The corrosion of UO_2 vs. ThO_2: a quantum mechanical investigation

Presented to:
Goldschmidt Geochemistry Conference

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May 21st, 2005
Moscow, Idaho

This presentation has been funded in whole or in part by the U.S. Department of Energy

Motivation

Why UO_2 versus ThO_2?

- Both are nuclear fuel materials
- Isostructural compounds
- Different electronic properties

Overview of the talk

- Electronic and crystalline structure of UO_2 and ThO_2
- Quantum mechanical calculation methods
- Surface energy comparison of UO_2 and ThO_2 (111) (110) and (100) surfaces
- Hydration and oxidation of the UO_2 and ThO_2 (111) surface:

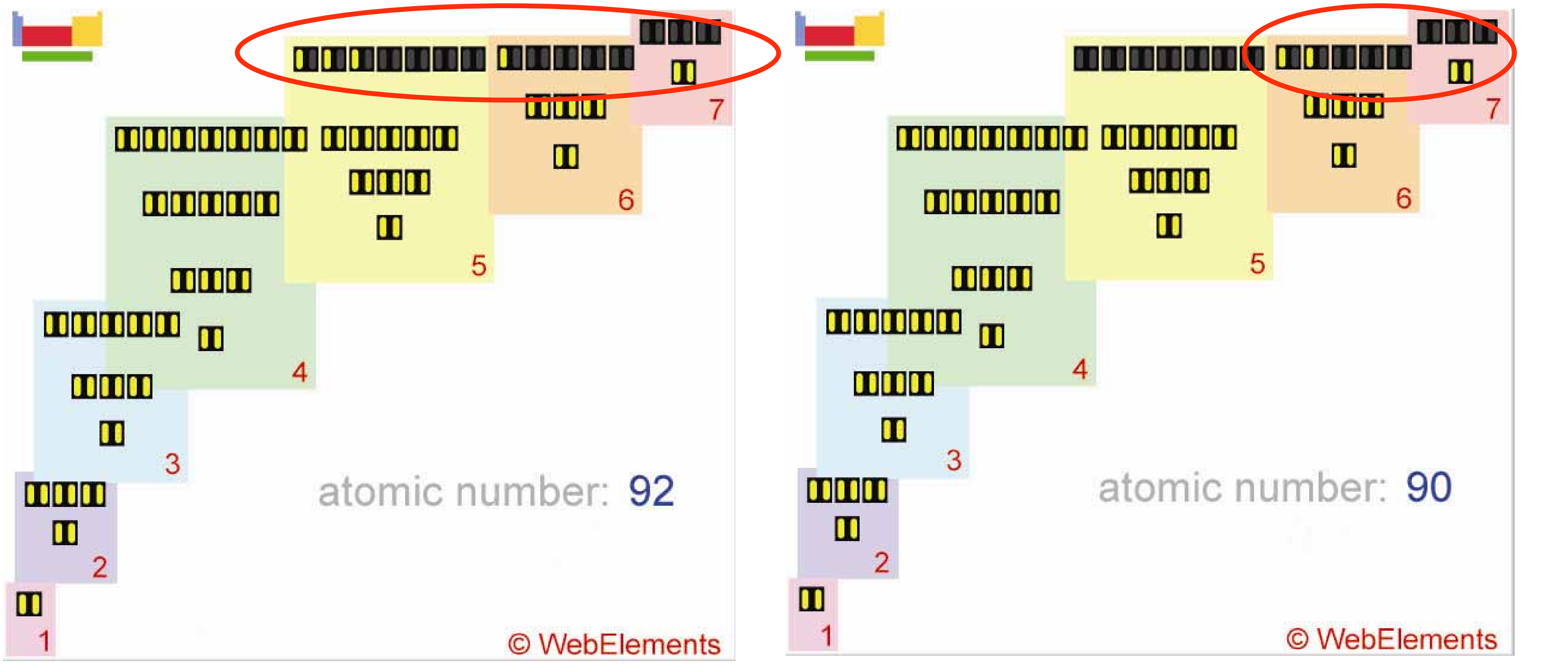
"How does electronic structure affect adsorption processes?"

- Summary and conclusions

The electronic structure of U versus Th

U: [Rn] $5f^3$ $6d^1$ $7s^2$

Th: [Rn] $6d^2$ $7s^2$



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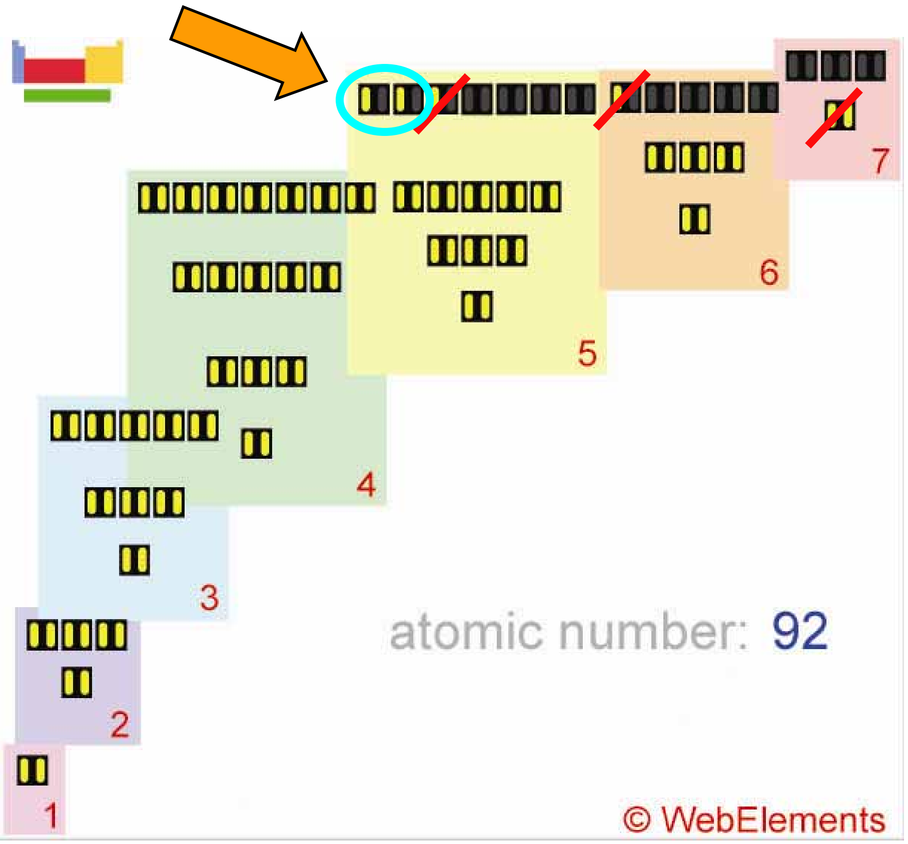
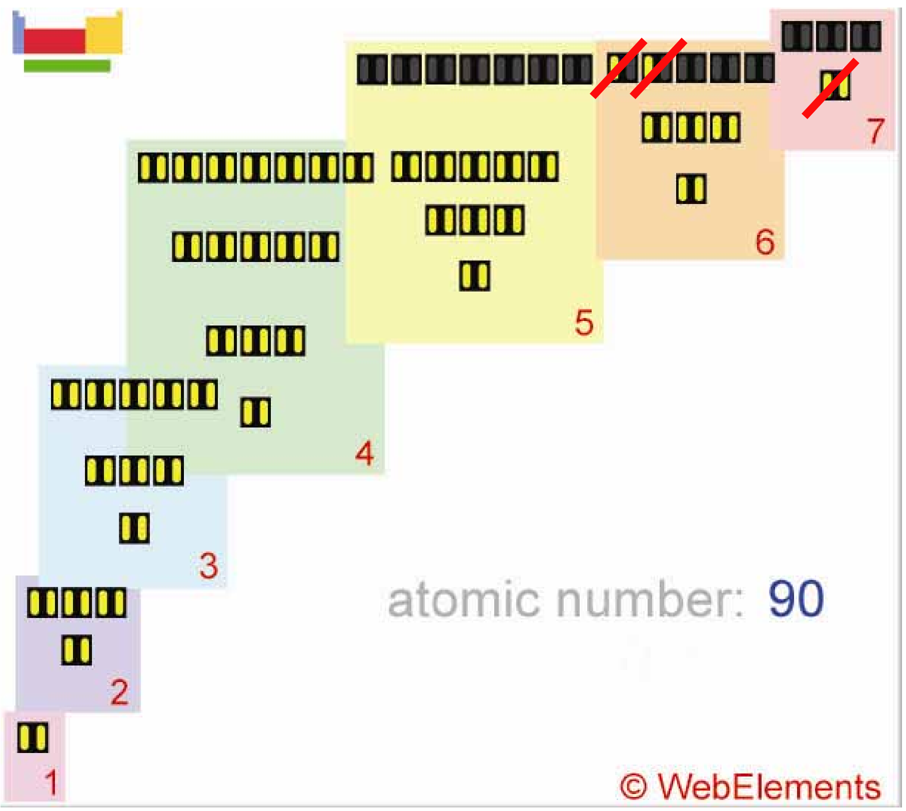
The electronic structure of U^{4+} versus Th^{4+}

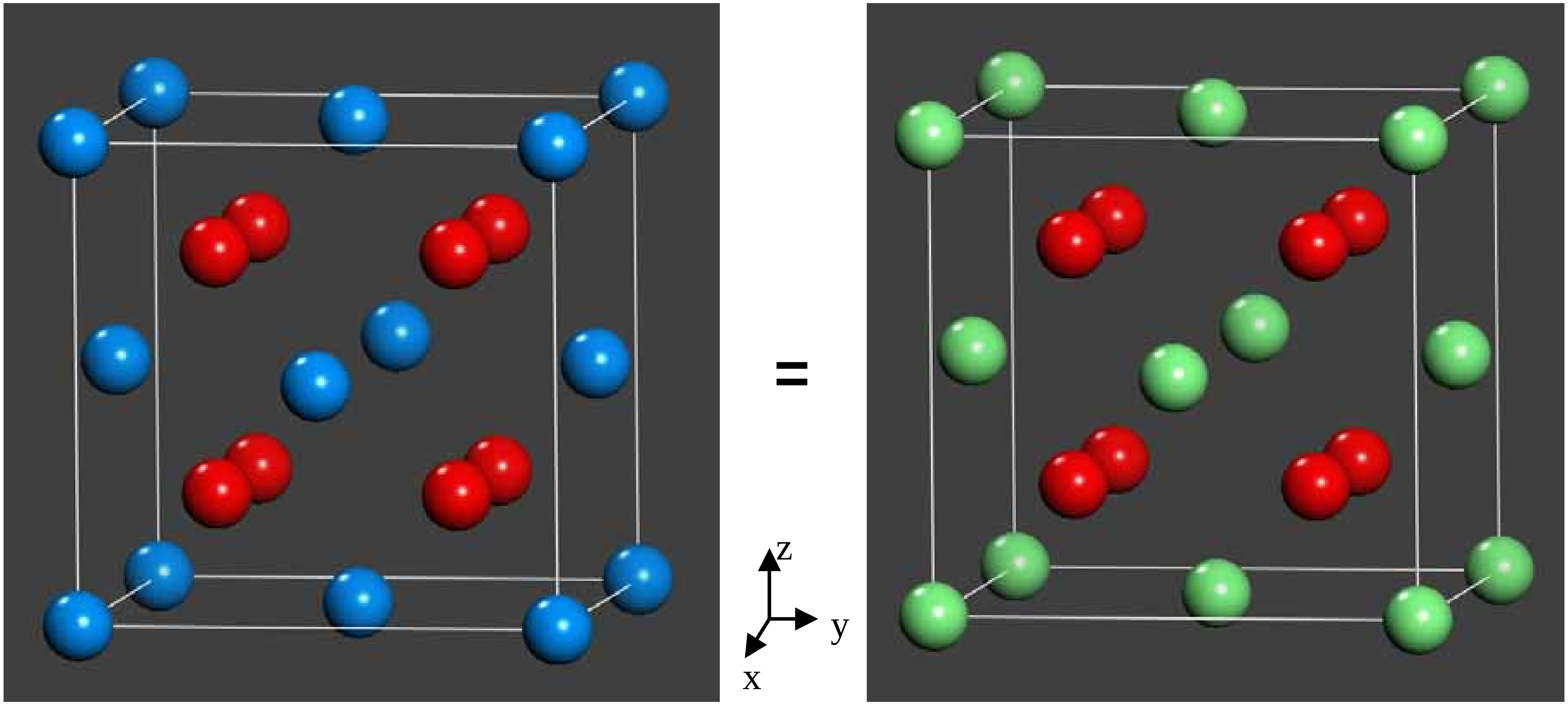
U^{4+}: [Rn] $5f^2$



Th^{4+}: [Rn]



Bulk structure of UO_2 and ThO_2



UO_2 a=b=c= 5.468 Å

ThO_2 a=b=c= 5.597 Å

= Uranium 4+ = Oxygen 2- = Thorium 4+

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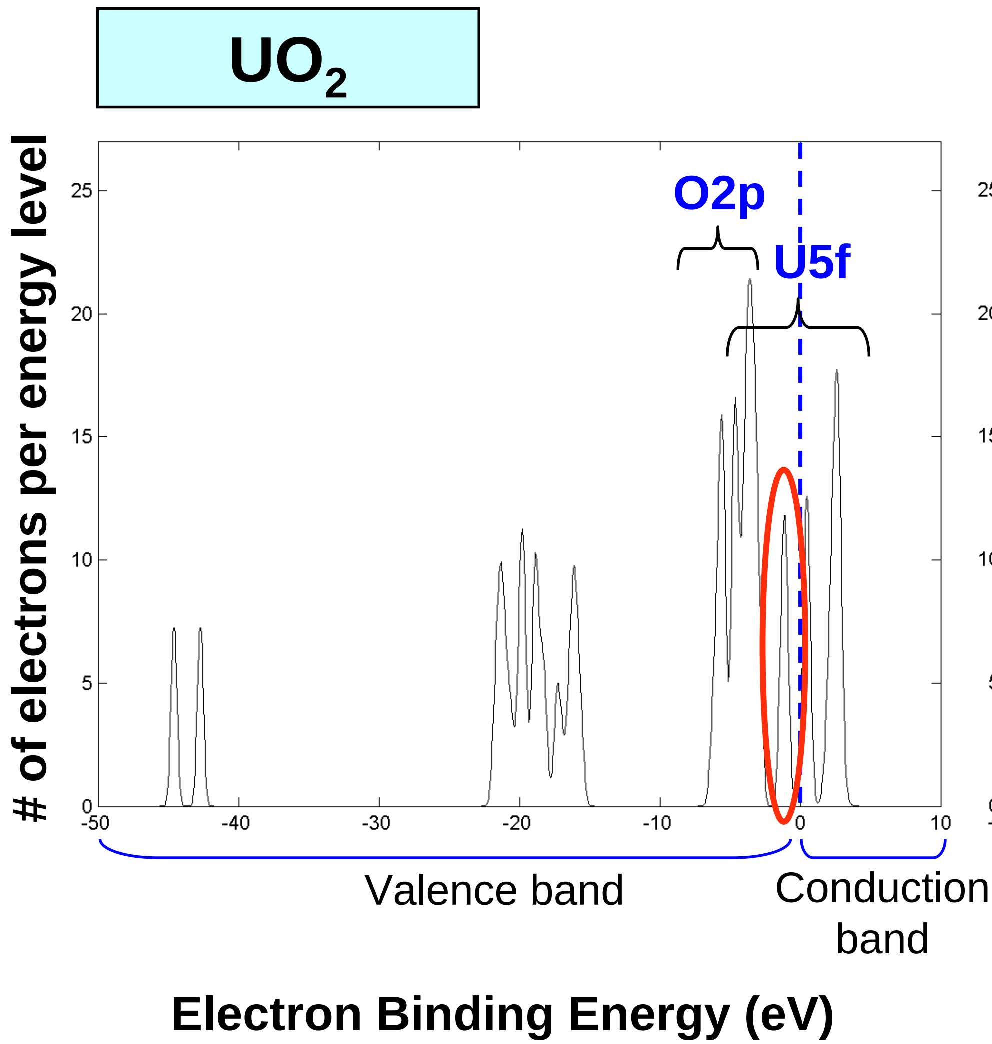
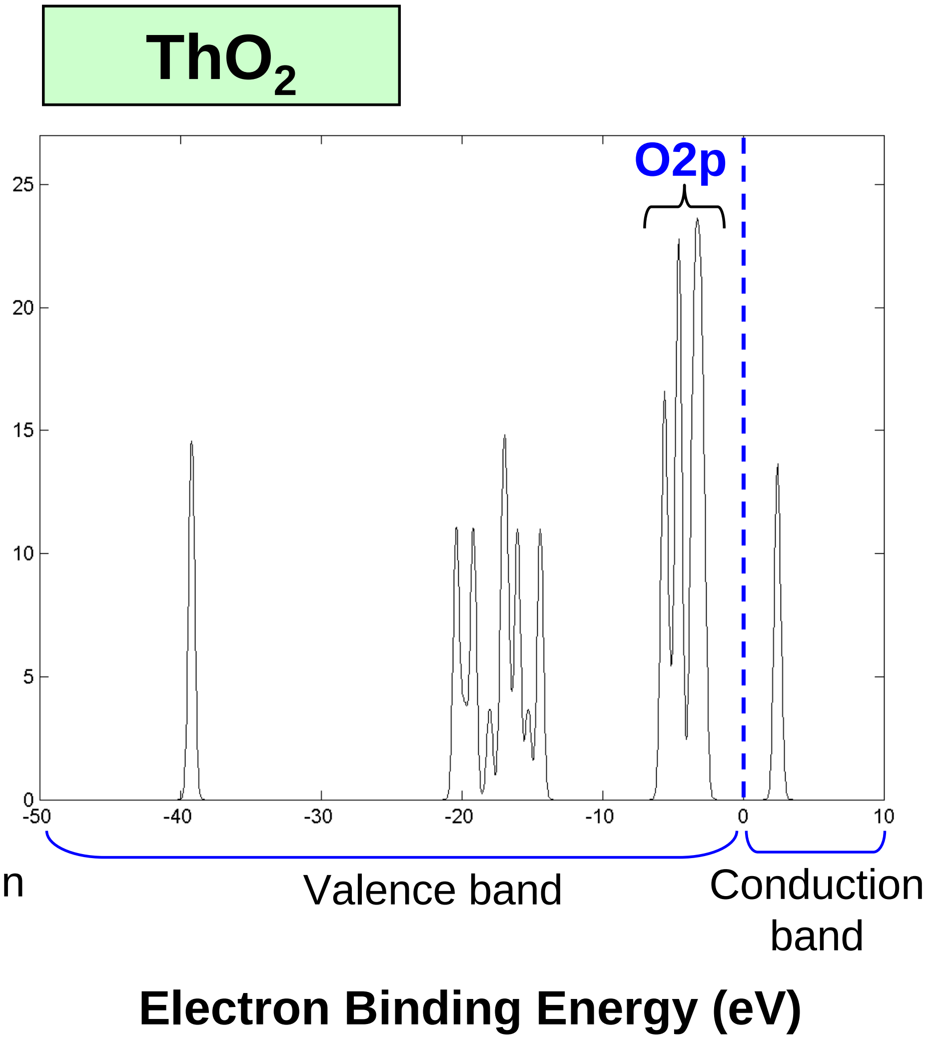
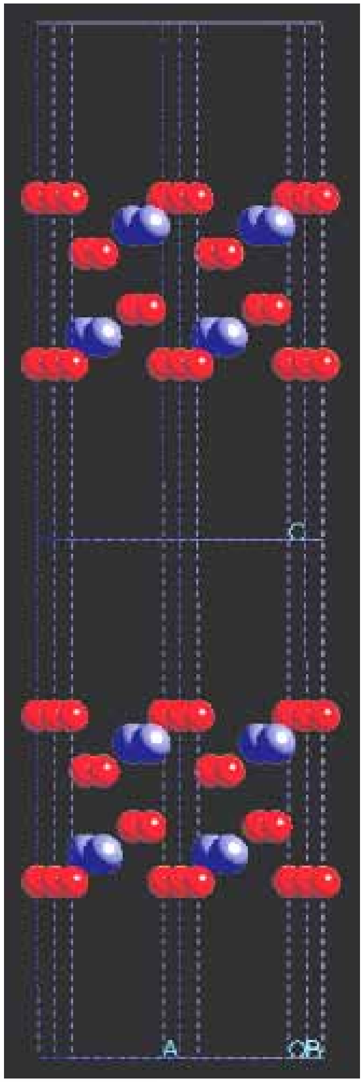
Electronic density of states





Quantum mechanical total energy code:



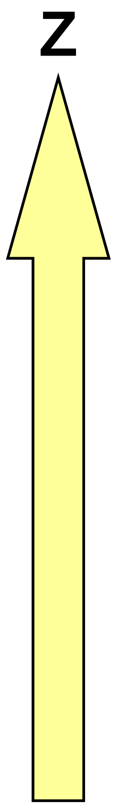
***CASTEP:**

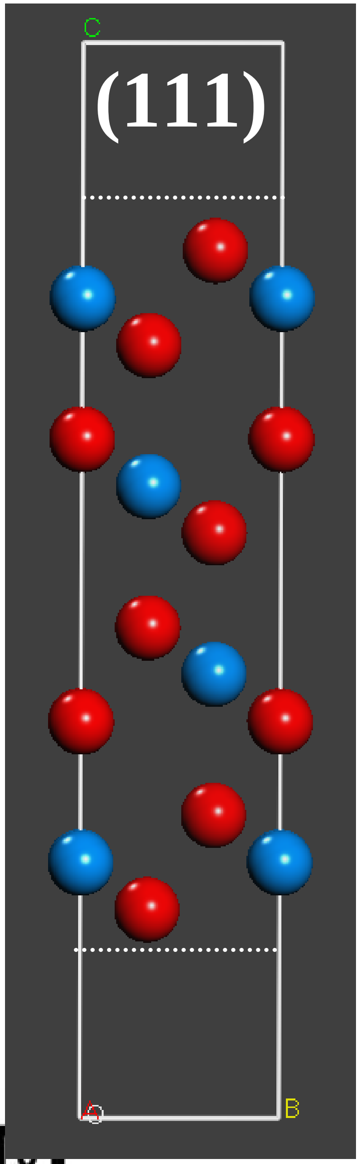
- **Density Functional Theory**
- **Generalized Gradient Approximation**
- **Perdew and Wang functional (1991)**
- **Plane waves and pseudopotentials**
- **Unrestricted spin GGA (for UO_2)**

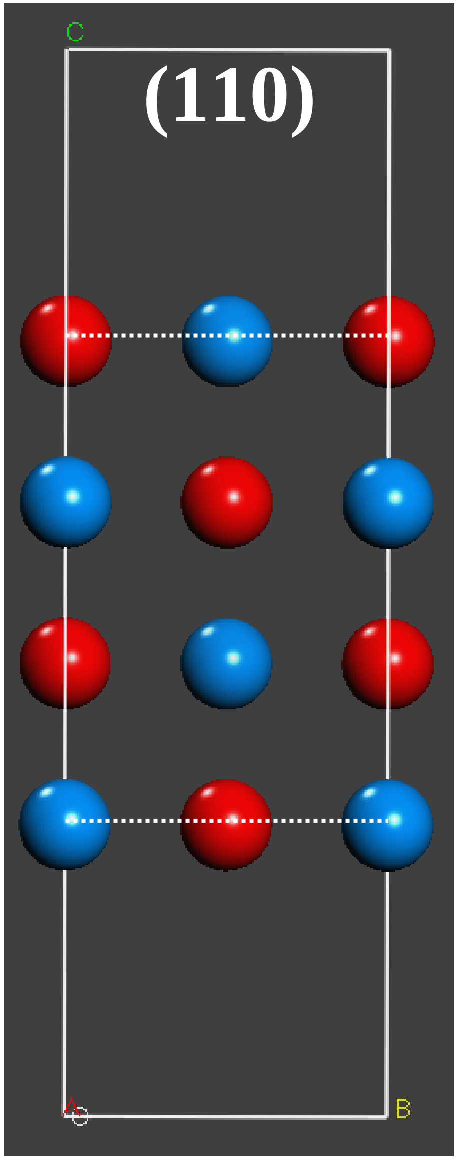
Purpose: Perform **geometry optimization** of bulk and surface slabs

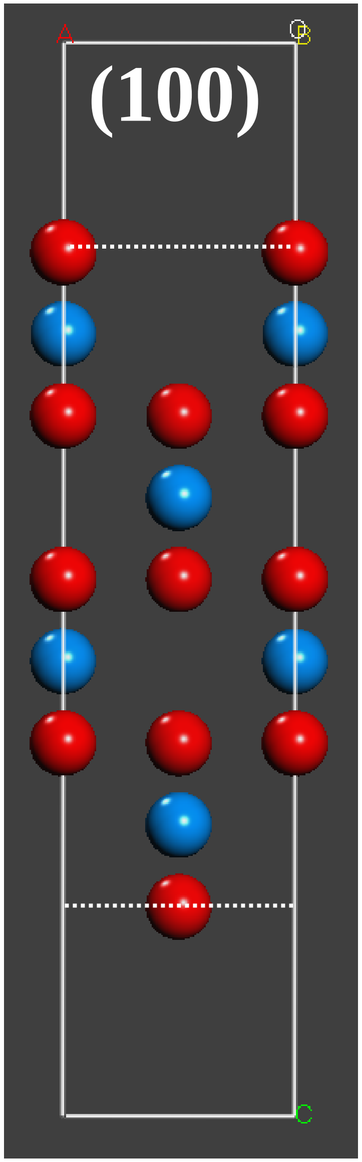
(*CASTEP: CAmbridge Serial Total Energy Package by Accelrys)

UO_2 and ThO_2 surface slab models

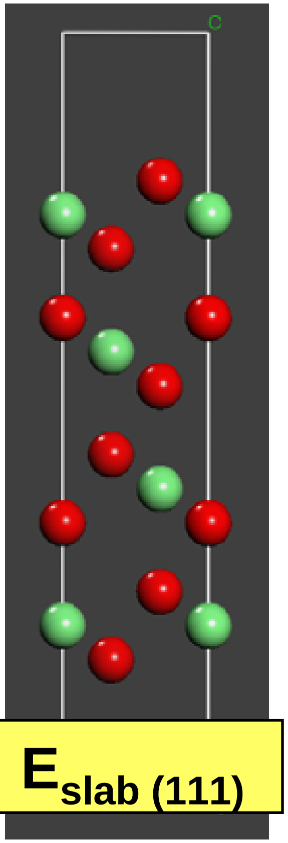




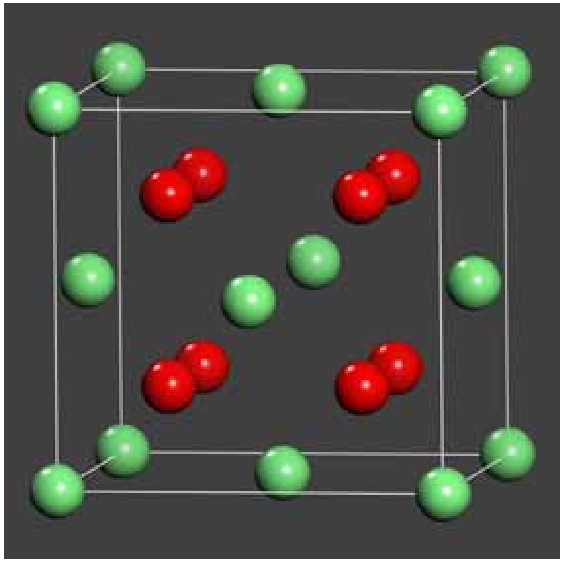




Surface energy calculations



$E_{slab\ (111)}$



E_{bulk}

Surface Energy = $E_{slab} - n \cdot E_{bulk}$

Normalized to slab surface area

Surface energy comparison

	(111)	<	(110)	<	(100)
ThO_2:	0.684 J/m^2		1.274 J/m^2		1.705 J/m^2
UO_2:	0.461 J/m^2		0.846 J/m^2		1.194 J/m^2

→ ***Decreasing Stability***

Adsorption on UO_2 and ThO_2 (111)

"How do UO_2 and ThO_2 surfaces interact with water and oxygen on the atomic scale?"

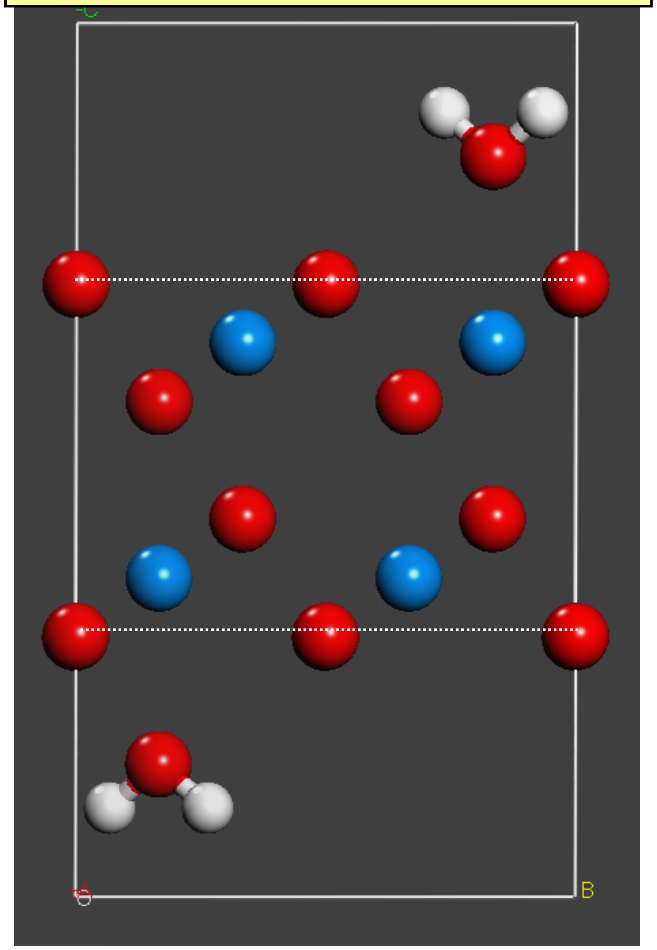
Case 1: Water adsorption

Case 2: Oxygen adsorption

Case 3: Combined adsorption

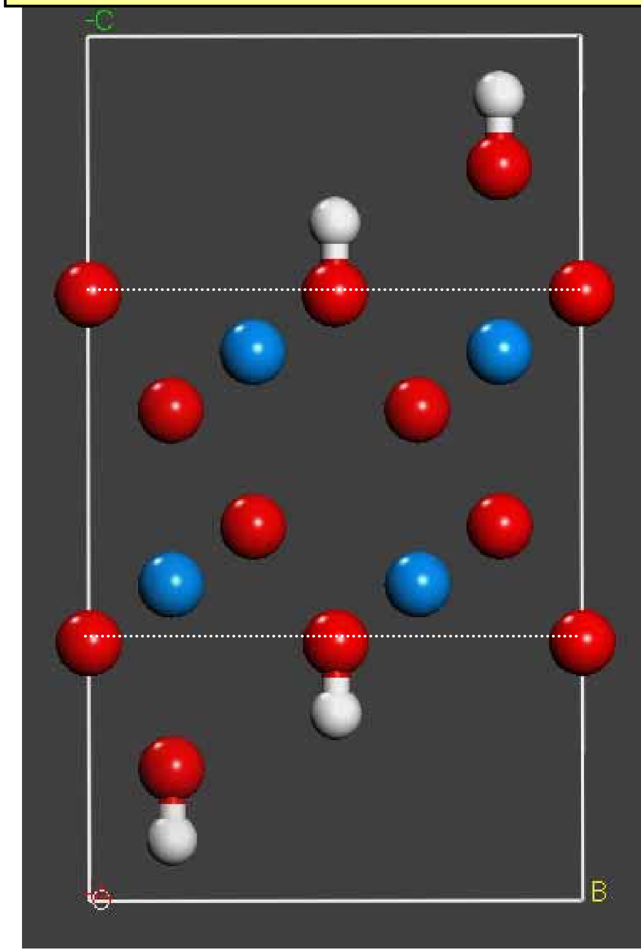
Case 1: The interaction of water with the UO_2 versus ThO_2 (111) surface

Molecular water case



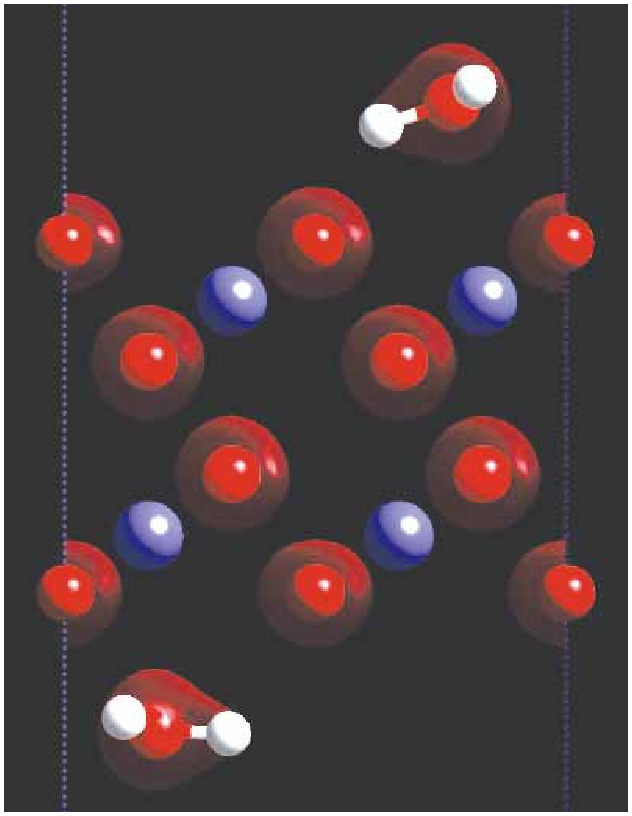
OR

Dissociated water case

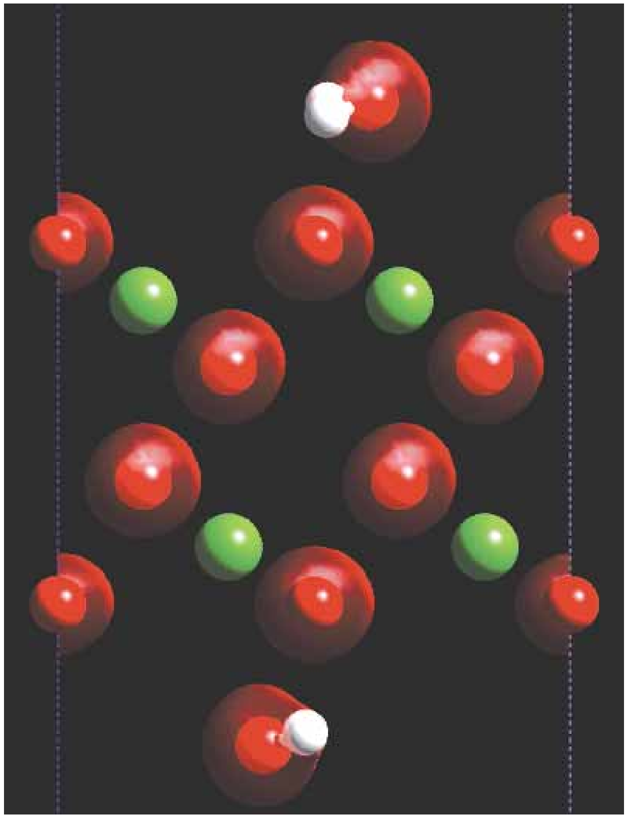


$$E_{slab + ads} - E_{slab} - E_{ads} = E_{adsorption}$$

Adsorption of molecular water is favored over dissociated water

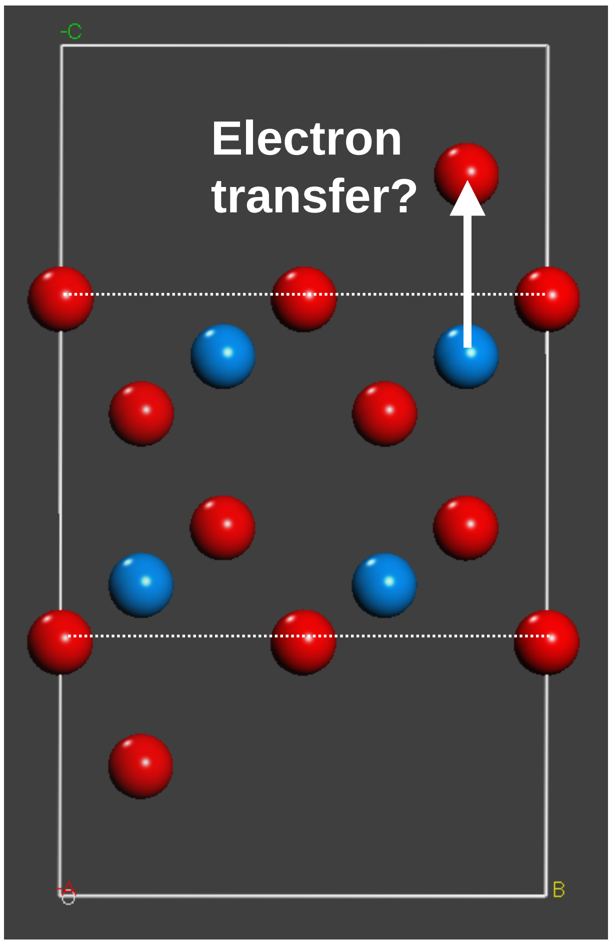


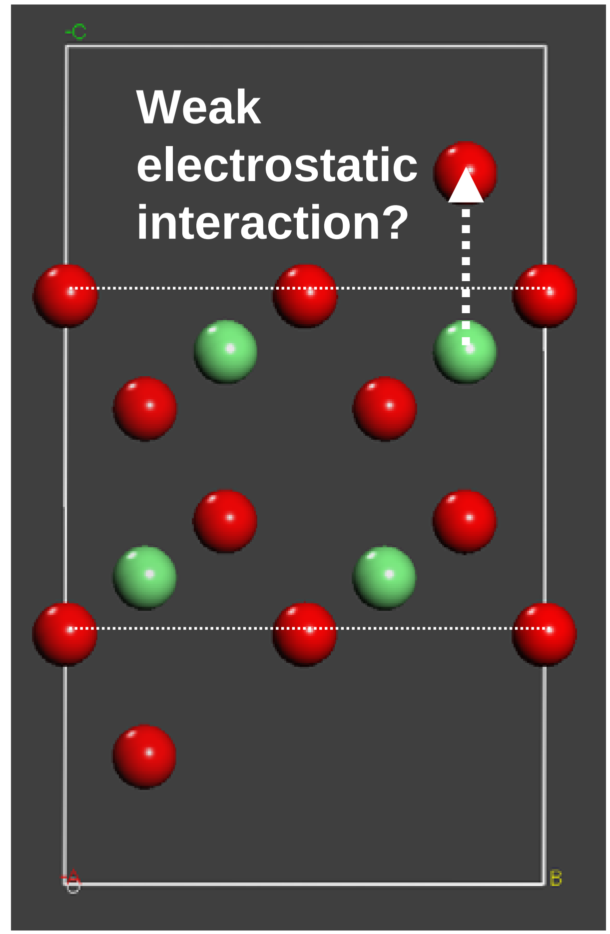
-0.59 eV
(-57.2 kJ/mol)
per H_2O molecule



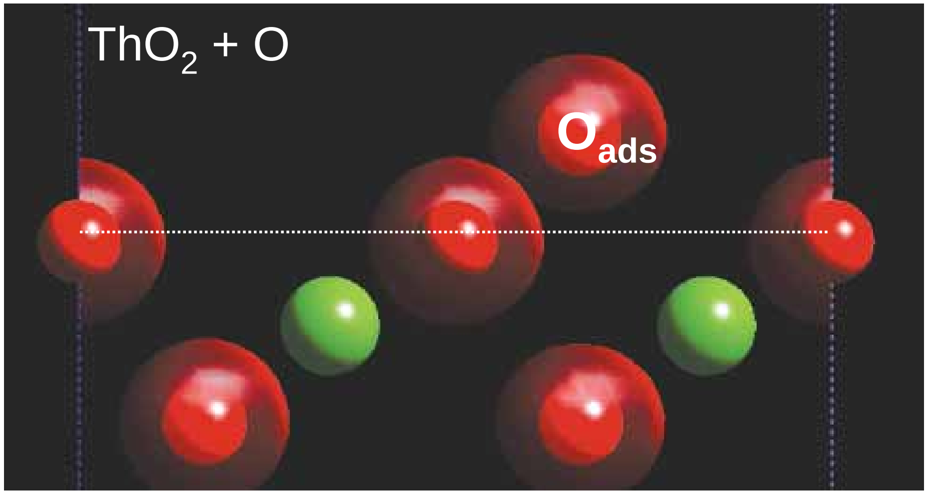
-0.60 eV
(-58.3 kJ/mol)
per H_2O molecule

Case 2: The interaction between UO_2 and ThO_2 (111) with oxygen





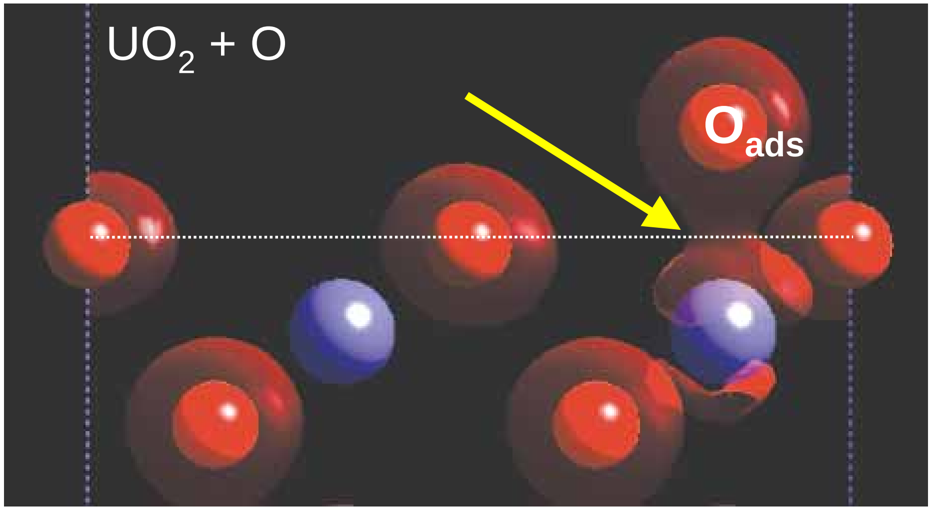
Oxygen interacts with UO_2 >> ThO_2



+73 kJ/mol per O atom

½O_2+ThO_2 → O-ThO_2
ΔH = +73 kJ/mol

O+ThO_2 → O-ThO_2
ΔH= **-176** kJ/mol



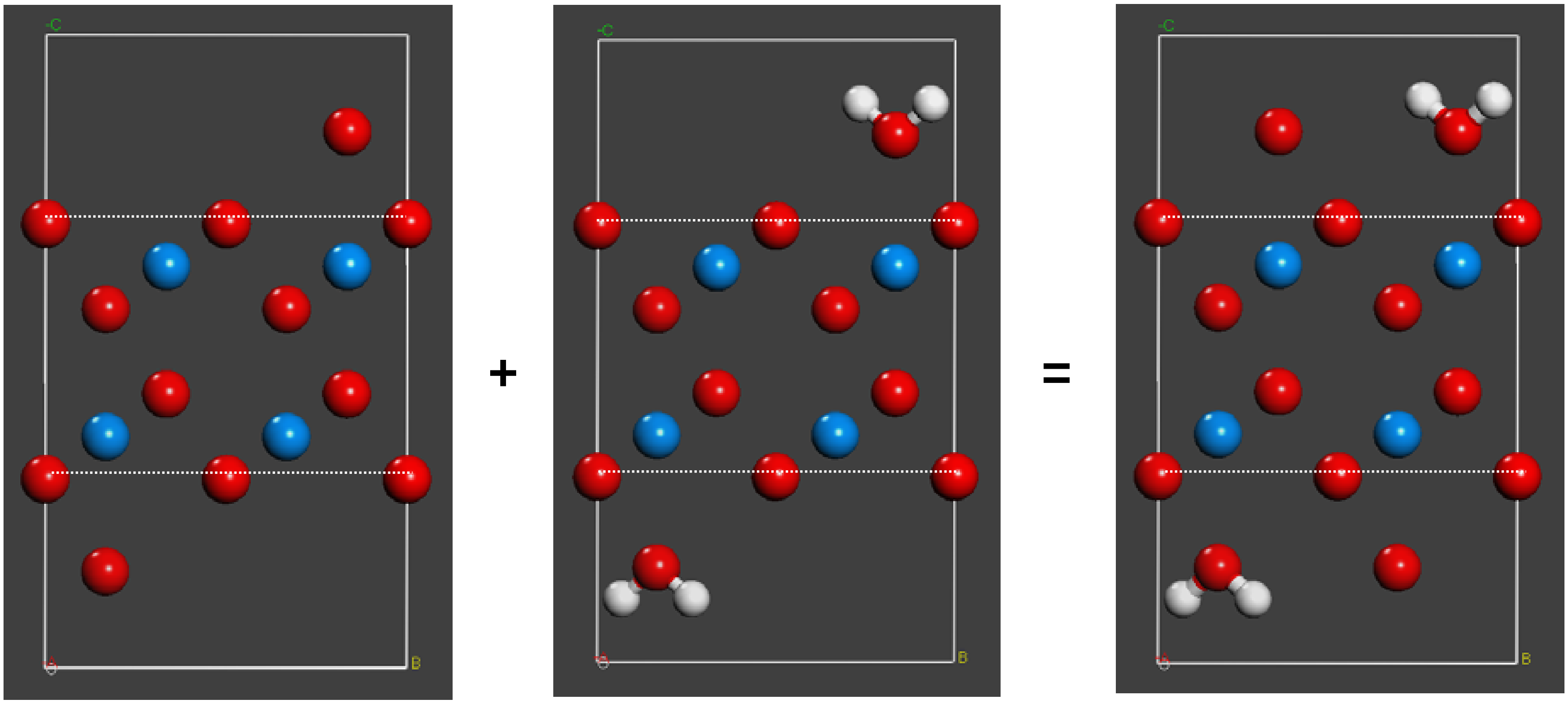
-27 kJ/mol per O atom

½O_2+UO_2 -> O-UO_2
ΔH = -27 kJ/mol

O+UO_2 -> O-UO_2
ΔH= **-276** kJ/mol

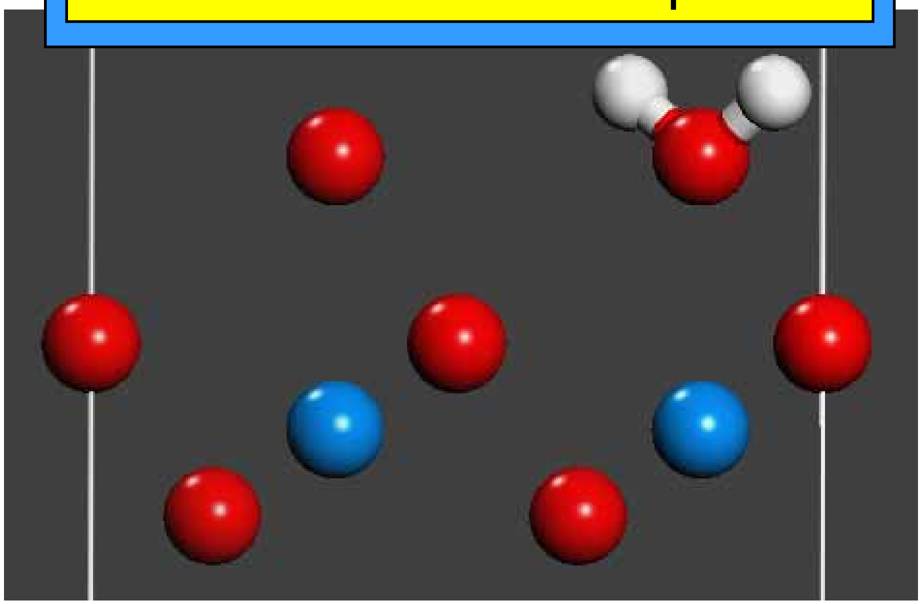
Case 3: Combined versus individual adsorption of water and oxygen

Oxygen alone + **Water alone** = **Combined case**



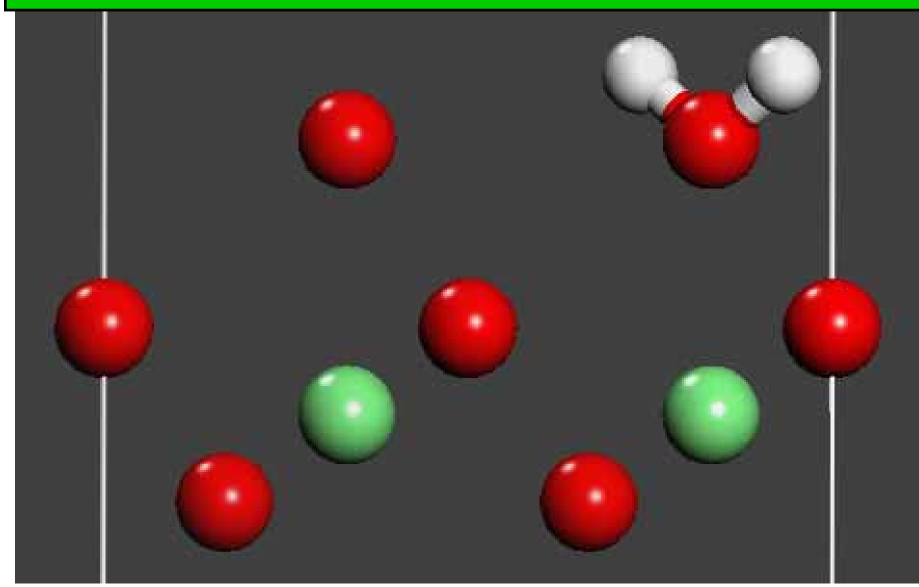
Oxidation is more favorable when water is present on UO_2 (111)

Combined case is **0.29 eV (28.1 kJ/mol)** more favorable than individual adsorption.



Combined: -1.16 eV per adsorbed atoms & molecules (**-111.6 kJ/mol**)

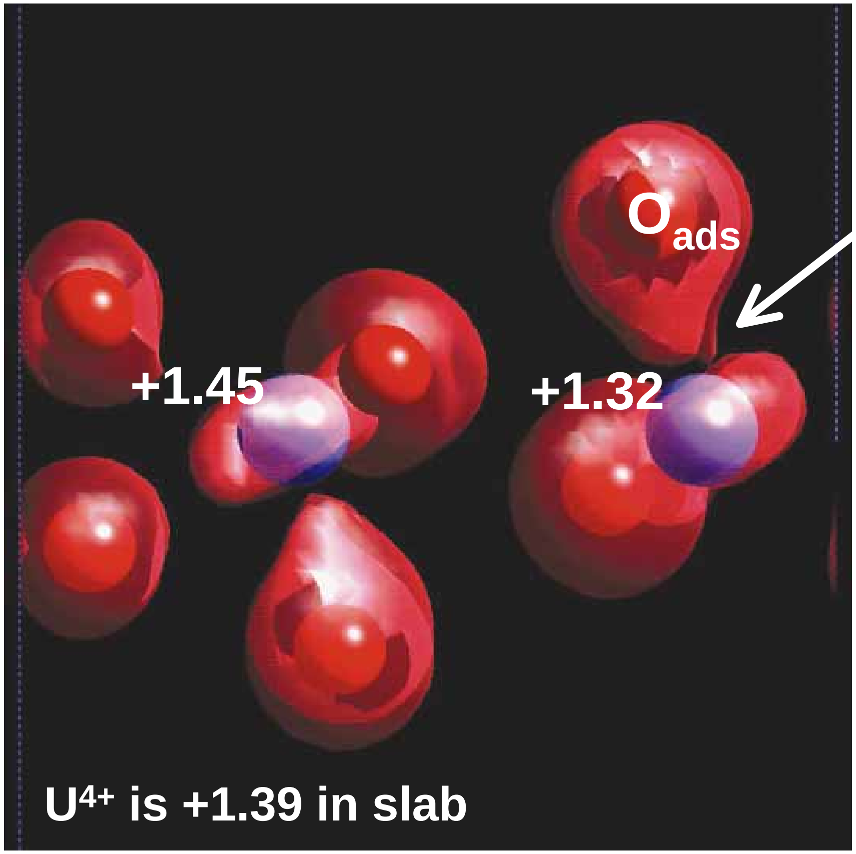
Combined case is nearly identical to sum of individual cases (**0.08 eV, 7.75 kJ/mol** lower).

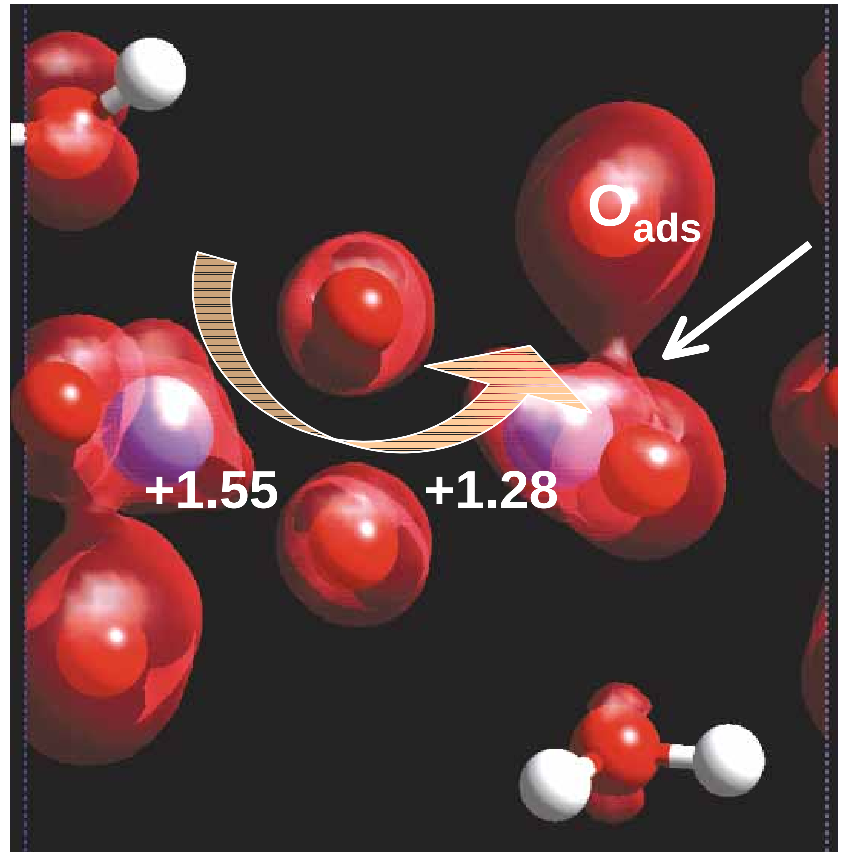


Combined: +0.069 eV per adsorbed atoms & molecules (**+6.66 kJ/mol**)

Nearby water enhances the adsorption of oxygen due to electron transfer

Oxygen only	Molecular water + oxygen





Summary and Conclusions

Clean surfaces:

- **Relative surface energy trends: (111) < (110) < (100) are observed for UO_2 and ThO_2**
- **UO_2 exhibits lower surface energy overall**

Surfaces + Adsorbates:

- **Adsorption trends on UO_2 and ThO_2 (111) are similar when electron transfer is not involved**
- **Adsorption of molecular water favored over dissociated water on defect free (111) surfaces**

Summary and conclusions cont.

Surfaces + Adsorbates (cont.):

- **UO_2 oxidizes more readily than ThO_2**
- **Adsorption interactions are stronger on UO_2 than ThO_2 when electron transfer is involved**

- **Electron transfer is important during the corrosion of semi-conducting materials (UO_2) – less significant on insulating surfaces (ThO_2)**