Supporting Information

Adsorption of Uranyl on Hydroxylated \( \alpha \)-SiO\(_2\)(001): A First-Principle Study

Hui Wang,\textsuperscript{a} Zhifang Chai,\textsuperscript{a,b} Dongqi Wang\textsuperscript{*a}

\textsuperscript{a}CAS Key Laboratory of Nuclear Radiation and Nuclear Energy Techniques, and Multidisciplinary Initiative Center, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China.

\textsuperscript{b}School of Radiation Medicine and Interdisciplinary Sciences (RAD-X), Soochow University, Suzhou 215123, China

E-mail address: dwang@ihep.ac.cn

1. Computational Details

The hydroxylated \( \alpha \)-SiO\(_2\)(001) surface was modeled by a periodic slab including three O-Si-O layers separated by a vacuum region of 15 Å. A \((2 \times 2)\) supercell with a dimension of \((10.02 \, \text{Å} \times 10.02 \, \text{Å} \times 21.36 \, \text{Å})\) was used to study the uranyl adsorption and a \((2 \times 2 \times 1)\) 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 H\(_2\)O, H\(_3\)O\(^+\) and [UO\(_2\)(H\(_2\)O)\(_5\)]\(^{2+}\) were optimized in the cubic unit cell of \(15 \times 15 \times 15\) Å\(^3\), the solvation effects of which were obtained from the work of Kremleva et al.\textsuperscript{1} as -29, -382, -811 kJ mol\(^{-1}\), respectively. The formation energy \(\Delta E\)\textsubscript{form} of the adsorption complex was estimated and details of its derivation is as follows: \textsuperscript{1}
Si(OH)$_2$ + [UO$_2$(H$_2$O)$_5$]$^{2+}$→[Si(OH)$_{2-n}$O]$_n$ - UO$_2$(H$_2$O)$_m$]$^{(2-n)^+}$ + n H$_2$O$^+$ + (5-n-m)H$_2$O (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:

Si(OH)$_2$ + [UO$_2$(H$_2$O)$_5$]$^{2+}$→Si(O)$_{2-n}$ - UO$_2$(H$_2$O)$_m$(2-n)+ (2-n)H$_2$O (2)

Si(O)$_{2-n}$ - UO$_2$(H$_2$O)$_m$+(2-n) H$_2$O$^+$→[Si(OH)$_{2-n}$O]$_n$ - UO$_2$(H$_2$O)$_m$]$^{(2-n)^+}$+(2-n)H$_2$O (3)

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

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

[Si(OH)$_3$O]$^-$ + H$_3$O$^+$ → Si(OH)$_4$ + H$_2$O (4)

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$_2$O, H$_3$O$^+$ and [UO$_2$(H$_2$O)$_5$]$^{2+}$, in eq 2 were $\Delta E_{\{H_2O\}}$, $\Delta E_{\{H_3O^+\}}$ and $\Delta E_{\{UO_2(H_2O)_5\}}$ respectively.

$\Delta E_1 = \Delta E_2 + \Delta E_3 \approx \Delta E_2 + (2-n)\Delta E_4 + 2\Delta E_{\{H_3O^+\}} - \Delta E_{\{UO_2(H_2O)_5\}} + (3-m)\Delta E_{\{H_2O\}}$

This approximate value is reported as $\Delta E_{\text{form}}$ in the paper.

The binding energy ($\Delta E_{\text{bind}}$) was calculated according to the method 2, which was considered more reliable, in Pan’s work: $^2$

$\Delta E_{\text{bind}} = E_{sc} - E_{sc}'$
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 $\Delta E_{\text{bind}}$. 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 $\Gamma$ 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 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$_2$O 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$_2$O 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 \(\alpha\)-SiO\(_2\)(001) surface with an isolated water monolayer. Q (in |e|) is the charge of the adsorption site.

<table>
<thead>
<tr>
<th>Model</th>
<th>Q</th>
<th>U-O(_{\text{surf}})</th>
<th>U-O(_{\text{sl}})</th>
<th>U-O(_{\text{wat}})</th>
<th>(\text{O}<em>\text{yl}-\text{H}</em>{\text{surf}})</th>
<th>H-O(_{\text{surf}})</th>
<th>(\Delta E_{\text{form}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOO</td>
<td>-2</td>
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<td>1.84,1.86</td>
<td>2.46,2.49,2.75</td>
<td>1.92</td>
<td>1.72,1.78</td>
<td>3.95</td>
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<td>2.26,2.59</td>
<td>1.83,1.84</td>
<td>2.38,2.52,2.62</td>
<td>2.04</td>
<td>1.73,1.96</td>
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<tr>
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<td>1.85,1.86</td>
<td>2.35,2.49,2.63</td>
<td>1.97</td>
<td>1.79,1.88</td>
<td>-4.05</td>
</tr>
<tr>
<td>SiO-SiO</td>
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<td>1.82,1.86</td>
<td>2.44,2.50,3.77</td>
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<td>1.72,1.78</td>
<td>3.10</td>
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<td>1.81,1.85</td>
<td>2.39,2.50,3.75</td>
<td>2.82</td>
<td>1.71,1.86</td>
<td>-1.33</td>
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<tr>
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<td>1.81,1.88</td>
<td>2.37,2.44,3.93</td>
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<tr>
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<tr>
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<td>2.57</td>
<td>1.66,1.89,2.02</td>
<td>-6.64</td>
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</tr>
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</table>

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


