Water Adsorption on Actinide Oxide Surfaces

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Outline

- Motivation
- Computational Method
- Results and Discussion
- Conclusions and Future Work
- Acknowledgements

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

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

- method development
- initial results

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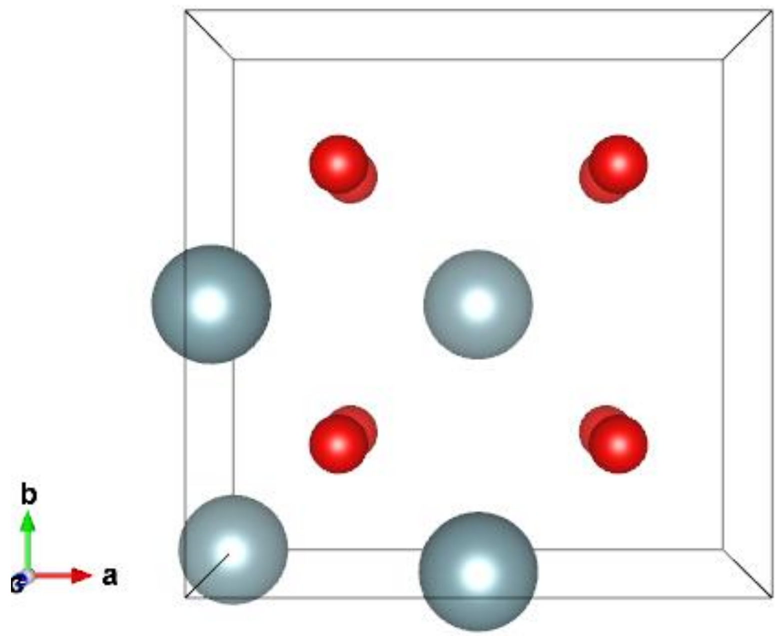
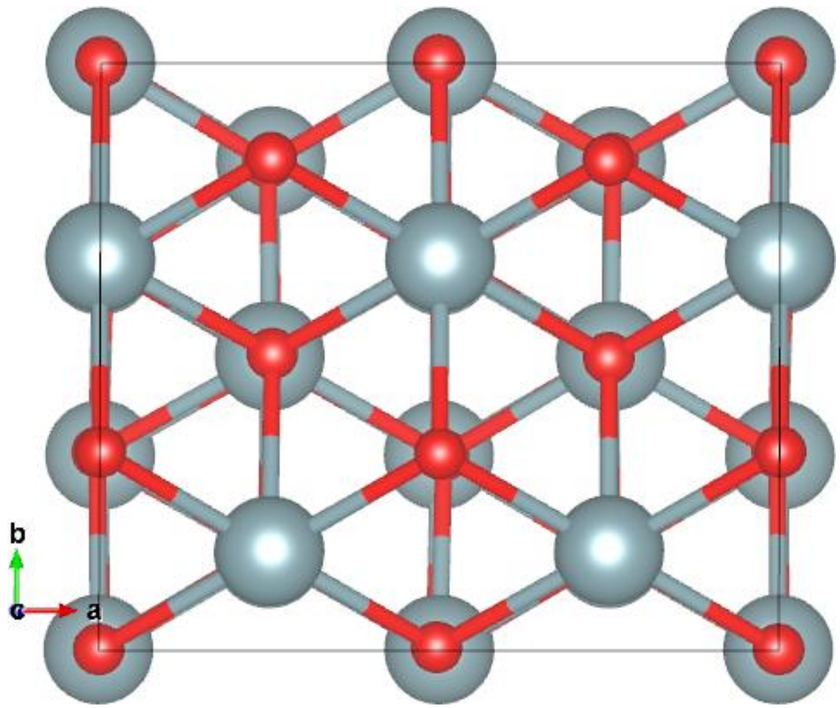
Computational Method

- Density Functional Theory
- VASP 5.4.1
- PAW-pseudopotentials
- Plane wave basis set
- k-point sampling of 1st BZ
- Spin-polarised
- DFT+*U* = PBE+*U*



Computational Method

- Surfaces are modelled using a repeating slab of 24 AnO_2 units 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.



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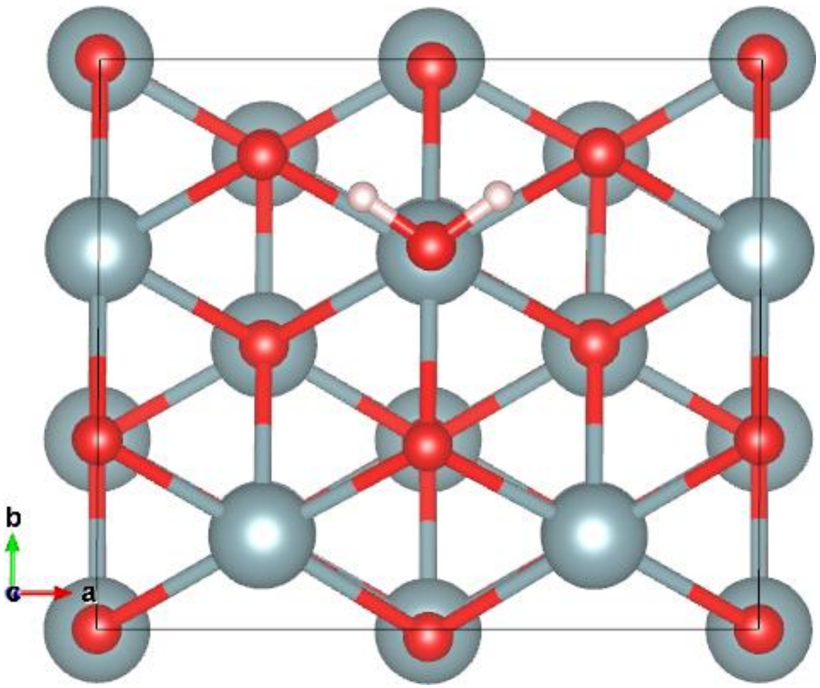
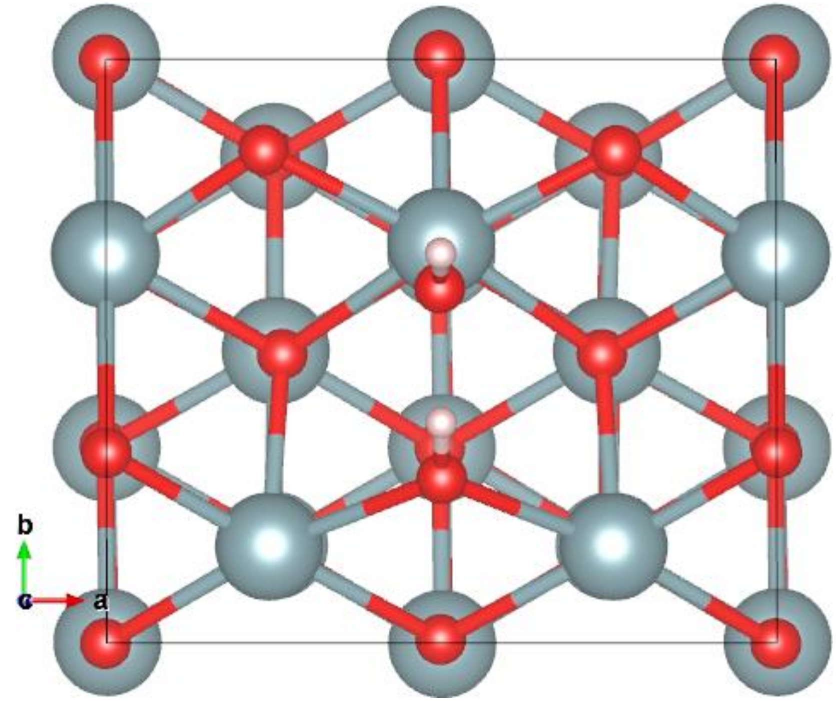
Results: Water on UO_2 / CeO_2 (111)





Molecular

Dissociative

25% coverage = ¼ ML

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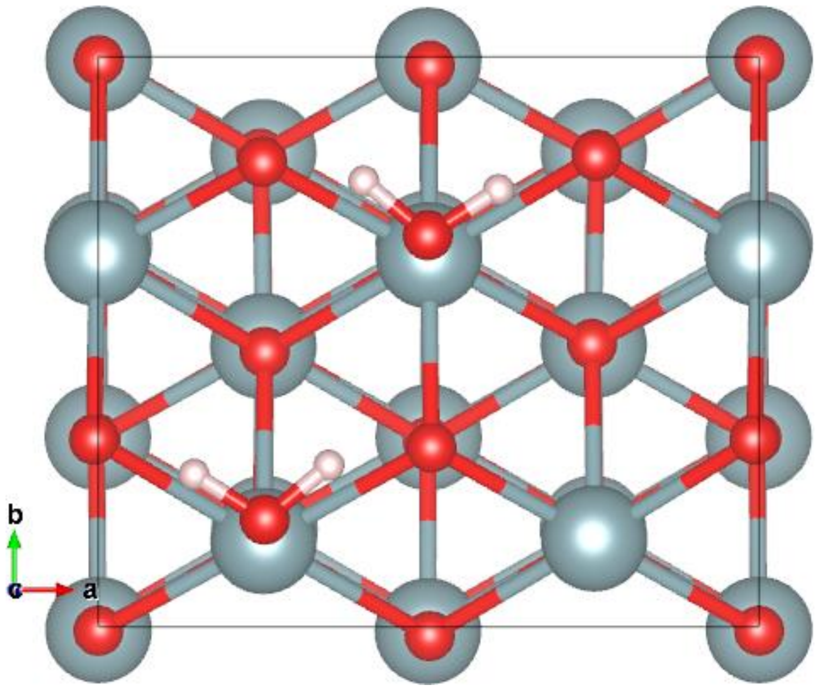
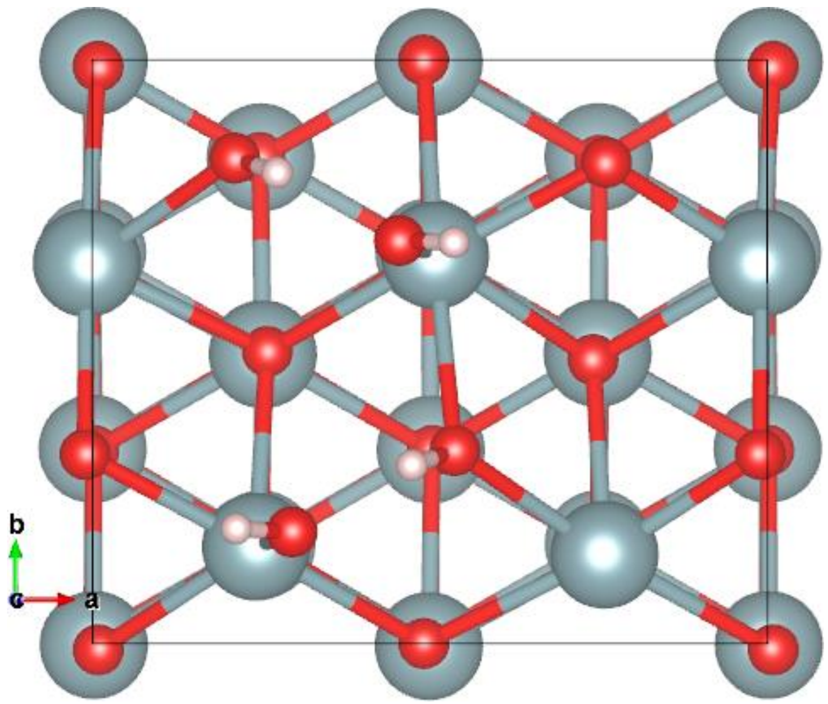


Molecular

50% coverage = ½ ML



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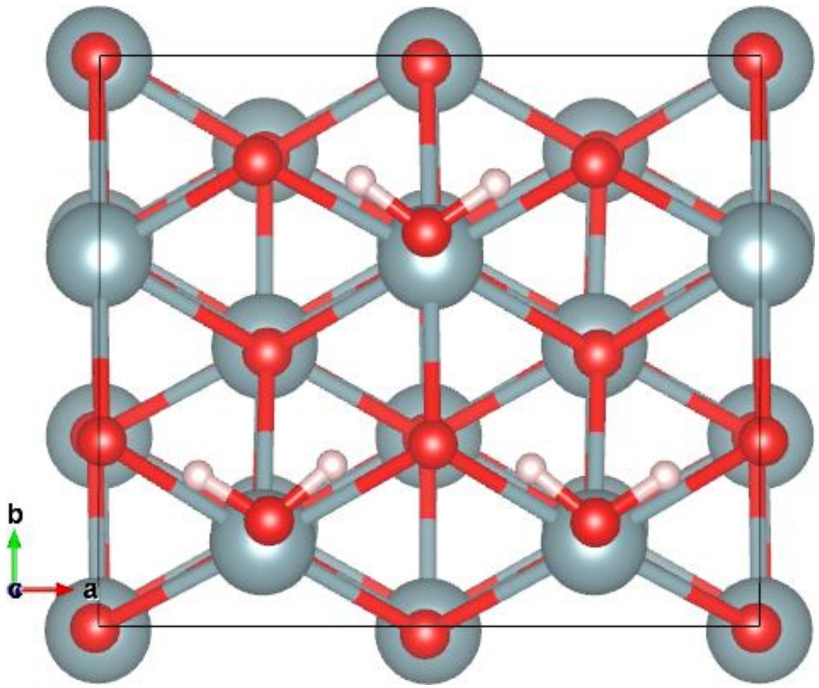

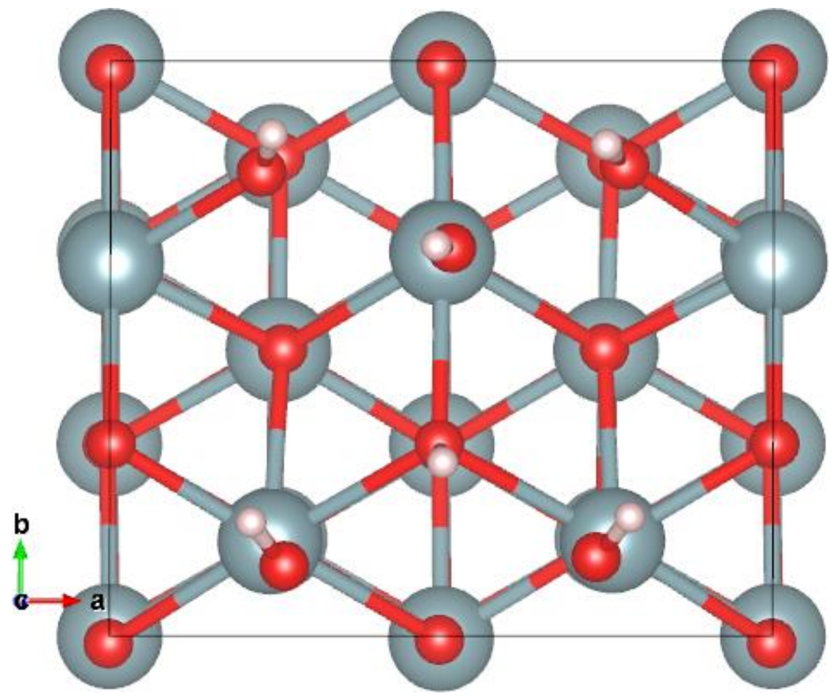

Molecular

75% coverage = ¾ ML

Dissociative

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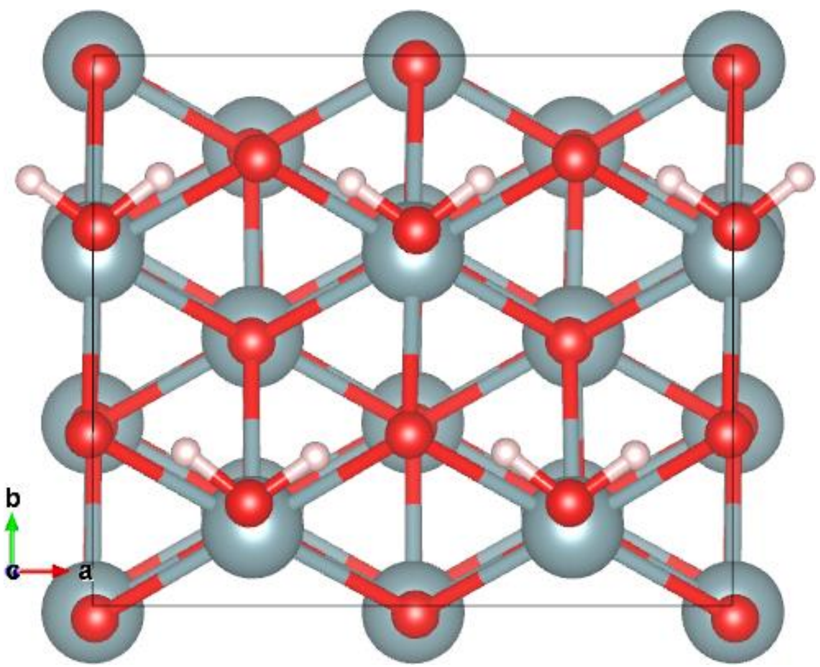
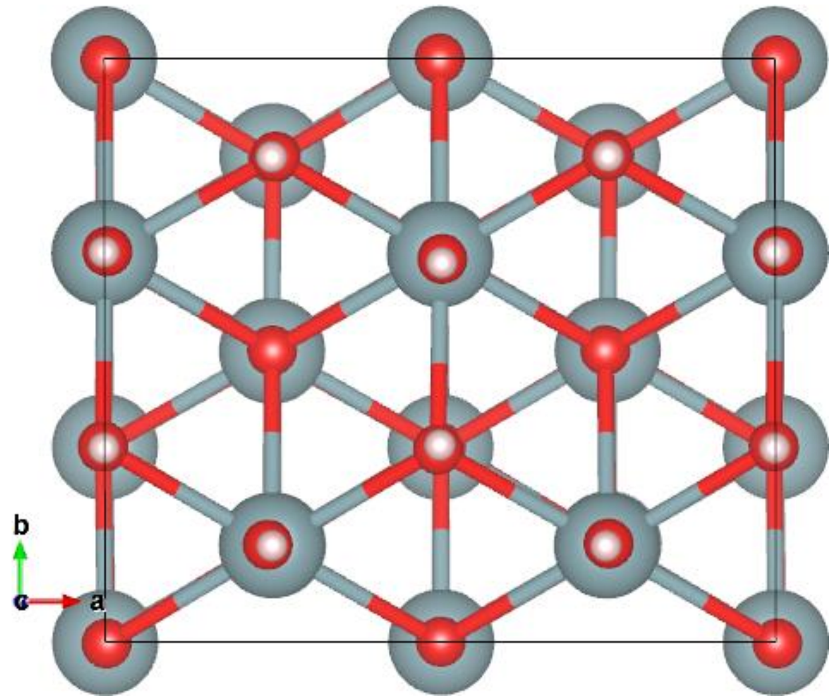
Results: Water on UO_2 / CeO_2 (111)





Molecular

100% coverage = 1 ML

Dissociative

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Results: Water on UO_2 (111)

Coverage	UO_2 (111) @ 0.25 ML	UO_2 (111) @ 0.50 ML	UO_2 (111) @ 0.75 ML	UO_2 (111) @ 1.00 ML
H_2O / nm^2	1.95	3.89	5.84	7.78
mg / m^2	0.058	0.12	0.17	0.23

Results: Water on UO_2 (111)

System	U_{eff} (eV)	0.25 ML	0.5 ML	0.75 ML	1.0 ML
$UO_2 + H_2O$	4.0	-0.53	-0.53	-0.53	-0.49
UO_2 + OH + H	4.0	-0.50	-0.41	-0.29	-0.15
$UO_2 + H_2O$ [1]	4.0	-0.61	N/A	N/A	-0.60
UO_2 + OH + H [1]	4.0	-0.68	N/A	N/A	-0.32

[1] T. Bo, J. Lan, Y. Zhao, Y. Zhang, C. He, Z. Chai and W. Shi, *J. Nucl. Mat*. **454** (2014) 446-454

Results: Water on UO_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	-0.53	-0.53	-0.53	-0.49
UO_2 + OH + H	4.0	-0.50	-0.41	-0.29	-0.15
$CeO_2 + H_2O$ [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

Results: Water on UO_2 / CeO_2 (111)

Distance (Å)	UO_2	CeO_2 [2]
$H_W – O_{1S}$	1.96 – 2.28	1.99 − 2.13
U_{1S} / $Ce_{1S} – O_W$	2.62 – 2.69	2.62
U_{1S} / $Ce_{1S} – O_WH_W$	2.18 – 2.26	2.22
U_{1S} / $Ce_{1S} – O_{1S}H_W$	2.33 – 2.44	2.41
$O_{1S}H_W – O_WH_W$	1.61 – 2.39	1.65

[2] M. Molinari, S. C. Parker, D. C. Sayle, and M. S. Islam,
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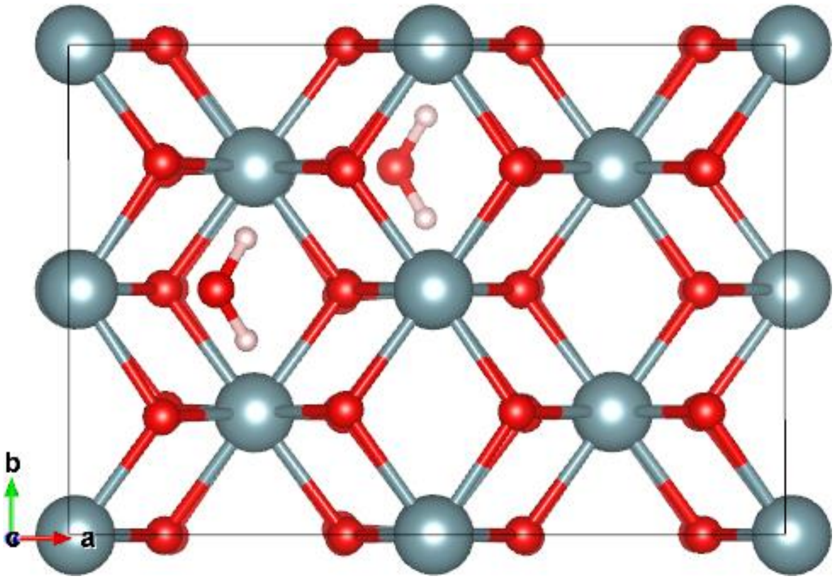
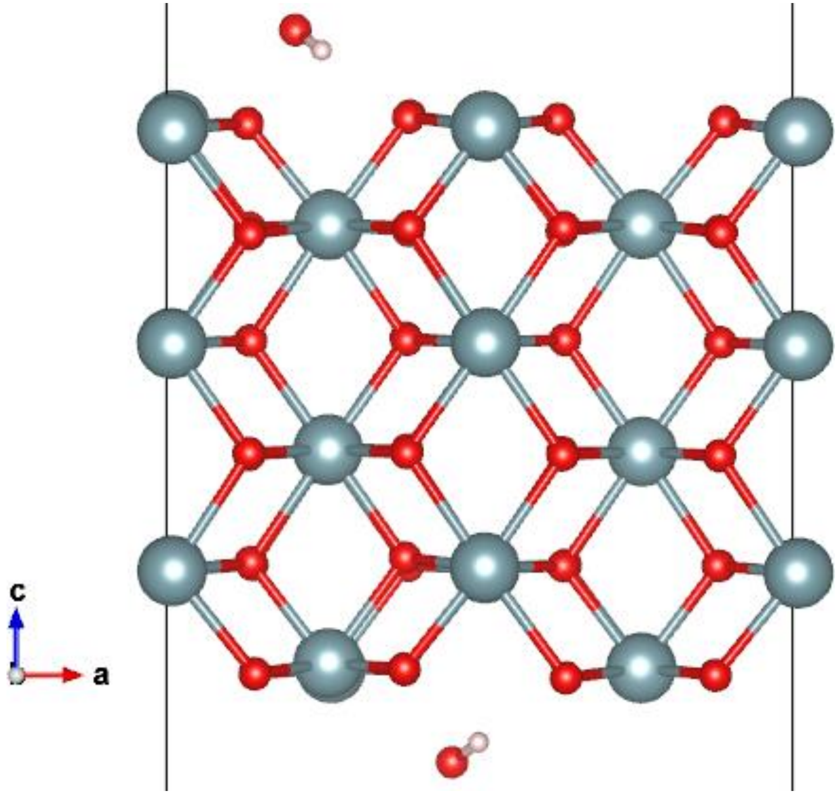
Results: Water on UO_2 / CeO_2 (110)





Molecular
25% Coverage = ¼ ML

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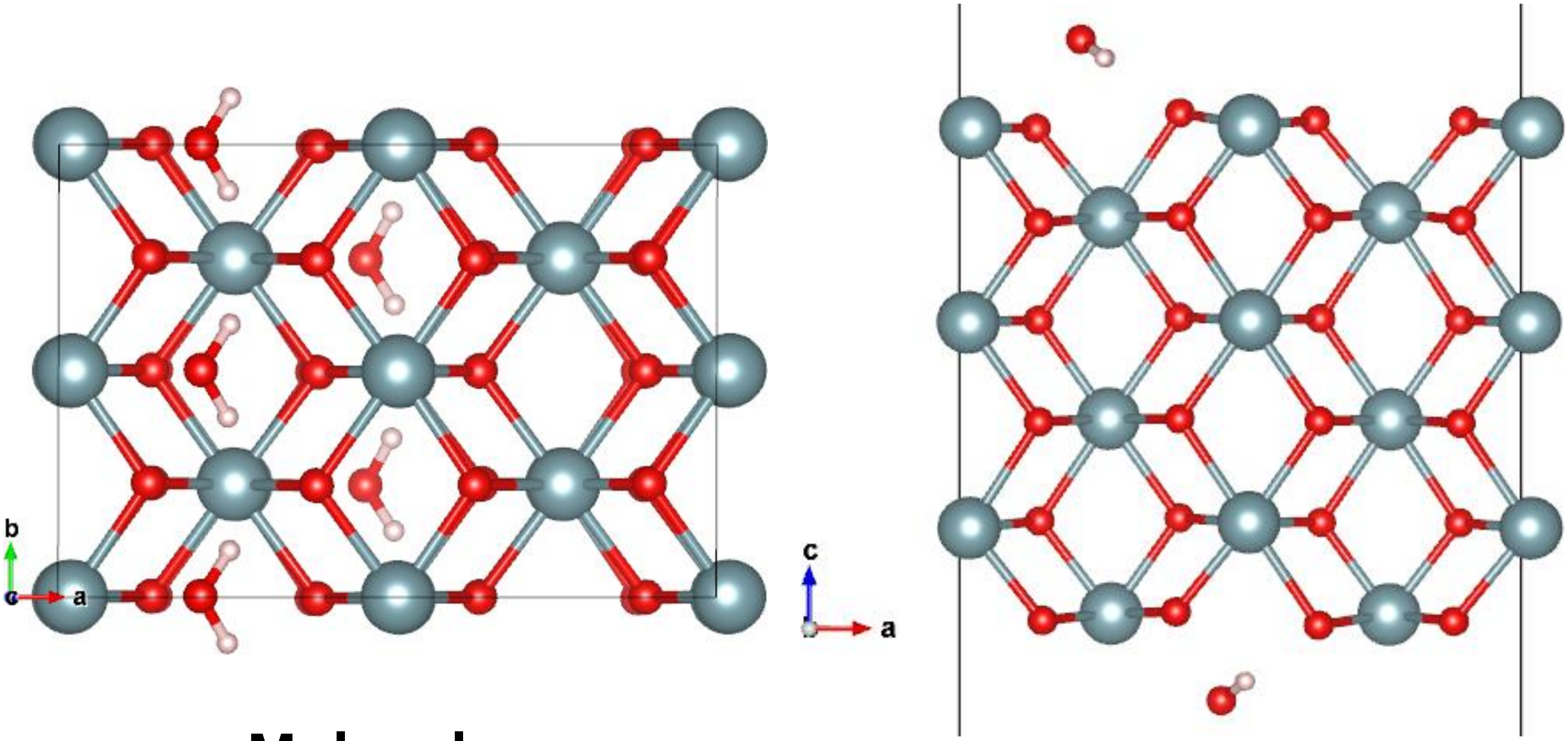

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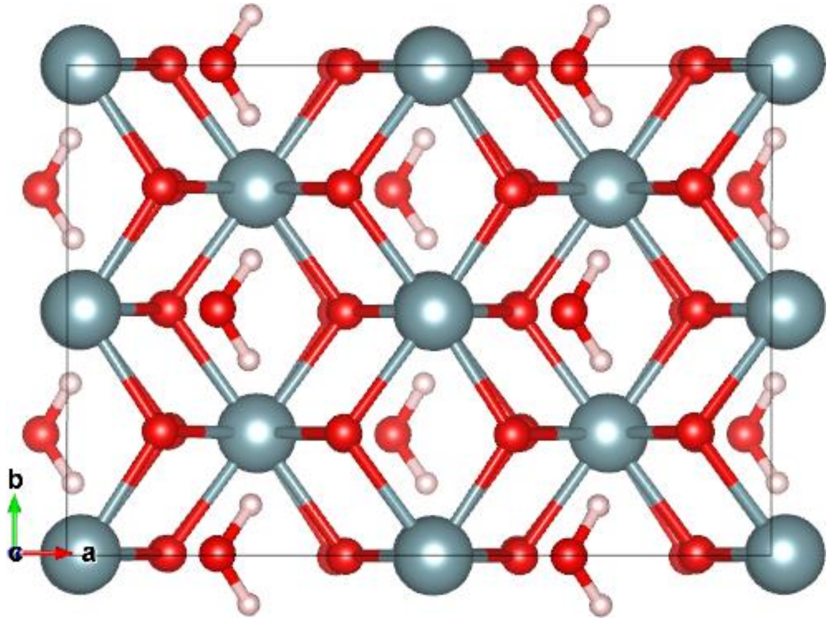
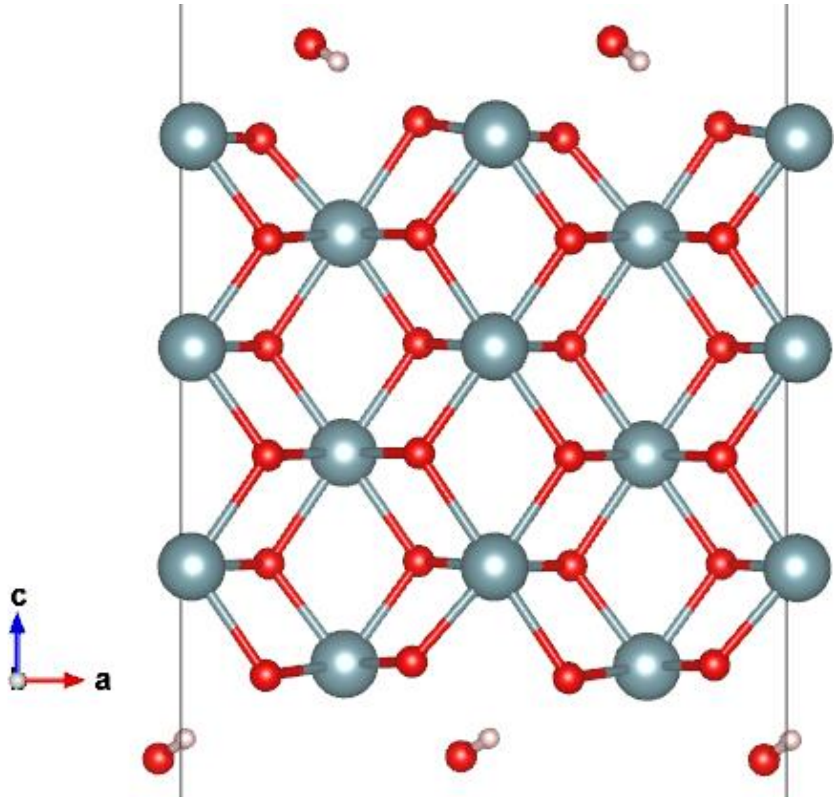
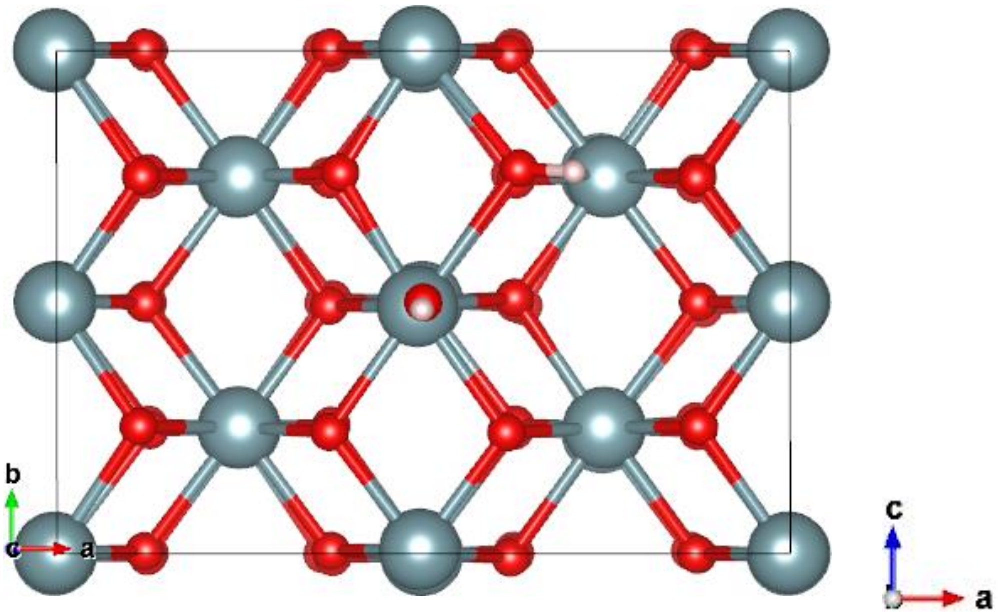




Molecular
100% Coverage = 1 ML

Results: Water on UO_2 / CeO_2 (110)



Dissociative
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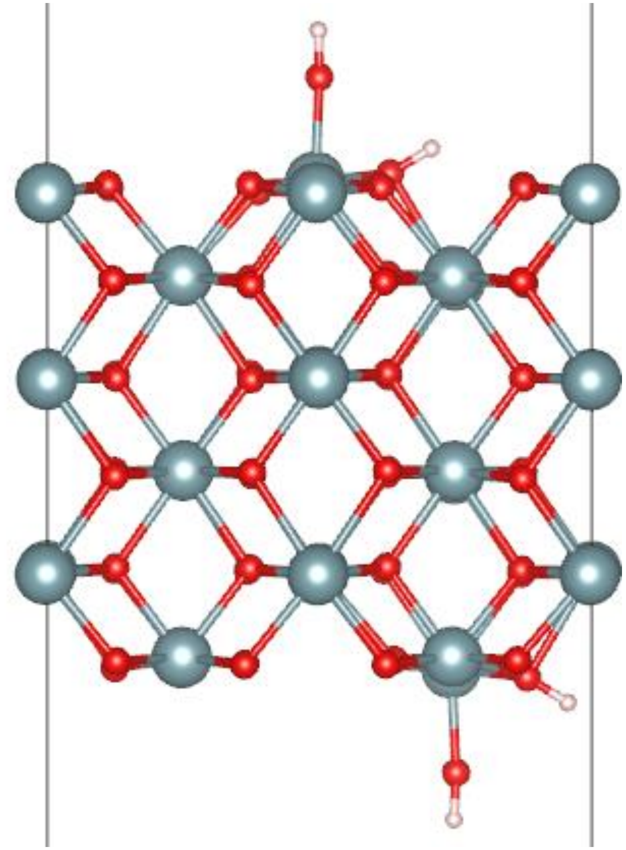

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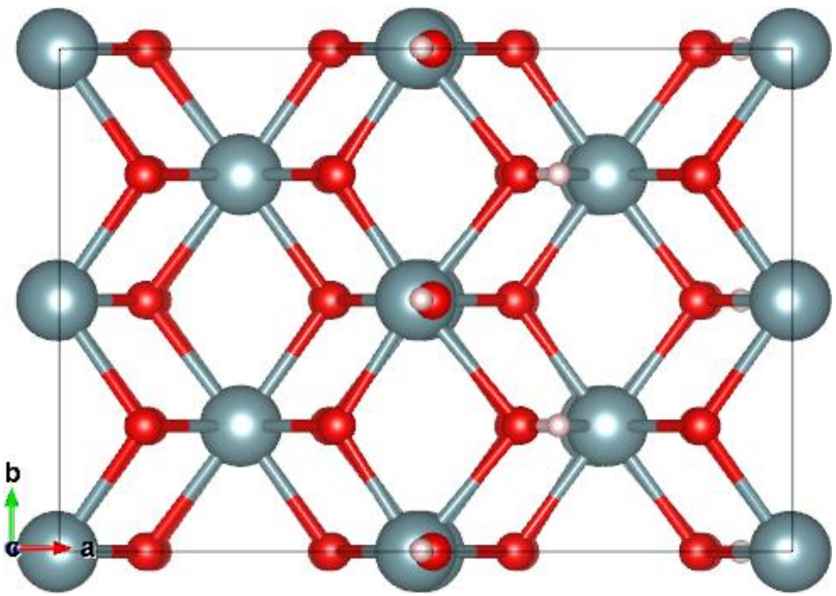

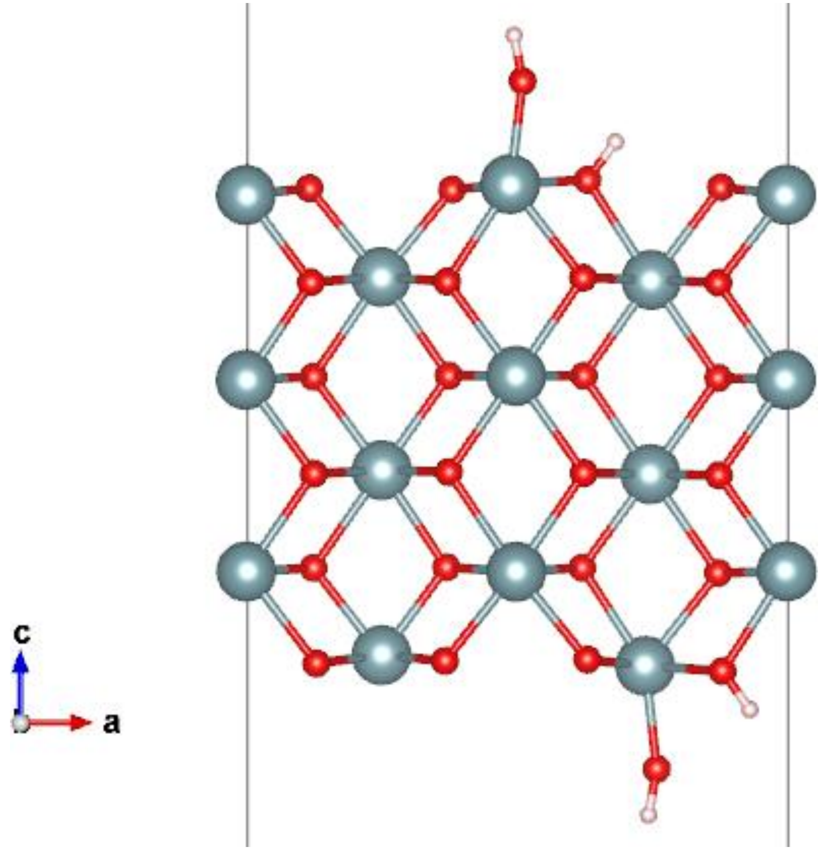

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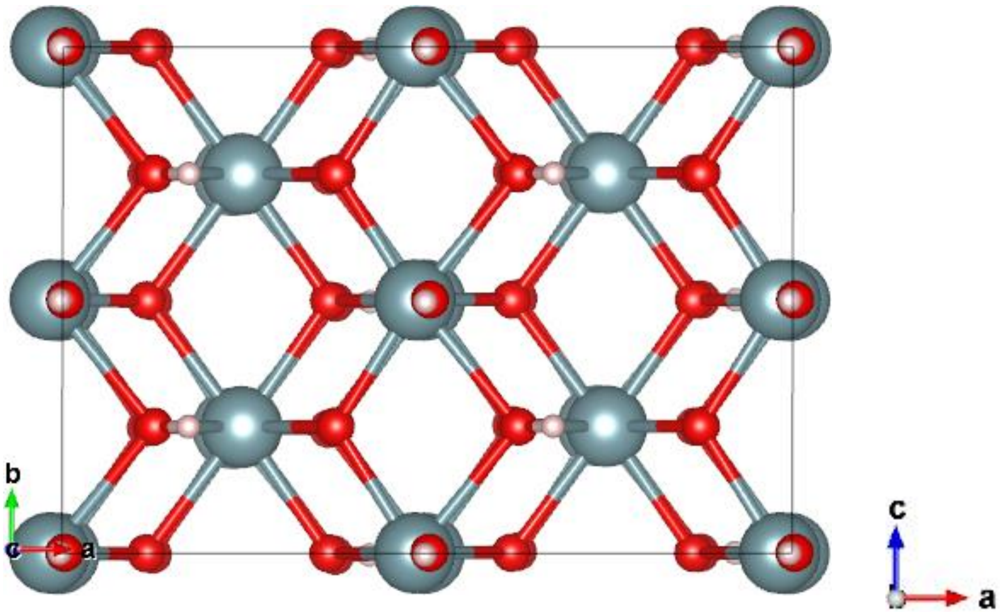

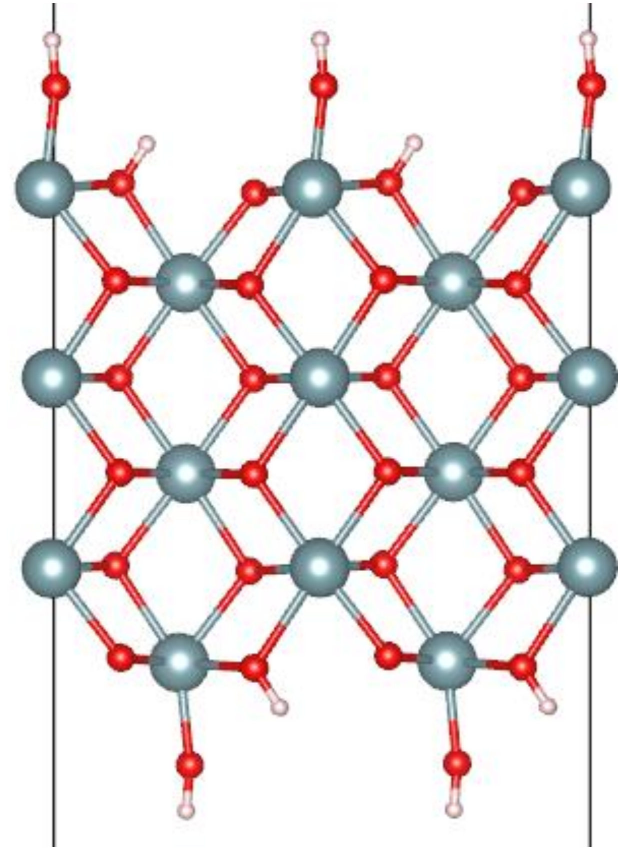

Dissociative
100% Coverage = 1 ML

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Results: Water on UO_2 (110)

Coverage	UO_2 (110) @ 0.25 ML	UO_2 (110) @ 0.50 ML	UO_2 (110) @ 1.00 ML
H_2O / nm^2	1.17	2.35	4.70
mg / m^2	0.035	0.070	0.14

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Results: Water on UO_2 / CeO_2 (110)

System	U_{eff} (eV)	0.25 ML	0.5 ML	1.0 ML
$UO_2 + H_2O$	4.0	-0.93	-0.74	-0.65
UO_2 + OH + H	4.0	-1.39	-1.05	-1.00
$CeO_2 + H_2O$ [2]	5.0	-0.85	-0.76	N/A
CeO_2 + OH + H [2]	5.0	-1.12	-1.00	-0.21

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

Results: Water on UO_2 / CeO_2 (110)

Distance (Å)	UO_2	CeO_2 [2]
$H_W - O_{1S}$	2.19 – 2.26	2.07
U_{1S} / $Ce_{1S} - O_W$	2.73 – 2.79	2.67
U_{1S} / $Ce_{1S} - O_W H_W$	2.17	2.14
U_{1S} / $Ce_{1S} - O_{1S} H_W$	2.59	2.48 – 2.58
$O_{1S} H_W - O_W H_W$	2.36	1.92

[2] M. Molinari, S. C. Parker, D. C. Sayle, and M. S. Islam,
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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 UO_2(111) and (110) surfaces suggest molecular adsorption on the (111) surface and dissociative adsorption on the (110) surface.
- Future work will focus on adsorption energies on the (100) uranium dioxide surface, followed by reduced surfaces.

Acknowledgements

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Helen Steele, Sellafield Ltd

Howard Sims, National Nuclear Laboratory

Results: Dry UO_2 Surfaces

Surface Energy	UO_2 (111)	UO_2 (110)	UO_2 (100)
meV / Å^2	40.76	65.69	82.79
J / m^2	0.65	1.05	1.33
J / m^2 [3]	0.78	1.05	1.47

[3] Zs. Rák, R.C. Ewing, and U. Becker, *Surface Science*, **608**, (2013), 180-187