

Supporting Information

Adsorption of Uranyl on Hydroxylated α -SiO₂(001): A First-Principle Study

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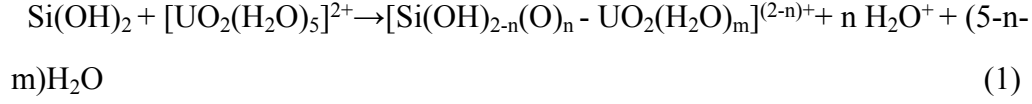
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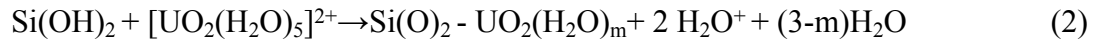
1. Computational Details

The hydroxylated α -SiO₂(001) surface was modeled by a periodic slab including three O-Si-O layers separated by a vacuum region of 15 Å. A (2 × 2) supercell with a dimension of (10.02 Å × 10.02 Å × 21.36 Å) was used to study the uranyl adsorption and a (2 × 2 × 1) k-point grid was used. The initial configuration of the complete hydroxylated surface was obtained by saturating the terminal O atoms on the top and bottom surfaces with hydrogen atoms. The two upper layers were allowed to fully relax while the bottom layer was fixed during optimization.

The gas species H₂O, H₃O⁺ and [UO₂(H₂O)₅]²⁺ were optimized in the cubic unit cell of 15 × 15 × 15 Å³, the solvation effects of which were obtained from the work of Kremleva et al.¹ as -29, -382, -811 kJ mol⁻¹, respectively. The formation energy ΔE_{form} of the adsorption complex was estimated and details of its derivation is as follows: ¹



Si(OH)_2 denotes the surface adsorption site, with two hydroxyl group described explicitly, n is the number of deprotonated surface OH group, and m counts the aqua ligands of the adsorbed uranyl. To calculate with neutral unite cells only, eq 1 may be decomposed formally into two sequential reactions:



$$\Delta E_1 = \Delta E_2 + \Delta E_3$$

The corresponding reaction energy of eq3 is obtained as the energy of reprotonation of a SiO^- moiety,



Thus, neglecting the solvation effects, the overall adsorption energy of uranyl is

$$\Delta E_1 = \Delta E_2 + \Delta E_3 \approx \Delta E_2 + (2-n)\Delta E_4$$

The solvation correction to eq2 is estimated by assuming that the solvation energy of the clean surface is equal to that of a surface with adsorbate. The solvation corrections for the molecular species H_2O , H_3O^+ and $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, in eq 2 were $\Delta E_{[\text{H}_3\text{O}^+]}$,

$\Delta E_{[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}}$ and $\Delta E_{[\text{H}_2\text{O}]}$ respectively.

$$\Delta E_1 = \Delta E_2 + \Delta E_3 \approx \Delta E_2 + (2-n)\Delta E_4 + 2\Delta E_{[\text{H}_3\text{O}^+]} - \Delta E_{[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}} + (3-m)\Delta E_{[\text{H}_2\text{O}]}$$

This approximate value is reported as ΔE_{form} in the paper.

The binding energy (ΔE_{bind}) was calculated according to the method 2, which was considered more reliable, in Pan's work: ²

$$\Delta E_{\text{bind}} = E_{\text{sc}} - E_{\text{sc}}'$$

where E_{sc} refers to the energy of the optimized surface complex and E'_{sc} corresponds to the energy of the system in which the actinyl and the surface are kept apart at about 6 Å. At a span of 6 Å, the interaction between the actinyl group and the surface is weak enough to mimic two non-interacting species to obtain a semi-quantitative value of ΔE_{bind} . Because the vacuum thickness is 15 Å, the interaction with the next periodic surface slab is also small.

Corresponding to a vacuum thickness of 15 Å between slabs, the liquid phase was represented with 44 water molecules with water density close to 1 g ml⁻¹. In order to allow long time AIMD simulations, the energy cutoff was reduced to 300 eV. The AIMD simulations with a time step of 1 fs were run with the NVT canonical ensemble, and the temperature was kept constant at 298.15 K using the Nose–Hoover thermostat.^{3,4} The Brillouin zone was integrated with one k point which corresponds to the Γ point. The whole simulation is 22 ps long, including an equilibration run of 2 ps and the following 20 ps of production run which started from the final configuration of the equilibration run.

According to Pan's work,² the interaction between $[\text{UO}_2(\text{H}_2\text{O})(\text{CO}_3)]^0$ and the $\text{TiO}_2(110)$ surface is stronger than that for $[\text{UO}_2(\text{H}_2\text{O})_2(\text{CO}_3)]^0$ and $[\text{UO}_2(\text{CO}_3)_2]^{2-}$. Our calculations also show that the complexes $[\text{UO}_2(\text{H}_2\text{O})_n(\text{CO}_3)]^0$ with one H_2O ligand is more preferential.

2. The models with the surface covered by a water layer:

In the bare surface model, the hydroxylated surface was covered by 8 H_2O molecules and a flat monolayer structure with two types of water molecules was

formed after optimization, as described in Yang's work.⁵ Then the water monolayer was added to the optimized adsorption systems of uranyl above with four to six water molecules of the monolayer shifted upward to construct a cavity to accommodate uranyl, as described as Martorell's work.⁶

Table S1. Structure parameters (in Å) and formation energies (in eV) of the inner-sphere and outer-sphere uranyl complexes adsorbed on the hydroxylated α -SiO₂(001) surface with an isolated water monolayer. Q (in |e|) is the charge of the adsorption site.

| Model | Q | U-O _{surf} | U-O _{yl} | U-O _{wat} | O _{yl} -H _{surf} | H-O _{surf} | ΔE_{form} |
|-----------|----|---------------------|-------------------|---------------------------|------------------------------------|---------------------|--------------------------|
| SiOO | -2 | 2.18,2.34 | 1.84,1.86 | 2.46,2.49,2.75 | 1.92 | 1.72,1.78 | 3.95 |
| | | <i>2.19,2.35</i> | <i>1.84,1.86</i> | <i>2.41,2.46,2.72</i> | <i>1.82</i> | <i>1.71,1.71</i> | |
| SiOOH | -1 | 2.26,2.59 | 1.83,1.84 | 2.38,2.52, 2.62 | 2.04 | 1.73,1.96 | -0.54 |
| SiOHOH | 0 | 2.57,2.77 | 1.85,1.86 | 2.35,2.49, 2.63 | 1.97 | 1.79,1.88 | -4.05 |
| SiO-SiO | -2 | 2.13,2.20 | 1.82,1.86 | 2.44,2.50,3.77 | 1.92 | 1.72,1.78 | 3.10 |
| SiO-SiOH | -1 | 2.17,2.43 | 1.81,1.85 | 2.39,2.50, 3.75 | 2.82 | 1.71,1.86 | -1.33 |
| SiOH-SiOH | 0 | 2.46,2.60 | 1.81,1.88 | 2.37,2.44, 3.93 | 2.12 | 1.68,2.09 | -4.57 |
| SiO | -1 | 2.81 | 1.81,1.84 | 2.40,2.49,2.50, 2.58 | | 1.59,1.68,1.81 | 0.57 |
| SiOH | 0 | 2.63 | 1.83,1.86 | 2.41,2.49,2.51,2.52 | | 1.72,1.75, 2.03 | -2.67 |
| SiOHOH | 0 | | 1.83,1.85 | 2.39,2.49,2.52,2.57, 2.57 | | 1.66,1.89, 2.02 | -6.64 |

The values in italic are obtained with the DFT-D3(BJ) method.

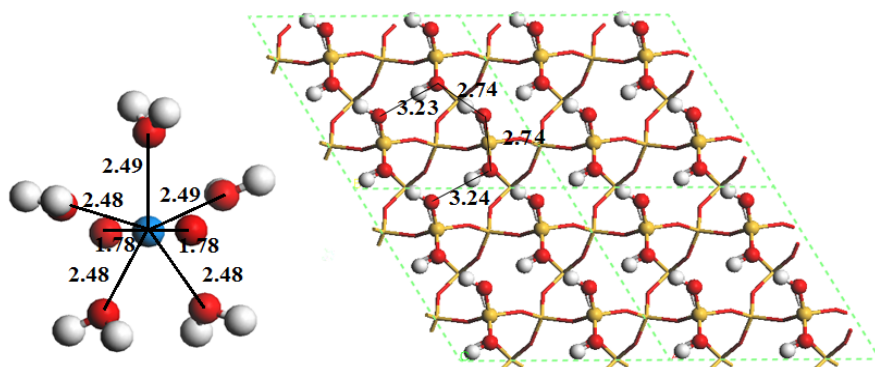


Figure S1 Optimized structures of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ and the hydroxylated $\alpha\text{-SiO}_2(001)$ surface. Color scheme: U(blue), O(red), Si(orange), H (white).

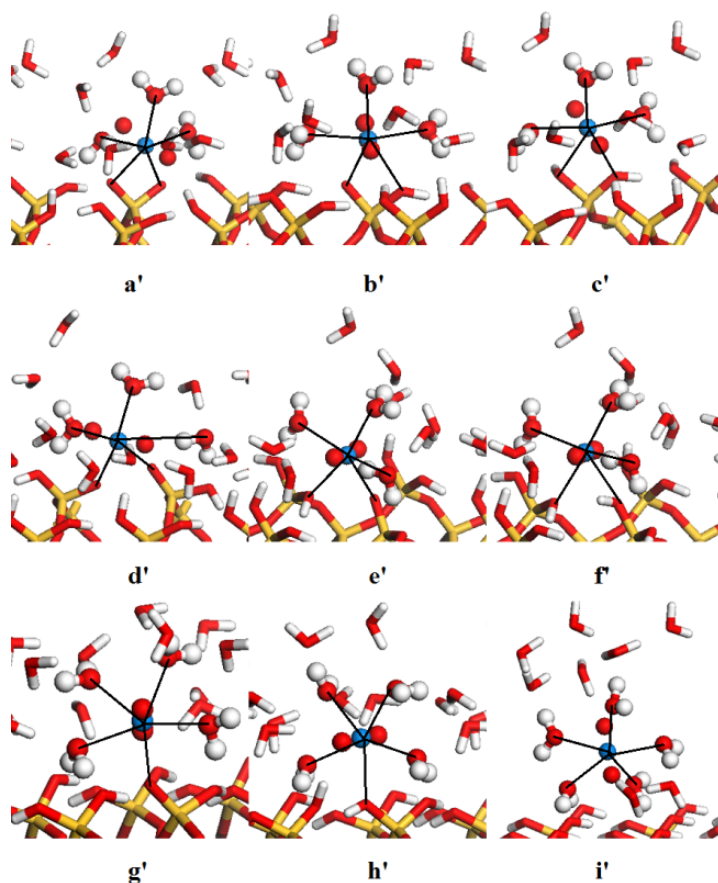


Figure S2 Configurations of uranyl adsorption on the hydroxylated $\alpha\text{-SiO}_2(001)$ surface with a water monolayer. Color scheme: U(blue), O(red), Si(orange), H (white).

References

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