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The Critical Role of Hydrogen on the Stability of Oxy-Hydroxyl Defect Clusters in Uranium Oxide

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Supplementary Information

The Choice of $UO_{2+x}H_n$ Structural Models. There are up to 35 million unique configurations of 1 to 4 hydrogen atoms in our chosen 32 UO_2 unit simulation cell. However, as the aim of this investigation is to determine whether oxygen defect clusters act as hydrogen trapping sites, we have limited the number of configurations studied to those where hydrogen is interacting solely with oxygen atoms belonging to defect clusters forming hydroxyl groups and where the position of the hydrogen serves to maximise the hydrogen bonding network. This generates 16 different configurations for hydrogen interacting with the 2:2:2 Willis (W_{222}) cluster and 8 for hydrogen interacting with the split di interstitial (I_2^x) cluster.

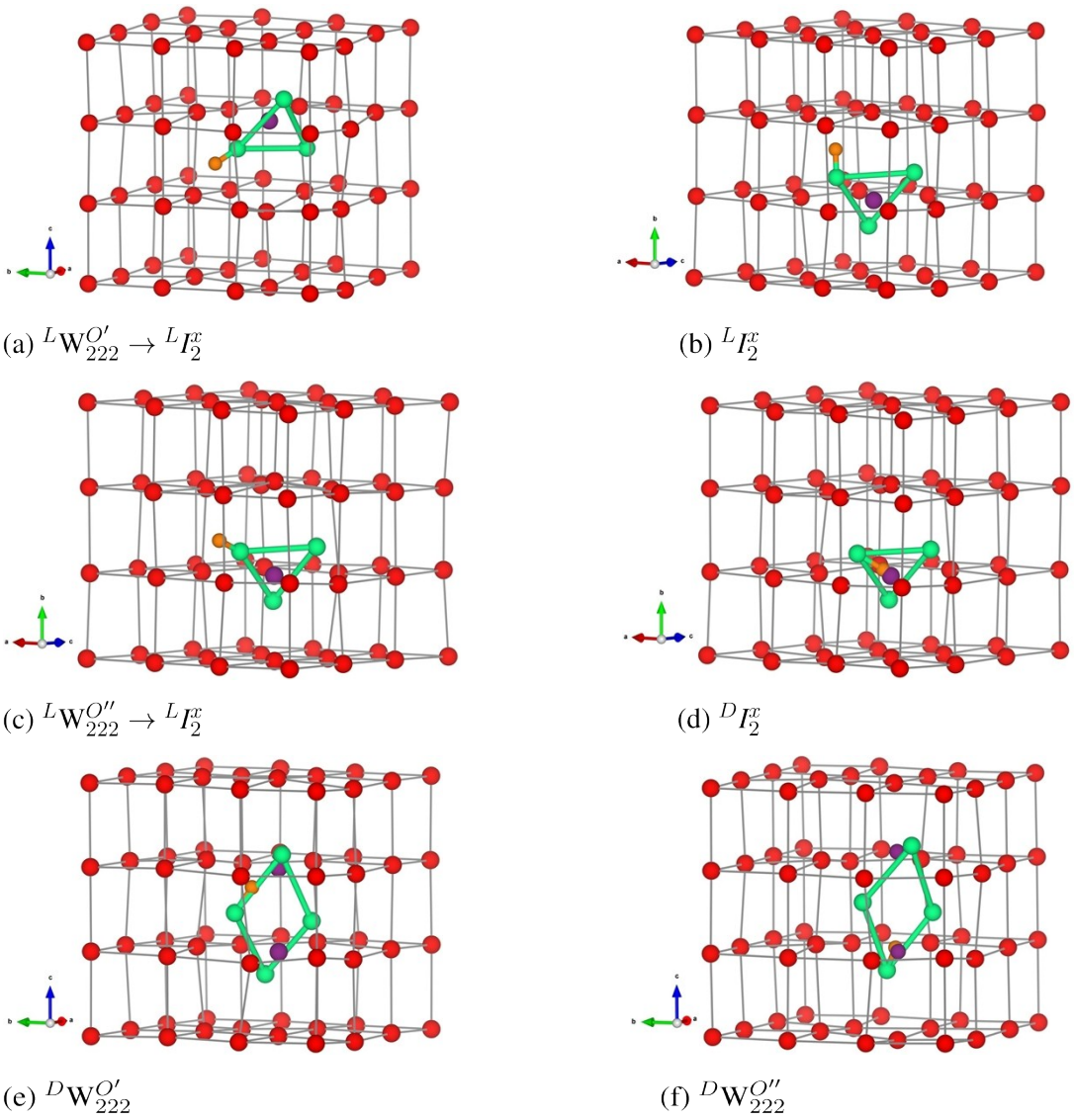
In our UO_{2+x} model, for each hydrogen inserted, one U^{5+} is reduced to U^{4+} to maintain charge neutrality. These charges can be localized on nearest neighbour (NN) uranium sites (*i.e.* U^{5+} belonging to the first coordination sphere) or next nearest neighbour (NNN) uranium sites (*i.e.* the U^{5+} is in the second coordination sphere), taking the centre of the defect cluster as the origin. We found that the positions of the compensating U^{5+} defects do not affect the geometry and energetics of the defect clusters.

Tables 1-4 summarise the structure of the hydrogen-oxygen (H-O) defect clusters and their corresponding solution and binding energies at hydrogen concentrations of 117 - 467 μgH / gUO_2. The number and strength of hydrogen bonds (H-bond) are calculated for each defect cluster. We consider a hydrogen bond to be between a hydrogen atom and an acceptor oxygen atom (an oxygen not bonded directly to the hydrogen atom). The strength of a hydrogen bond is based on the oxygen-hydrogen distance, with a strong H-bond defined as 1.2-1.5 Å, a medium one 1.5-2.2 Å and a weak one 2.2-3.0 Å.[1]

Oxy-hydroxyl defect clusters at 117 μgH / gUO_2

Supplementary Table 1. Oxy-hydroxyl defect cluster configurations at 117 μgH / gUO_2. An arrow denotes where a change in the initial H-O cluster geometry has occurred (*i.e.* relaxation to a different type of cluster). ΔV is the change in calculated volume compared to stoichiometric UO_2. [U^{5+}] is the U^{5+} defect concentration localized on nearest neighbour (NN) or next nearest neighbour (NNN) uranium sites. Formation and binding energies per hydrogen and number of strong, medium and weak hydrogen bonds are also presented. Ω is the degeneracy of the oxy-hydroxyl cluster.

Cluster	Configuration	ΔV / H Å^3	[U^{5+}] mgU^{5+} / gUO_2		Energy / H eV		Hydrogen Bonds			Ω
			NN	NNN	Formation	Binding	Strong	Medium	Weak	
1	${}^{L}\mathrm{W}_{222}^{O'} \rightarrow {}^{L}I_2^x$	3.74	55	28	-1.52	0.72	0	0	4	3
2	${}^{L}I_2^x$	2.13	0	83	-1.44	0.80	0	1	3	6
3	${}^{L}\mathrm{W}_{222}^{O''} \rightarrow {}^{L}I_2^x$	3.57	55	28	-1.27	0.97	0	2	2	3
4	${}^{D}I_2^x$	2.92	83	0	-0.58	1.65	0	2	1	3
5	${}^{D}\mathrm{W}_{222}^{O'}$	4.35	55	28	-0.91	1.33	1	0	2	4
6	${}^{D}\mathrm{W}_{222}^{O''}$	5.51	55	28	-0.58	1.66	0	2	2	2



(a) ${}^{L}\mathrm{W}_{222}^{O'} \rightarrow {}^{L}I_2^x$ (b) ${}^{L}I_2^x$

(c) ${}^{L}\mathrm{W}_{222}^{O''} \rightarrow {}^{L}I_2^x$ (d) ${}^{D}I_2^x$

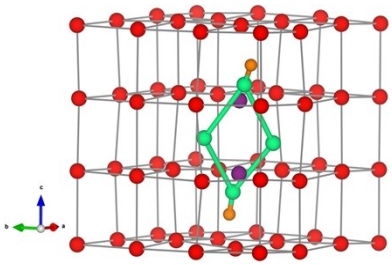
(e) ${}^{D}\mathrm{W}_{222}^{O'}$ (f) ${}^{D}\mathrm{W}_{222}^{O''}$

Supplementary Figure 1 | Configurations of oxy-hydroxyl clusters at 117 μgH / gUO$_2$. Uranium ions have been omitted for clarity, lattice oxygen shown in red, O_i in green, V_O shown in purple and hydrogen shown in orange. Bonds have been drawn to highlight defect cluster geometries.

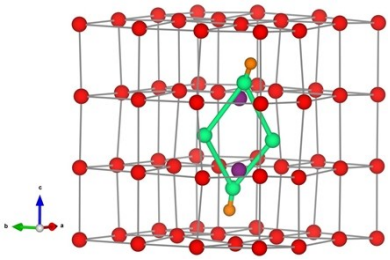
Oxy-hydroxyl defect clusters at 234 *μ*gH / gUO$_2$

Supplementary Table 2 | Oxy-hydroxyl defect cluster configurations at 234 μgH / gUO$_2$. An arrow denotes where a change in the initial H-O cluster geometry has occurred (*i.e.* relaxation to a different type of cluster). ΔV is the change in calculated volume compared to stoichiometric UO_2. [U^{5+}] is the U^{5+} defect concentration localized on nearest neighbour (NN) or next nearest neighbour (NNN) uranium sites. Formation and binding energies per hydrogen and number of strong, medium and weak hydrogen bonds are also presented. Ω is the degeneracy of the oxy-hydroxyl cluster.

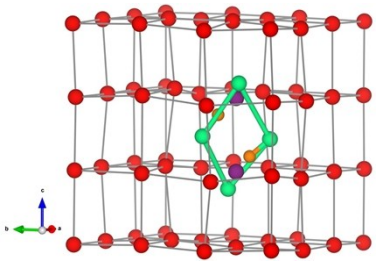
Cluster	Configuration	ΔV / H Å^3	[U^{5+}] mgU^{5+} / gUO_2		Energy / H eV		Hydrogen Bonds			Ω
			NN	NNN	Formation	Binding	Strong	Medium	Weak	
7	$^{L}\mathrm{W}_{222}^{2O''}$	5.19	28	28	-1.23	-0.21	0	3	3	2
8	$^{L}\mathrm{W}_{222}^{2O'}$	4.91	0	55	-0.64	0.37	0	2	7	1
9	$^{D}\mathrm{W}_{222}^{2O'}$	5.97	55	0	-0.79	0.23	1	2	1	2
10	$^{D}\mathrm{W}_{222}^{2O''}$	7.43	55	0	-0.27	0.74	0	4	4	1
11	$^{L}I_2^x$	4.36	0	55	-1.07	-0.05	0	2	5	3
12	$^{L}\mathrm{W}_{222}^{O',O''} \rightarrow {}^{L}I_2^x$	4.71	0	55	-1.01	0.01	0	2	6	3
13	$^{D}\mathrm{W}_{222}^{O',O''} \rightarrow {}^{D}I_2^x$	5.07	0	55	-0.61	0.40	1	2	3	2
14	$^{D}I_2^x$	5.45	0	55	-0.59	0.42	2	0	3	3



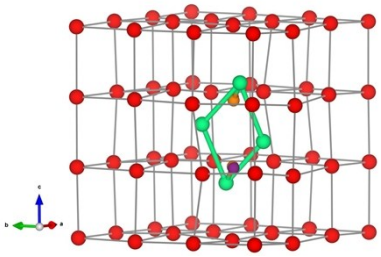
(a) ${}^{L}\mathrm{W}_{222}^{2O''}$



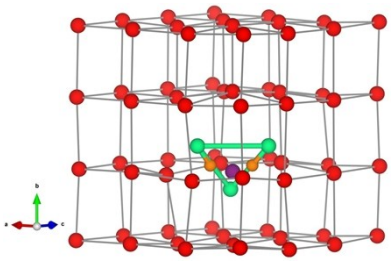
(b) ${}^{L}\mathrm{W}_{222}^{2O'}$



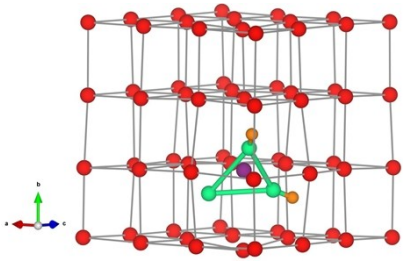
(c) ${}^{D}\mathrm{W}_{222}^{2O'}$



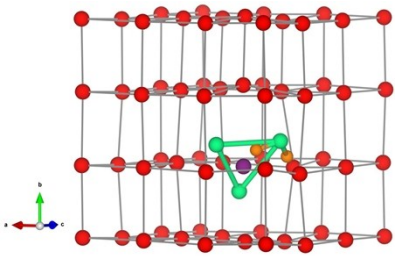
(d) ${}^{D}\mathrm{W}_{222}^{2O''}$



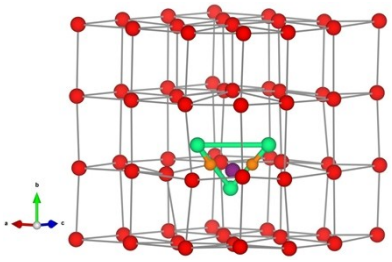
(e) ${}^{L}I_2^x$



(f) ${}^{L}\mathrm{W}_{222}^{O',O''} \rightarrow {}^{L}I_2^x$



(g) ${}^{D}\mathrm{W}_{222}^{O',O''} \rightarrow {}^{D}I_2^x$



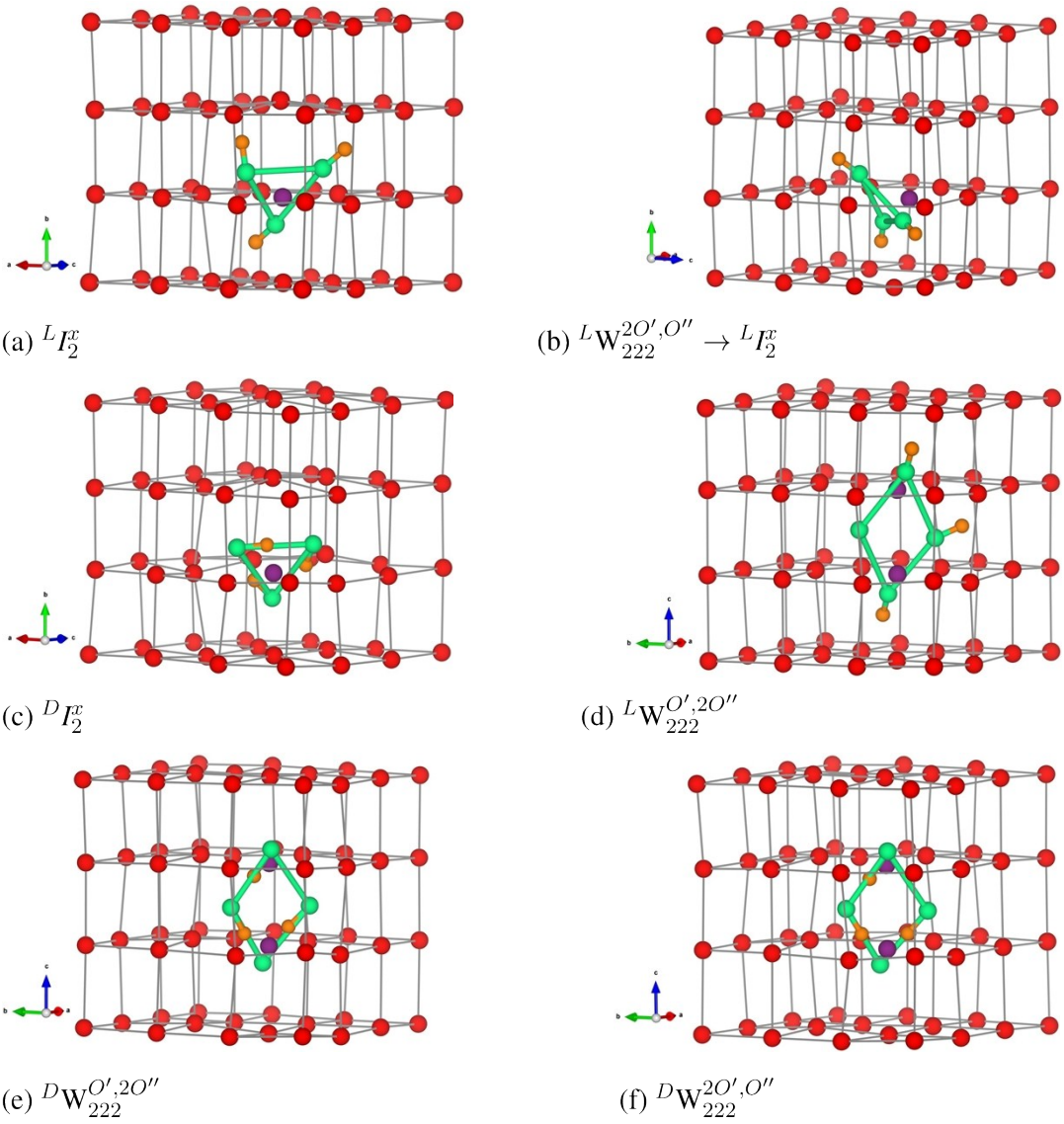
(h) ${}^{D}I_2^x$

Supplementary Figure 2 | Configurations of oxy-hydroxyl clusters at 234 *μ*gH / gUO$_2$. Uranium ions have been omitted for clarity, lattice oxygen shown in red, O_i in green, V_O shown in purple and hydrogen shown in orange. Bonds have been drawn to highlight defect cluster geometries.

Oxy-hydroxyl defect clusters at 351 μgH / gUO_2

Supplementary Table 3 | Oxy-hydroxyl defect cluster configurations at 351 μgH / gUO_2. An arrow denotes where a change in the initial H-O cluster geometry has occurred (*i.e.* relaxation to a different type of cluster). ΔV is the change in calculated volume compared to stoichiometric UO_2. [U^{5+}] is the U^{5+} defect concentration localized on nearest neighbour (NN) or next nearest neighbour (NNN) uranium sites. Formation and binding energies per hydrogen and number of strong, medium and weak hydrogen bonds are also presented. Ω is the degeneracy of the oxy-hydroxyl cluster.

Cluster	Configuration	ΔV / H Å^3	[U^{5+}] mgU^{5+} / gUO_2		Energy / H eV		Hydrogen Bonds			Ω
			NN	NNN	Formation	Binding	Strong	Medium	Weak	
15	$^{L}I_2^x$	4.64	0	28	-0.97	-0.36	0	3	7	1
16	$^{L}\mathrm{W}_{222}^{2O',O''} \rightarrow {}^{L}I_2^x$	5.28	0	28	-0.86	-0.25	0	1	12	1
17	$^{D}I_2^x$	6.02	0	28	-0.42	0.19	0	5	3	2
18	$^{L}\mathrm{W}_{222}^{O',2O''}$	5.43	0	28	-0.78	-0.17	0	2	10	2
19	$^{D}\mathrm{W}_{222}^{O',2O''}$	5.76	0	28	-0.59	0.02	2	1	5	2
20	$^{D}\mathrm{W}_{222}^{2O',O''}$	6.02	0	28	-0.58	0.03	3	0	4	2



(a) ${}^{L}I_2^x$ (b) ${}^{L}\mathrm{W}_{222}^{2O',O''} \rightarrow {}^{L}I_2^x$

(c) ${}^{D}I_2^x$ (d) ${}^{L}\mathrm{W}_{222}^{O',2O''}$

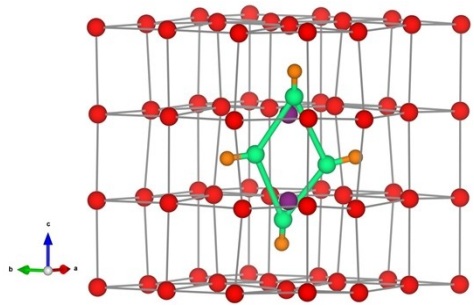
(e) ${}^{D}\mathrm{W}_{222}^{O',2O''}$ (f) ${}^{D}\mathrm{W}_{222}^{2O',O''}$

Supplementary Figure 3 | Configurations of oxy-hydroxyl clusters at 351 *μ*gH / gUO$_2$. Uranium ions have been omitted for clarity, lattice oxygen shown in red, O_i in green, V_O shown in purple and hydrogen shown in orange. Bonds have been drawn to highlight defect cluster geometries.

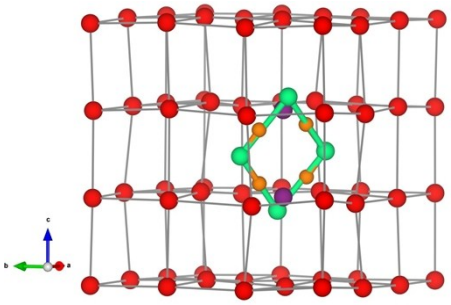
Oxy-hydroxyl defect clusters at 467 μgH / gUO_2

Supplementary Table 4. Oxy-hydroxyl defect cluster configurations at 467 μgH / gUO_2. An arrow denotes where a change in the initial H-O cluster geometry has occurred (*i.e.* relaxation to a different type of cluster). ΔV is the change in calculated volume compared to stoichiometric UO_2. $[U^{5+}]$ is the U^{5+} defect concentration localized on nearest neighbour (NN) or next nearest neighbour (NNN) uranium sites. Formation and binding energies per hydrogen and number of strong, medium and weak hydrogen bonds are also presented. Ω is the degeneracy of the oxy-hydroxyl cluster.

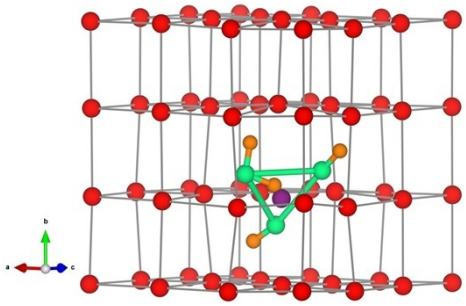
Cluster	Configuration	ΔV /H Å^3	$[U^{5+}]$ mgU^{5+} / gUO_2		Energy / H eV		Hydrogen Bonds			Ω
			NN	NNN	Formation	Binding	Strong	Medium	Weak	
21	$^{L}\mathrm{W}_{222}^{2O',O''}$	5.88	0	0	-0.79	-0.39	0	2	14	1
22	$^{D}\mathrm{W}_{222}^{2O',O''}$	6.21	0	0	-0.50	-0.10	4	0	6	2
23	$^{L}I_2^x$	5.41	0	0	-0.60	-0.20	0	6	6	3
24	$^{D}I_2^x \rightarrow {}^{D}I_3^x$	3.35	28	28	0.09	0.50	1	4	4	1



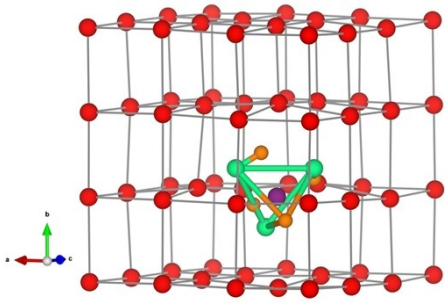
(a) ${}^{L}\mathrm{W}_{222}^{2O',O''}$



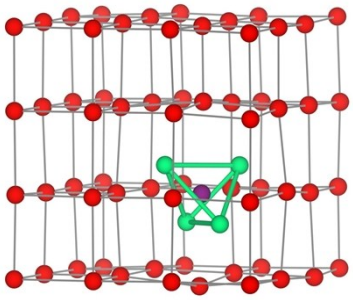
(b) ${}^{D}\mathrm{W}_{222}^{2O',O''}$



(c) ${}^{L}I_2^x$



(d) ${}^{D}I_2^x \rightarrow {}^{D}I_3^x$



(e) I_3^x

Supplementary Figure 4 | Configurations of oxy-hydroxyl clusters at 467 *μ*gH / gUO$_2$. Uranium ions have been omitted for clarity, lattice oxygen shown in red, O_i in green, V_O shown in purple and hydrogen shown in orange. Bonds have been drawn to highlight defect cluster geometries.

Supplementary References

1. Jeffrey, G.A., An Introduction to hydrogen bonding, Oxford University Press, 1997.