $Fe(III)$ centers, with the least stable (001) surface completely composed of only four coordinate $Fe(III)$ centres.

Incomplete coordination of the exposed $Fe(III)$ ions at the surface is most likely responsible for the high surface energies of terminations, such as those of the (111) and (001) surfaces. $Fe(III)$ ions at these surfaces that are not fully coordinated will carry a net charge (q), the value of which can be simply calculated by assigning to each oxygen atom a charge of -2

Table 3. Calculated surface energies (J/m^2) of the goethite crystal.

Face	Cleavage depth (unit cell fractions)	Surface energy	
		Unrelaxed	Relaxed
(010)	0.250	3.17	1.89
	0.500	1.26	0.81
(101)	0.500	2.93	1.55
(120)	0.500	4.69	1.50
(110)	0.500	3.36	1.40
(001)	0.250	3.40	2.15
(111)	0.338	6.03	2.08
(100)	0.500	5.62	1.96
	0.250	11.63	1.99
	0.500	8.02	2.42

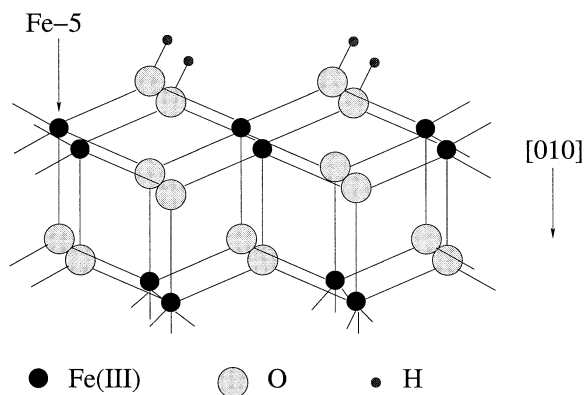


Fig. 2. Side view of the relaxed (010) surface, with the coordination number of the surface Fe(III) ions shown.

and to each hydroxyl group a charge of -1.0 , giving the charge on an Fe(III) surface ion:

$$3 - \left(a \frac{1}{x} (-2) + b \frac{1}{y} (-1) \right) = q. \quad (2)$$

Here, a and b are the numbers of Fe–O(H) bonds, and x and y

are the numbers of Fe(III) centres to which the oxygen and hydroxyl group is also bound. The value of 3 in the equation corresponds to the assigned cation charge. Eqn. 2 was used to calculate the residual charge on the iron centres that terminate the “dry” (110) and (001) surfaces. As iron hydroxide surfaces are known to hydrate easily, a full coordination shell and cancellation of this charge could be obtained by the addition of OH groups to the Fe(III) centres.

5. STRUCTURE OF URANYL SURFACE COMPLEX

5.1. (010) Surface

The most stable surface and correspondingly the most abundant surface of goethite is the (010) surface (Fig. 2), which consists of five coordinate Fe(III) atoms bound to bridging hydroxyl groups that lie parallel to the surface, slightly below which are fully coordinated oxygen atoms. The $\text{UO}_2^{2+} \cdot (\text{H}_2\text{O})_5$ species was initially docked between the two surface hydroxyl groups, and to ensure charge neutrality, two other surface hydroxyl groups had their protons removed and their assigned charge changed from -1 to -2 . This structure, when optimised, had two $\text{U}-\text{O}_{\text{surf}}$ distances of $\sim 2.5 \text{ \AA}$ and an Fe–U distance of 3.0 \AA . The experimentally measured Fe–U distance is close to 3.5 \AA . Other positions for the uranyl complex along

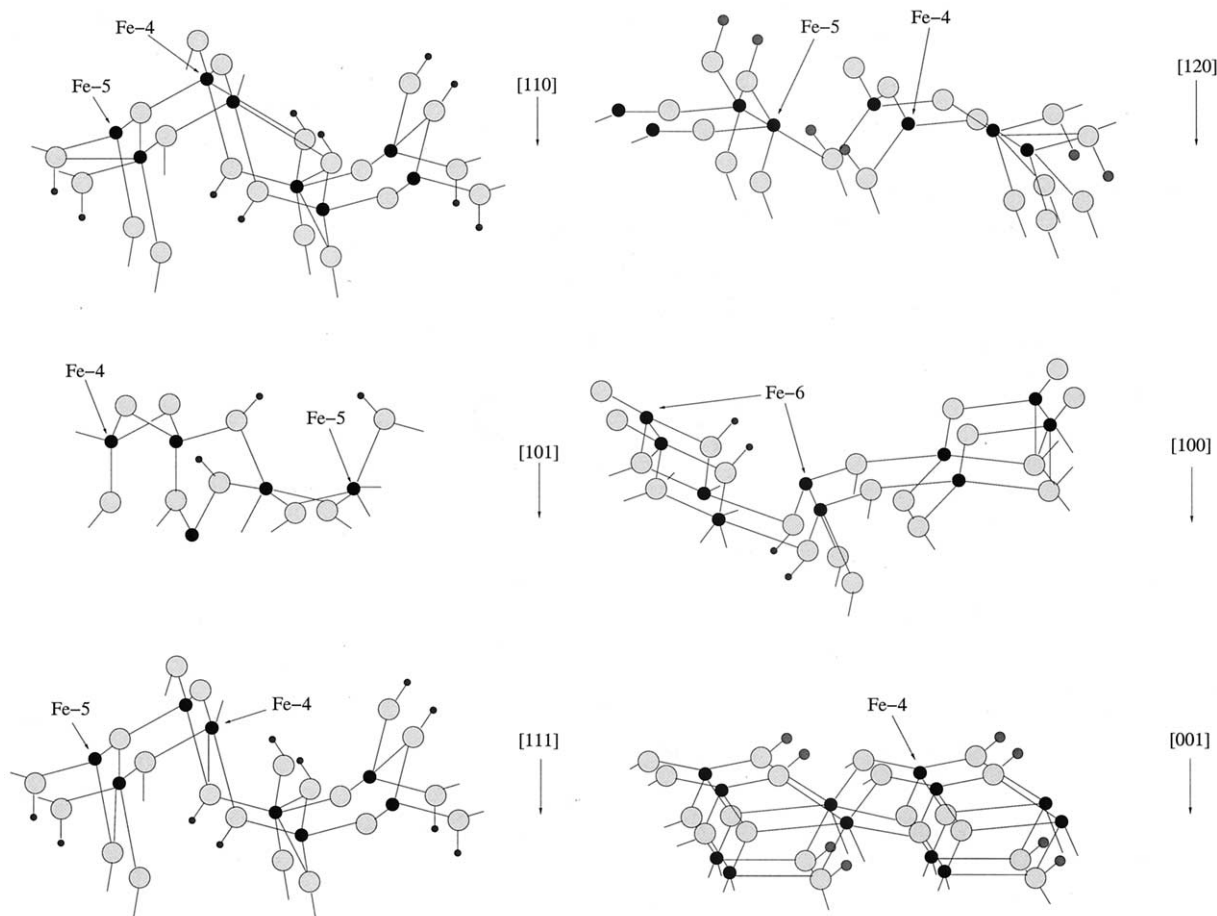


Fig. 3. A schematic view of the relaxed surfaces of goethite, with the Fe coordination number indicated.

the surface were sampled, but no sorption structure contained U–Fe nearest-neighbour distances in close agreement with those found experimentally. As a number of studies suggest that goethite surfaces are made up of a contiguous layer of singly coordinated OH groups, such a structure was modelled by reconstructing the (010) surface so that each bridging surface hydroxyl group was localised on a single Fe(III) centre and then relaxed. This singly coordinated surface was found to be 0.19 eV per unit cell (0.1%) less stable than the bridging configuration, and when UO_2^{2+} was docked on this surface, the Fe–U separation increased to 3.9 Å, a value considerably larger than experimentally obtained.

5.2. (110) Surface

The (110) surface is the second most stable goethite termination, having hydroxyl ions at the surface bound to fivefold coordinate Fe(III) ions and oxide ions bound to Fe(III) ions, with a total of four oxygen bonds (Fe-4), as shown in Figure 3. Two possible binding sites were studied. The uranyl molecule was first docked between the two uppermost oxide ions of the (110) surface, to which two hydroxyl groups had been added to maintain charge neutrality. The lowest energy relaxed structure had two U–O_{surf} distances of 2.48 Å and three U–O_{water} bonds of ~2.4 Å, with a nearest Fe–U distance of 2.68 Å. A second structure, with the hydrated uranyl ion binding between the two singly coordinated OH groups added to the Fe-4 sites, resulted in a minimum energy structure, with a longer U–Fe distance of 3.57 Å and two U–O_{surf} distances of 2.49 Å and three U–O_{water} distances of ~2.4 Å, giving a structure for adsorption on the hydrated (110) surface in closer agreement with the experimental atom-atom distances than was found using the (010) surface.

5.3. (001) Surface

The (001) surface has a relaxed surface energy of 2.15 J/m² and is therefore the least stable of all the surfaces considered here. The Fe(III) ions on the surface of the (001) plane are coordinated to only four O atoms, two OH and two O. The Fe(III) ions on the surface have an effective charge (Eqn. 2) of 0.5. Cancellation of this charge was achieved by the addition of both an extra OH group directly to each of the Fe(III) ions at the surface and a H⁺ ion to the surface oxygen atoms, thereby simulating the hydration of the (001) surface. The coordination of the Fe(III) ions now becomes five, and the charge becomes zero, with the overall surface remaining neutral and being stabilised. The uranyl species, with its waters of hydration, was docked between two hydroxyl groups, with charge neutrality being conserved by exchanging two hydroxide ions for oxide ions. For this structure (Fig. 4), the calculated U–Fe bond lengths (3.40 to 3.50 Å) are close to those found experimentally. In addition, the distances between the uranium atom and the oxygen atom of the two surface hydroxyl groups (2.5 Å) is somewhat longer than between the oxygen atoms of the water molecules and the uranium ion (2.4 Å). Such differences are in line with EXAFS data (Waite et al., 1994) and are consistent with uranyl binding to the hydrated surface.

6. DISCUSSION

A molecular mechanics approach has been used to study the adsorption of uranyl ions onto a selected number of fully

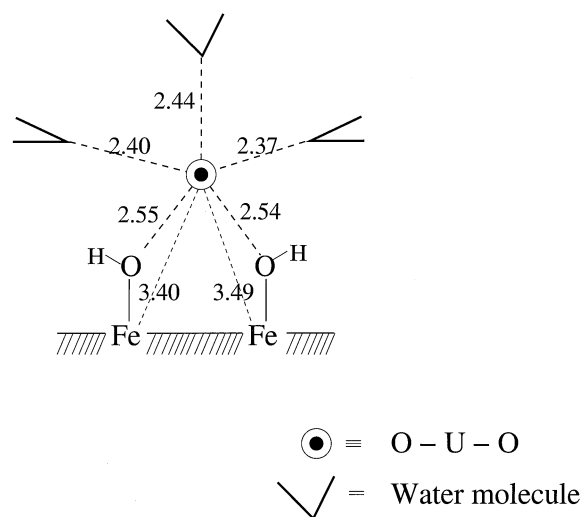


Fig. 4. A schematic view of the adsorption of uranyl onto the (001) surface of goethite. The distances shown are in angstroms.

periodic surfaces. This technique does not allow charge transfer to be modelled and relies upon the quality of the force field employed. However, the force field used here has been validated by its successful prediction of the bulk goethite structure, enabling a comprehensive study of the stable faces of goethite to be investigated. We find the order of stability to be (010) > (110) > (120) > (101) > (100) > (111) > (001), the most stable surface being the (010) perfect cleavage plane. The stability of this surface with respect to the other planes may be explained by there being no “unsaturated” charge on the Fe(III) ions that terminate this surface. The Fe atoms of the least stable (001) surface carry a charge of 0.5 because of incomplete coordination. This charge can be balanced by the addition of singly coordinated OH groups to the terminating Fe(III) ions and by the corresponding addition of H⁺ ions to the surface oxide groups; such hydration of the (001) surface stabilises it with respect to the “dry” surface.

Direct binding of the hydrated uranyl species to both the (010) and (110) nonhydrated surfaces results in sorption structures with U–Fe separations that are short compared to those found experimentally. The introduction of the products of water dissociation, OH[−] and H⁺, which stabilise the (110) and (001) surfaces, allows binding of the uranyl species via these singly coordinated OH groups. The sorption structures obtained now give much better agreement with experimental U–Fe distances than had been found for the “dry” and more stable (010) surfaces. A definite difference between the two sets of U–O bond lengths was found, with the distances to the surface oxygens being a little longer than those coordinated to water, in agreement with experiment. Agreement between our predicted Fe–U and U–O distances and experimental EXAFS data would suggest that the uranyl species is likely to be bound to the hydrated (110) or (001) surface rather than to the more abundant (010) face of goethite.

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