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Periodic Density Functional Theory Investigation of the Uranyl Ion Sorption on the TiO_2 Rutile (110) Face

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Periodic density functional theory calculations have been performed in order to study the uranyl ion sorption on the TiO_2 rutile (110) face. From experimental measurements, two uranyl surface complexes have been observed and the two corresponding sorption sites have been identified. However, from a crystallographic point of view, three different sorption sites can be considered on this face. The corresponding three surface bidentate complexes were modeled and optimized, and their relative energies were calculated. Only 5 kJ/mol separates the two most stable structures, which correspond to the experimental ones. The third surface complex is nearly 10 kJ/mol less stable, in agreement with the fact that it was not observed experimentally.

Within the framework of nuclear waste storage in a geological repository, the safety assessment requires a complete knowledge of the mechanisms involved at the aqueous solution−mineral interface. Because radionuclide migration through the geosphere is mainly governed by sorption and precipitation phenomena, it is of first importance to investigate these mechanisms. In this study, the retention process was investigated with both experimental and theoretical approaches. Atomic calculations can provide support to the experimental data by bringing complementary insights to better understand the interfacial interactions. The TiO_2 rutile (110) face has been chosen here as a methodological solid because (i) it is a sparingly soluble oxide, (ii) the (110) face is the most stable one (60% of the natural rutile powder) according to Jones and Hockey,[1] and (iii) single crystals are available for experimental investigations. In addition, the TiO_2 rutile substrate has already been the subject of several experimental and theoretical investigations (see the review paper in ref 2 and references cited therein). The uranyl ion, UO_2^{2+}, is an interesting adsorbate because it is a representative actinide molecular ion and, moreover, the U(VI)−TiO_2 (110) system has already been experimentally studied by grazing extended X-ray absorption fine structure (EXAFS).[3] This previous investigation gave structural information and thus allows one a direct comparison between experimental and further theoretical calculations. Current X-ray photoelectron spectroscopy (XPS) and time-resolved laser fluorescence spectroscopy studies have revealed that there are only two uranyl surface complexes on the TiO_2 rutile (110) single-crystal face.[4] Moreover, from the U speciation diagram, only the free aquo uranyl ion, $[UO_2(H_2O)_5]^{2+}$, can react with the surface sites at low pH. During the sorption process, two water molecules are lost and replaced by two surface O atoms. These experimental investigations[4] have allowed one to characterize the surface atoms involved in the interaction: the major surface complex corresponds to the uranyl ion sorbed between two O_b atoms (called in this study the *bb* site), while for the second one (the *bt* site), it is sorbed between one O_b and one added O atom on the top of a neighboring Ti(5) (see Figure 1).

In this study, all calculations were performed with periodic density functional theory (DFT) using the Vienna ab initio Simulation Package, VASP 4.6,[5] using the gradient-corrected formalism (GGA) as defined by Perdew and Wang (PW91)[6] for exchange-correlation energy evaluation. All atoms were described using pseudopotentials, taken from the VASP library, generated with the projector augmented wave[7] method, with U ($6s^26p^67s^25f^56d^1$), Ti ($4s^23d^2$), O ($2s^22p^4$),

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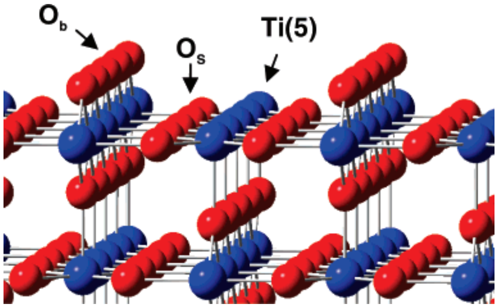

Figure 1. The dry TiO_2 rutile (110) face (Ti atoms in blue and O atoms in red).

and H ($1s^1$) valence electrons. For the U atom, relativistic effects are directly included in the exchange-correlation functional.[8] The Brillouin zone was integrated using the Monkhorst-Pack sets of k-points[9] centered at the Γ point. The bulk structural parameters have been determined and the convergence has been checked with respect to the number of k-points and the energy cutoff. For surfaces, all supercells were built from direct bulk cleavage and the atomic coordinates have been relaxed at constant volume by using the conjugate gradient method with a 300 eV energy cutoff. Adsorbates were introduced on only one side of the slabs.

The bulk rutile and the dry (110) face (Figure 1) were first studied. The unit cell was relaxed, and the optimized bulk parameters ($a = b = 4.649$ Å, $c = 2.972$ Å, and $x = 0.304$) were used to build the surface systems. The (110) face unit area is $a\sqrt{2} \times c$. The surface (110) is found to be more stable than the (100), (101), and (001) surfaces, in agreement with experimental observations[1] and previous theoretical calculations.[10] As already noted by Bates et al.[11] and Bredow et al.,[12] the surface energy of the fully relaxed slabs oscillates with the number of layers used in the model. However, by the introduction of internal constraints, obtained by freezing some of the most internal layers to the bulk positions, the surface energies and properties are stabilized from five-layer systems. Because the sorption process occurs in aqueous solution, the sorption of water should be established beforehand. According to recent XPS measurements,[13] a new O surface species (called here terminal oxygen, O_t) is created on the dry TiO_2 (110) face when water molecules are added (see Figure 2). Following the results obtained on the dry surface, the addition of internal constraints stabilizes correctly the sorption of water: the molecular sorption is supported compared to the dissociation. These results are in agreement with experimental data[14] and previous theoretical works.[15] These first steps lead to the selection of a five-layer system, with its most internal layer frozen to bulk positions, as a good hydrated surface model that will be used for studying of the sorption of the uranyl ion on a large surface. The details on the modeling of this hydrated surface will be given in an upcoming paper.[13]

Table 1. Pentahydrated Uranyl Ion $[UO_2(H_2O)_5]^{2+}$ Optimized from GGA Calculations (All Distances are in Å and Angles in Degrees)

	GGA	LDA[a]	MP2[b]	EXAFS[c]
U=O	1.78	1.77[d]	1.77	1.77 ± 0.02[d]
O=U=O	179.7	171	180	180
$U-O_{water}$	2.46[d]	2.41[d]	2.46	2.42 ± 0.02[d]

[a] Reference 16. [b] Reference 17. [c] Reference 3. [d] Average distances.

From EXAFS data,[3] the uranyl ion is known to be pentahydrated in aqueous solution while it sorbs as a bidentate complex with an inner-sphere mechanism (the U atom is directly linked with two surface O atoms) with three water molecules to saturate its first hydration shell (see Figure 2). Calculations were performed on the hydrated uranyl ion with several numbers of water molecules (up to six). Several structures with water molecules in the first and second hydration shells were considered. For these calculations, the molecular systems were placed in a (10 Å)^3 supercell with a 2+ net charge. The pentahydrated structure has been determined as the most stable one, and the optimized bond lengths are in good agreement with experimental data and previous theoretical calculations (see Table 1).

Looking at the hydrated (110) face, from a crystallographic point of view, two surface O types are supposed to be reactive (bridging and terminal), leading to three different possible bidentate sorption sites (see Figure 2): bridging-bridging (*bb*), bridging-terminal (*bt*), and terminal-terminal (*tt*). Experimentally, only two of them were observed with uranyl ions and attributed to bridging-bridging and bridging-terminal sites. In addition, for low pH (<3), the bridging-bridging site is the most reactive, but a stability inversion occurs when the pH increases (pH ≈ 4). This result shows that the reactivity between uranyl ions and these two sites depends clearly on the pH of the solution.[4]

The sorption simulations were performed on the hydrated surface model as defined previously. The surface dimension is $2a\sqrt{2} \times 3c$, equivalent to 13.2×8.9 Å^2 (the total supercell contains up to 200 atoms calculated at the Γ point). On this large surface, the uranyl ion should not interact with its images [$d(\text{U}-\text{U})_{\text{min}} = 8.9$ Å], in agreement with EXAFS data where no U−U interaction was detected.[3] Low-pH conditions were simulated by saturating, with protons, all reactive surface O species: terminal (bridging) O atoms were saturated with two (one) protons, while none were added when these O atoms were linked to the uranyl ion. Some additional DFT calculations have been performed in order to check these behaviors: the sorption energies are decreasing with the saturation of these O atoms by H atoms. Moreover, the first hydration sphere of the uranyl ion was saturated with three water molecules to keep its pentadentate equatorial structure. The three structures displayed in Figure 2 were optimized: the bond lengths were compared to the EXAFS results, and the relative uranyl sorption energies were calculated (see Table 2).

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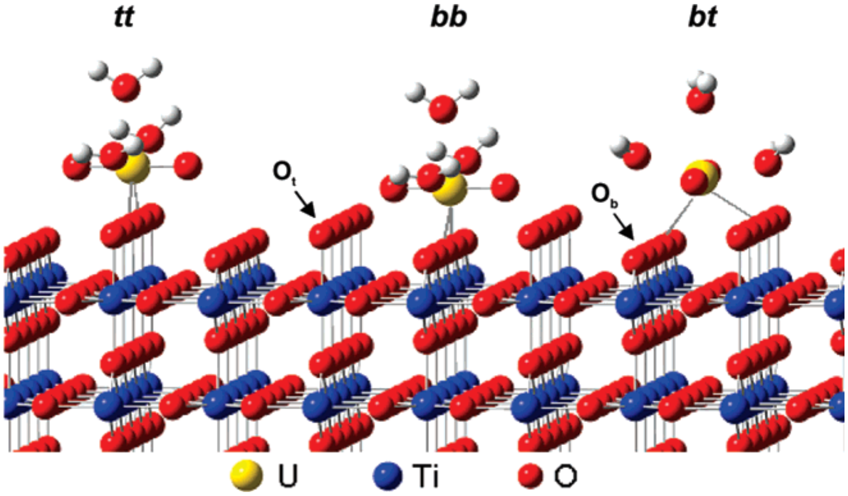

Figure 2. The three possible bidentate sorption sites for the uranyl ion on the TiO_2 rutile (110) face (from left to right): terminal-terminal (*tt*), bridging-bridging (*bb*), and bridging-terminal (*bt*). H atoms used to saturate the surface (on terminal and bridging O atoms) are not represented here for clarity.

Table 2. Optimized Geometries (Distances in Å, Angles in Degrees) and Relative Energies (in kJ/mol) for the Three Bidentate Sorption Sites

	bb	*bt*	*tt*	EXAFS[e]
U═O[a]	1.92	1.90	1.86	1.78 ± 0.02
O═U═O	167.0	172.4	176.1	180
$U-O_{surface}$	2.28[b]	2.21[b]/2.28[c]	2.17[c]	2.31 ± 0.02[a]
$U-O_{water}$[a]	2.59	2.62	2.64	2.46 ± 0.02
$E_{relative}$[d]	0.0	+5.0	+13.6	

[a] Average distances. [b,c] Average bond lengths with the bridging and the terminal oxygen atoms respectively. [d] The *bb* structure is taken as reference energy. [e] Reference 3.

The sorbed uranyl ion is not linear, contrary to the pentahydrated form, as was also recently calculated by Moskaleva et al. on alumina surfaces[16] (see Table 1). This bending decreases the overlap between the U atom and the two axial O atoms, leading to a larger U═O bond length: the more the uranyl ion is bent, the larger the U═O distances are. The easy bending of the uranyl ion is certainly related to the low bending frequency calculated (between 100 and 180 cm^{-1} according to the exchange-correlation functional used).[17] Such a lengthening is also partially due to the GGA formalism, which is known to slightly overestimate the distances. The local density approximation (LDA) leads to relatively shorter distances by up to 0.02 Å only. However, the GGA approximation provides more accurate energy than the LDA for molecular species. The calculations have thus been consistently performed in GGA. Furthermore, the $U-O_{water}$ distance overestimation (~0.15 Å) is certainly due to a lack of solvent effects. Finally, looking at the $U-O_{surface}$ distances, the EXAFS average distance (obtained from the two $U-O_{surface}$ bonds: 2.31 ± 0.02 Å) is consistent with the calculated average distances of the *bb* and *bt* structures (2.28 and 2.25 Å, respectively).

Regarding the relative sorption energies of the uranyl ion, it appears that the *bb* and *bt* structures are the most stable ones and are energetically very close. The third structure, the *tt* one, is nearly 10 kJ/mol less stable than the *bt* one, which is in agreement with the experimental results: only two uranyl surface complexes, on the two most reactive sorption sites (*bb* and *bt*), were observed on the TiO_2 (110) face. Finally, even if the two most stable surface complexes are close in energy, the uranyl sorption, on the *bb* site, corresponds to the most stable structure, which agrees with the experimental data.[4]

As a conclusion, the uranyl sorption site relative stabilities are well reproduced using this methodology for the three bidentate complexes. In addition, the atomic distances corresponding to the different kinds of chemical bonds are coherent with the experimental observations within an average error of ~0.1 Å. Having complementary experimental surface second-harmonic generation data of the uranyl sorption on the TiO_2 (001) face,[18] this theoretical approach will be used to provide support to the experimental interpretations. These combined approaches will contribute to a better understanding of the retention processes of radionuclides on the mineral surface through these model systems at the molecular level.

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