Hydroxylation induced surface stability of AnO$_2$ (An=U, Np Pu) from first-principles

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Why study AnO$_2$ surfaces?

- **technological importance:**
  - most common fuel forms used for the nuclear energy production
  - the AnO$_2$ surface reactivity $\rightarrow$ fabrication of the fuel pellets, storage in pools or geologic disposal;
  - surface-water interaction $\rightarrow$ corrosion, leaching of radionuclides

- **fundamental scientific interest:**
  - presence of partially filled 5f orbitals – at the boundary between localized and itinerant behavior
Outline

- **Methodology**
  - surface energy calculations
  - \( f - \) electrons/DFT+\( U \) method

- **Results**
  - optimized surface geometry
  - surface/adsorption energetics

- **Conclusions**
Computational parameters

- Projector Augmented Wave (PAW) method – implemented in VASP code
- Generalized Gradient Approximation (GGA – PBE)
- DFT+$U$; $U = 4.5$ eV, $J = 0.5$ eV for uranium
  
  $U = 4.0$ eV, $J = 0.5$ eV for neptunium and plutonium
- The (111), (110), and (100) surfaces of $\text{AnO}_2$ ($\text{An} = \text{U, Np, Pu}$) are simulated by periodic slabs
- The Brillouin zones (BZ) sampling: (111), (110), and (100) slabs
  
  $6\times6\times1$, $6\times4\times1$, and $4\times4\times1$ k-points

\[
\begin{array}{c}
(111) \\
\text{---O---O---O---O---} \\
\text{U---U---U---U---} \\
\text{---O---O---O---O---} \\
\text{---O---O---O---O---} \\
\text{U---U---U---U---} \\
\text{---O---O---O---O---} \\
\end{array}
\]

\[
\begin{array}{c}
(110) \\
\text{-O-\text{U-O-O-U-O-}} \\
\text{-O-U-O-O-U-O-} \\
\text{-O-U-O-O-U-O-} \\
\text{-O-\text{U-O-O-U-O-}} \\
\end{array}
\]

\[
\begin{array}{c}
(100) \\
\text{---O---O---O---O---} \\
\text{---U---------U----} \\
\text{---O---O---O---O---} \\
\text{U---------U---------U} \\
\text{---O---O---O---O---} \\
\text{---U---------U----} \\
\end{array}
\]
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• Generalized Gradient Approximation (GGA – PBE)
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\[ 6 \times 6 \times 1, \ 6 \times 4 \times 1, \ \text{and} \ 4 \times 4 \times 1 \text{ k-points} \]
Convergent surface energy

The surface energy can be calculated as:

$$\sigma(N) = \frac{1}{2} \left( E_{\text{slab}}^N - N E_{\text{bulk}} \right)$$

Boettger:¹

$$E_{\text{bulk}} = E_{\text{slab}}^N - E_{\text{slab}}^{N-1}$$

Fiorentini and Methfessel:²

$$E_{\text{slab}}^N \approx 2\sigma + N E_{\text{bulk}}$$

If the slab and bulk systems are calculated with the same high accuracy all three methods converge to the same surface energy

\[ \sigma(N) = \frac{1}{2} \left( E_{slab}^N - N E_{bulk} \right) \]  

(1)

(1 × 1) slabs containing 6 f.u. are used to model the AnO₂ surfaces
The orbital dependent Hamiltonian (DFT+U method) leads to multiple self-consistent solutions - “metastable states”

- the case of UO$_2$
  - 2 $f$-electrons ($U^{4+}$)
  - 7 $f$-orbitals (spin degenerate)

\[
\frac{7!}{2!5!} = 21
\]

Methods that deal with the metastability
- **constrained density matrix method** – set up the initial orbital occupations and choose the lowest energy solution
- **$U$-ramping method** – start from $U=0$ and gradually increase $U$ until integer band occupation$^3$

Surface relaxation

Relaxations of the outmost atomic layers of the AnO$_2$ (An = U, Np, Pu) surfaces relative to the ideal bulk geometries

<table>
<thead>
<tr>
<th></th>
<th>(111)-dry</th>
<th>(111)-wet</th>
<th>(110)-dry</th>
<th>(110)-wet</th>
<th>(100)-dry</th>
<th>(100)-wet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>An</td>
<td>O</td>
<td>An</td>
<td>O$_{II}$</td>
<td>O</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>0.12</td>
<td>0.07</td>
<td>0.04</td>
<td>-0.01</td>
<td>0.05</td>
<td>0.18</td>
</tr>
<tr>
<td>NpO$_2$</td>
<td>0.06</td>
<td>0.03</td>
<td>0.09</td>
<td>0.05</td>
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<td>0.18</td>
</tr>
<tr>
<td>PuO$_2$</td>
<td>0.08</td>
<td>0.04</td>
<td>0.05</td>
<td>0</td>
<td>0.03</td>
<td>0.16</td>
</tr>
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<td>0.11</td>
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### Surface energies

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<th>NpO₂</th>
<th></th>
<th>PuO₂</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(111)</td>
<td>(110)</td>
<td>(100)</td>
<td>(111)</td>
<td>(110)</td>
<td>(100)</td>
</tr>
<tr>
<td>Clean Surf. Energy</td>
<td>0.78</td>
<td>1.05</td>
<td>1.47</td>
<td>0.51</td>
<td>1.00</td>
<td>1.52</td>
</tr>
<tr>
<td>Ads. Energy</td>
<td>-0.35</td>
<td>-0.77</td>
<td>-1.34</td>
<td>-0.40</td>
<td>-0.80</td>
<td>-1.62</td>
</tr>
<tr>
<td>Hydrox. Surf. Energy</td>
<td>0.43</td>
<td>0.28</td>
<td>0.13</td>
<td>0.11</td>
<td>0.20</td>
<td>-0.10</td>
</tr>
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![Graph 1: Clean Surface Energy](image1.png)

![Graph 2: Wet Surface Energy](image2.png)
Conclusions

- The dry surface energies of AnO₂ (An=U, Np, Pu) reinforce the well-established trend observed in metal-dioxides with fluorite structure: (111) < (110) < (100)

- The relative stability of the dry surfaces is inversely correlated with the surface relaxations; the (111) surface is the most “bulk-like”

- Dissociated water is adsorbed preferentially on the (100) surface for all AnO₂

- Water adsorption changes the surface stability to: (100) < (110) < (111). This probably influences the morphology of the AnO₂ crystallites

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allminerals.com
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