Water Adsorption on Actinide Oxide Surfaces

Bengt Tegner
School of Chemistry
The University of Manchester

DISTICTIVE Theme 2 Meeting
12th November 2015
Lancaster University

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

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.

"*worker performing general housekeeping and relocating storage cans in the interim storage vault noticed a plutonium bearing storage can was* ***bulging on both ends****"*

Lawrence Livermore National Laboratory 1994

- 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

⇒Model the interaction of water on PuO_2 surfaces at the atomic level

- method development
- initial results

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Outline

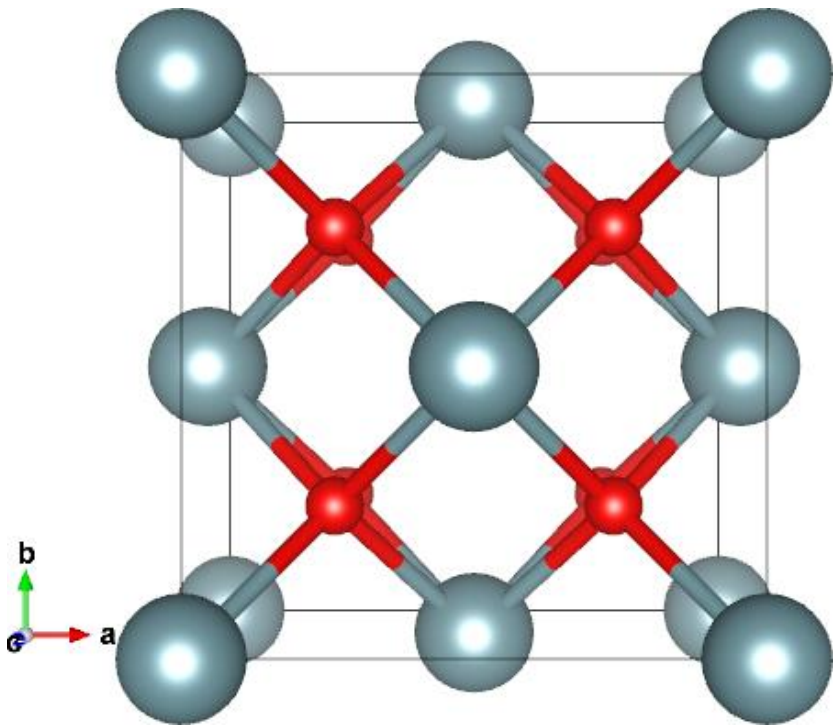
- Introduction and Research Aims
- Background and Methodology
- Results and Discussion
- Conclusions and Future Work

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Introduction and Research Aims

- Fluorite (CaF_2) structure
- Insulators, bandgap 2 - 3 eV
- Research Aims: Study water dynamics on actinide oxide surfaces, using density functional theory.

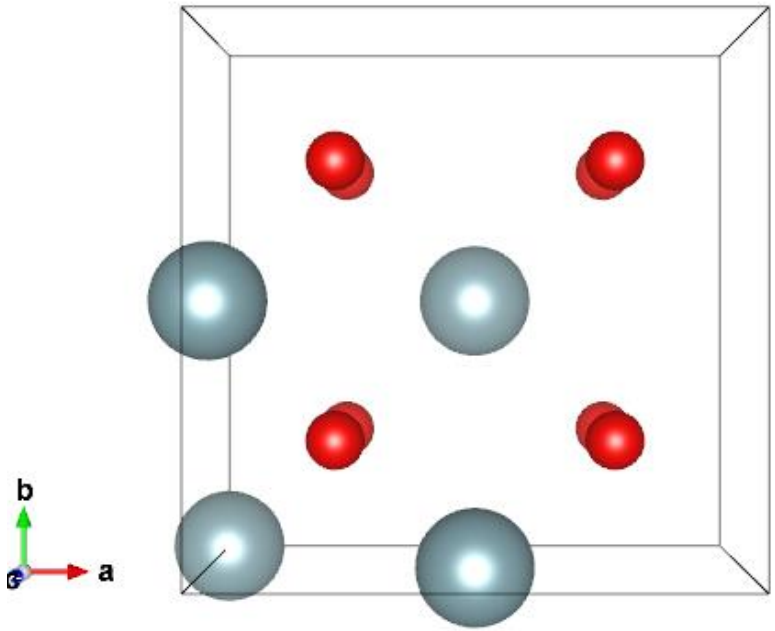


Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Periodic Calculations

- VASP 5.3.5
- PAW-pseudopotentials
- Plane wave basis set
- k-point sampling of 1st BZ
- Spin-polarised
- DFT+*U*



Research Councils UK Energy For a Low Carbon Future

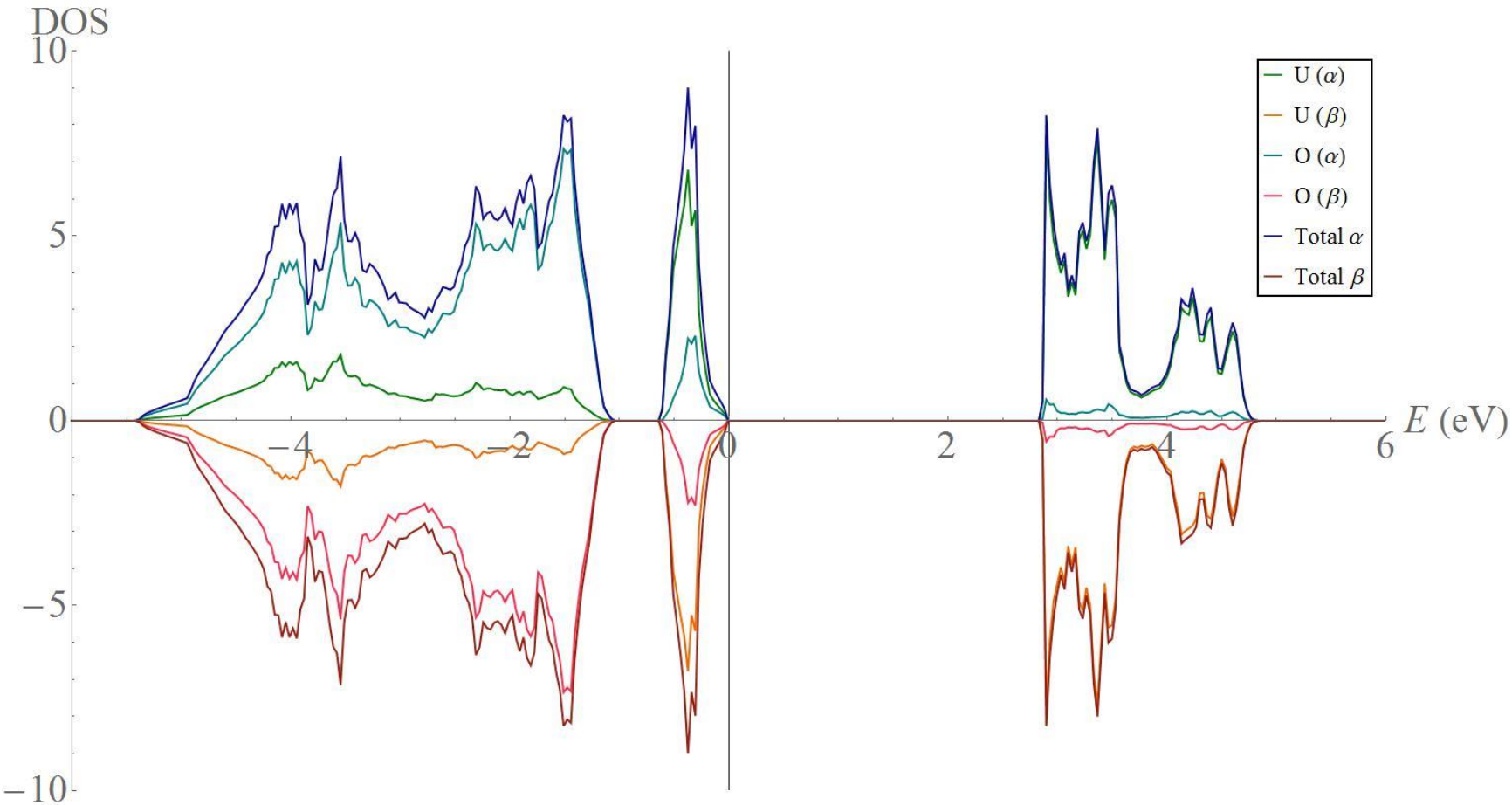
DISTINCTIVE

Results: Lattice Parameters

System	PBE+*U* (Å)	Other Calcs. (Å) (PBE+*U*, HSE [1])	Expt. (Å) [1]
UO_2	5.566	5.568, 5.458	5.470
NpO_2	5.498	5.498, 5.412	5.420
PuO_2	5.435	5.465, 5.383	5.398

[1] X.-D. Wen, R. L. Martin, T. M. Henderson, and G. E. Scuseria, *Chem. Rev*. 113:1063, 2013.

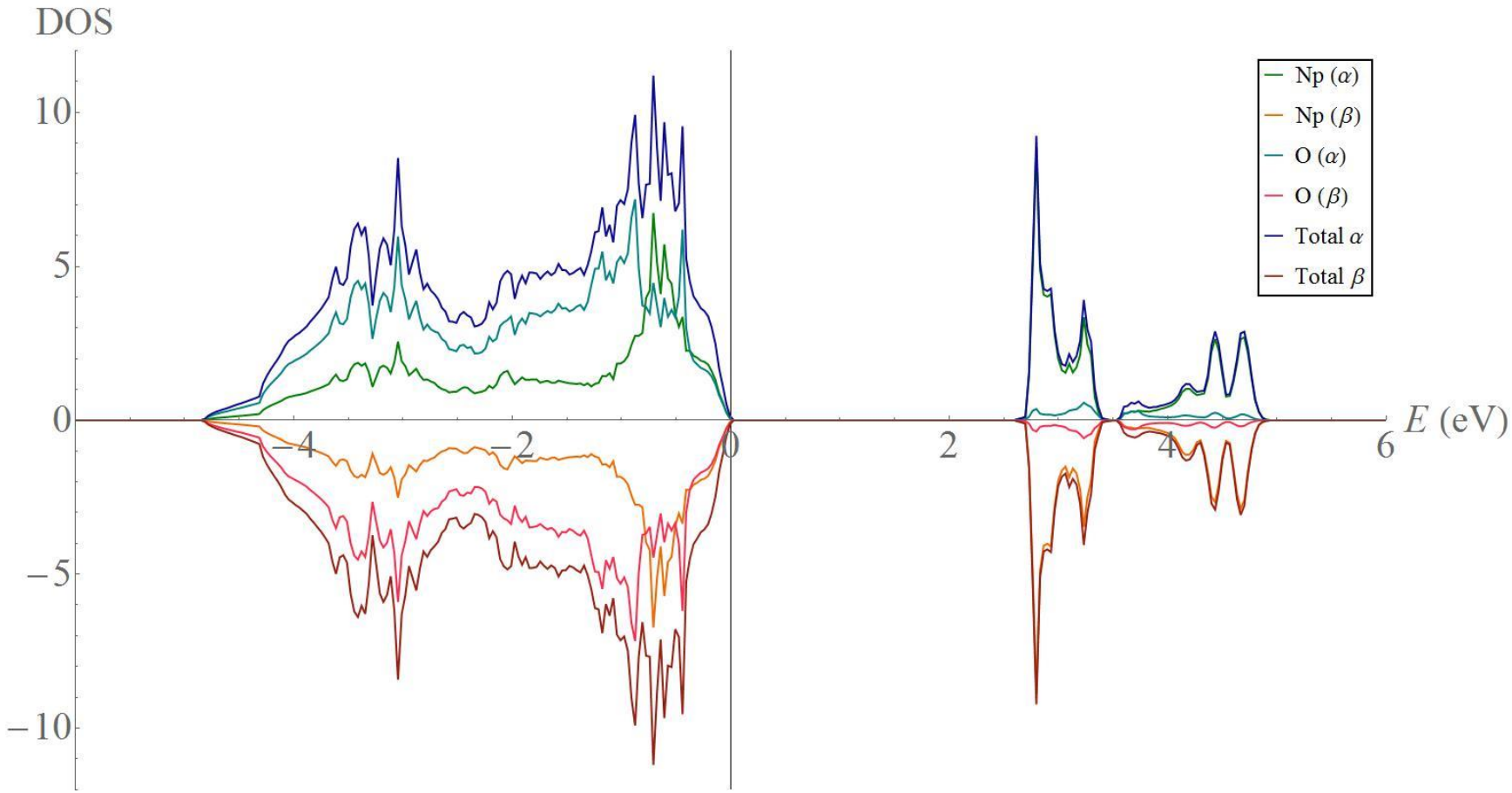
Results: UO_2 AFM DOS



Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

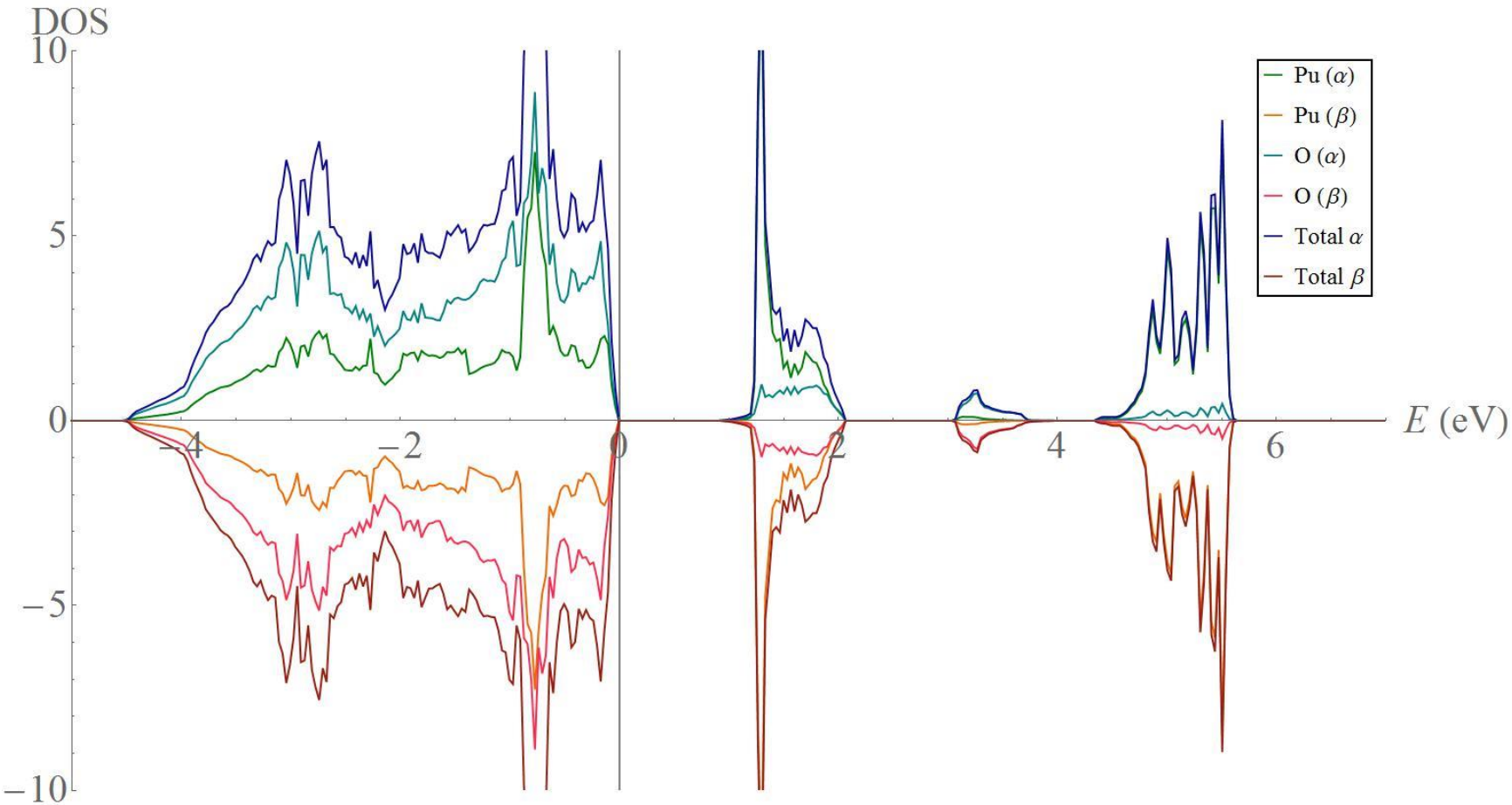
Results: NpO_2 AFM DOS



Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: PuO_2 AFM DOS



Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Band Gaps

System	PBE+*U* (eV)	Other Calcs. (eV) (PBE+*U*, HSE [1])	Expt. (eV) [1]
UO_2	2.80	2.30, 2.40	2.10
NpO_2	2.60	2.60, 2.40	2.80
PuO_2	1.30	1.60, 2.40	2.85

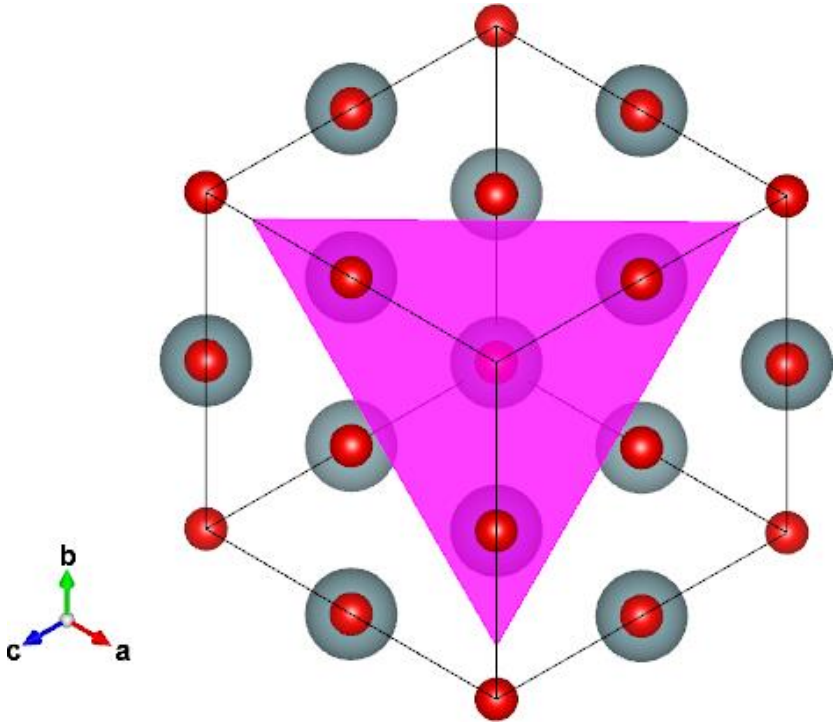
[1] X.-D. Wen, R. L. Martin, T. M. Henderson, and G. E. Scuseria, *Chem. Rev*. 113:1063, 2013.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

The AnO_2 (111) Surface

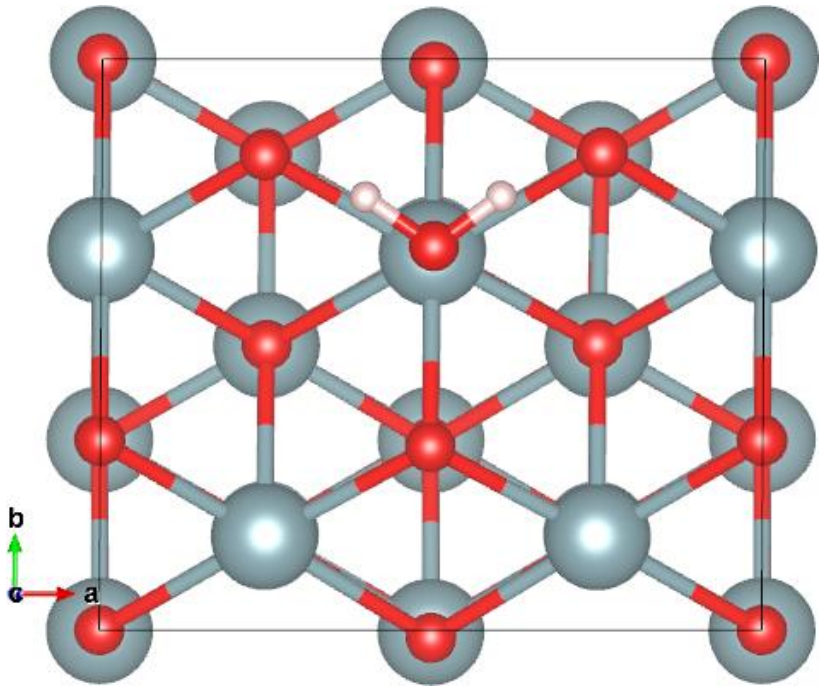
- Close-packed surface
- Oxygen terminated
- Stable



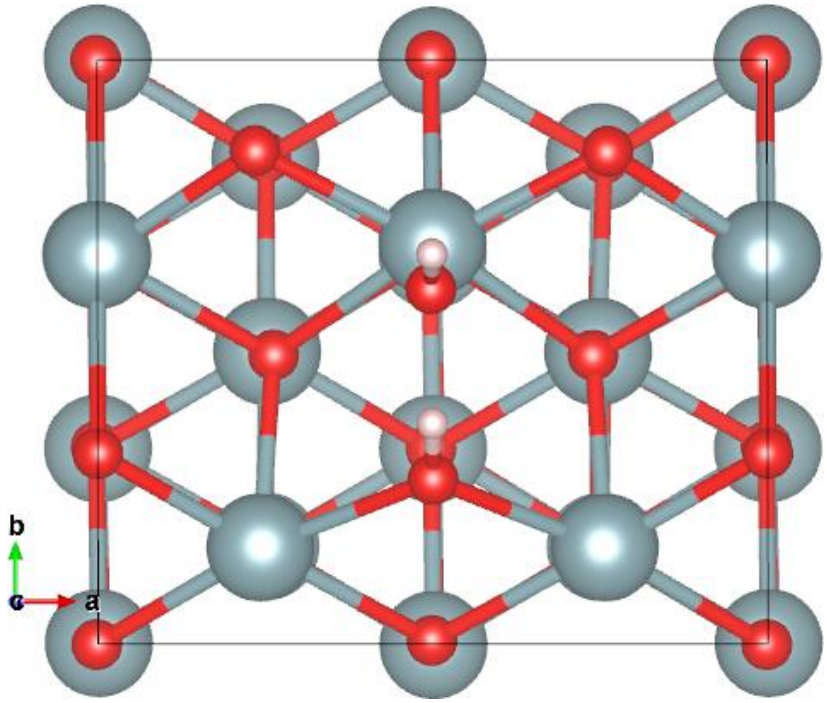
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Water on AnO_2 / CeO_2 (111)



Molecular

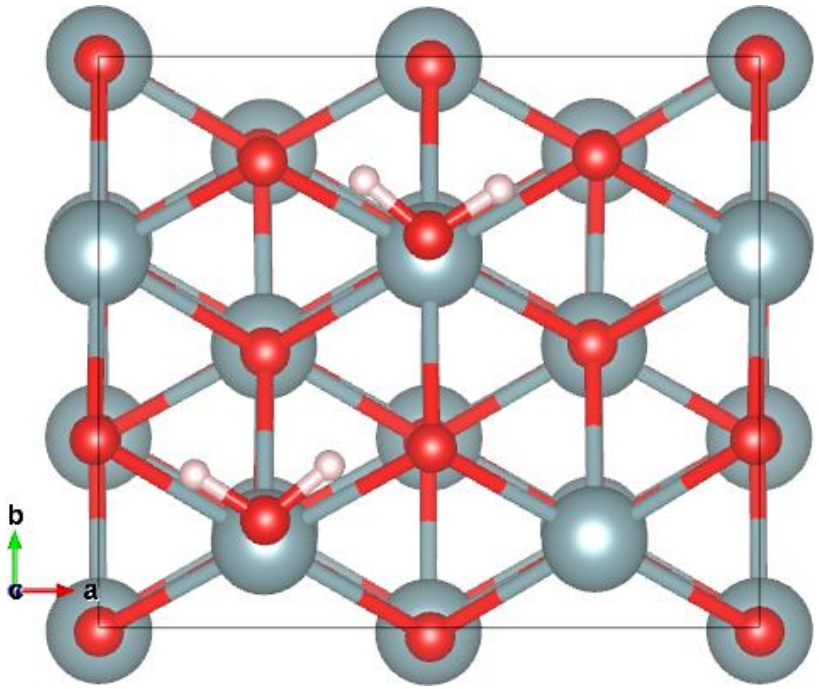


Dissociative

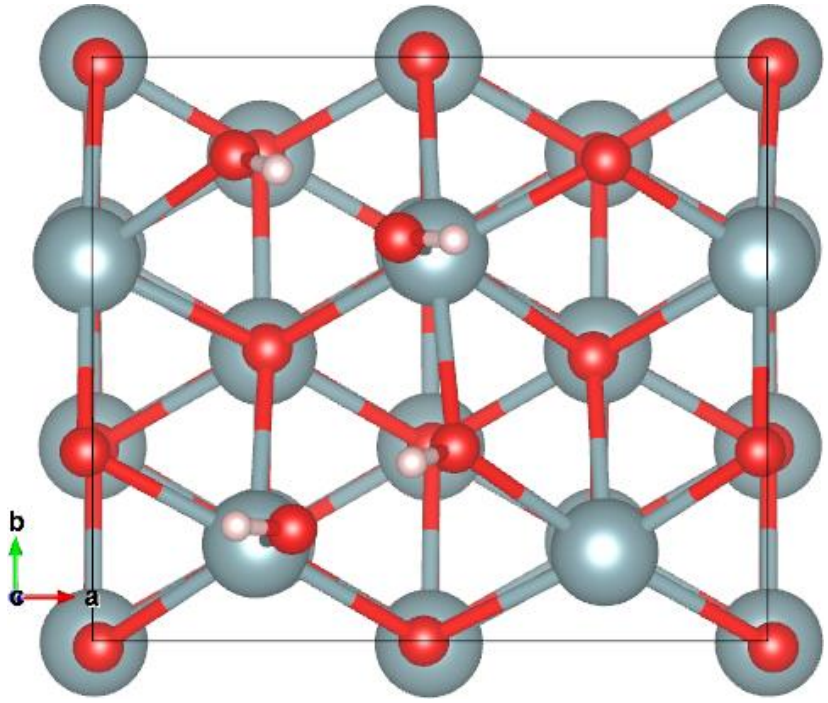
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Water on AnO_2 / CeO_2 (111)



Molecular

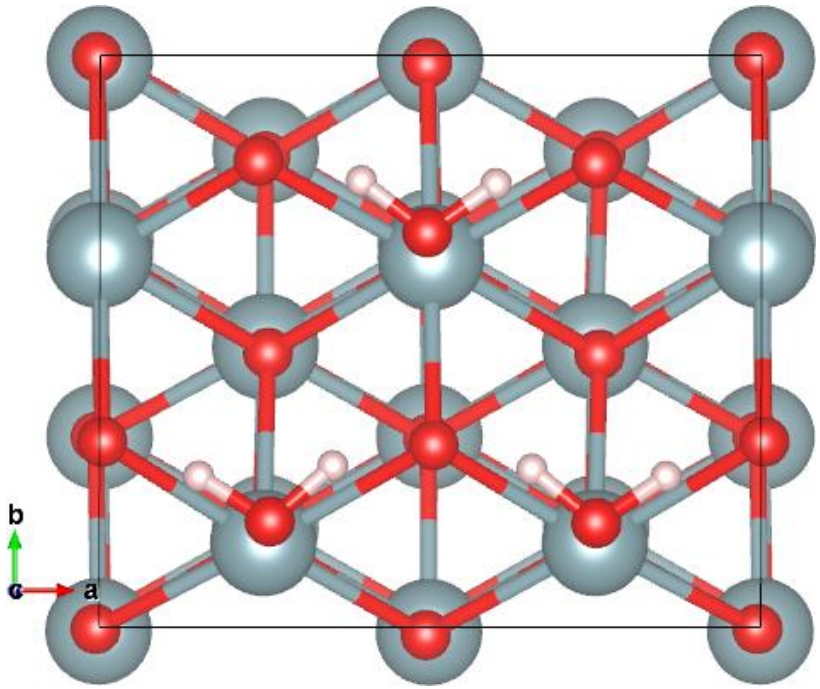


Dissociative

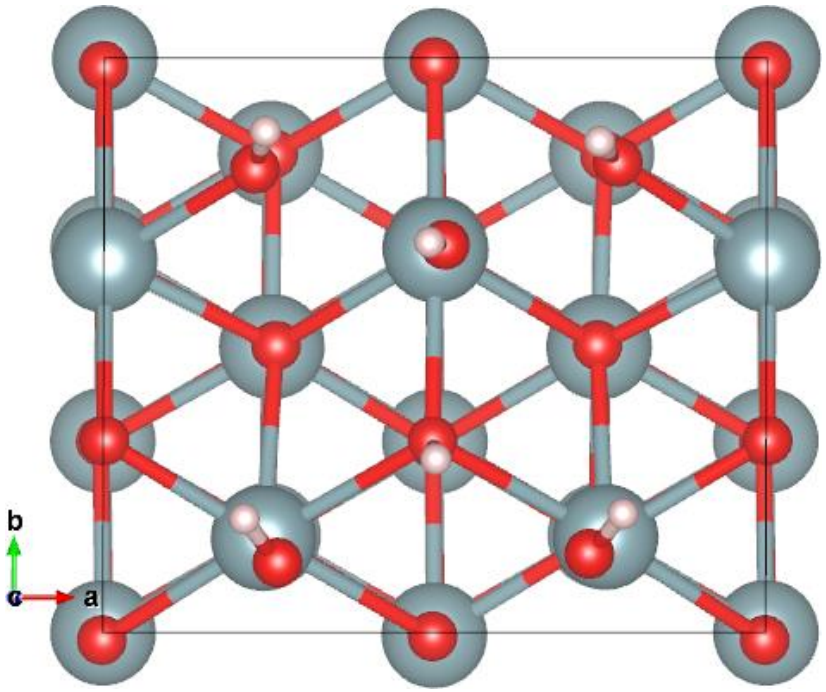
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Water on AnO_2 / CeO_2 (111)



Molecular

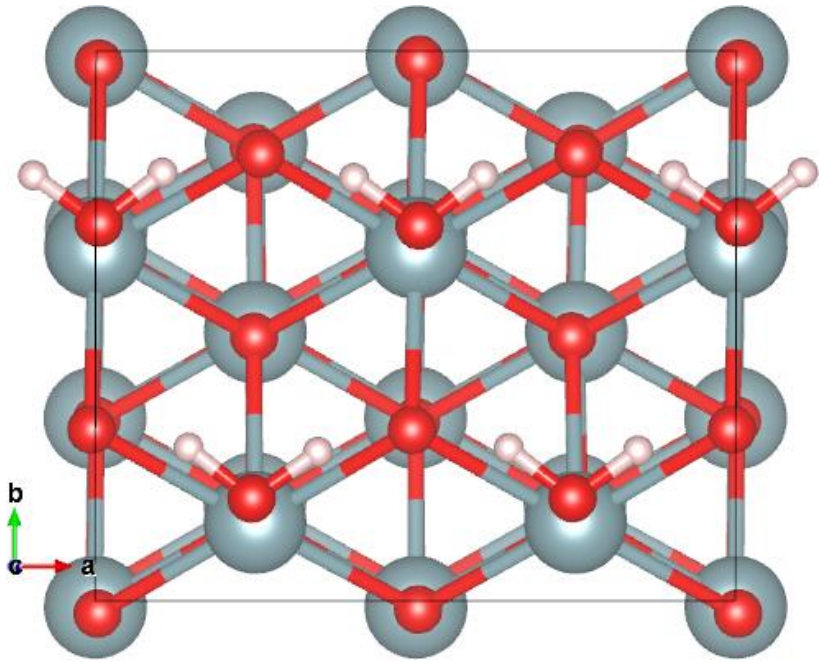


Dissociative

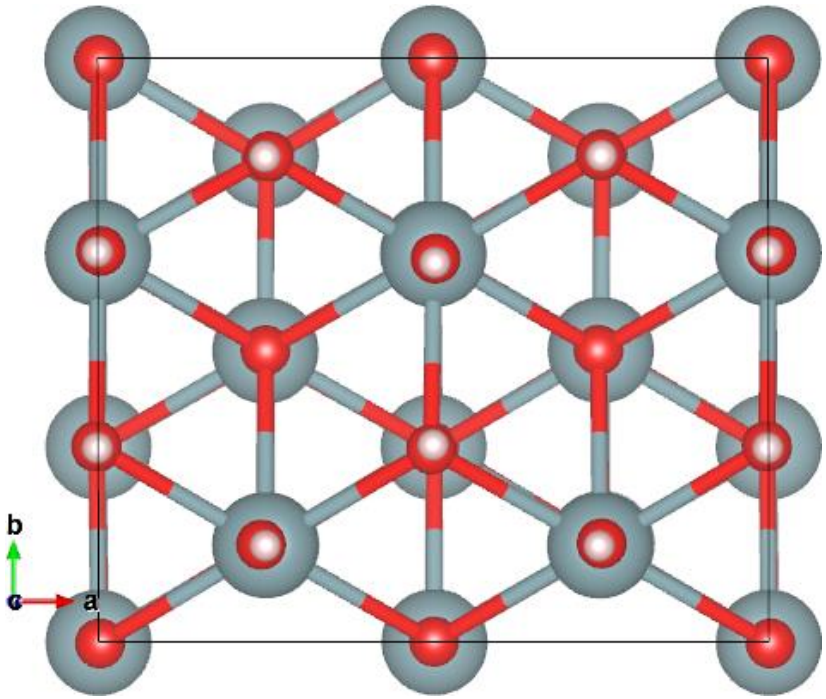
Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Water on AnO_2 / CeO_2 (111)



Molecular



Dissociative

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Water on AnO_2 / CeO_2 (111)

System	U_{eff} (eV)	0.25 ML	0.5 ML	0.75 ML	1.0 ML
$UO_2 + H_2O$	4.0	-0.36	-0.51	-0.52	-0.49
$UO_2 + OH + H$	4.0	-0.44	-0.40	-0.26	-0.13
$NpO_2 + H_2O$	4.0	-1.24	-0.92	-0.76	-0.71
$NpO_2 + OH + H$	4.0	-1.27	-0.77	-0.56	-0.32
$PuO_2 + H_2O$	4.0	-0.42	-0.49	-0.44	-0.43
$PuO_2 + OH + H$	4.0	-0.27	-0.32	-0.14	-0.05
$CeO_2 + H_2O$ [2]	5.0	-0.56	-0.60	N/A	-0.57
$CeO_2 + OH + H$ [2]	5.0	-0.59	N/A	N/A	-0.15

[2] M. Molinari, S. C. Parker, D. C. Sayle, and M. S. Islam,
The Journal of Physical Chemistry C **2012** *116* (12), 7073-7082

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Results: Water on AnO_2 / CeO_2 (111)

Distance (Å)	UO_2	NpO_2	PuO_2	CeO_2 [2]
$H_W – O_{1S}$	1.96 – 2.28	2.05 – 2.22	2.00 – 2.23	1.99 – 2.13
An_{1S} / $Ce_{1S} – O_W$	2.62 – 2.69	2.60 – 2.67	2.62 – 2.68	2.62
An_{1S} / $Ce_{1S} – O_WH_W$	2.18 – 2.26	2.20 – 2.28	2.20 – 2.26	2.22
An_{1S} / $Ce_{1S} – O_{1S}H_W$	2.33 – 2.44	2.31 – 2.39	2.30 – 2.43	2.41
$O_{1S}H_W – O_WH_W$	1.61 – 2.39	1.56 – 2.50	1.57 – 2.29	1.65

[2] M. Molinari, S. C. Parker, D. C. Sayle, and M. S. Islam,
The Journal of Physical Chemistry C **2012** *116* (12), 7073-7082

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE

Conclusions and Future Work

- Studying the actinide oxides using DFT remains a challenge.
- Careful use of the DFT+*U* method allows calculation of structural and electronic properties.
- First results on the AnO_2(111) surfaces suggest molecular adsorption.
- Future work will focus on adsorption energies on the (110) and (100) actinide oxide surfaces, followed by reduced surfaces.

Research Councils UK Energy For a Low Carbon Future

DISTINCTIVE