Water Layers on Actinide Oxide Surfaces

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Outline

- Motivation and Method
- Water on Pristine AnO_2
- Water on Reduced AnO_2
- More Water Layers on AnO_2
- Summary and Conclusions
- Acknowledgements

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Motivation

- The UK's stock of civil plutonium is stored as PuO_2 powder in multi layer steel cans in Sellafield.
- Under certain circumstances, gas generation may occur within the cans, with consequent pressurisation.
- Several proposed routes to gas production, including:

(i) steam produced by H_2O desorption from hygroscopic PuO_2 due to self-heating

(ii) radiolysis of adsorbed water

(iii) generation of H_2 by reaction of PuO_2 with H_2O, producing a "postulated" PuO_{2+x} phase

All involve PuO_2/H_2O interactions and are complex, inter-connected and poorly understood

$\Rightarrow$ Model the interaction of water on PuO_2 surfaces at the atomic level.

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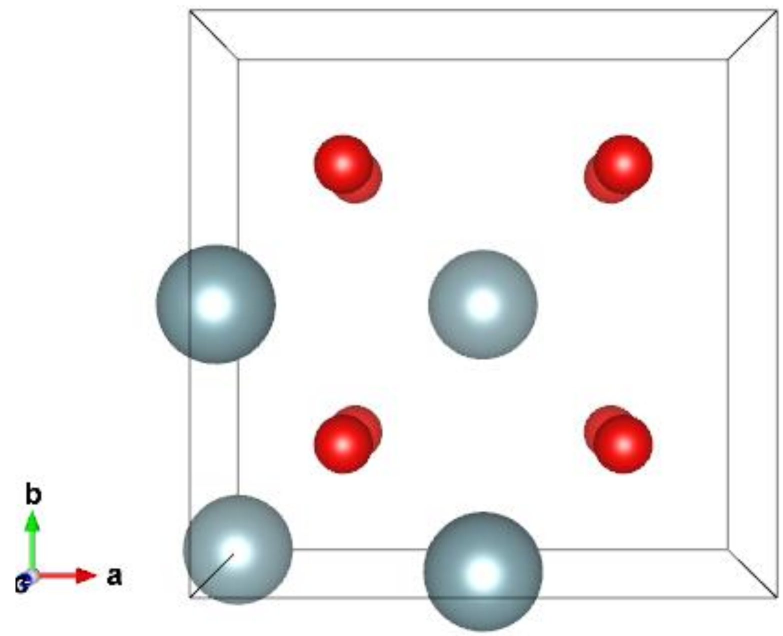
Computational Method

- Density Functional Theory
- VASP 5.4.1
- Plane wave basis set
- PAW-pseudopotentials
- k-point sampling of 1st Brillouin zone
- Spin-polarised
- DFT+U = PBE+U
- $U_{eff} = (U - J) = 4.0$ eV



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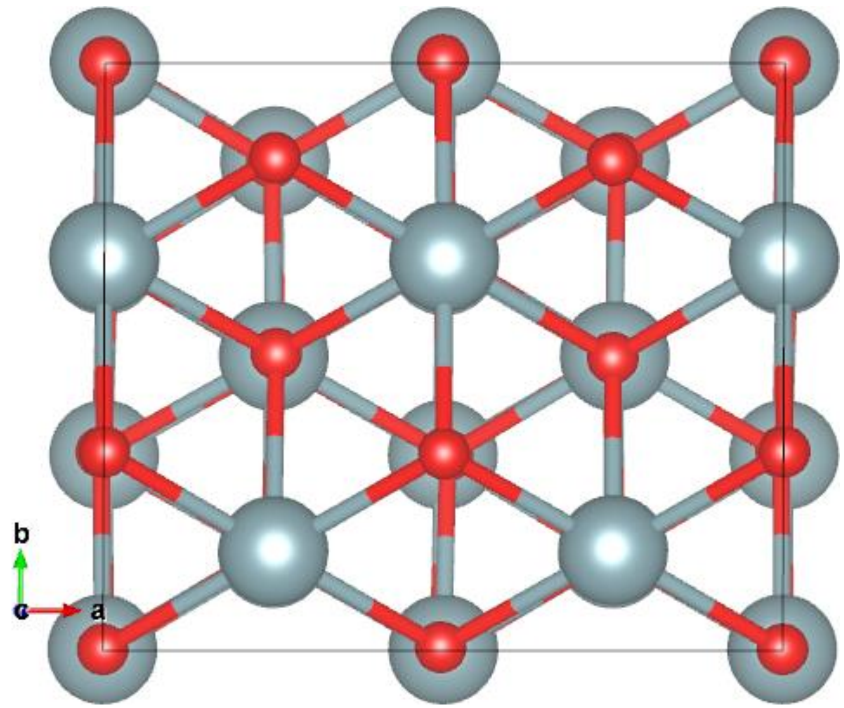
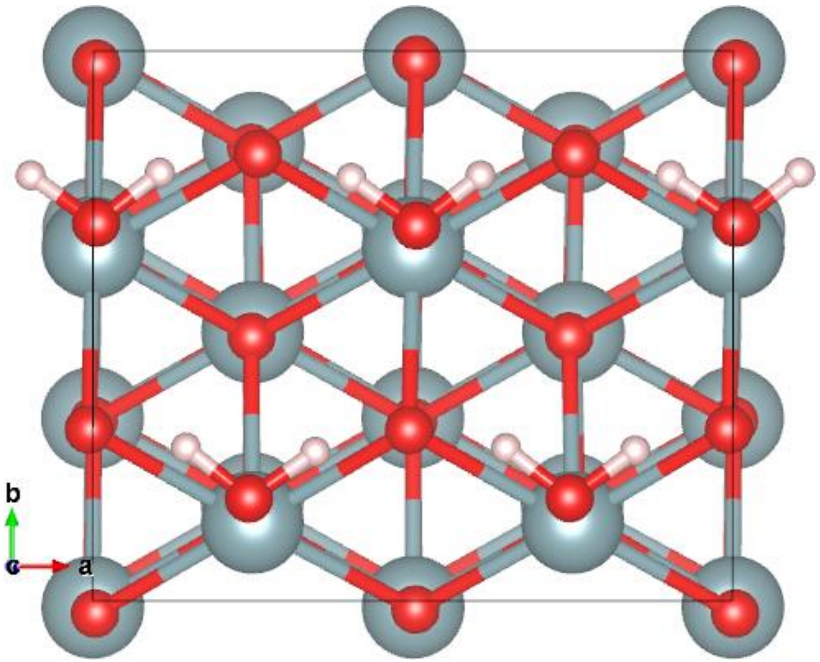
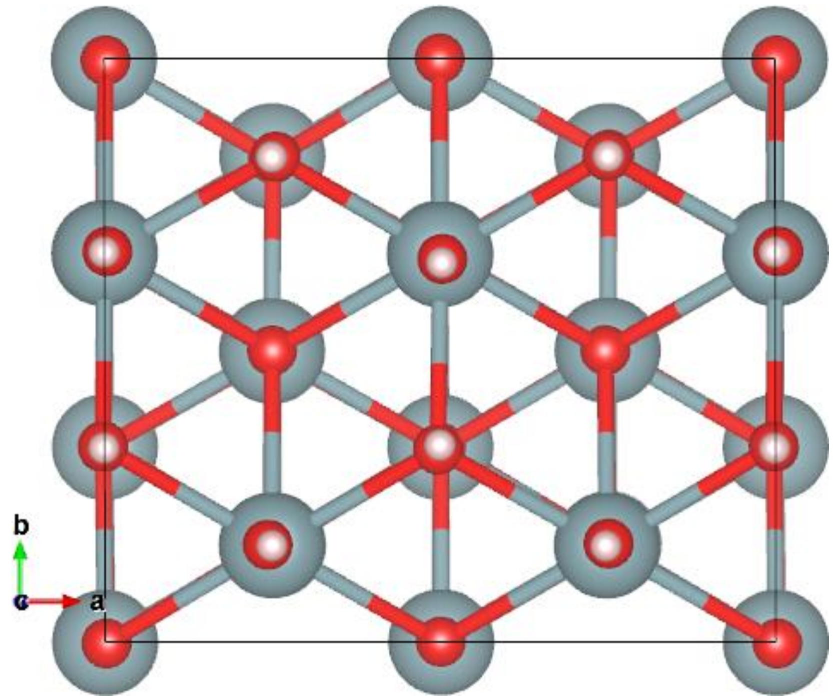
Computational Method

- Surfaces are modelled using a repeating slab of 24 AnO_2 units (An = U or Pu) with 18 Å of vacuum between each slab.
- Water is adsorbed on both sides of the slab to ensure the system has no net dipole moment.



Water on Pristine AnO_2 (111)



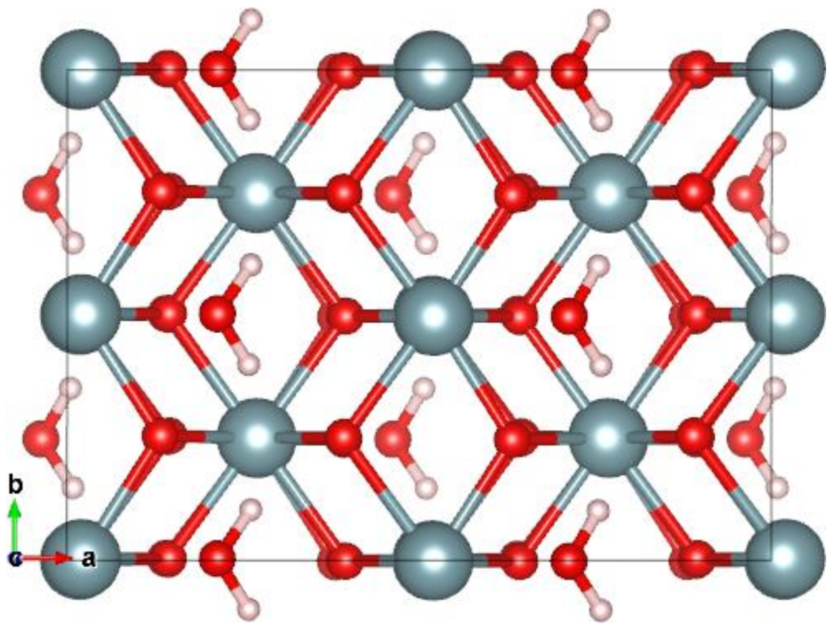


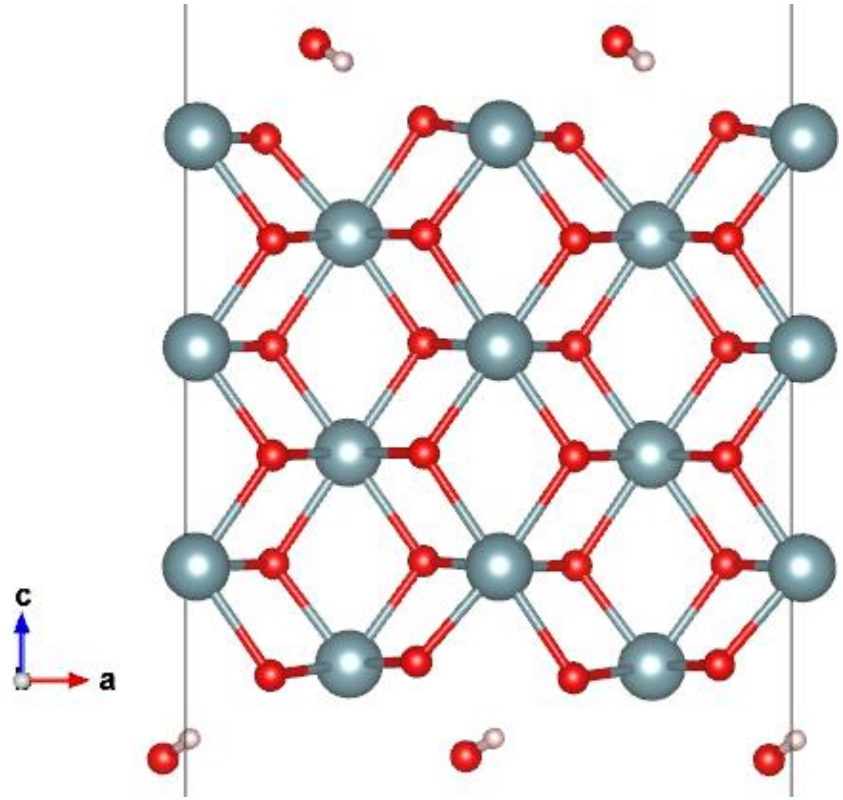
Molecular

Dissociative

100% coverage = 1 Monolayer

Water on Pristine AnO_2 (110)





Molecular
100% Coverage = 1 Monolayer

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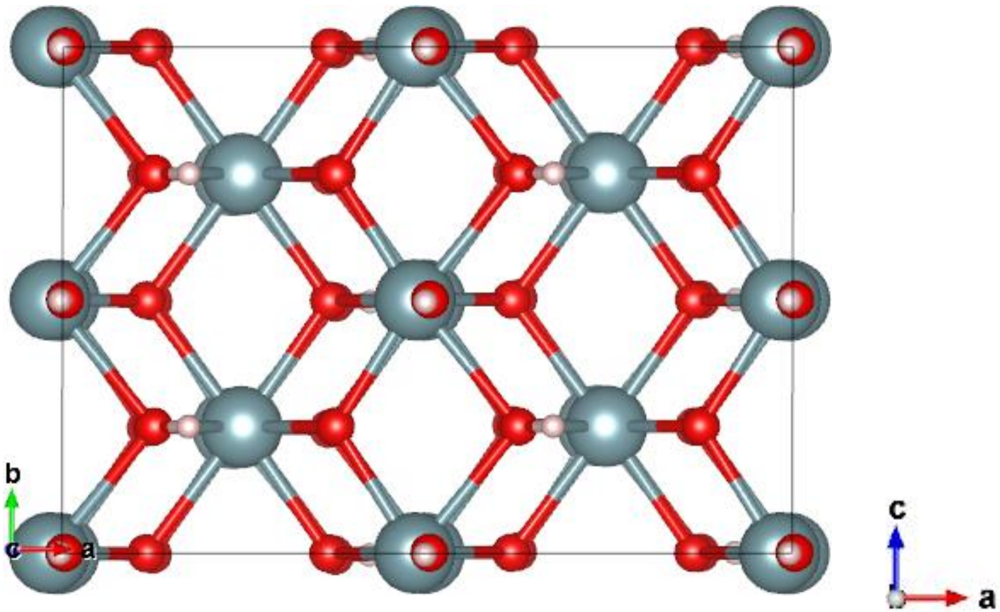
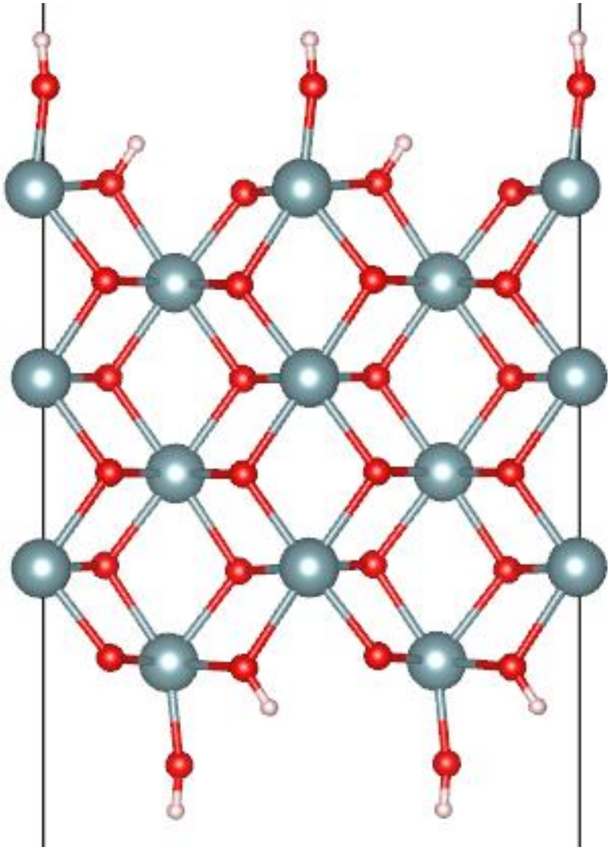
Water on Pristine AnO_2 (110)





Dissociative
100% Coverage = 1 Monolayer

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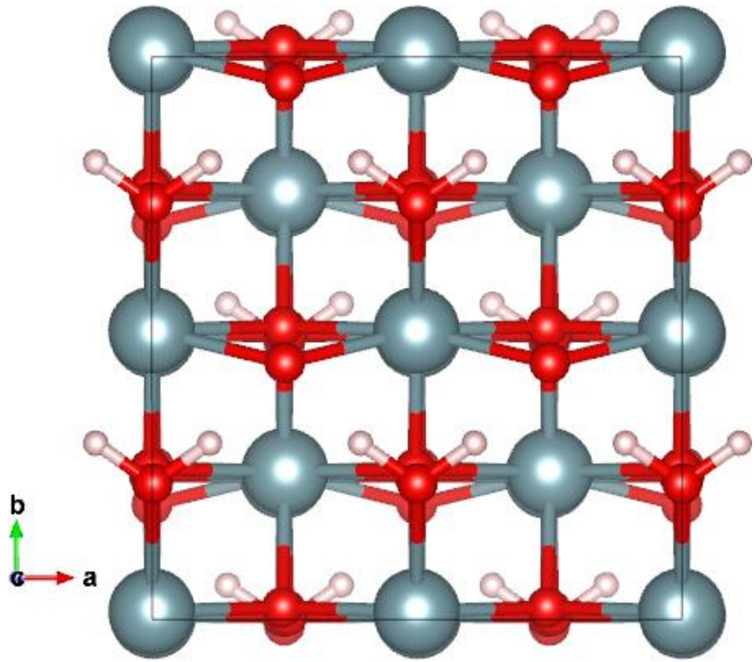
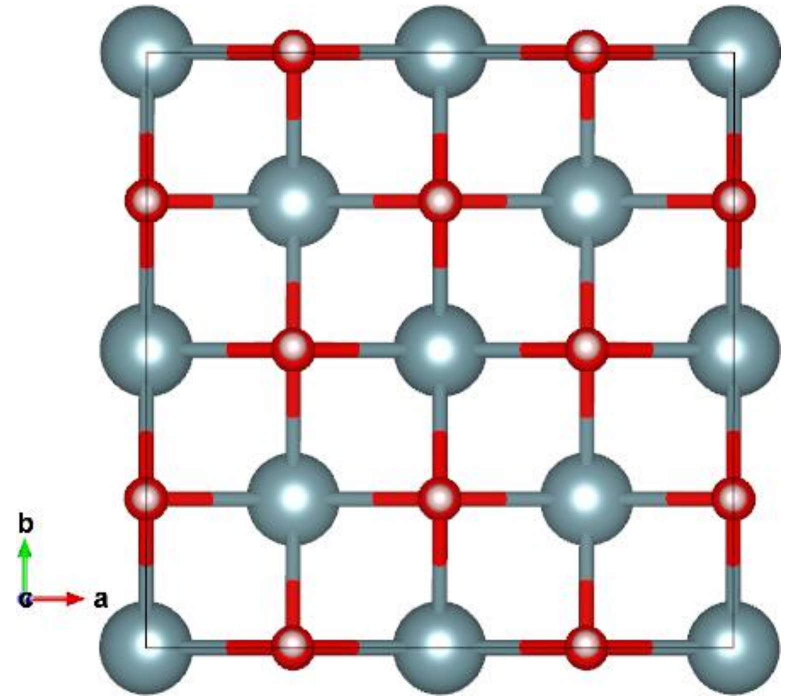
Water on Pristine AnO_2 (100)



Molecular



Dissociative

100% coverage = 1 Monolayer

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Water on Pristine AnO_2

- Results on the pristine AnO_2 (111), (110) and (100) surfaces suggest mixed (i.e. both molecular and dissociative) adsorption on the (111) surface, and dissociative adsorption on the (110) and (100) surfaces.
- Using these results we calculate water desorption temperatures for the most stable configurations on each surface at various pressures.
- These results have been written up and published in the Journal of Physical Chemistry C **121** (2017) 1675.

AnO_2 Surface Oxygen Vacancies

Oxygen vacancy formation energies in eV.

Surface	(111)	(110)	(100)	Bulk
UO_2 (1st O layer)	6.45	5.69	5.93	-
UO_2 (2nd O layer)	5.88	6.25	6.22	-
UO_2 [1]	-	-	-	6.14
PuO_2 (1st O layer)	3.35	2.49	2.50	-
PuO_2 (2nd O layer)	3.40	2.75	3.27	-
PuO_2 [2]	-	-	-	3.76

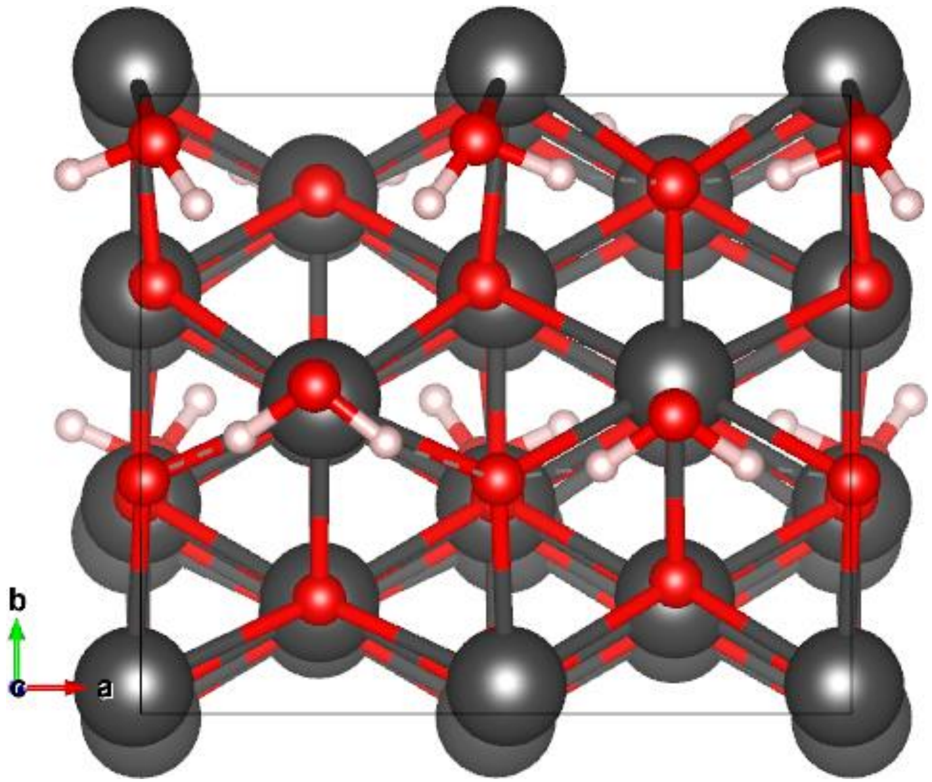
$U^{4+} + e^- \rightleftharpoons U^{3+}$ $E = -0.52$ V

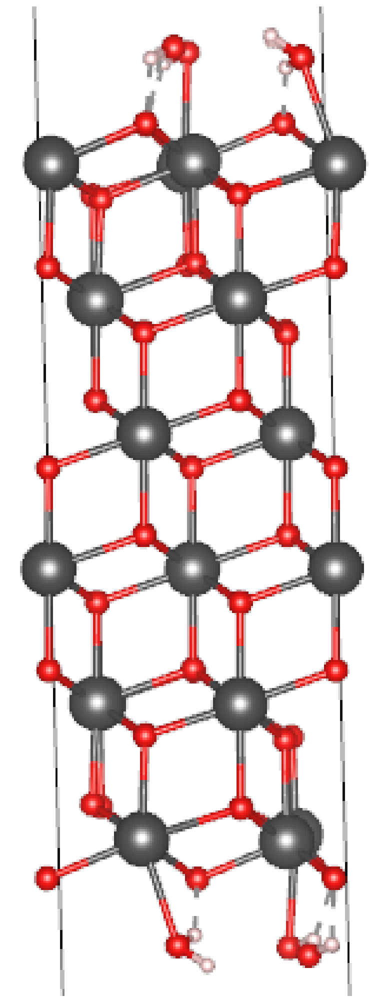
$Pu^{4+} + e^- \rightleftharpoons Pu^{3+}$ $E = +1.01$ V

[1] Bo *et al*. *J. Phys. Chem. C* **2014**, *118*, 21935–21944.

[2] Ao *et al*. *Comput. Mater. Sci.* **2016**, *122*, 263–271.

Water on Reduced AnO_2 (111)





Molecular

100% Coverage = 1 Monolayer

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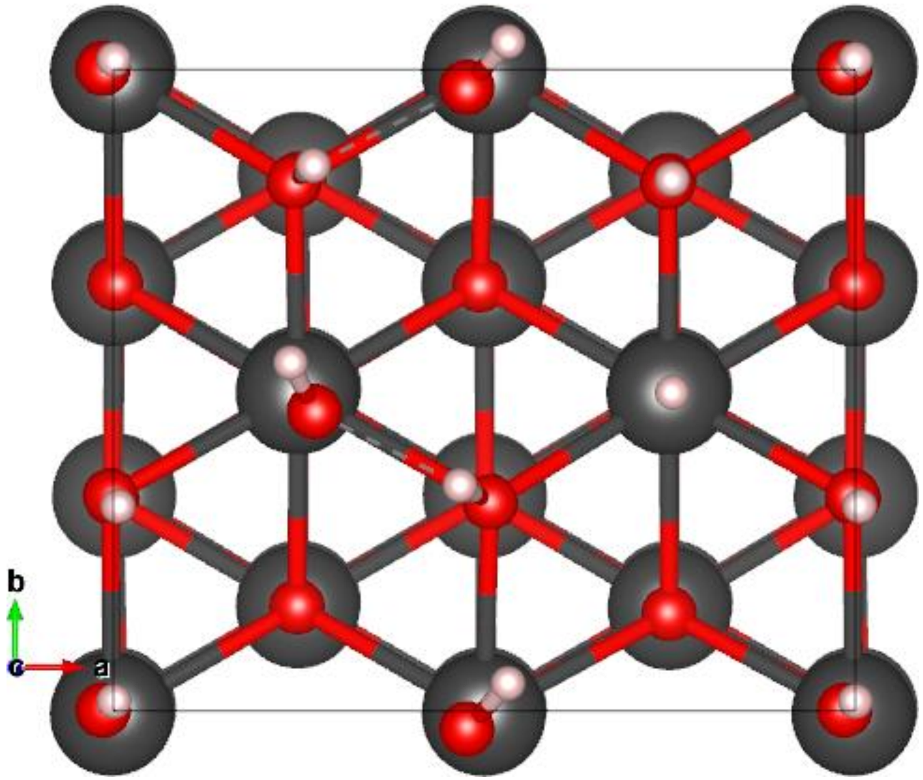
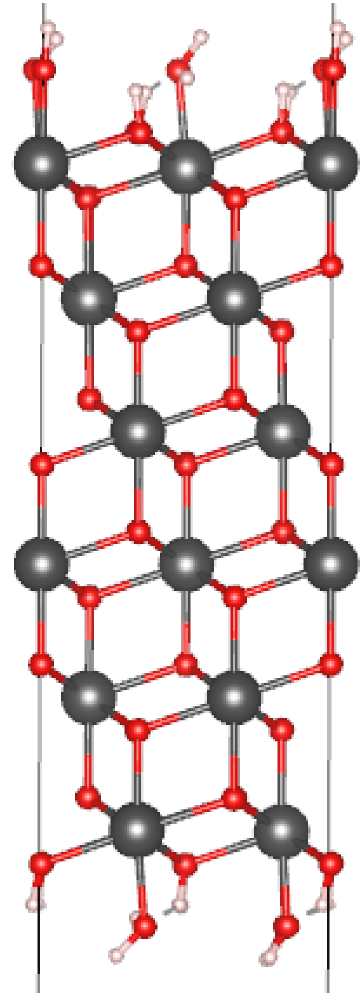
Water on Reduced AnO_2 (111)





Dissociative

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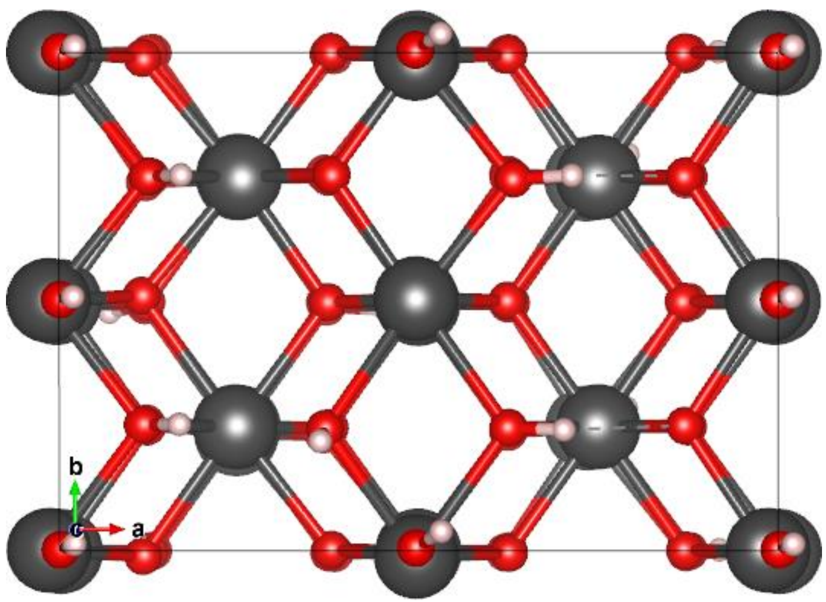
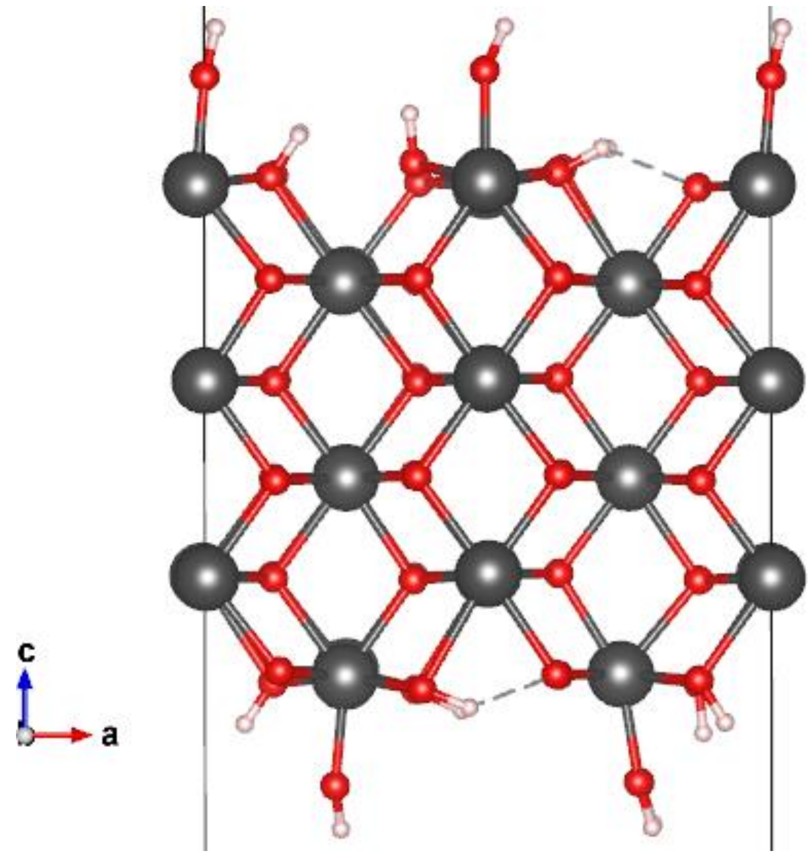
Water on Reduced AnO_2 (111)

Adsorption energies in eV per water molecule.

System	0.25 Monolayer	1.0 Monolayer
Pristine UO_2 + H_2O	-0.53	-0.49
Pristine UO_2 + OH + H	-0.50	-0.15
Reduced UO_2 + H_2O	-0.90	-0.66
Reduced UO_2 + OH + H	-2.23	-0.91
Pristine PuO_2 + H_2O	-0.40	-0.44
Pristine PuO_2 + OH + H	-0.32	-0.07
Reduced PuO_2 + H_2O	-0.60	-0.62
Reduced PuO_2 + OH + H	-2.10	-0.07

Water on Reduced AnO_2 (110)





Dissociative

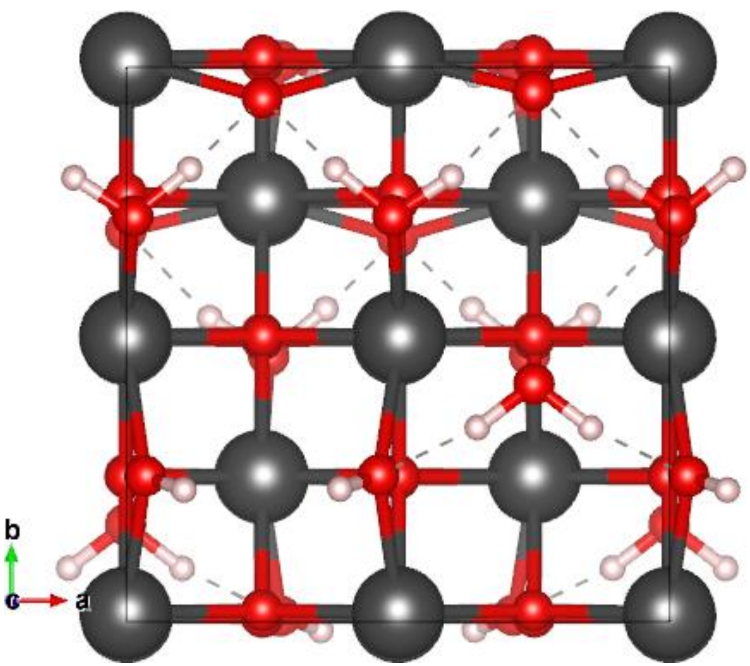
100% Coverage = 1 Monolayer

Water on Reduced AnO_2 (110)

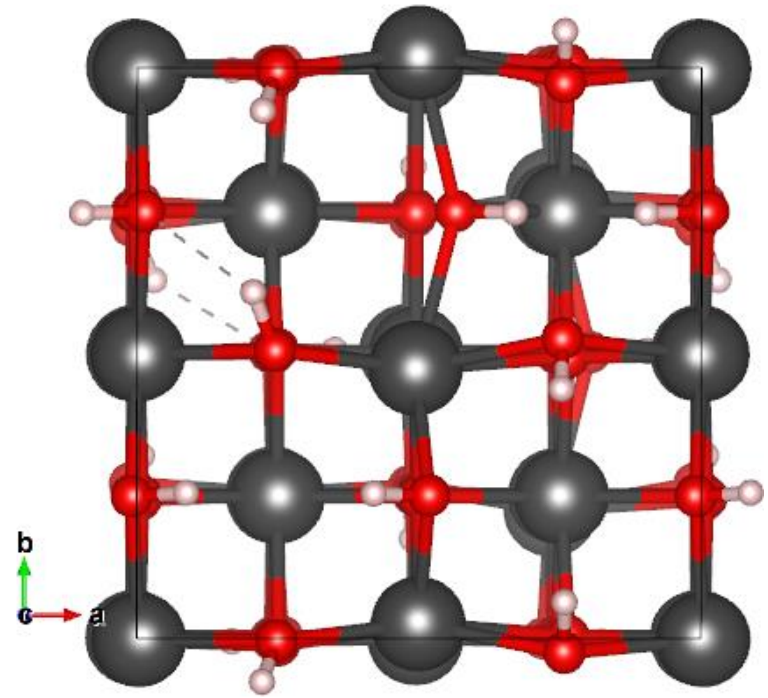
Adsorption energies in eV per water molecule.

System	0.25 Monolayer	1.0 Monolayer
Pristine UO_2 + H_2O	-0.93	-0.65
Pristine UO_2 + OH + H	-1.39	-1.00
Reduced UO_2 + H_2O	-0.82	-0.74
Reduced UO_2 + OH + H	-1.50	-1.01
Pristine PuO_2 + H_2O	-0.88	-0.39
Pristine PuO_2 + OH + H	-1.14	-0.91
Reduced PuO_2 + H_2O	-0.44	-0.75
Reduced PuO_2 + OH + H	-1.51	-1.10

Water on Reduced AnO_2 (100)



Molecular



Dissociative

100% coverage = 1 Monolayer

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Water on Reduced AnO_2 (100)

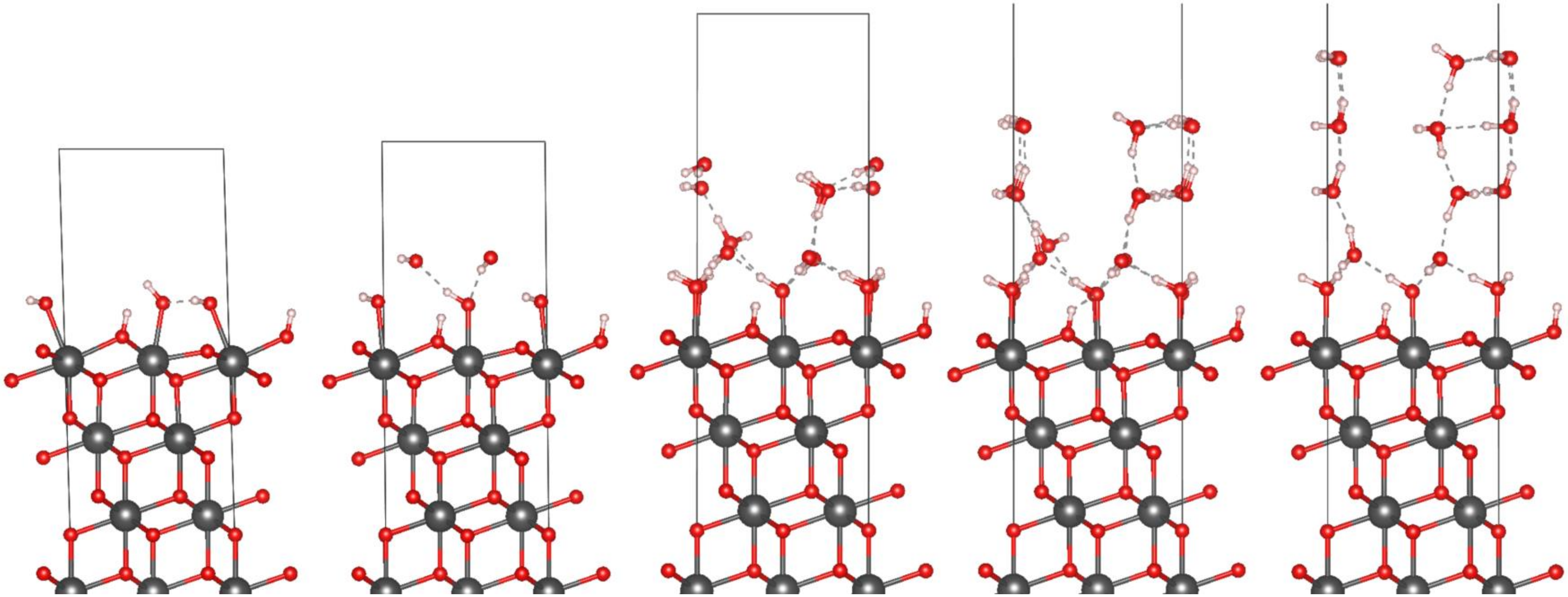
Adsorption energies in eV per water molecule.

System	0.25 Monolayer	1.0 Monolayer
Pristine UO_2 + H_2O	-0.97	-0.86
Pristine UO_2 + OH + H	-1.55	-1.01
Reduced UO_2 + H_2O	-1.62	-1.12
Reduced UO_2 + OH + H	-2.43	-1.78
Pristine PuO_2 + H_2O	-1.12	-0.95
Pristine PuO_2 + OH + H	-1.76	-1.37
Reduced PuO_2 + H_2O	-2.59	-1.29
Reduced PuO_2 + OH + H	-2.82	-1.31

Water on Reduced AnO_2

- It is energetically easier to form oxygen vacancies in PuO_2 compared with UO_2.
- Results on the reduced AnO_2 (111), (110) and (100) surfaces suggest a strong preference for dissociative adsorption on all three surfaces.
- Water might spontaneously dissociate near an oxygen vacancy on the (100) surface, potentially forming hydrogen gas.
- These results have been written up and published in the Journal of Physical Chemistry C **122** (2018) 7149.

More Water Layers on AnO_2 (111)



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More Water Layers on AnO_2 (111)

Adsorption energies per layer in eV per water molecule.

System	1st Layer: 100% H_2O, 50% / 50% H_2O / OH + H, or 100% OH + H	2nd Layer: 100% H_2O	3rd Layer: 100% H_2O	4th Layer: 100% H_2O	5th Layer: 100% H_2O
$PuO_2 + H_2O$	-0.45	-0.57	-0.65	-0.48	-0.65
PuO_2 + 50% H_2O + 50% OH + H	-0.57	-0.06	-0.91	-0.59	-0.46
PuO_2 + OH + H	-0.17	-0.58	-0.38	-0.59	-0.77

More Water Layers on AnO_2 (111)

Average adsorption energies in eV per water molecule.

System	1st Layer: 100% H_2O, 50% / 50% H_2O / OH + H, or 100% OH + H	2nd Layer: 100% H_2O	3rd Layer: 100% H_2O	4th Layer: 100% H_2O	5th Layer: 100% H_2O
$PuO_2 + H_2O$	-0.45	-0.51	-0.56	-0.54	-0.56
PuO_2 + 50% H_2O + 50% OH + H	-0.57	-0.31	-0.51	-0.53	-0.52
PuO_2 + OH + H	-0.17	-0.38	-0.38	-0.43	-0.50

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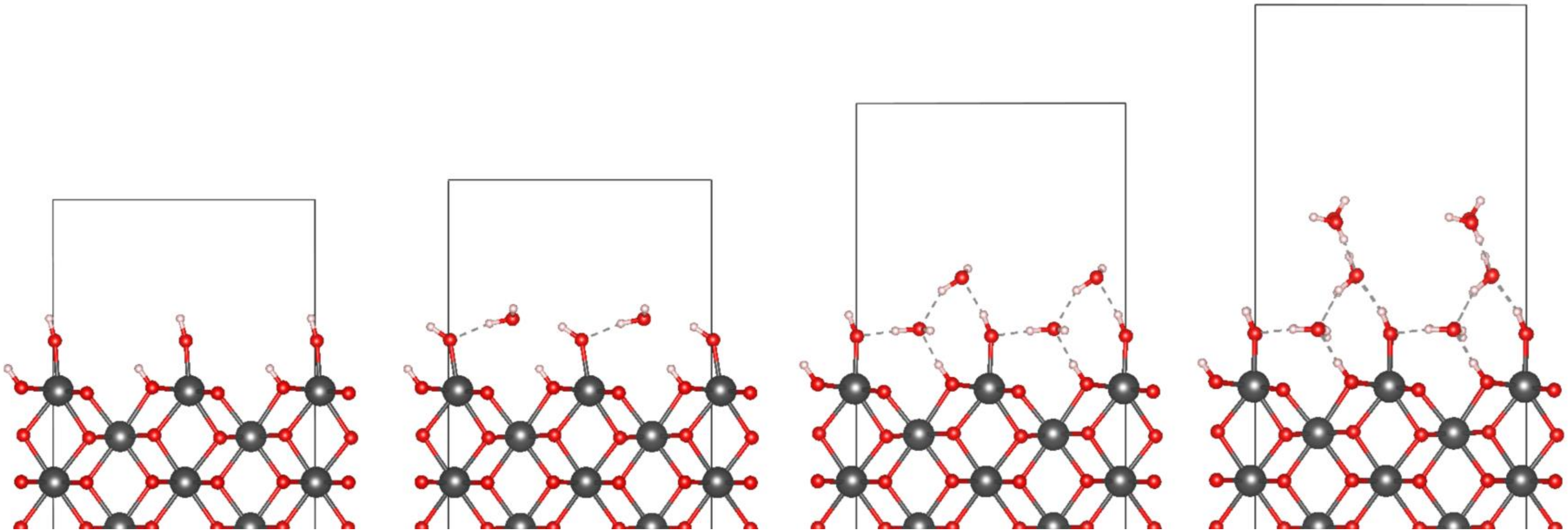
More Water Layers on AnO_2 (110)



More Water Layers on AnO_2 (110)

Adsorption energies per layer in eV per water molecule.

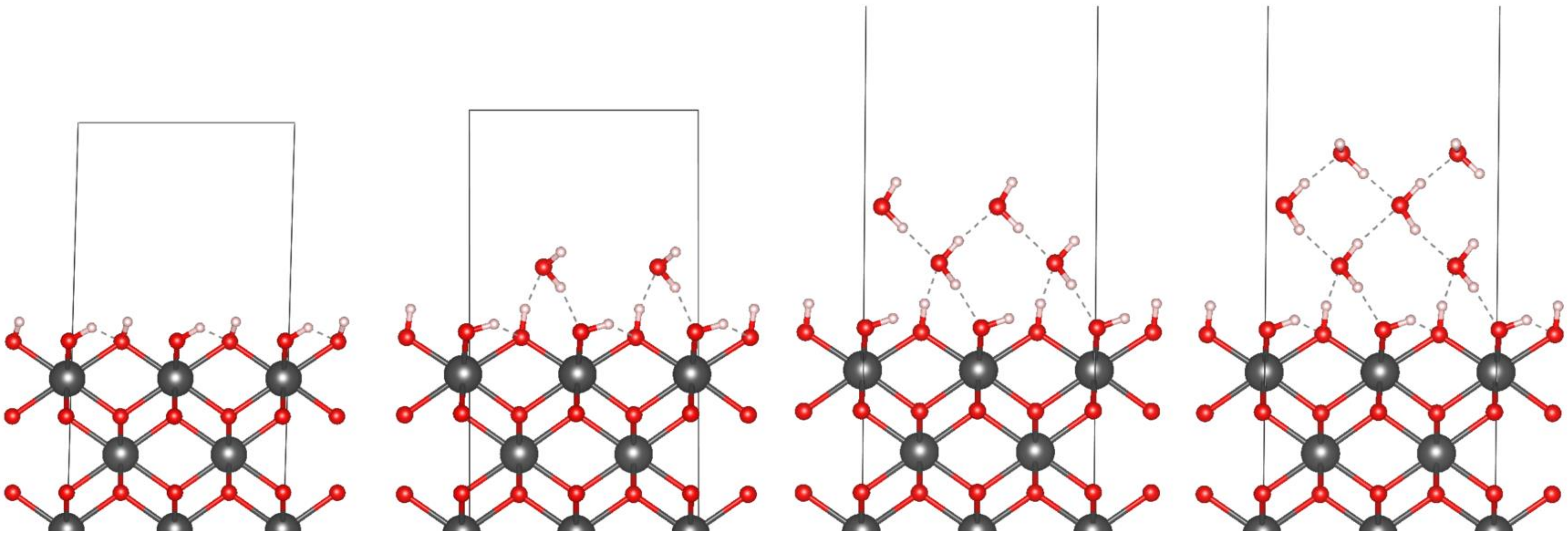
System	1st Layer: 100% H_2O or 100% OH + H	2nd Layer: 100% H_2O	3rd Layer: 100% H_2O	4th Layer: 100% H_2O
$PuO_2 + H_2O$	-0.39	N/A	N/A	N/A
PuO_2 + OH + H	-0.91	-0.60	-0.44	-0.51

More Water Layers on AnO_2 (110)

Average adsorption energies in eV per water molecule.

System	1st Layer: 100% H_2O or 100% OH + H	2nd Layer: 100% H_2O	3rd Layer: 100% H_2O	4th Layer: 100% H_2O
$PuO_2 + H_2O$	-0.39	N/A	N/A	N/A
PuO_2 + OH + H	-0.91	-0.76	-0.65	-0.62

More Water Layers on AnO_2 (100)



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More Water Layers on AnO_2 (100)

Adsorption energies per layer in eV per water molecule.

System	1^{st} Layer: 100% H_2O or 100% OH + H	2^{nd} Layer: 100% H_2O	3^{rd} Layer: 100% H_2O	4^{th} Layer: 100% H_2O
$PuO_2 + H_2O$	-0.95	N/A	N/A	N/A
PuO_2 + OH + H	-1.37	-0.52	-0.17	-0.79

More Water Layers on AnO_2 (100)

Average adsorption energies in eV per water molecule.

System	1^{st} Layer: 100% H_2O or 100% OH + H	2^{nd} Layer: 100% H_2O	3^{rd} Layer: 100% H_2O	4^{th} Layer: 100% H_2O
$PuO_2 + H_2O$	-0.95	N/A	N/A	N/A
PuO_2 + OH + H	-1.37	-0.94	-0.69	-0.72

Summary and Conclusions

- Results on the pristine AnO_2(111), (110) and (100) surfaces suggest mixed adsorption on the (111) surface and dissociative adsorption on the (110) and (100) surfaces.
- It is energetically easier to form oxygen vacancies in PuO_2 compared with UO_2.
- Adsorption at defects suggest a strong preference for dissociative adsorption on all three surfaces and may provide a mechanism for H_2 formation.
- Adsorption of additional water layers suggest a hydrogen bond network forming after just a few layers on all three surfaces.

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