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Multiple Water Layers on AnO_2 {111}, {110} and {100} Surfaces (An = U, Pu); A Computational Study

Bengt E. Tegner and Nikolas Kaltsoyannis*

School of Chemistry, The University of Manchester,

Oxford Road, Manchester, M13 9PL, UK

*Correspondence: nikolas.kaltsoyannis@manchester.ac.uk

The geometries and energies of the adsorption of up to five layers of water on the {111}, {110} and {100} surfaces of UO_2 and PuO_2 are studied computationally with Hubbard U -corrected density functional theory.

Abstract

The geometries and energies of adsorption of up to five layers of water on the {111}, {110} and {100} surfaces of stoichiometric UO_2 and PuO_2 are studied computationally with Hubbard U -corrected density functional theory within the periodic boundary condition framework. The work builds on our recent study of the surface-bound water monolayers [J. Phys. Chem. C, **121**, 1675 (2017)], and the water geometries within this first layer are used as the starting point for the present calculations. Significant variations are found in the per-layer adsorption energies, as a result of differing extents of intra- and inter-layer hydrogen bonding. After the adsorption of several additional layers, the effect of the surface-bound water geometries diminishes, and the average adsorption energy per water molecule is c. 0.5-0.6 eV (similar to that in bulk water) irrespective of the surface.

Introduction

The reprocessing of UO_2 -based spent nuclear fuel in the UK has led to the accumulation, over several decades, of significant quantities of highly radioactive PuO_2 . Indeed, the UK holds about half the world's civil inventory of PuO_2 (126 tonnes Pu), stored as a powder in stainless steel containers, while the government decides its long term fate. Options include storage in a geological disposal facility, or reuse in mixed oxide fuel, but for the time being the material is kept in the steel containers pending a final decision. However, some have buckled, leading to the hypothesis that gas build up has occurred, which might be water vapour due to desorption from the PuO_2 , or hydrogen gas from the radiolysis of water or the reaction of water with PuO_2 . It is essential that we fully understand the causes of the container distortions and, as experimental measurements are extremely challenging, computational approaches have a very valuable role. As part of this project, we have previously considered the adsorption of up to a monolayer of water on stoichiometric^{1,2} and reduced³ low Miller-index surfaces of the actinide oxides UO_2 and PuO_2 , using density functional theory, within both periodic boundary condition (PBC) and embedded cluster frameworks. In this contribution, we report our PBC investigations of the adsorption of multiple layers of water on the same low-index surfaces of UO_2 and PuO_2 , as there is experimental evidence for multiple water layers adsorbed onto PuO_2 ⁴, as well as on other metal oxides.^{5,6,7} We start with a brief description of the computational methodology used, followed by a brief discussion of previous results. We then describe adsorption geometries and energies of up to five layers of water on the stoichiometric {111}, {110} and {100} surfaces, with particular focus on the hydrogen bonding networks that this creates.

Computational Details

All calculations were performed using VASP 5.4.1,^{8–11} a plane-wave DFT code using Projector-Augmented Wave (PAW)-pseudopotentials^{12,13} to describe the ions, and Monkhorst-Pack (MP)¹⁴ grids for the k -space integration. A plane wave cut-off of 650 eV was used, and a minimum MP-grid of $5 \times 5 \times 1$ k -points for the Brillouin zone sampling for the surface simulations and $11 \times 11 \times 11$ for the bulk calculations. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)¹⁵ was used for the exchange-correlation energy, with a Hubbard U correction for the 5f electrons.^{16,17} We used an effective U value $U_{\text{eff}} = (U - J) = 4$ eV for both uranium and plutonium, in accordance with earlier work summarized by Wen *et al.*¹⁸ While Pegg and co-workers¹⁹ have recently suggested that other values of U are more appropriate, we have not adopted their recommendations (3.35 eV for UO_2 and 6.35 eV for PuO_2 , in conjunction with the PBE-Sol functional) as (a) these values were arrived at following analysis solely of bulk properties and (b) we have used $U = 4$ eV for all of our previous work,^{2,3} and have established that variations in U have only minimal effects on water adsorption geometries and energies.

The AnO_2 surfaces are constructed using repeating slabs of 24 AnO_2 units arranged in six layers, with 18 Å of vacuum between each slab. The atom positions are allowed to relax until the net inter-atomic forces are below 0.001 eV/Å. We use 1- k co-linear magnetic ordering with a net magnetic moment of zero, allowing us to treat the total system as anti-ferromagnetic and thereby reach the correct ground state.^{20,21} We neglect spin-orbit coupling, as earlier results by Rák and co-workers²² indicate that this has only a very small effect on the surface stability. Adsorbing species are introduced on both sides of the slab to minimize dipole effects.

The adsorption energy E_{ads} is calculated using the following expression:

$$E_{ads} = \frac{1}{n} (E_{Slab+Mols} - E_{Slab} + n E_{Mol}) \quad (1)$$

where $E_{Slab+Mols}$ is the energy of the system with n extra molecules adsorbed, E_{Slab} is the energy of the slab without the added molecules and E_{Mol} is the energy of a single molecule, in our case a water molecule in an empty box with a 20 Å side.

All the water adsorption images were made using VESTA.²³

Results and Discussion

There has been some debate in the literature as to whether the first monolayer of water is adsorbed molecularly or dissociatively on the defect-free AnO_2 {111} surface or its LnO_2 analogues. Bo *et al.*^{24,25} suggest a mixture of molecular and dissociative adsorption on UO_2 and NpO_2 {111} surfaces whereas Molinari *et al.*²⁶ suggest molecular adsorption on the CeO_2 {111} surface. Previous work from our group^{1,2} confirms Bo and co-workers' suggestion that a mixed configuration is the most stable at this coverage for the {111} surface. Bo *et al.*^{24,25} suggest a mixture is also the most stable on the {110} surface, with dissociative adsorption dominating on the {100} surface. By contrast, we find dissociative adsorption to be the most stable on both the {110} and {100} surfaces. For reduced surfaces (*i.e.* those with surface oxygen vacancies), previous studies by both Bo *et al.*^{24,25} and by Molinari *et al.*²⁶, as well as recent work by our group,³ suggest dissociative adsorption is preferred in the vicinity of oxygen vacancies on all three surfaces.

Multiple water layers have not, to our knowledge, been studied computationally on actinide or lanthanide oxides, although there is some very recent work on yttria-stabilised zirconia,^{27,28} a system which is isostructural with the lanthanide and actinide oxides. This paucity is in stark contrast to water adsorption on other metal oxides such as Cassiterite (SnO_2) and rutile (TiO_2), which has been studied extensively.^{5,6,7}

We used the results from our previous work² to set up the starting geometries of the first adsorbed monolayer of water on each surface. Even though the most stable configuration on the {111} surface is likely to be a mix of molecular and dissociative adsorption, we also considered the fully molecular and fully dissociative cases for the initial layer on this surface; the former because the difference in the adsorption energy in favour of the mixed case is only 0.12 eV for PuO₂ and 0.14 eV for UO₂, and the latter for a more complete comparison with the {110} and {100} surfaces, which our previous work² suggests will be fully hydroxylated.

Multiple water layers on the {111} surface

Figure 1a shows side-on views of the adsorption geometries of up to four additional layers of water above a mixed molecular/dissociative first layer on the PuO₂ {111} surface. The analogous geometries for adsorption on fully molecular and fully dissociative first layers are shown in figures 1b and 1c. The corresponding geometries for UO₂, are shown in figures S1 to S3 of the supplementary information. The corresponding adsorption energies for each system are shown in figure 2, with the data also provided in tables S1 to S4. There is a large variation in adsorption energy per layer in the mixed case. This is due to differing amounts of intra-layer hydrogen bonding, as seen in figure 1a. For example, formation of the second layer disrupts the hydrogen bonding in the first layer, causing the adsorption energy per layer to drop significantly. By contrast, addition of the third layer generates substantial additional hydrogen bonding. The arrangement of water molecules in the first three layers is little perturbed by the addition of the fourth and fifth layers, and a regular pattern begins to emerge in these layers.

Figure 1: Multiple water layers on the PuO_2 {111} surface. Plutonium atoms are dark grey, oxygen atoms are red, and hydrogen atoms are white. Dashed lines indicate hydrogen bonds. The first layer is (a) a mix of molecular and dissociative adsorption (b) molecularly adsorbed and (c) dissociatively adsorbed.

The fully molecular case is quite different (figure 1b). Here, a much smaller variation between the first and second layer is observed. There are no intra-first layer hydrogen bonds to break, and the creation of the second layer causes a change in the first layer such that it is bound to the surface only by hydrogen bonds. The third layer causes another change in first layer/surface interaction, with reformation of the An–O bonds, which persist as subsequent water layers are added. As with the mixed first layer case, by five layers a clear and regular hydrogen bonding network has formed.

The fully dissociative case (shown in figure 1c) has only weak binding at one monolayer coverage, though this increases significantly for the second layer, presumably because of the strong hydrogen bonds between surface hydroxyls and second layer waters. The reduction in adsorption energy for the third layer reflects the weaker H₂O–H₂O hydrogen bonds. As four and five layers bind, there is an increase in the hydrogen bonding within the water network, and the adsorption energies steadily increase.

Averaging the adsorption energy over all water molecules, as seen in figure 2, shows that all three first layer configurations arrive at a similar value of about 0.6 eV / H₂O for UO₂ and 0.5 eV / H₂O for PuO₂ once five water layers are present. In agreement with our previous studies,² the average adsorption energy is somewhat lower on PuO₂ compared to UO₂. Moreover, the observation that the average adsorption energy approaches a constant value is in agreement with earlier work on TiO₂ {110} by Liu and co-workers,⁶ and also with the BET theory of gas adsorption on a solid surface, which assumes that the adsorbates interact only with the adjacent layers.²⁹

Figure 2: Adsorption energies (eV/molecule) per layer, and averaged over all water molecules, on the AnO₂ {111} surfaces. The top panel shows the UO₂ data, the bottom panel the PuO₂.

Multiple water layers on the {110} surface

On the {110} surface, the initial layer is dissociatively adsorbed. Side-on views of the adsorption geometries for multiple water layers on PuO_2 are shown in figure 3. The corresponding geometries for UO_2 are very similar, and are shown in figure S4. The adsorption energies per layer are shown in figure 4 and collected in tables S5 to S8. Figure 4 shows that the variation in adsorption energy per layer is much smaller and more monotonous than on the {111} surface. Here there are no hydrogen bonds to break in the first layer and a hydrogen bond network builds up more gradually as more water is added. By three layers we see three hydrogen bonds per molecule. Similar adsorption motifs have been seen on hydroxylated Cassiterite {110}, as reported by Vlcek *et al.*,⁵ and on SiO_2 , as reported by Asay and Kim.³⁰

Figure 3: Multiple water layers on the PuO_2 {110} surface. The first layer is dissociatively adsorbed. Plutonium atoms are dark grey, oxygen atoms are red, and hydrogen atoms are white. Dashed lines indicate hydrogen bonds.

Figure 4: Adsorption energies (eV/molecule) per layer, and averaged over all water molecules, on the UO₂ and PuO₂ {110} surfaces. The first layer is dissociatively adsorbed.

The average adsorption energy again approaches a constant value after three to four layers. This is about 0.2 eV larger compared to the {111} surface, due to the tighter binding of the first hydroxylated layer on the {110} surface. Removing the first layer data, the average adsorption energy per molecule for the subsequent layers is 0.52 eV for UO₂ and 0.55 eV for PuO₂, similar to the {111} surface. The difference between UO₂ and PuO₂ is smaller than on the {111} surface. Note that the much smaller variation in the per layer adsorption energies meant that we considered only four water layers on {110}.

Multiple water layers on the {100} surface

As with the {110} surface, the first monolayer of water on the {100} surface is fully dissociated, followed by subsequent layers of molecular water. Side-on views of the resulting adsorption geometries for PuO_2 are shown in figure 5, and for UO_2 in figure 6. The corresponding adsorption energies are shown in figure 7 and gathered in tables S9 to S12. For UO_2 , there is a monotonic decrease in both the per layer and average adsorption energies as the water network builds up. By contrast, there is much greater variation for PuO_2 , possibly as a result of variations in intra-first layer hydrogen bonding. This is present for both layers one and two but, as figure 5 shows, weakens at three layers before reforming at four layers. The difference between UO_2 and PuO_2 may well be a consequence of the smaller lattice parameter in the latter, which results in the surface hydroxyls being closer together and hence more able to participate in intra-first layer hydrogen bonding.

The average adsorption energy for both UO_2 and PuO_2 is a little larger than on the {110} surface, again due to the strong adsorption of the first hydroxyl layer on these surfaces. Omitting the first layer data, the average adsorption energy per molecule for the subsequent layers on the {100} surface is 0.46 eV for PuO_2 and 0.62 eV for UO_2 , within 0.1 eV of the corresponding data for the other two surfaces.

Figure 5: Multiple water layers on the PuO_2 {100} surface. The first layer is dissociatively adsorbed. Plutonium atoms are dark grey, oxygen atoms are red, and hydrogen atoms are white. Dashed lines indicate hydrogen bonds.

Figure 6: Multiple water layers on the UO_2 {100} surface. The first layer is dissociatively adsorbed. Uranium atoms are grey, oxygen atoms are red, and hydrogen atoms are white. Dashed lines indicate hydrogen bonds.

Figure 7: Adsorption energies (eV/molecule) per layer, and averaged over all water molecules, on the $\text{AnO}_2 \{100\}$ surface ($\text{An} = \text{U}, \text{Pu}$). The first layer is dissociatively adsorbed.

Conclusions

In this study, we have calculated the geometries and energies for adsorption of several layers of water on three low-index UO_2 and PuO_2 surfaces, starting from the stable configurations we have previously established for the surface-bound monolayers. Significant variations are found in the per-layer adsorption energies, which we rationalise in terms of intra- and inter-layer hydrogen bonding. After the adsorption of several additional layers, the effect of the surface adsorption configuration diminishes, and the average adsorption energy per water molecule is c. 0.5-0.6 eV, irrespective of the surface. This is in agreement with earlier work on other metal oxide surfaces, and also with one of the assumptions of BET theory, *i.e.* that each adsorbed molecule interacts only with the adjacent layer.

Previous studies of other metal oxide surfaces have reported a change in the water adsorption geometries from an initial “ice-like” double layer to more “liquid-like” water.³⁰ Such behaviour is most noticeable in our work for the {111} surface (figure 1), and is not inconsistent with data from experimental study of water/ PuO_2 (Figure 1 in ref 4). Moreover, the average water-water binding energy in liquid water, assuming 2.5 hydrogen bonds per molecule,³⁰ is 0.54 eV,^{31,32} which compares very favourably with our data for the layers above the surface-bound monolayer. We hope that the structures provided in this paper prove useful starting points for simulations of water radiolysis above AnO_2 surfaces.

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Data supporting this study, including the geometries presented in Figures 1, 3, 5, 6 and the SI Figures, are openly available from <http://dx.doi.org/10.17632/mc85ht5wpf.1>

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