Water Adsorption on AnO_2 {111}, {110} and {100} Surfaces (An = U, Pu); A DFT+*U* Study

Supplementary Information

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Conf. / Pressure	**4 × H_2O**	**3 × H_2O + 1 × (OH + H)**	**2 × H_2O + 2 × (OH + H)**	**1 × H_2O + 3 × (OH + H)**	**4 × (OH + H)**
p = 10^{-13} bar	117	122	138	102	37
p = 10^{-7} bar	159	165	186	139	52
p = 1 bar	260	270	300	230	93
p = 3 bar	271	281	313	240	98
p = 5 bar	276	287	319	245	101

Table S1: Desorption temperatures (K) on UO_2 {111} at various pressures.

Conf. / Pressure	**4 × H_2O**	**3 × H_2O + 1 × (OH + H)**	**2 × H_2O + 2 × (OH + H)**	**1 × H_2O + 3 × (OH + H)**	**4 × (OH + H)**
p = 10^{-13} bar	107	112	120	89	19
p = 10^{-7} bar	145	152	162	121	26
p = 1 bar	239	250	265	203	50
p = 3 bar	250	261	277	213	53
p = 5 bar	255	267	282	217	54

Table S2: Desorption temperatures (K) on PuO_2 {111} at various pressures.

Conf. / Pressure	**4 × H_2O**	**3 × H_2O + 1 × (OH + H)**	**2 × H_2O + 2 × (OH + H)**	**1 × H_2O + 3 × (OH + H)**	**4 × (OH + H)**
p = 10^{-13} bar	153		193	193	228
p = 10^{-7} bar	205		257	256	301
p = 1 bar	329		406	405	472
p = 3 bar	342		422	421	490
p = 5 bar	349		430	429	499

Table S3: Desorption temperatures (K) on UO_2 {110} at various pressures.

Conf. / Pressure	**4 × H_2O**	**3 × H_2O + 1 × (OH + H)**	**2 × H_2O + 2 × (OH + H)**	**1 × H_2O + 3 × (OH + H)**	**4 × (OH + H)**
p = 10^{-13} bar	94		191	180	208
p = 10^{-7} bar	128		255	240	276
p = 1 bar	214		402	381	434
p = 3 bar	224		418	396	452
p = 5 bar	228		426	404	460

Table S4: Desorption temperatures (K) on PuO_2 {110} at various pressures.

Conf. / Pressure	**4 × H_2O**	**3 × H_2O + 1 × (OH + H)**	**2 × H_2O + 2 × (OH + H)**	**1 × H_2O + 3 × (OH + H)**	**4 × (OH + H)**
p = 10^{-13} bar	197	220	227	271	229
p = 10^{-7} bar	262	291	300	356	303
p = 1 bar	413	457	470	555	475
p = 3 bar	429	475	488	577	494
p = 5 bar	437	483	497	587	503

Table S5: Desorption temperatures (K) on UO_2 {100} at various pressures.

Conf. / Pressure	**4 × H_2O**	**3 × H_2O + 1 × (OH + H)**	**2 × H_2O + 2 × (OH + H)**	**1 × H_2O + 3 × (OH + H)**	**4 × (OH + H)**
p = 10^{-13} bar	216	202	265	284	302
p = 10^{-7} bar	287	269	348	374	396
p = 1 bar	450	423	543	581	615
p = 3 bar	468	440	564	603	638
p = 5 bar	477	448	575	615	650

Table S6: Desorption temperatures (K) on PuO_2 {100} at various pressures.

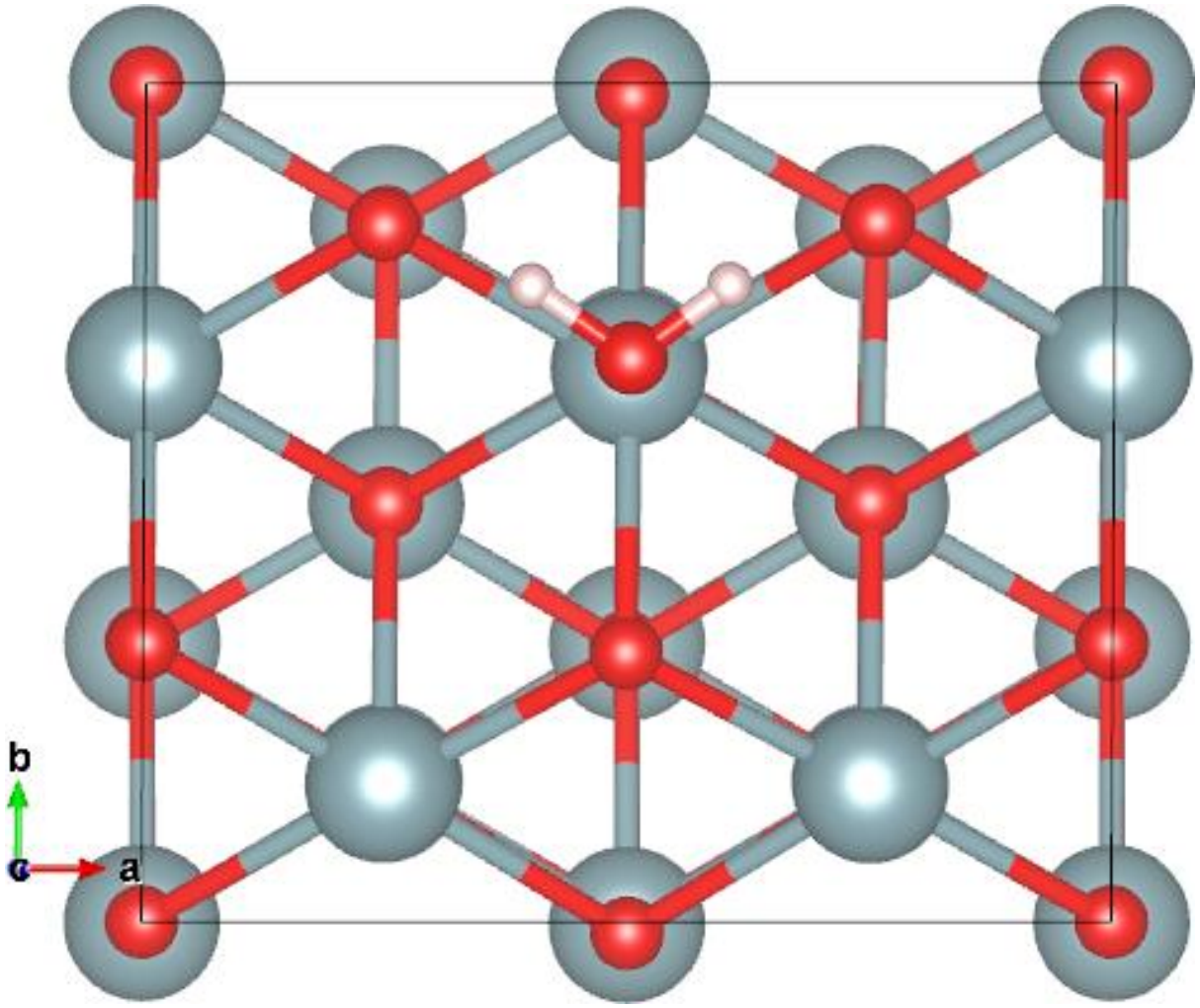

Figure S1: Single water molecule adsorbed molecularly on the 2 × 2 UO_2 {111} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

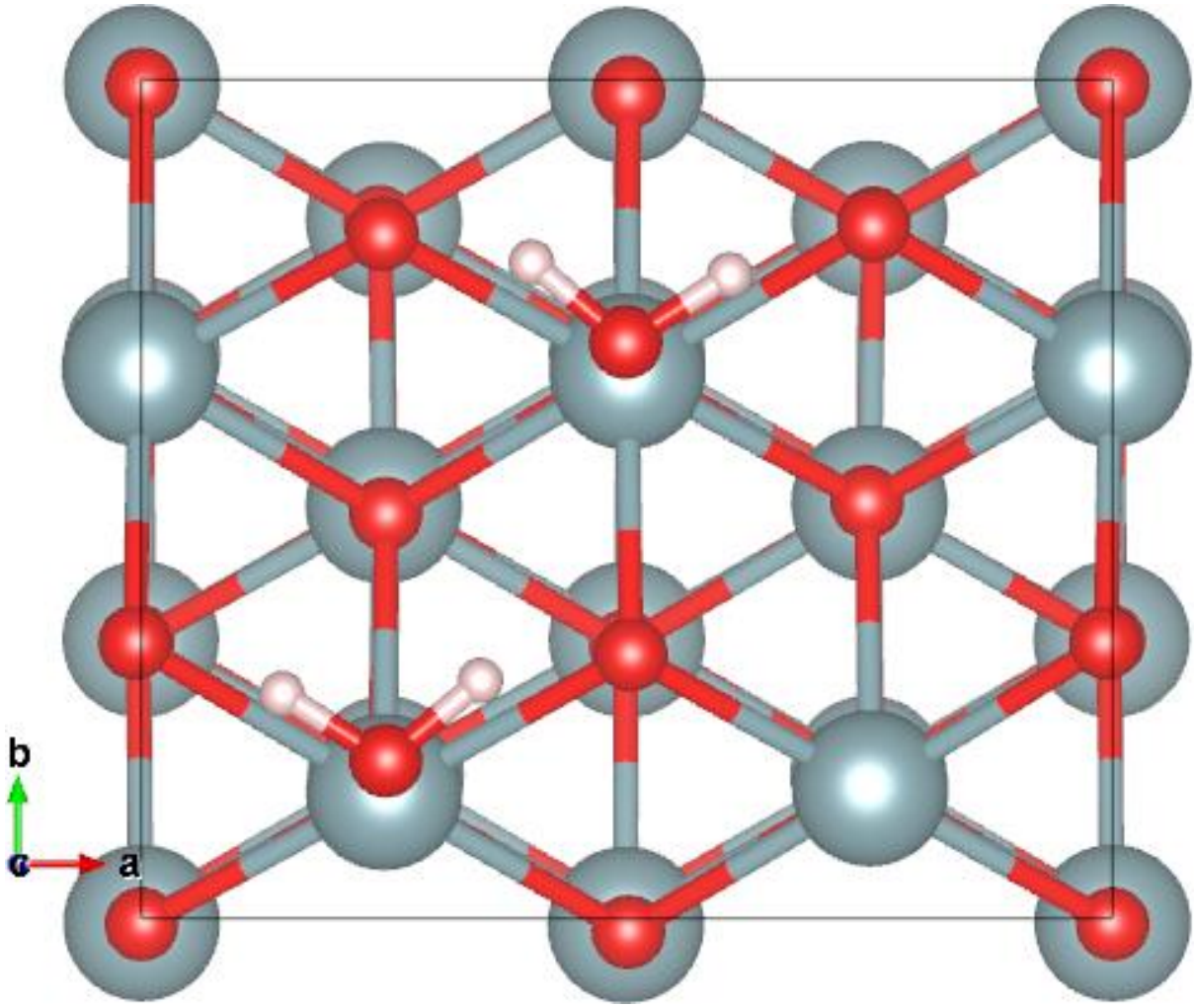

Figure S2: Two water molecules adsorbed molecularly on the 2 × 2 UO_2 {111} surface, yielding a coverage of 50%, i.e. half a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

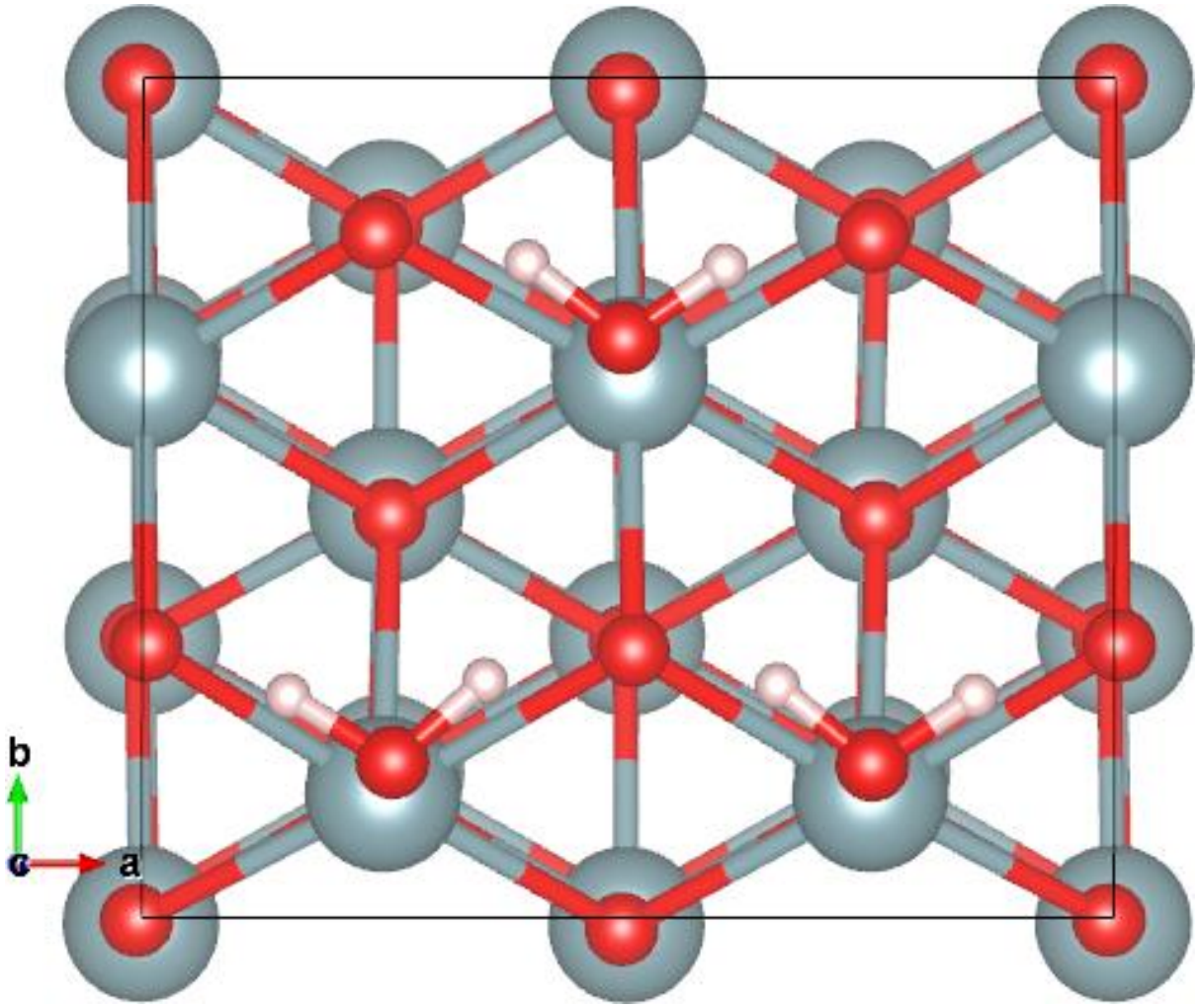

Figure S3: Three water molecules adsorbed molecularly on the 2 × 2 UO_2 {111} surface, yielding a coverage of 75%, i.e. ¾ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

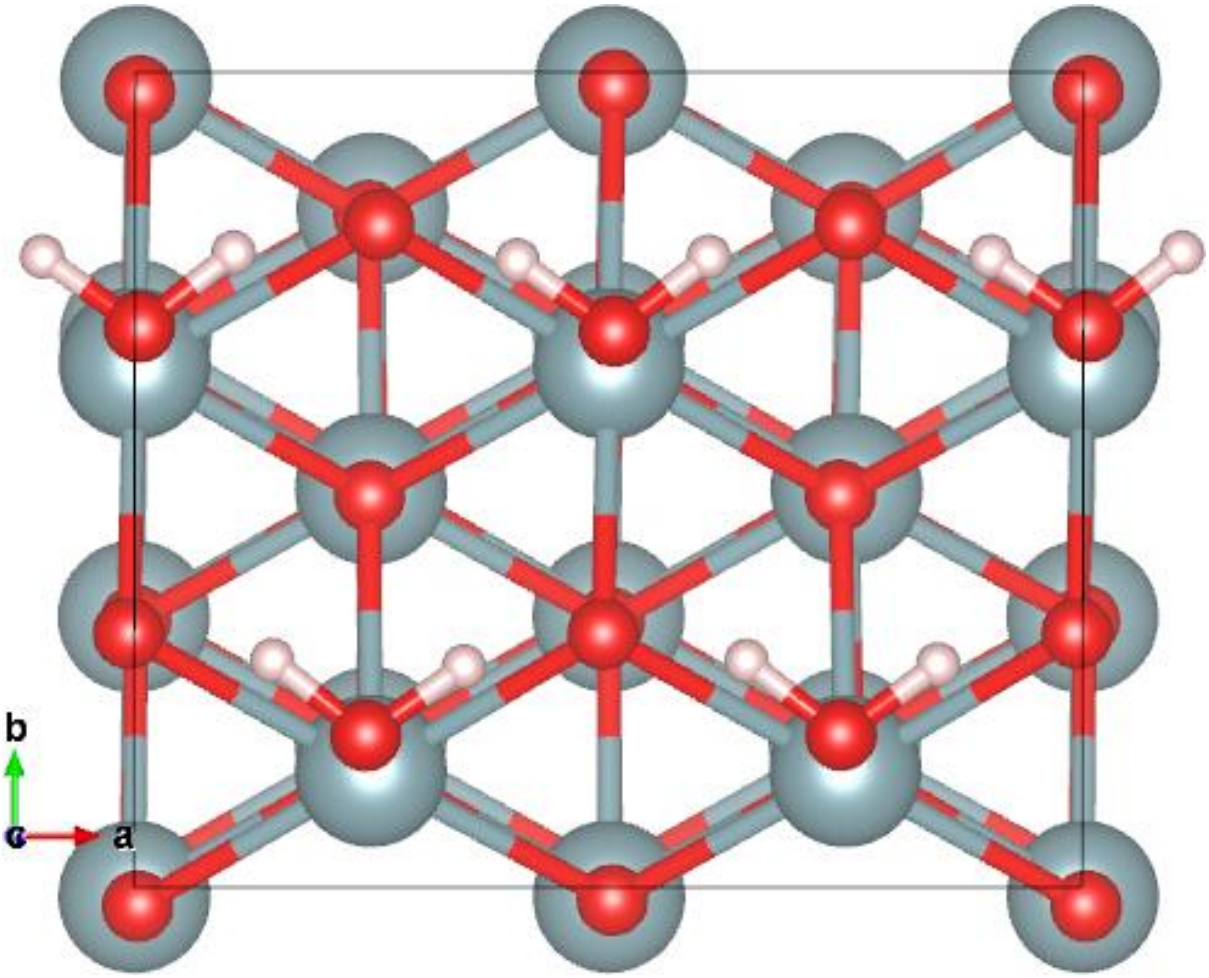

Figure S4: Four water molecules adsorbed molecularly on the 2 × 2 U O_2 {111} surface, yielding a coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

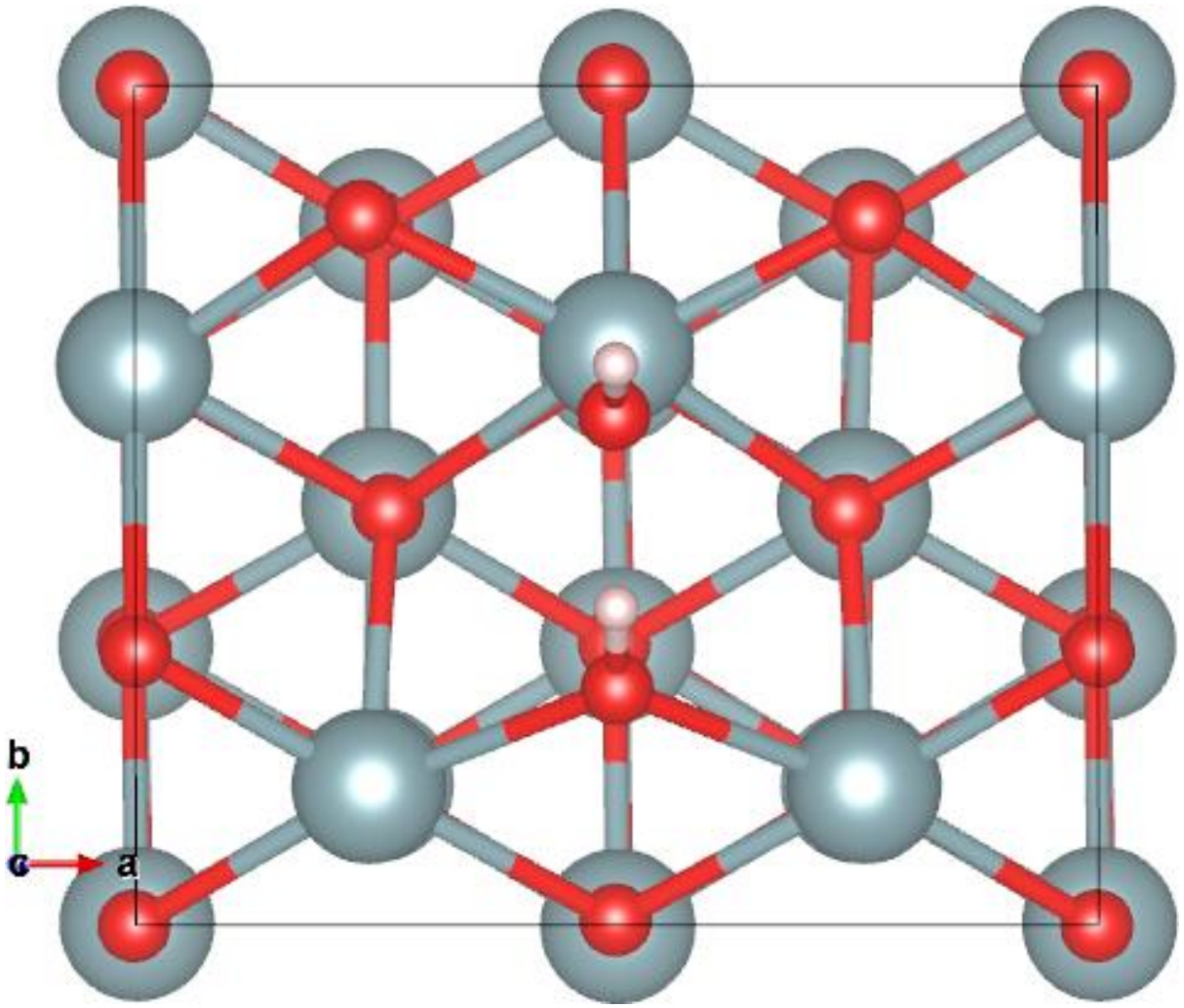

Figure S5: Single water molecule adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

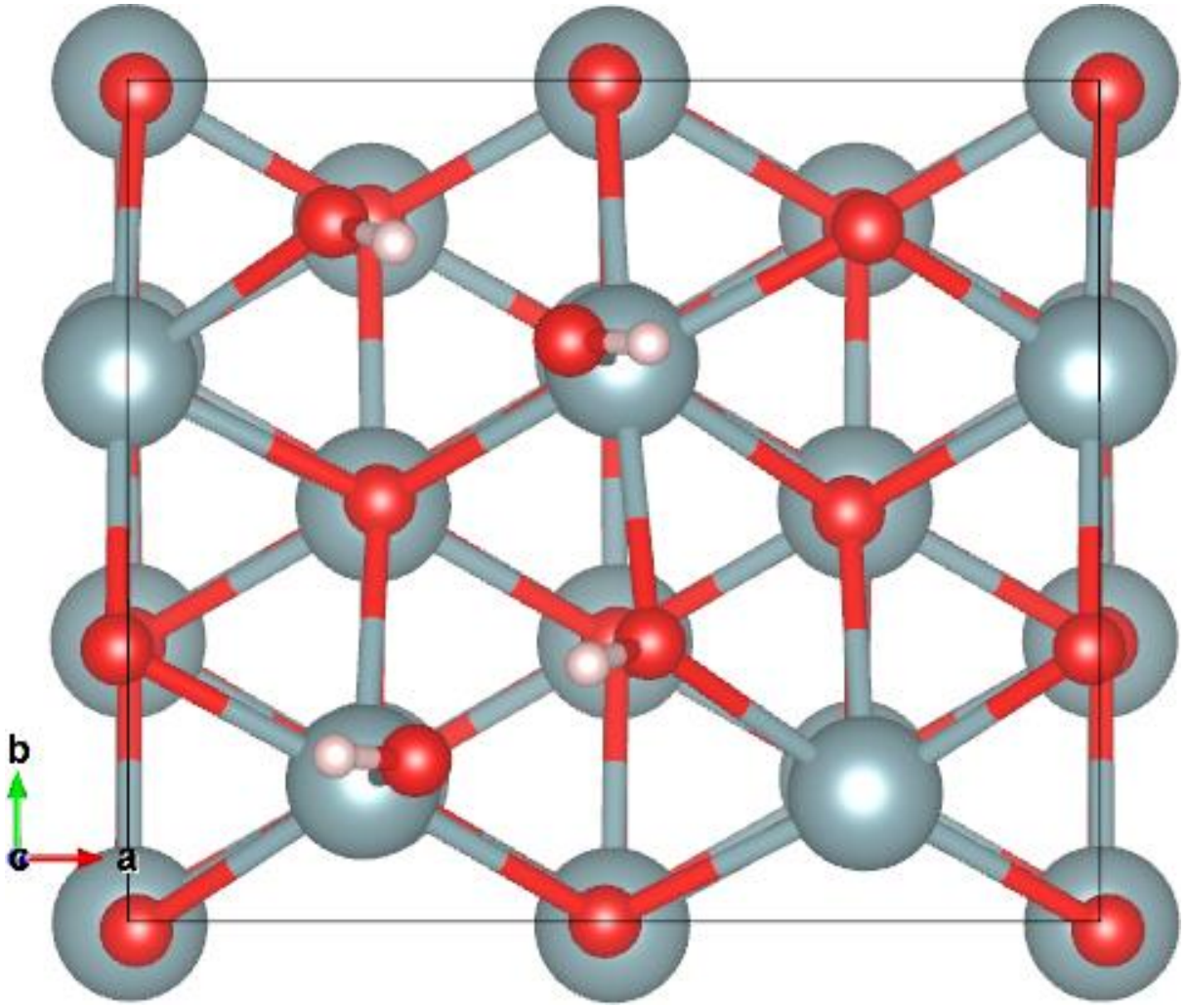

Figure S6: Two water molecules adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 50%, i.e. half a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

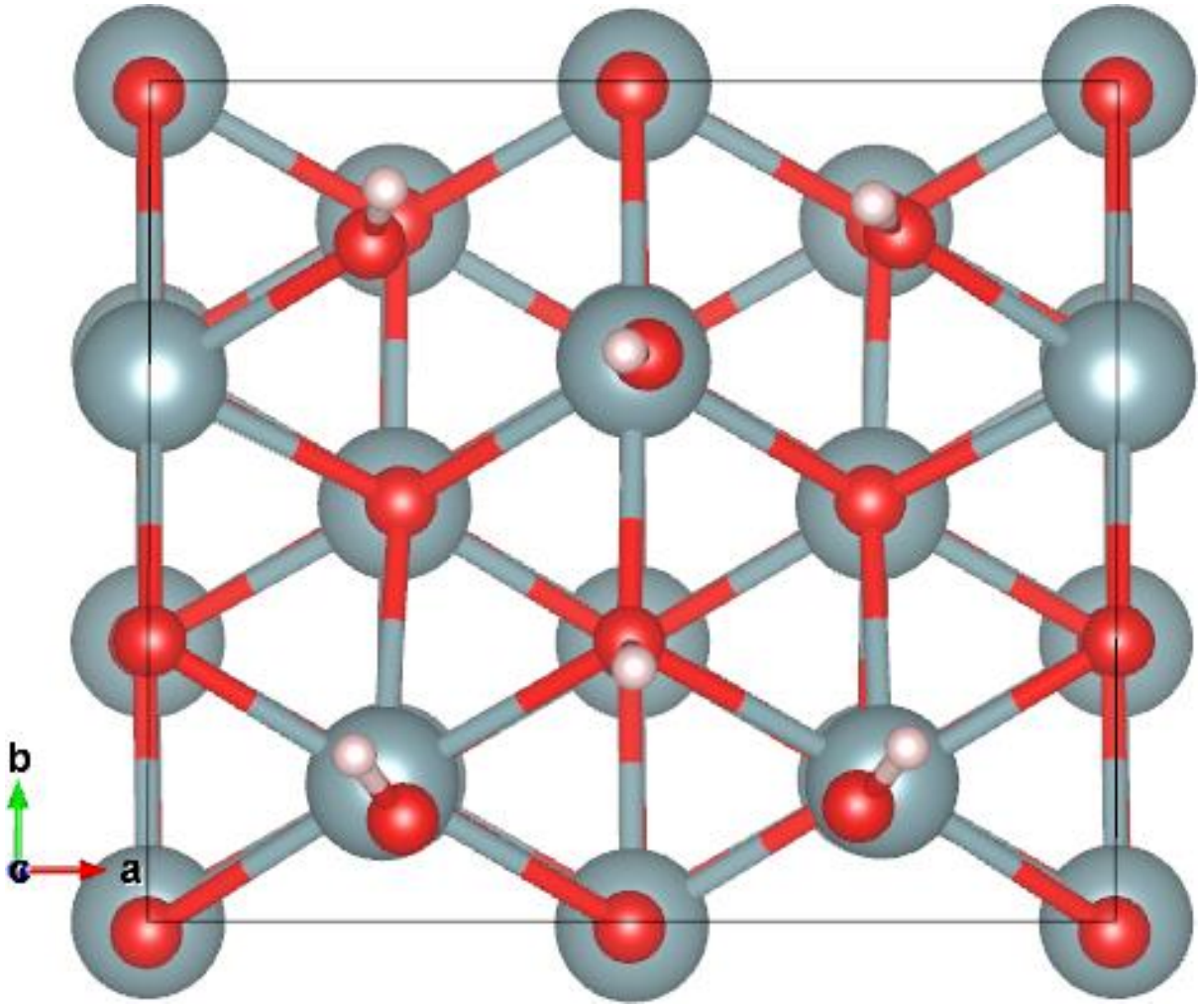

Figure S7: Three water molecules adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 75%, i.e. ¾ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

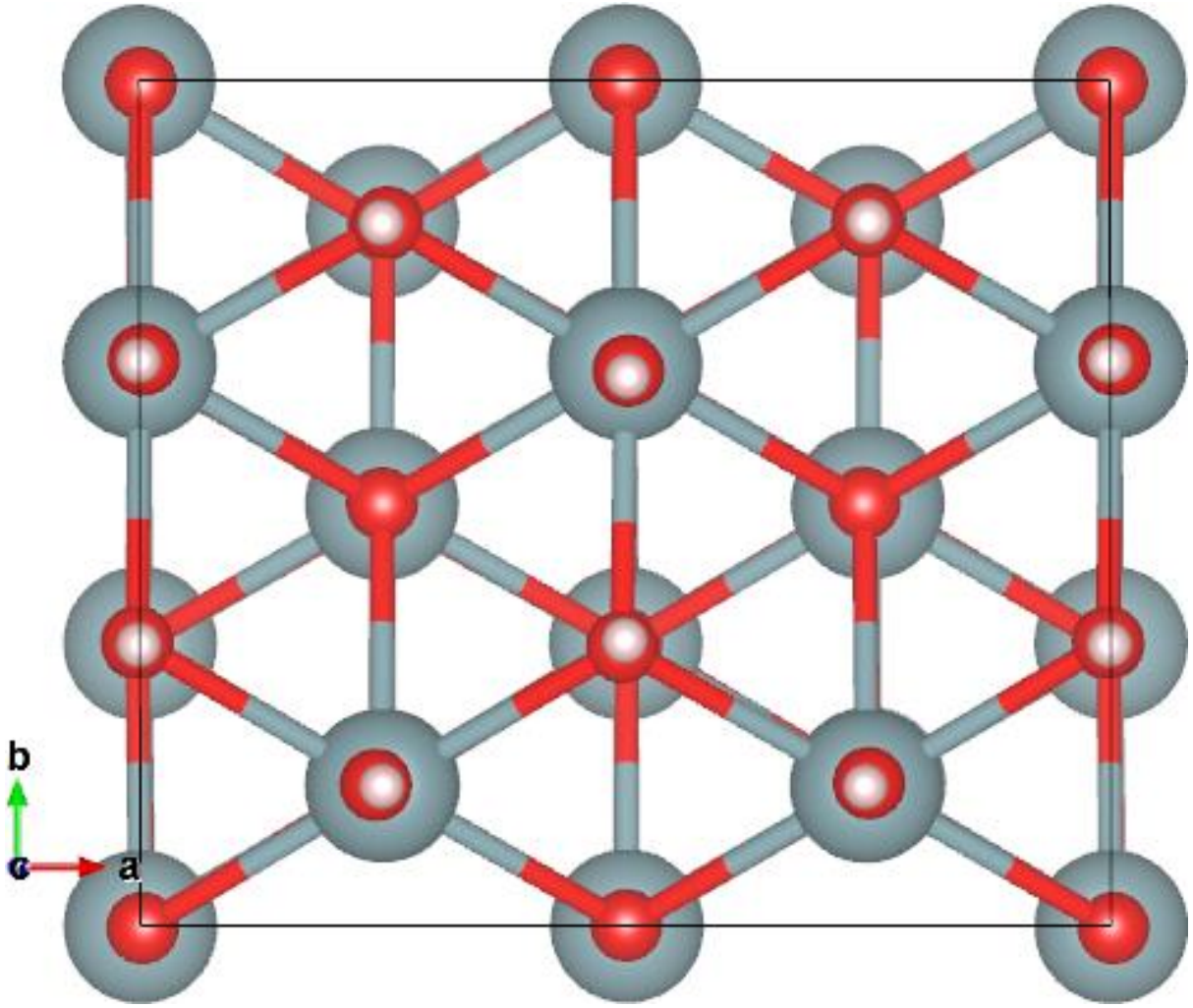

Figure S8: Four water molecules adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

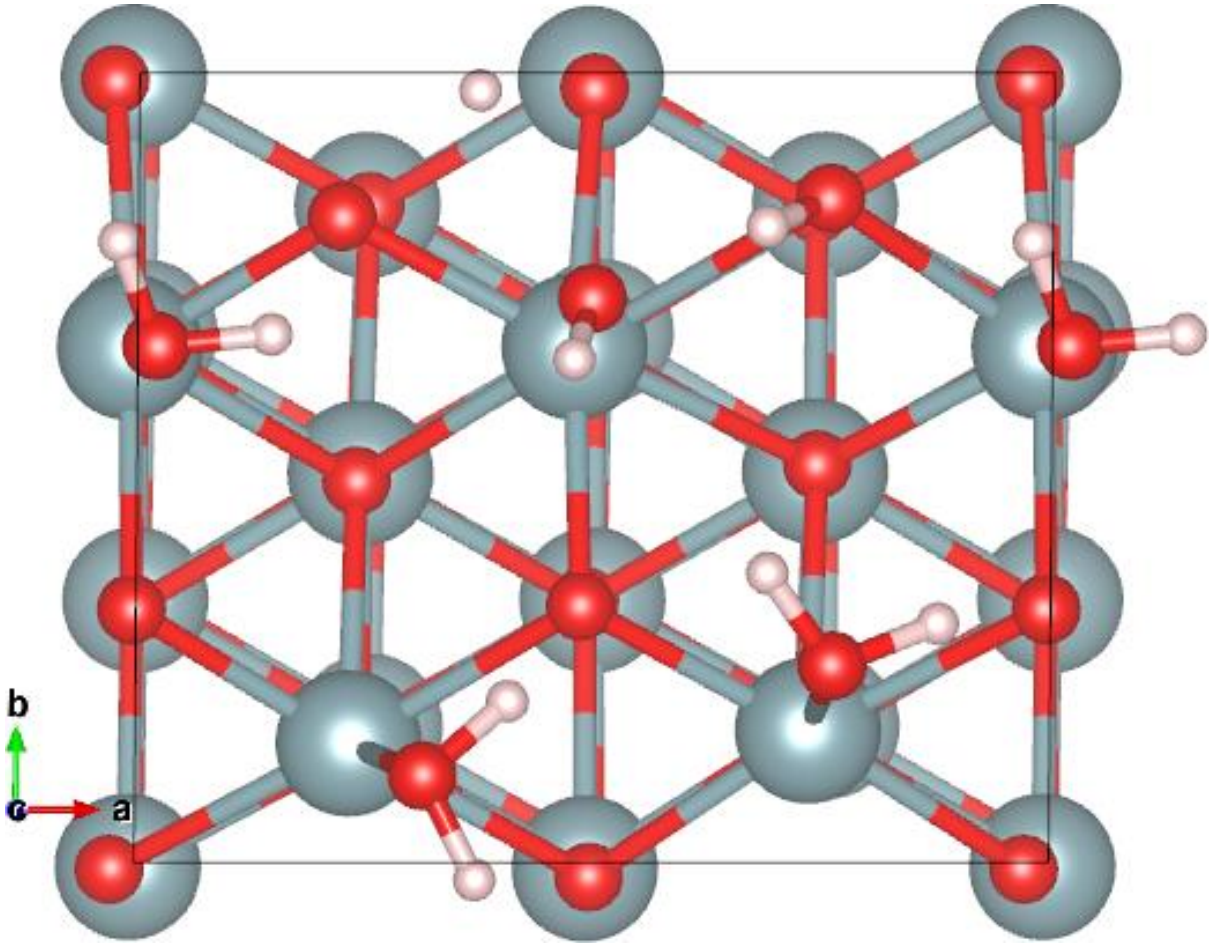

Figure S9: Three water molecules adsorbed molecularly and one water molecule adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 100%, i.e. one monolayer. U atoms in gray, oxygen in red and hydrogen in white.

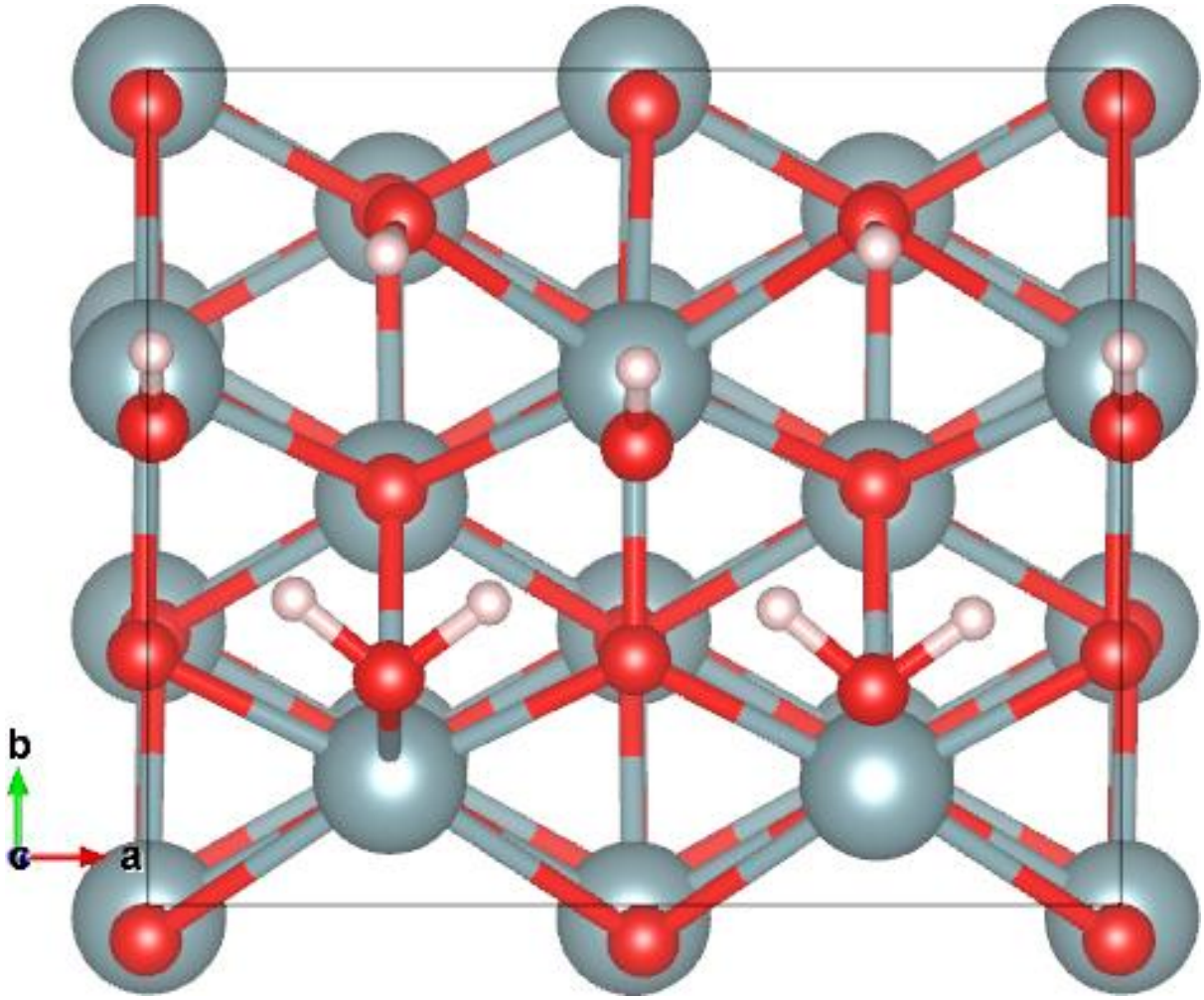

Figure S10: Two water molecules adsorbed molecularly and two water molecules adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 100%, i.e. one monolayer. U atoms in gray, oxygen in red and hydrogen in white.

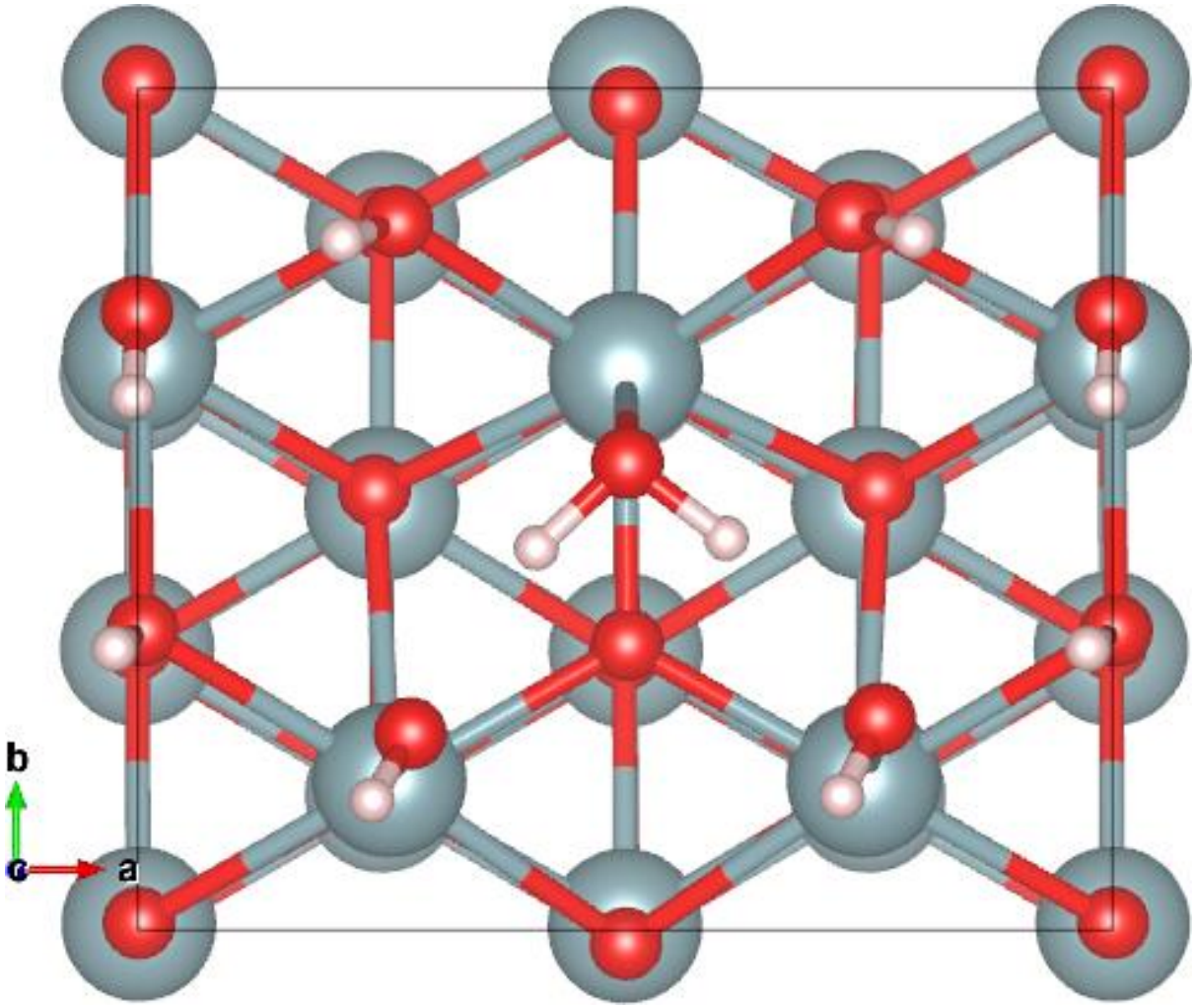

Figure S11: One water molecule adsorbed molecularly and three water molecules adsorbed dissociatively on the 2 × 2 UO_2 {111} surface, yielding a coverage of 100%, i.e. one monolayer. U atoms in gray, oxygen in red and hydrogen in white.

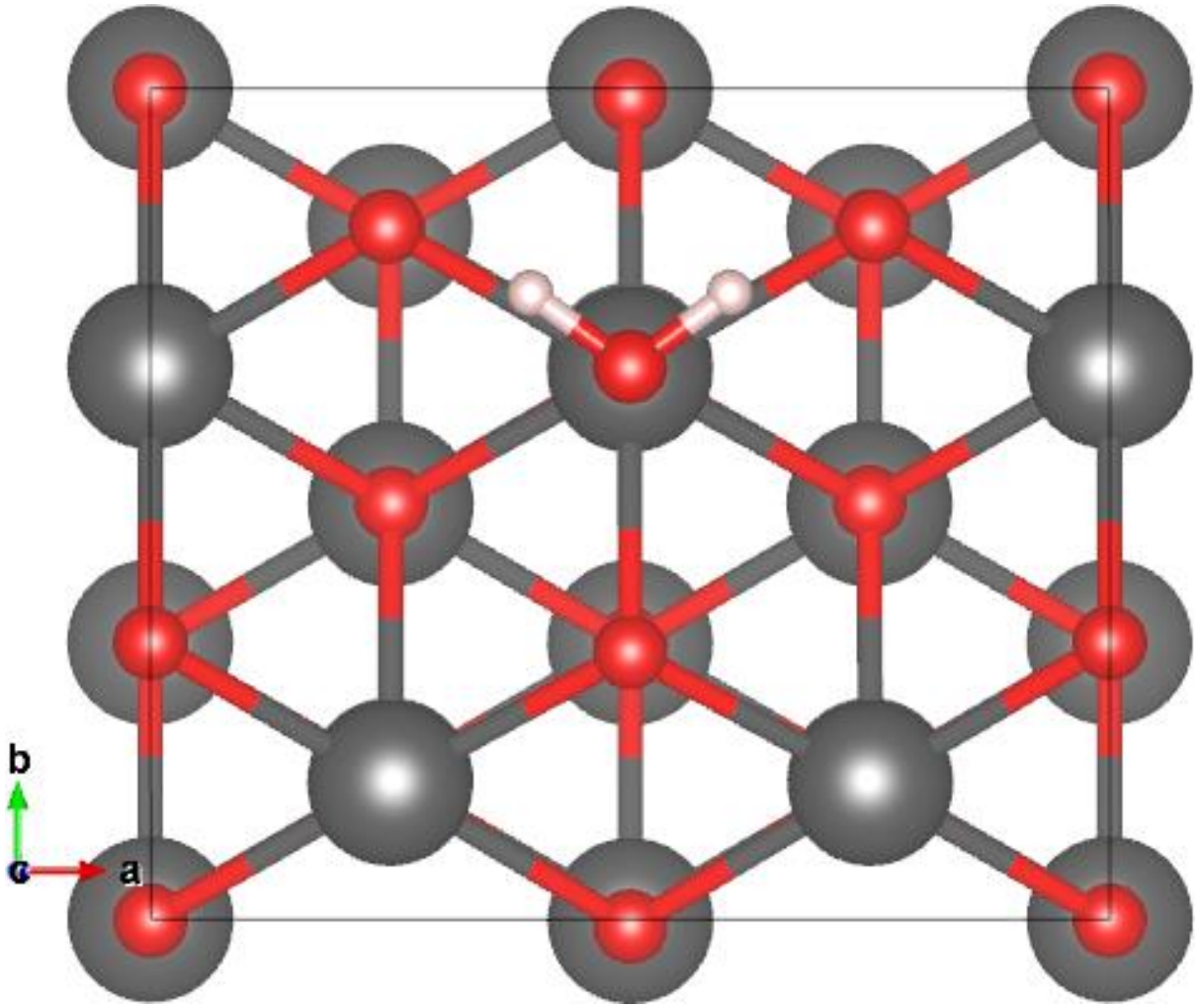

Figure S12: Single water molecule adsorbed molecularly on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

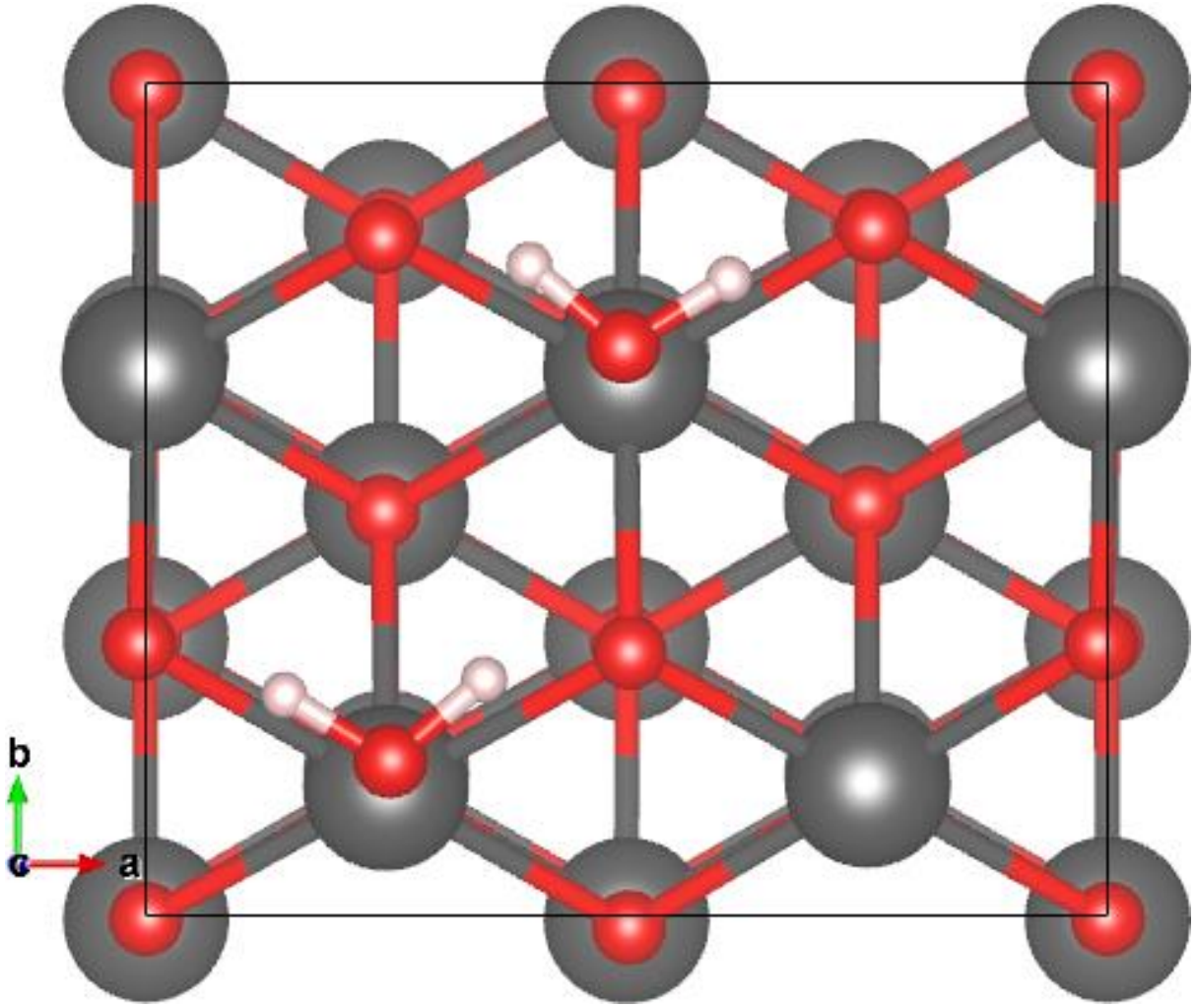

Figure S13: Two water molecules adsorbed molecularly on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 50%, i.e. half a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

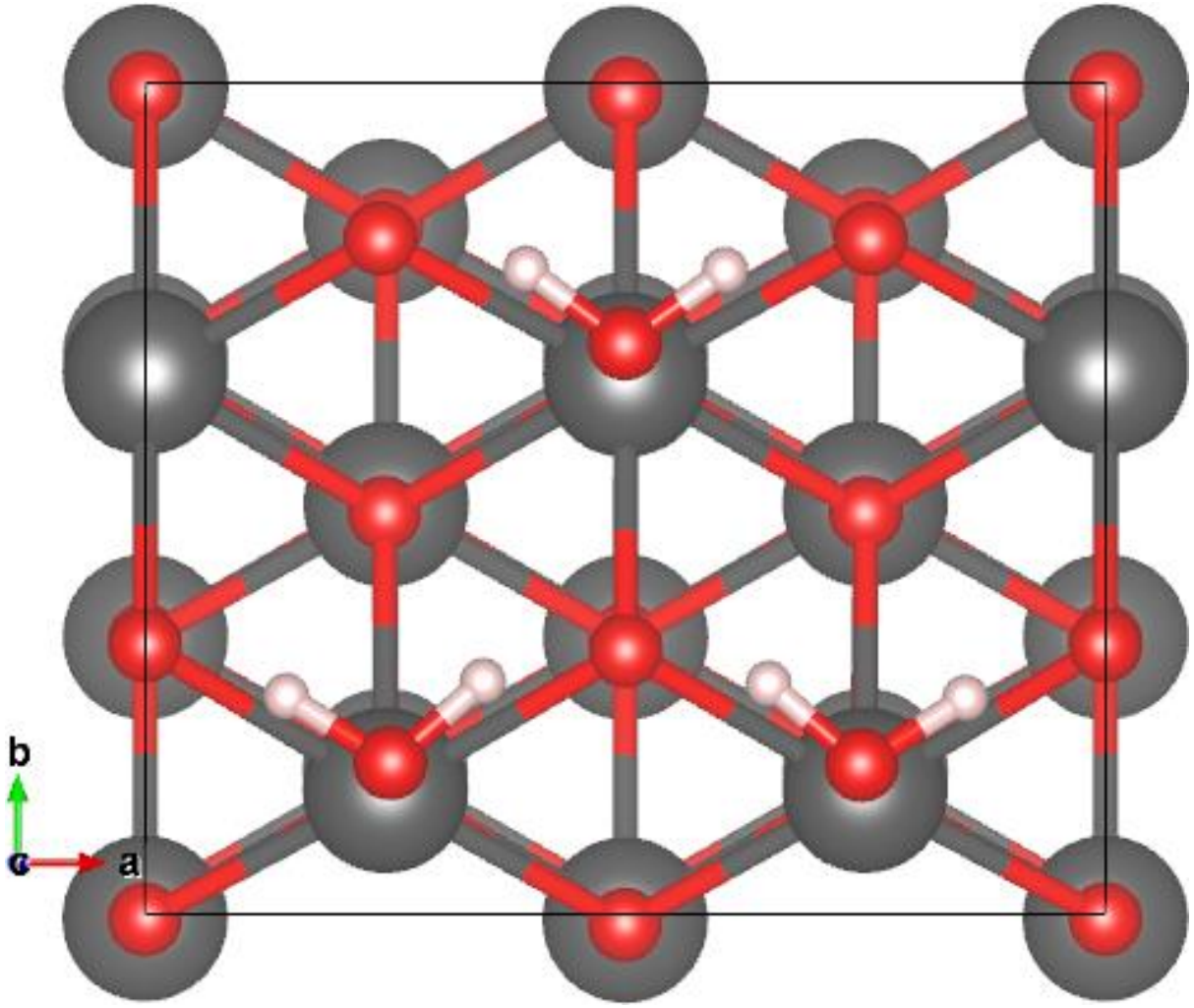

Figure S14: Three water molecules adsorbed molecularly on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 75%, i.e. ¾ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

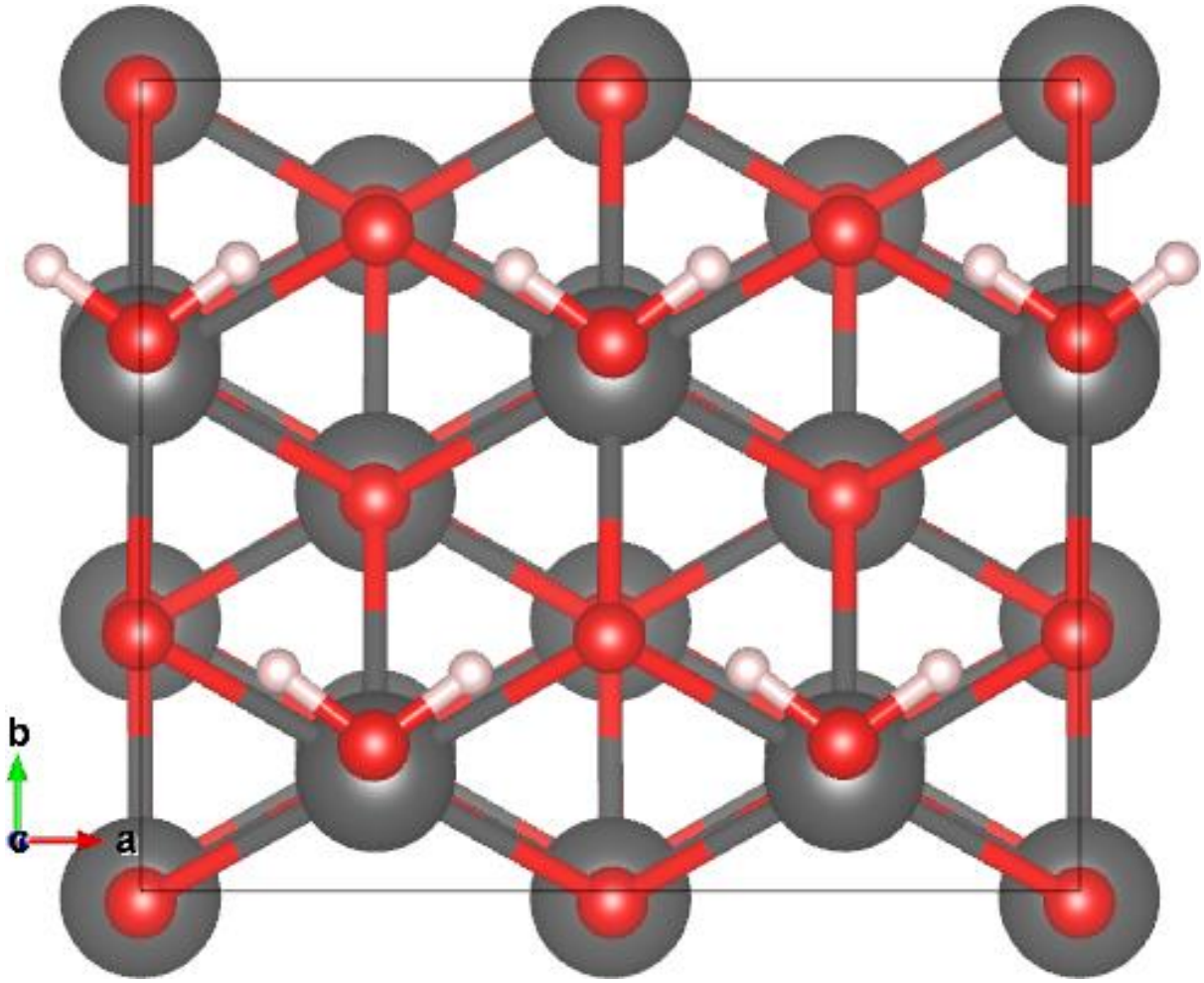

Figure S15: Four water molecules adsorbed molecularly on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

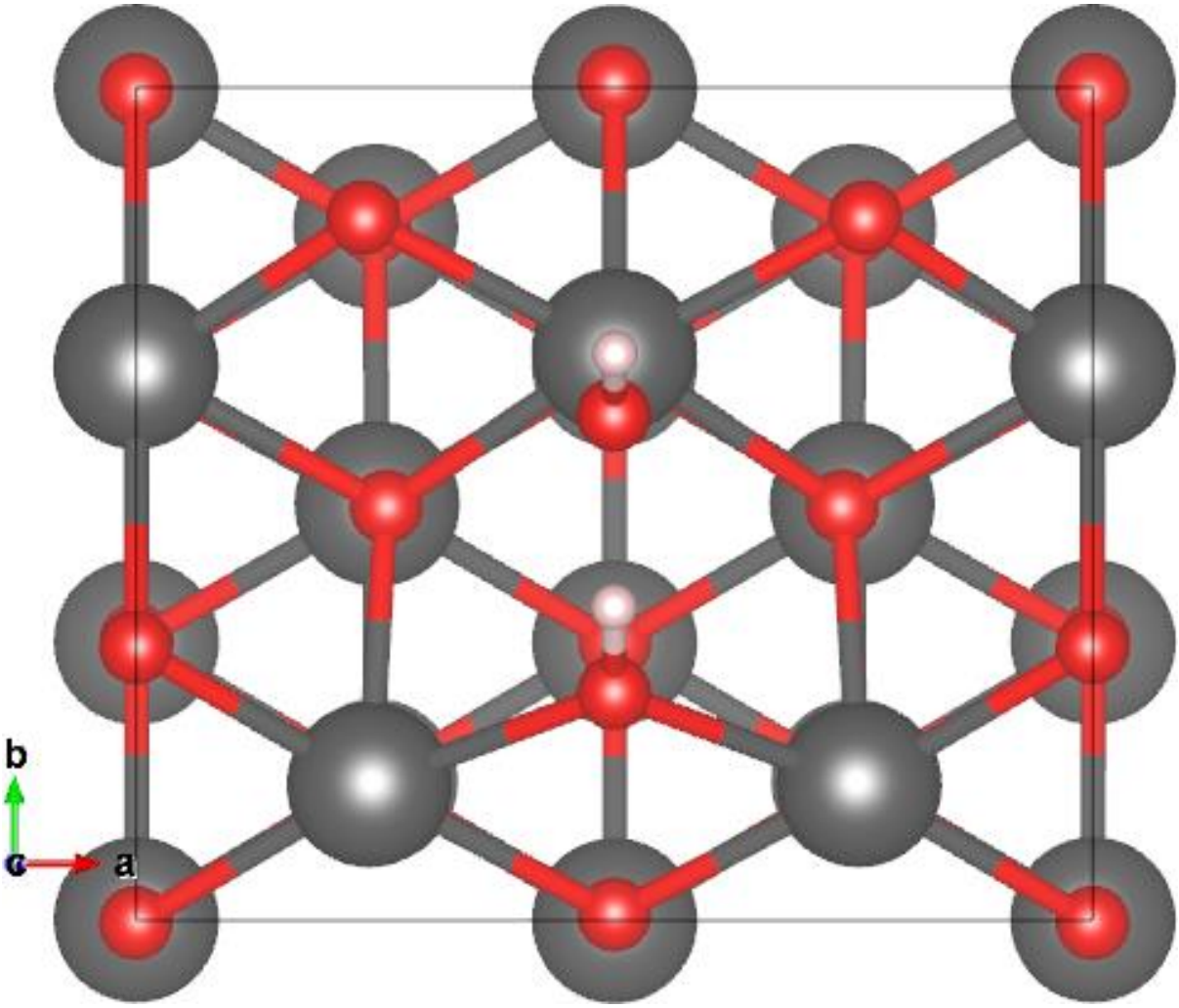

Figure S16: Single water molecule adsorbed dissociatively on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

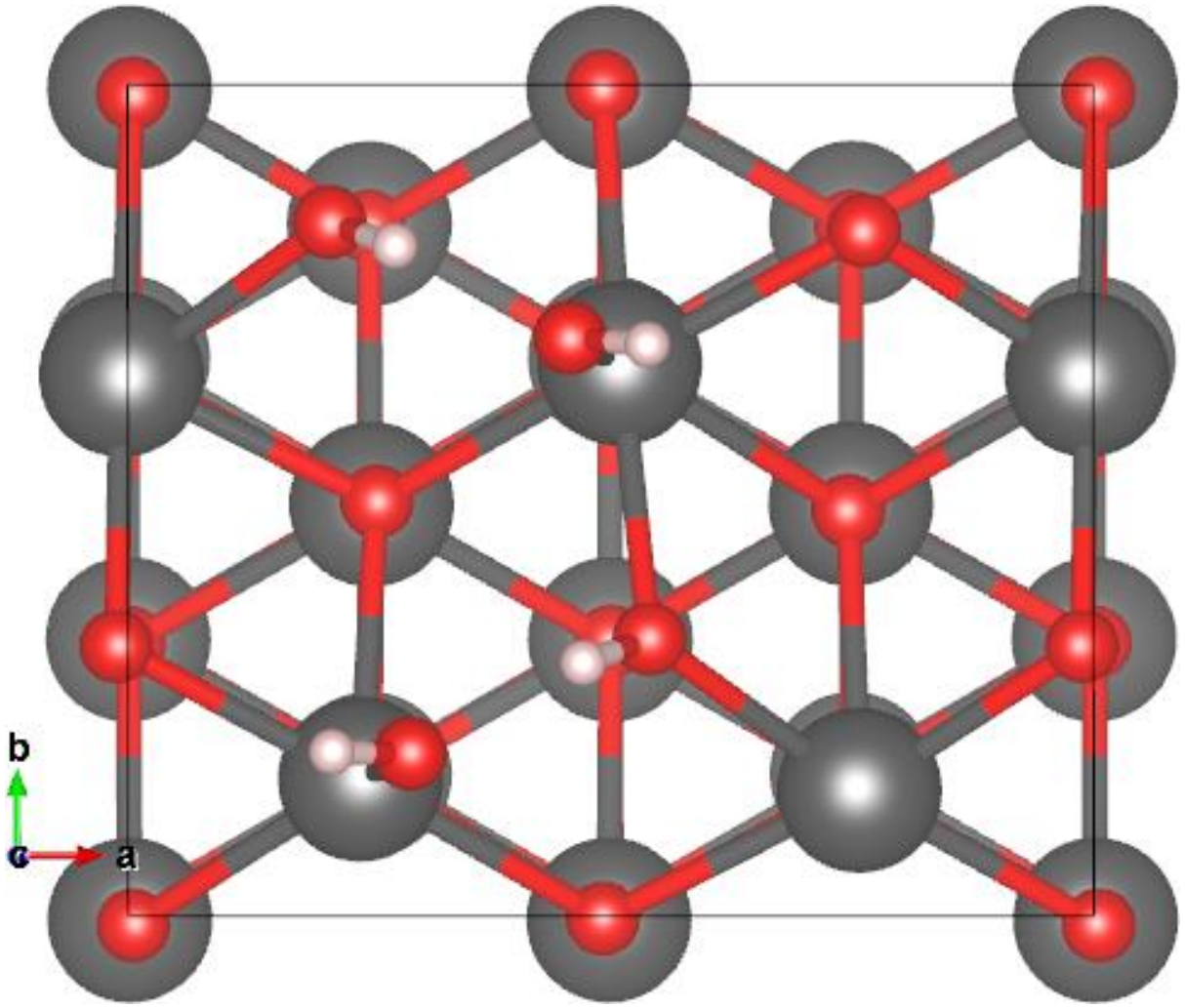

Figure S17: Two water molecules adsorbed dissociatively on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 50%, i.e. half a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

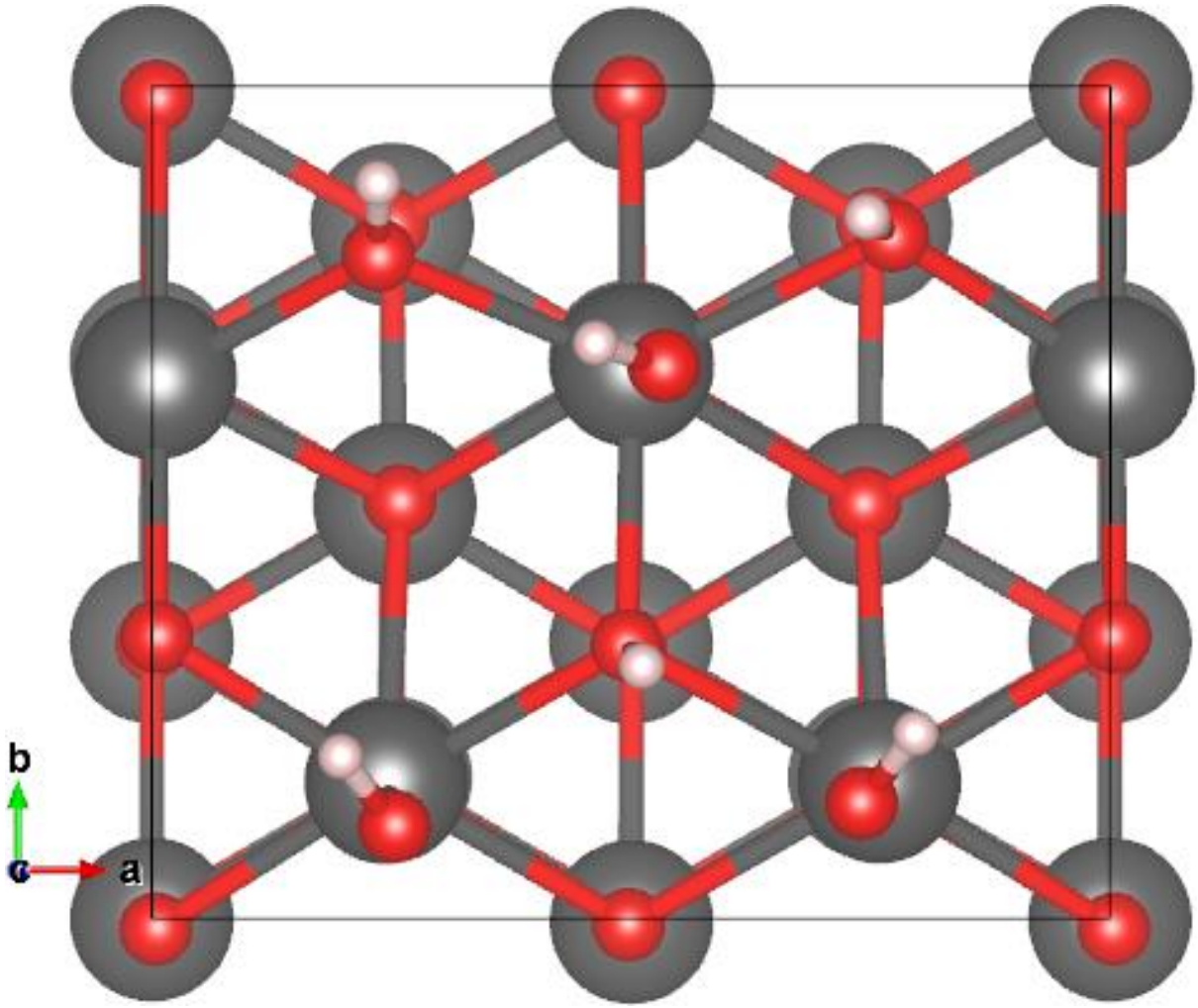

Figure S18: Three water molecules adsorbed dissociatively on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 75%, i.e. ¾ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

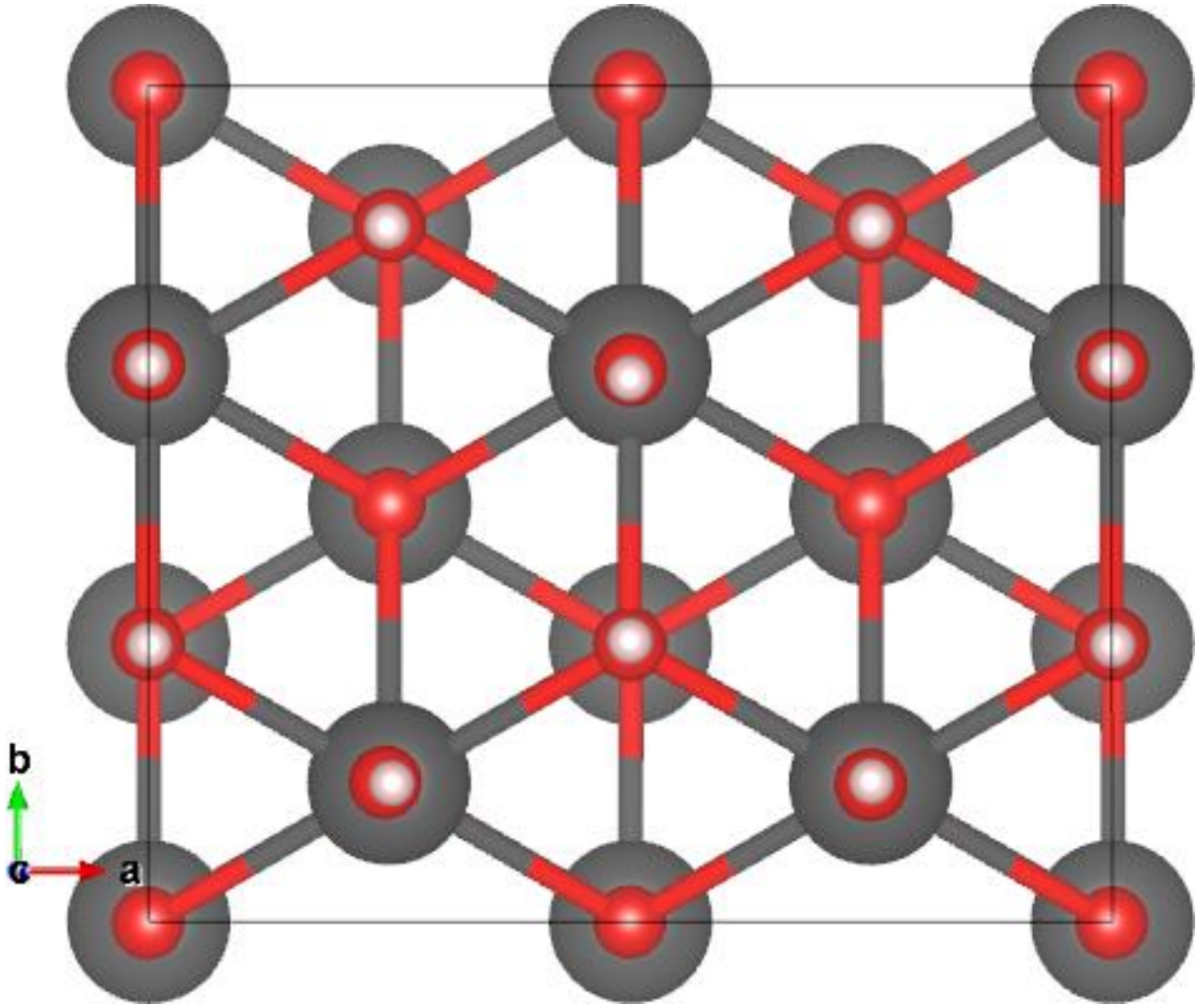

Figure S19: Four water molecules adsorbed molecularly on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

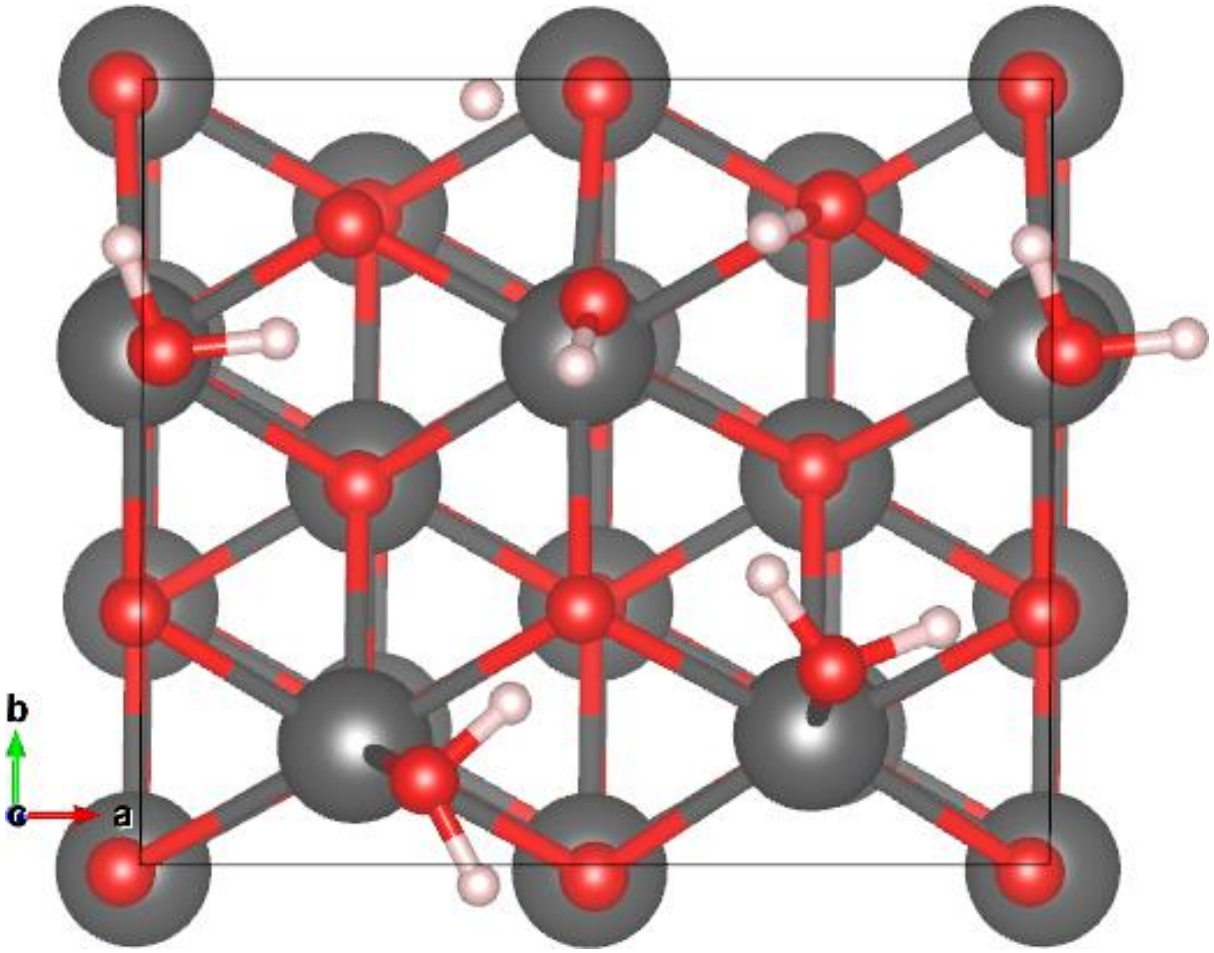

Figure S20: Three water molecules adsorbed molecularly and one water molecule adsorbed dissociatively on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 100%, i.e. one monolayer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

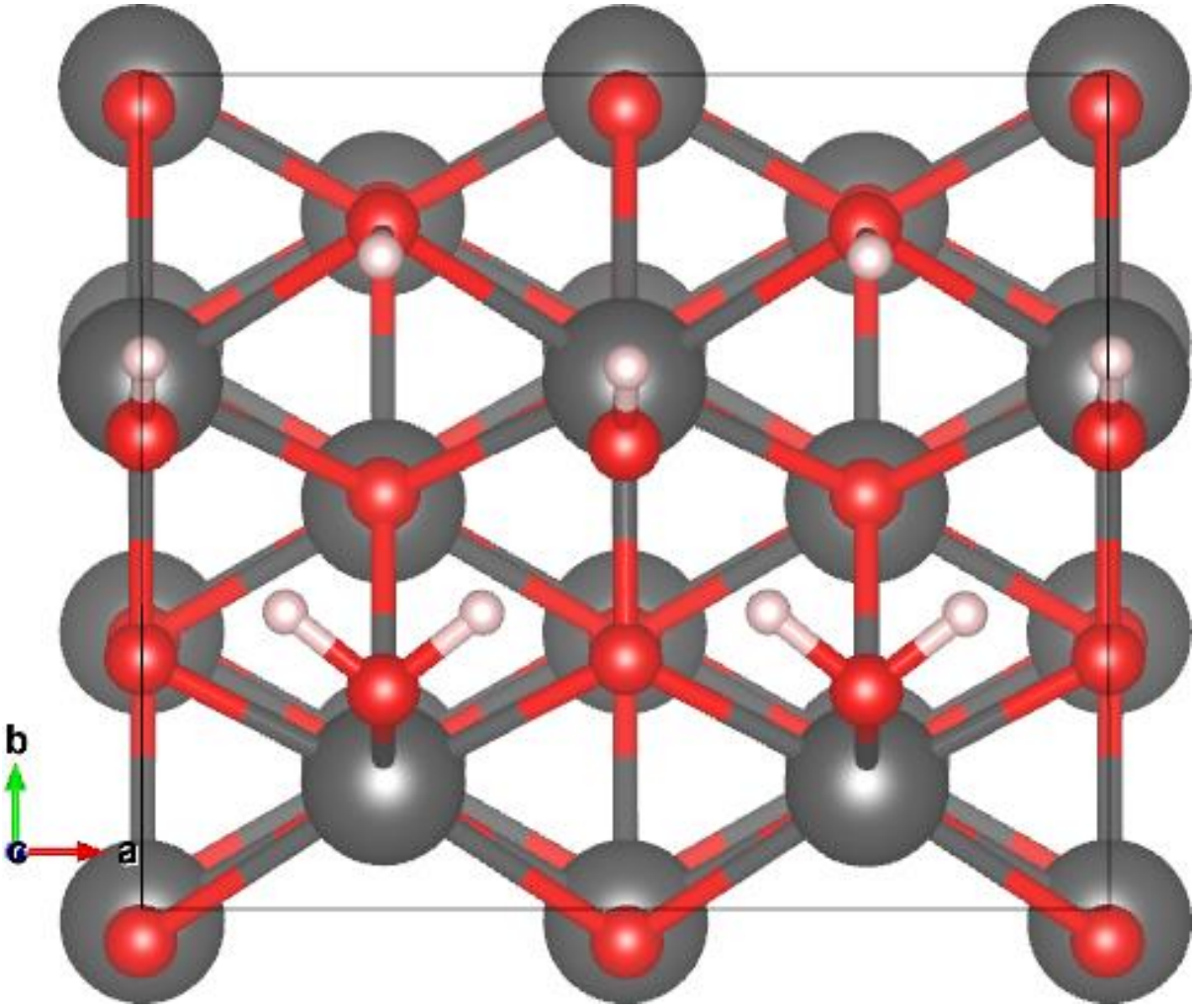

Figure S21: Two water molecules adsorbed molecularly and two water molecules adsorbed dissociatively on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 100%, i.e. one monolayer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

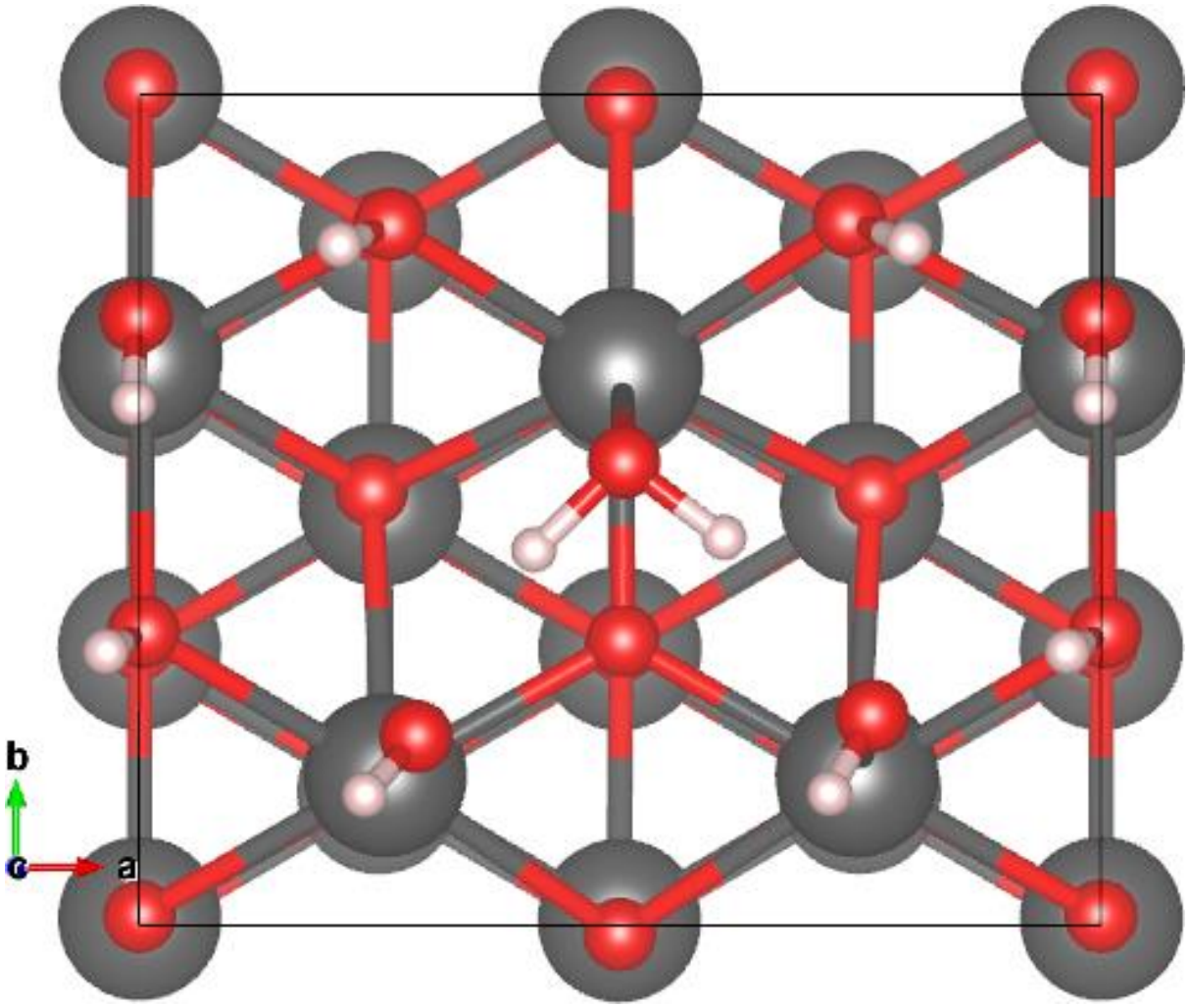

Figure S22: One water molecule adsorbed molecularly and three water molecules adsorbed dissociatively on the 2 × 2 PuO_2 {111} surface, yielding a coverage of 100%, i.e. one monolayer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

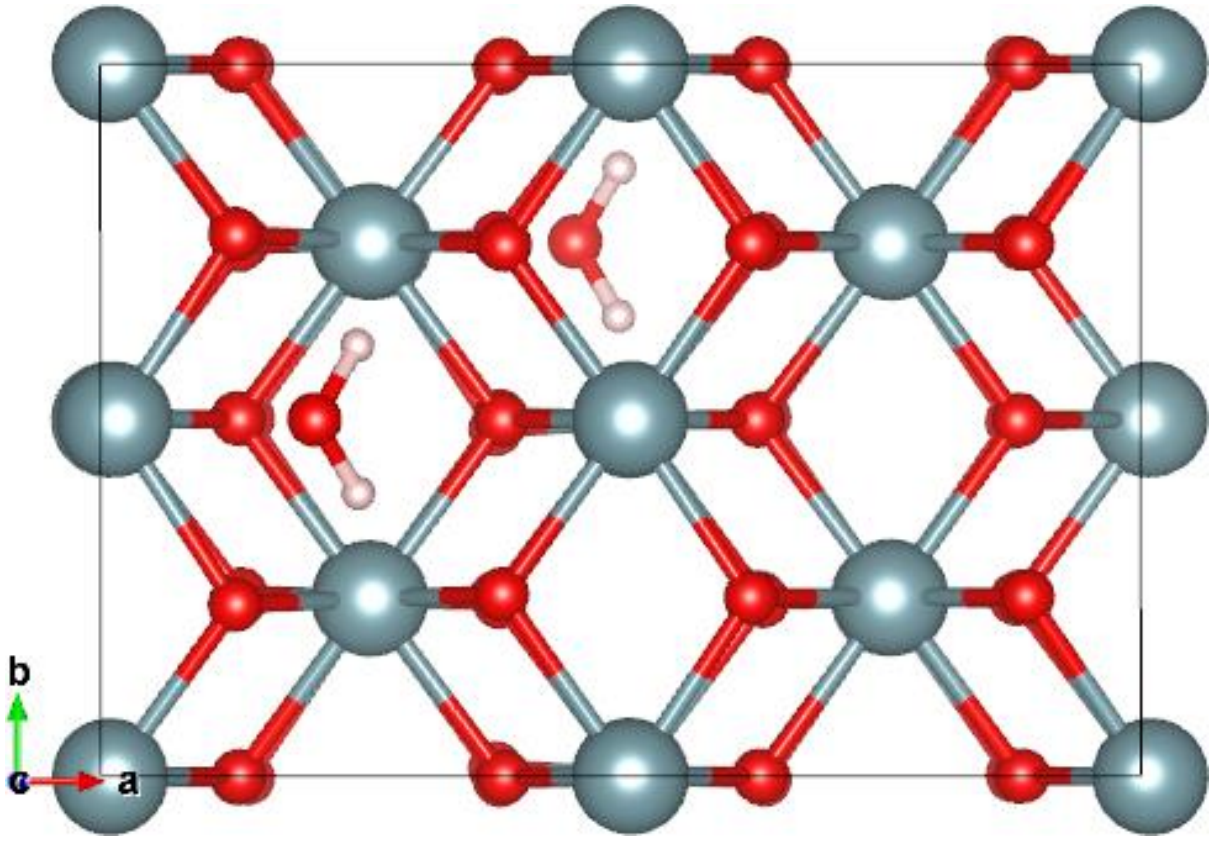

Figure S23: Water adsorbed molecularly on the 2 × 2 UO_2 {110} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

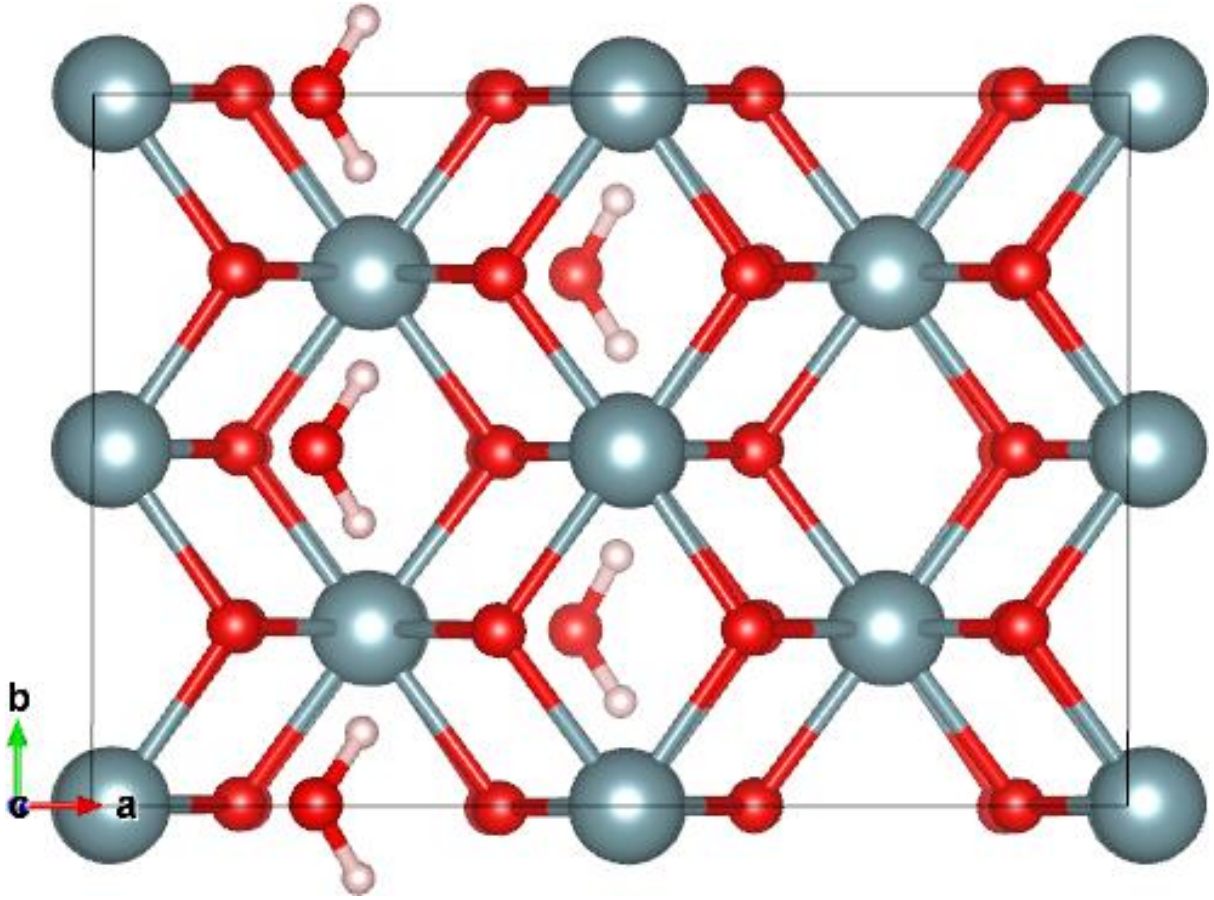

Figure S24: Water adsorbed molecularly on the 2 × 2 UO_2 {110} surface, yielding a coverage of 50%, i.e. half a mono-layer. U atoms in gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

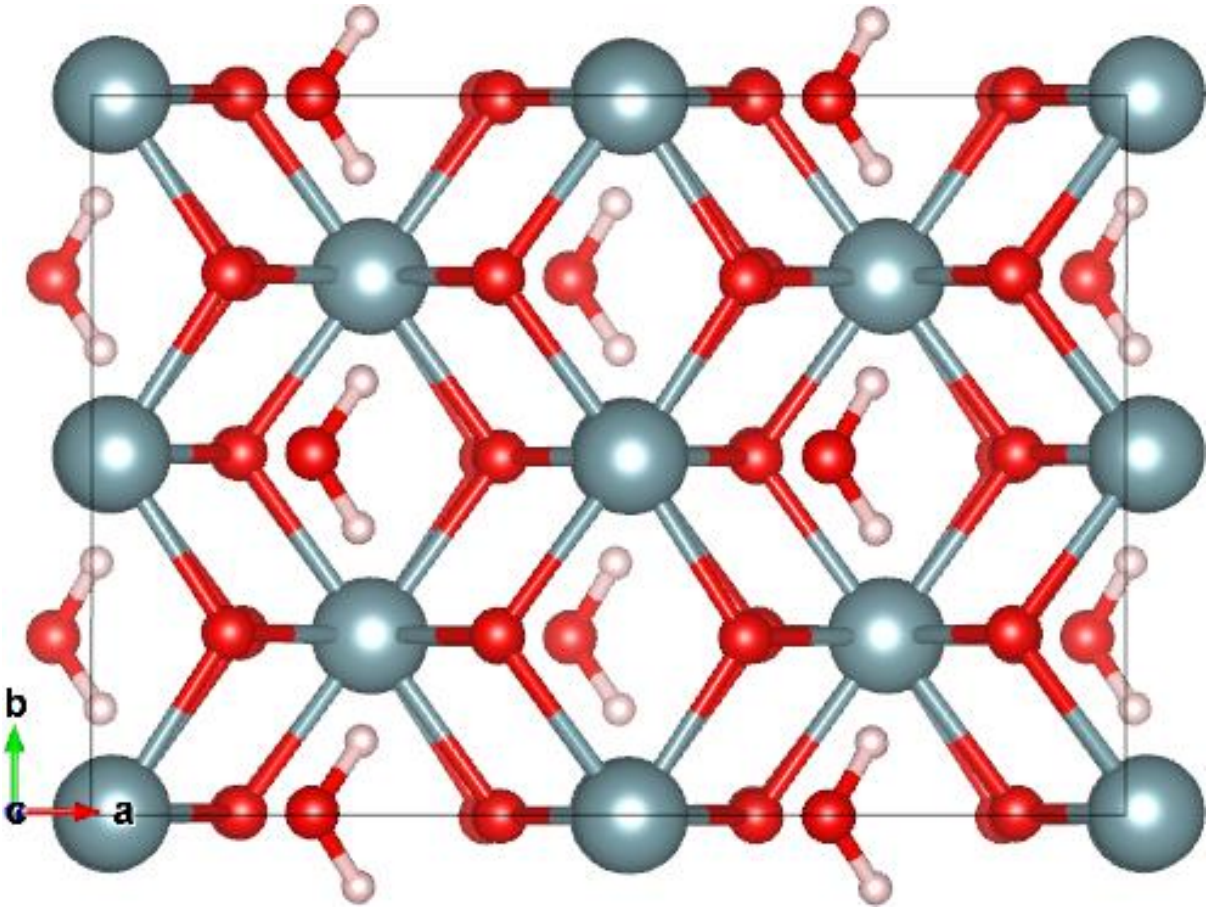

Figure S25: Water adsorbed molecularly on the 2 × 2 UO_2 {110} surface, yielding a coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

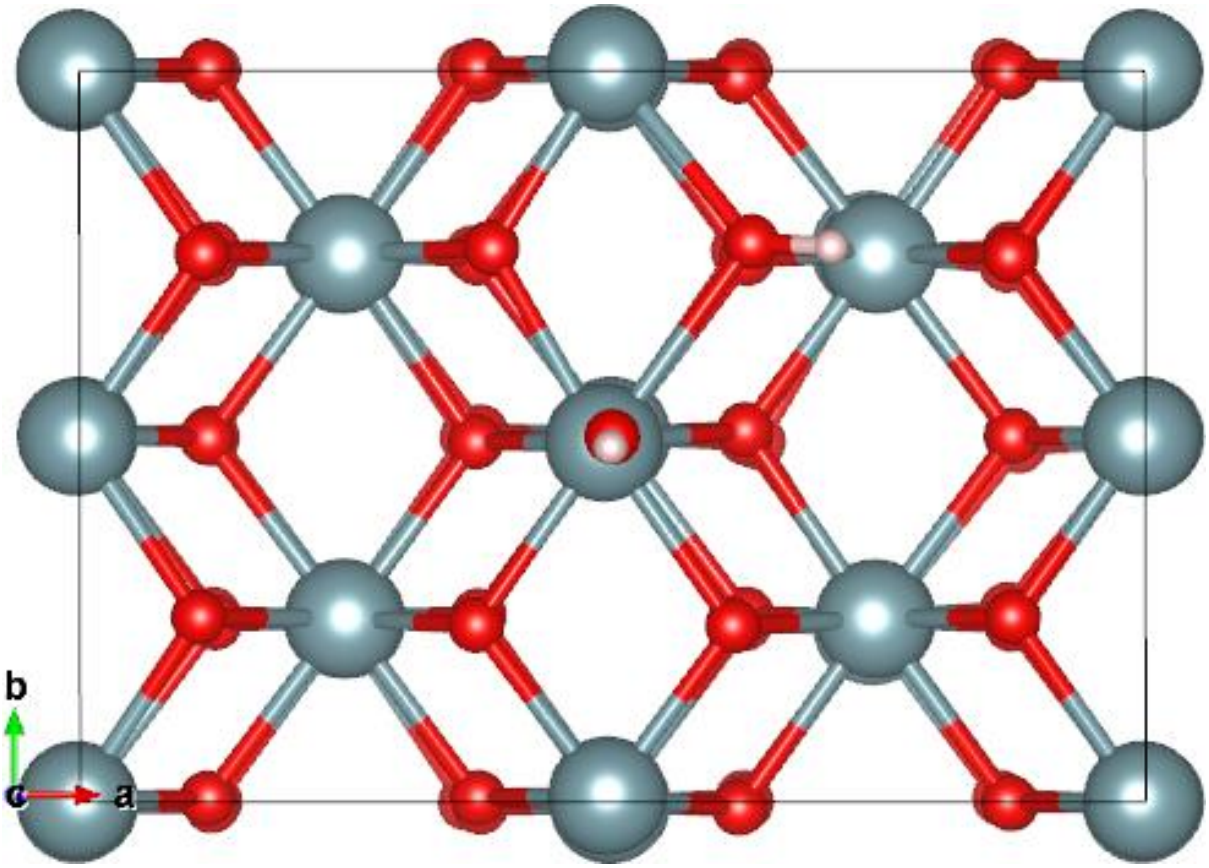

Figure S26: Water adsorbed dissociatively on the 2 × 2 UO_2 {110} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

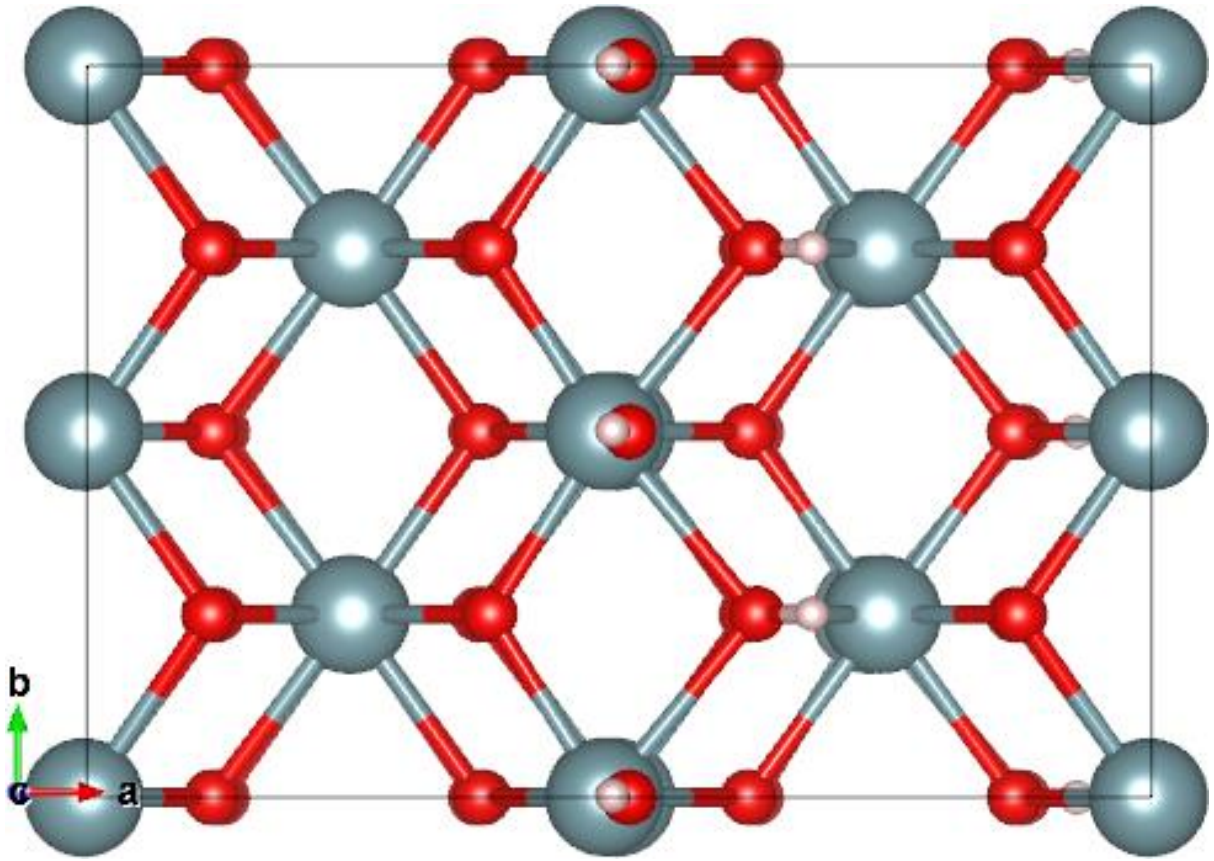

Figure S27: Water adsorbed dissociatively on the 2 × 2 UO_2 {110} surface, yielding a coverage of 50%, i.e. half a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

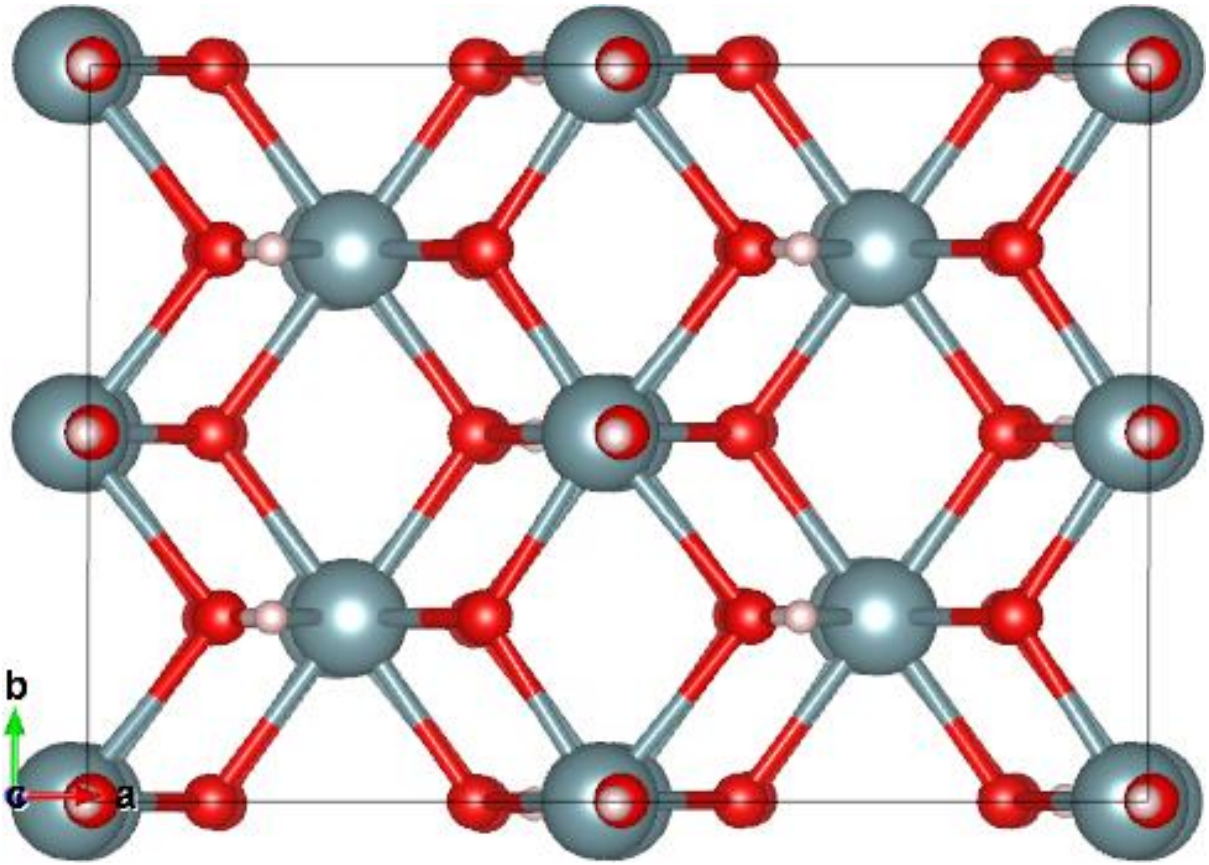

Figure S28: Water adsorbed dissociatively on the 2 × 2 UO_2 {110} surface, yielding a coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

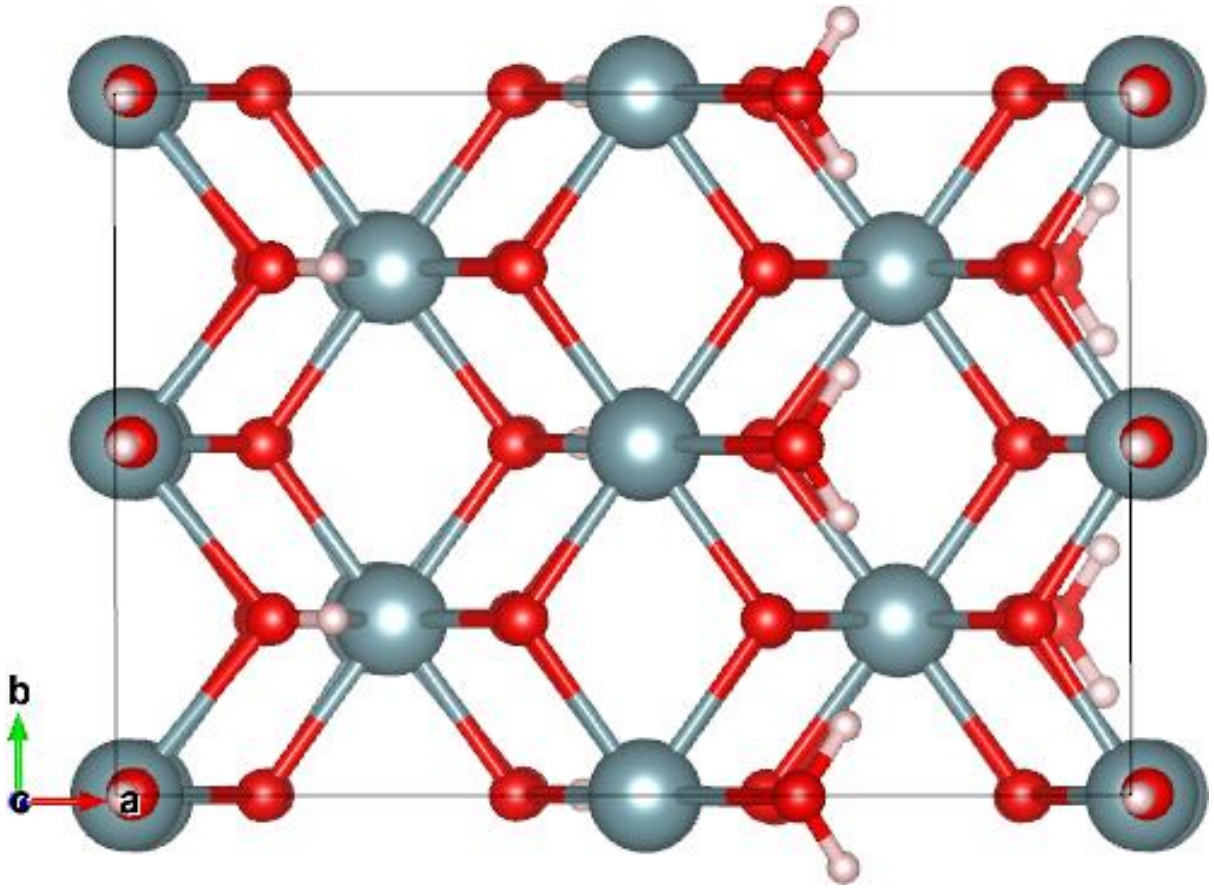

Figure S29: Water adsorbed 50% molecularly and 50% dissociatively on the 2 × 2 UO_2 {110} surface, yielding a total coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

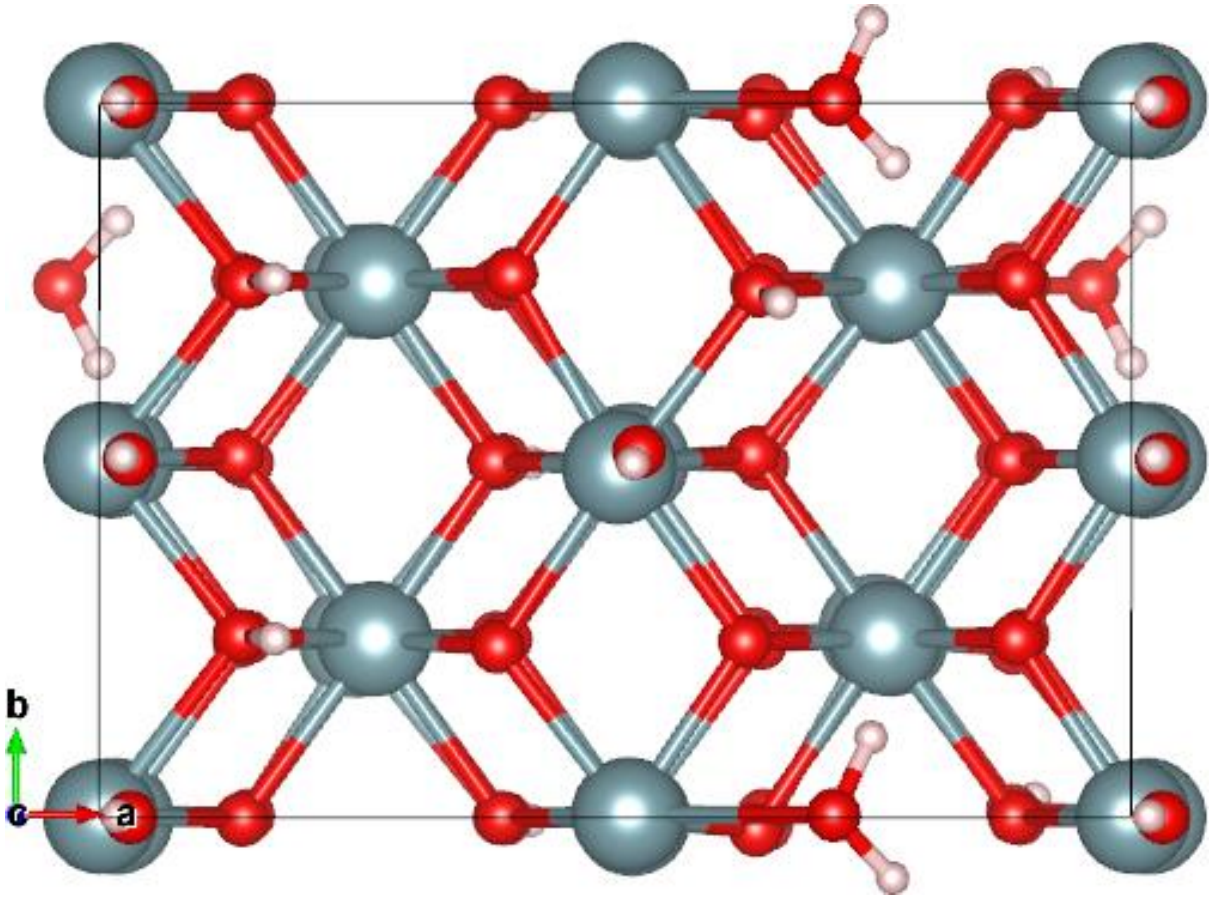

Figure S30: Water adsorbed 25% molecularly and 75% dissociatively on the 2 × 2 UO_2 {110} surface, yielding a total coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

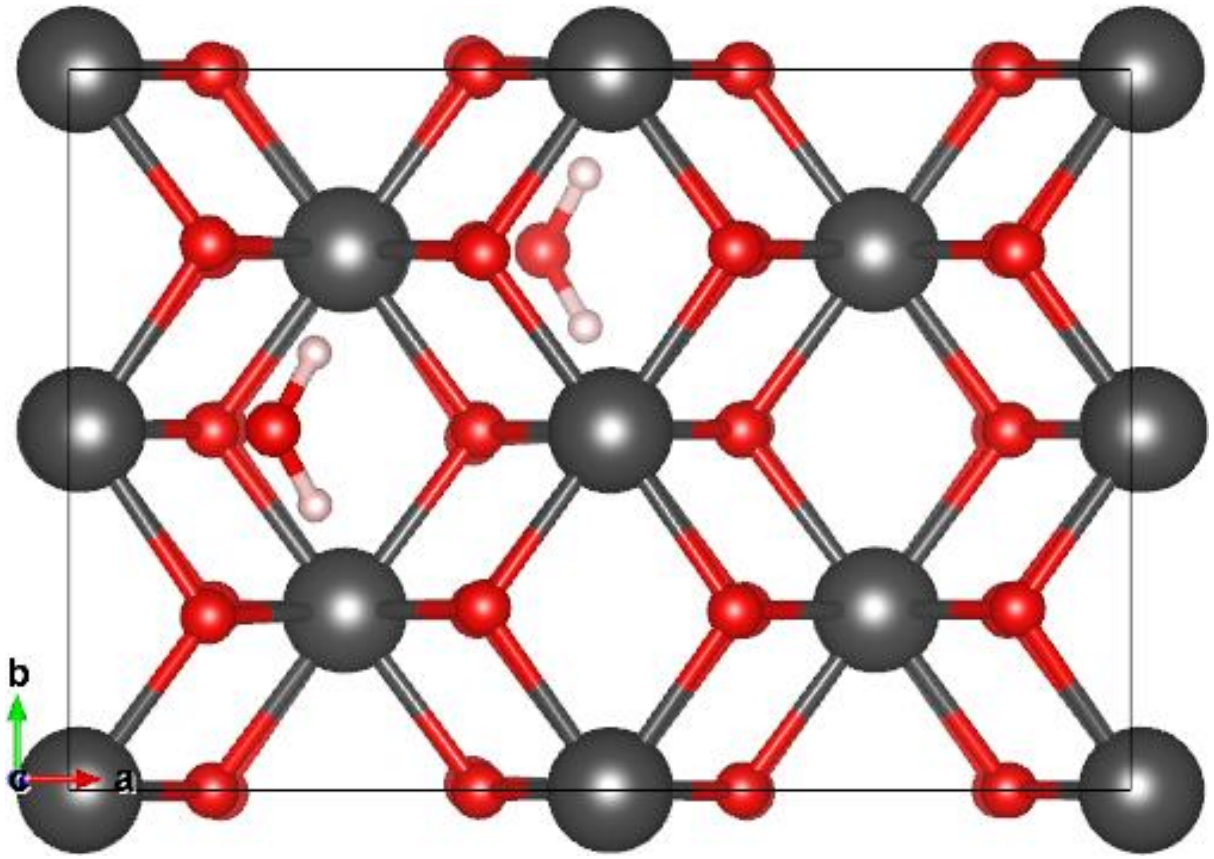

Figure S31: Water adsorbed molecularly on the 2 × 2 PuO_2 {110} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

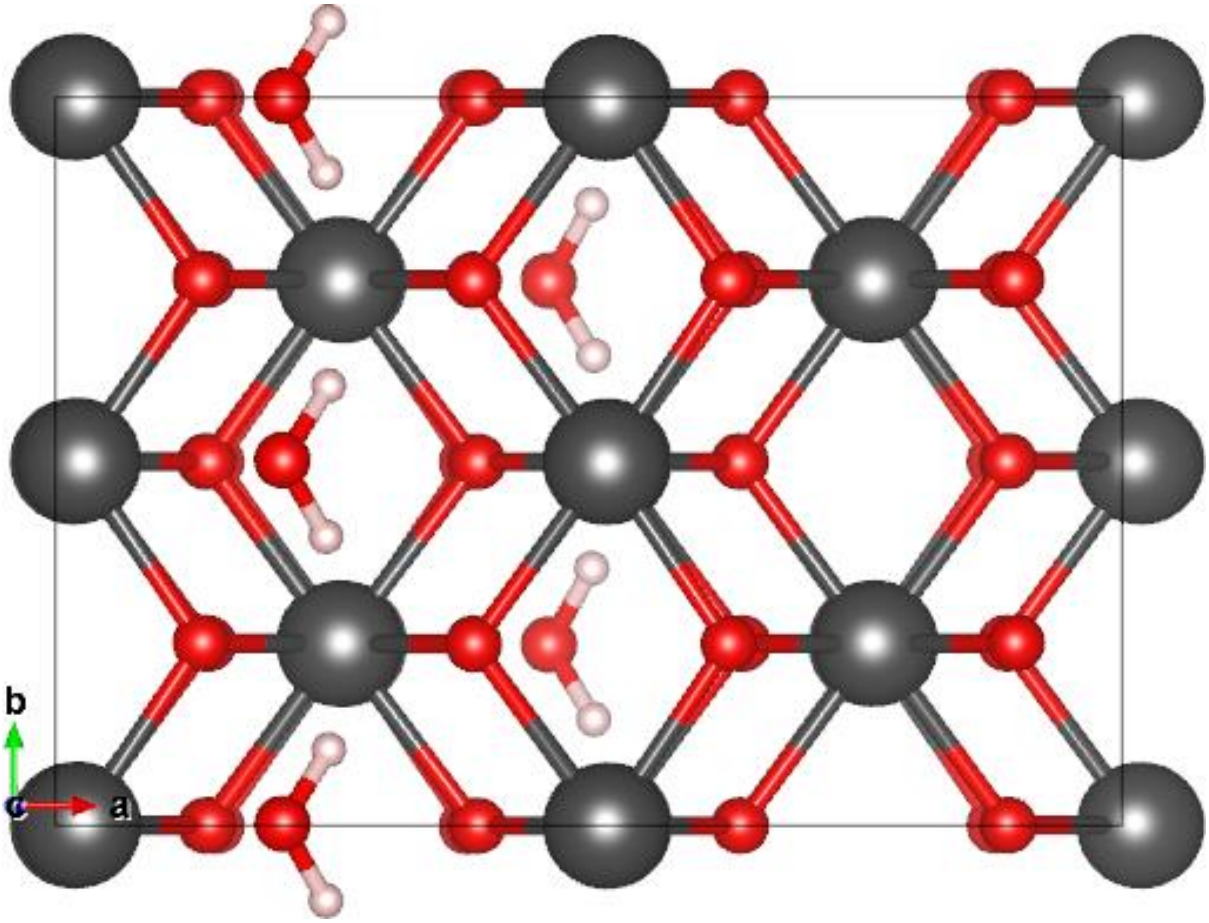

Figure S32: Water adsorbed molecularly on the 2 × 2 PuO_2 {110} surface, yielding a coverage of 50%, i.e. half a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

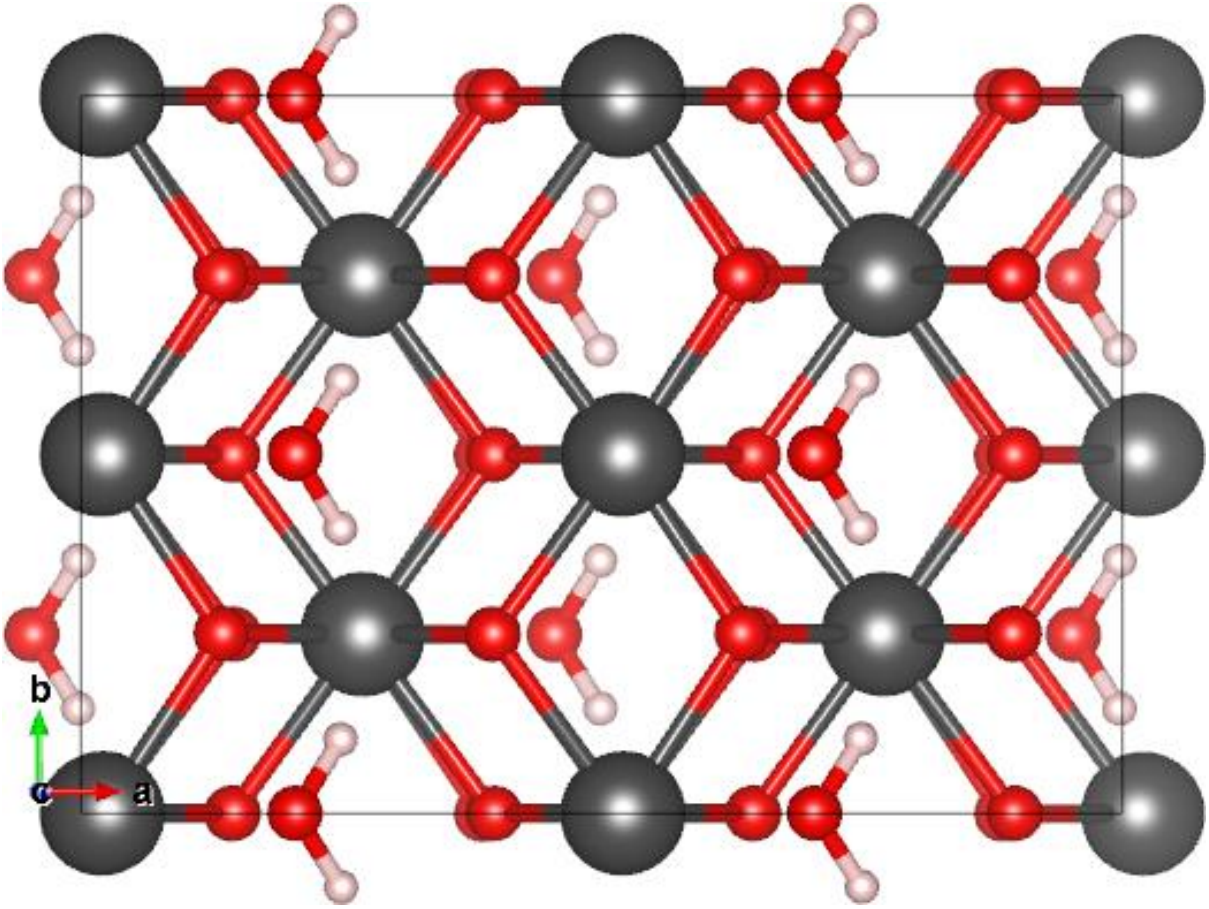

Figure S33: Water adsorbed molecularly on the 2 × 2 PuO_2 {110} surface, yielding a coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

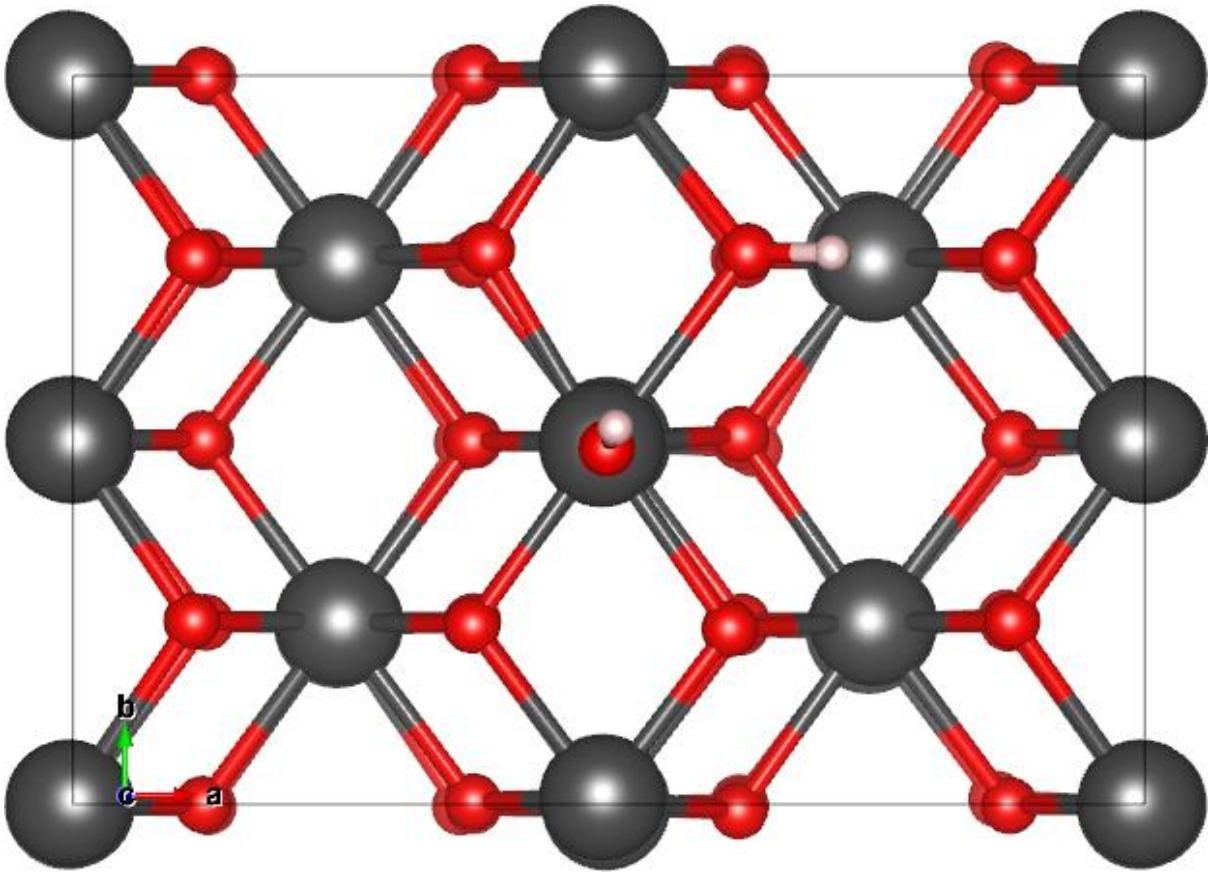

Figure S34: Water adsorbed dissociatively on the 2 × 2 PuO_2 {110} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

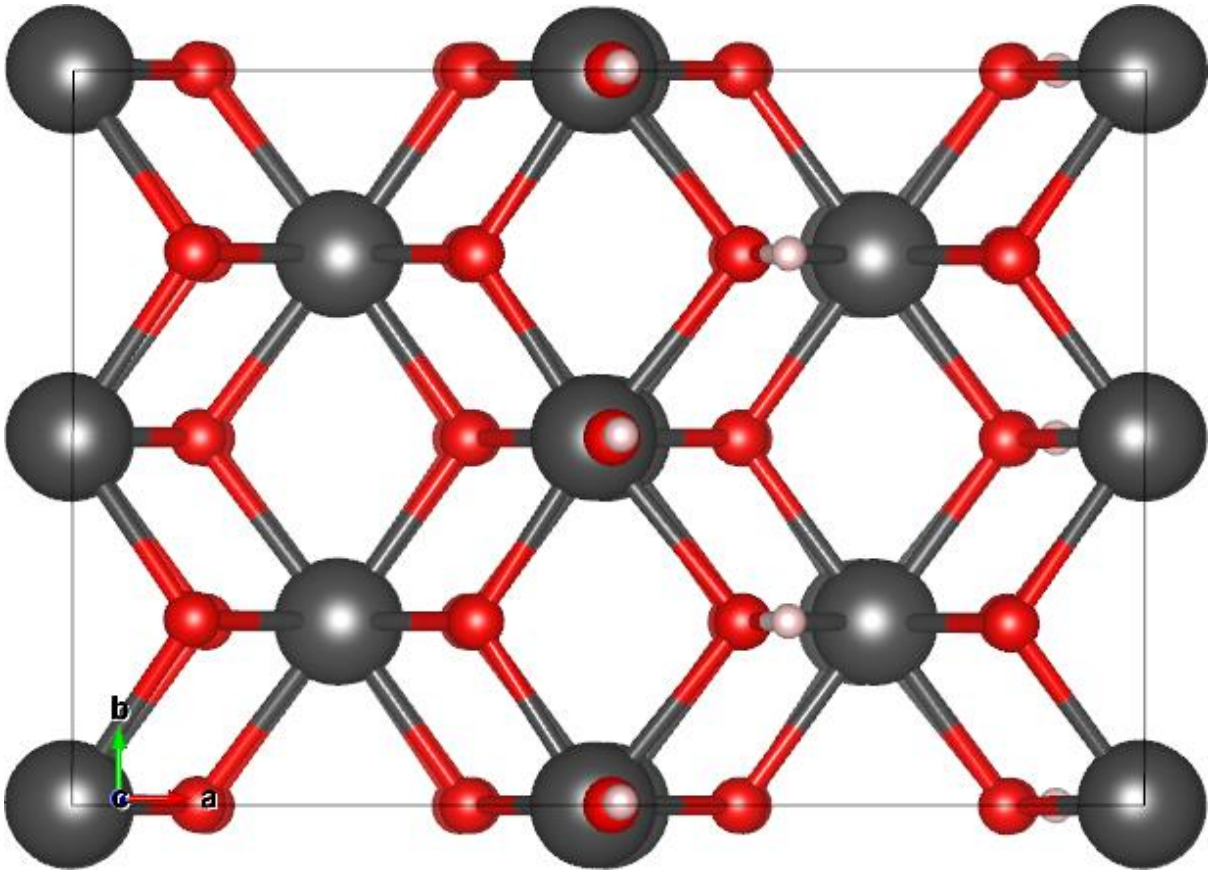

Figure S35: Water adsorbed dissociatively on the 2 × 2 PuO_2 {110} surface, yielding a coverage of 50%, i.e. half a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

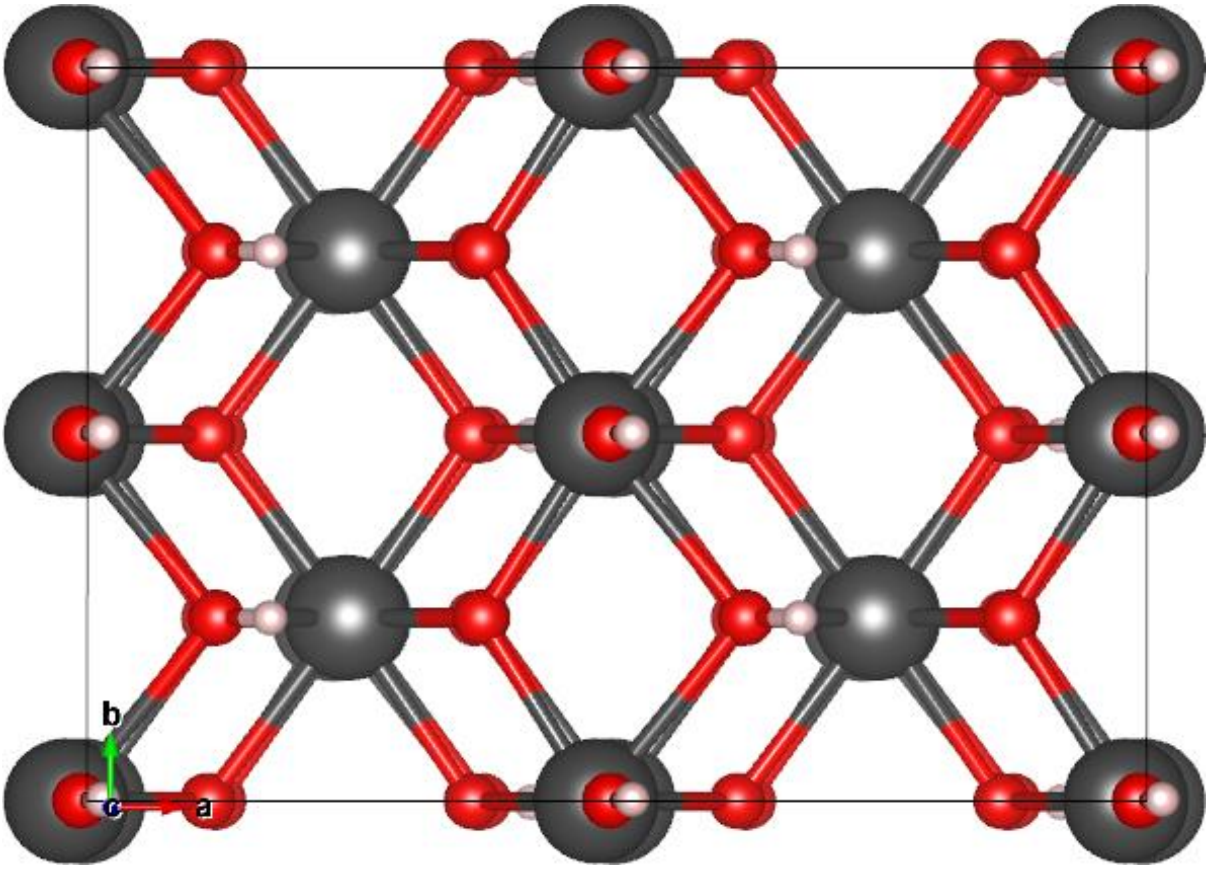

Figure S36: Water adsorbed dissociatively on the 2 × 2 PuO_2 {110} surface, yielding a coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

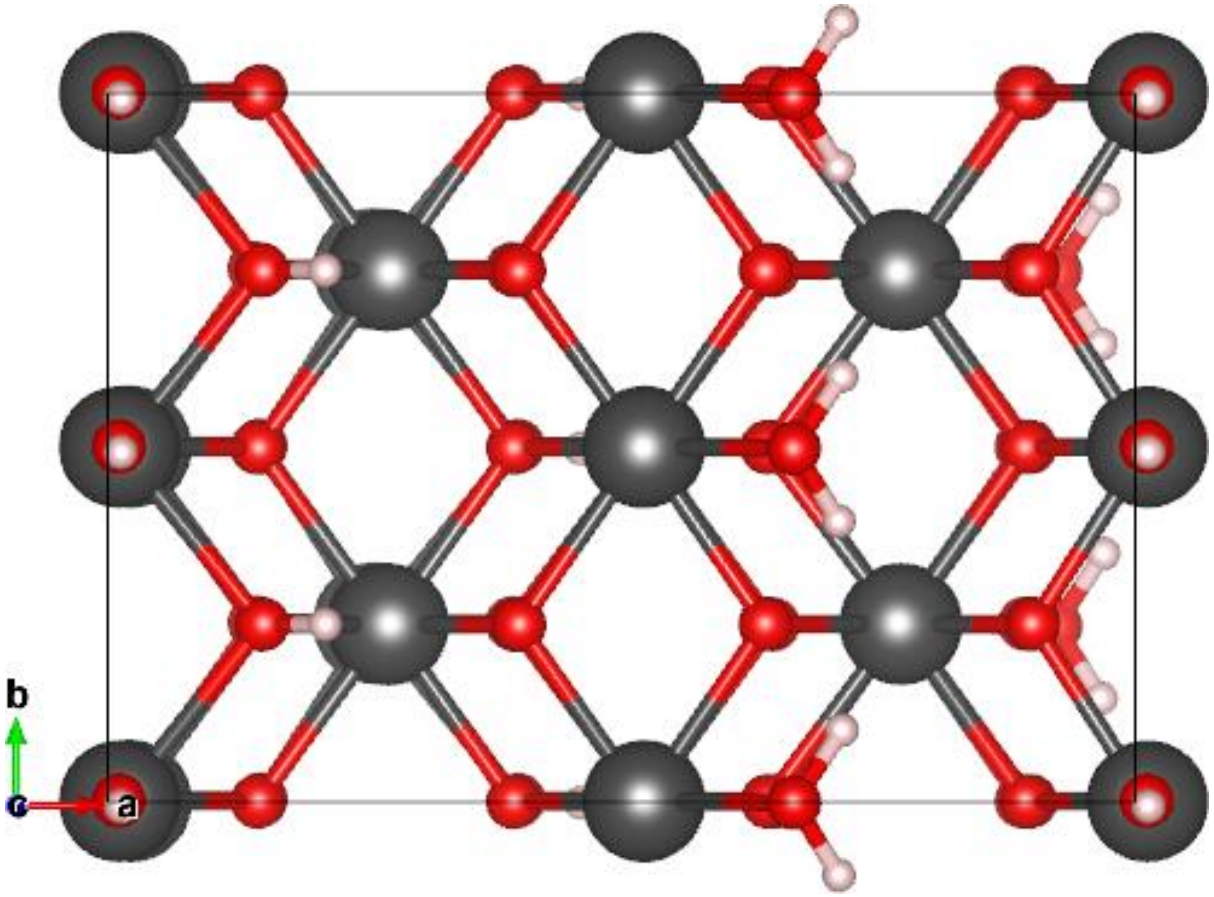

Figure S37: Water adsorbed 50% molecularly and 50% dissociatively on the 2 × 2 PuO_2 {110} surface, yielding a total coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

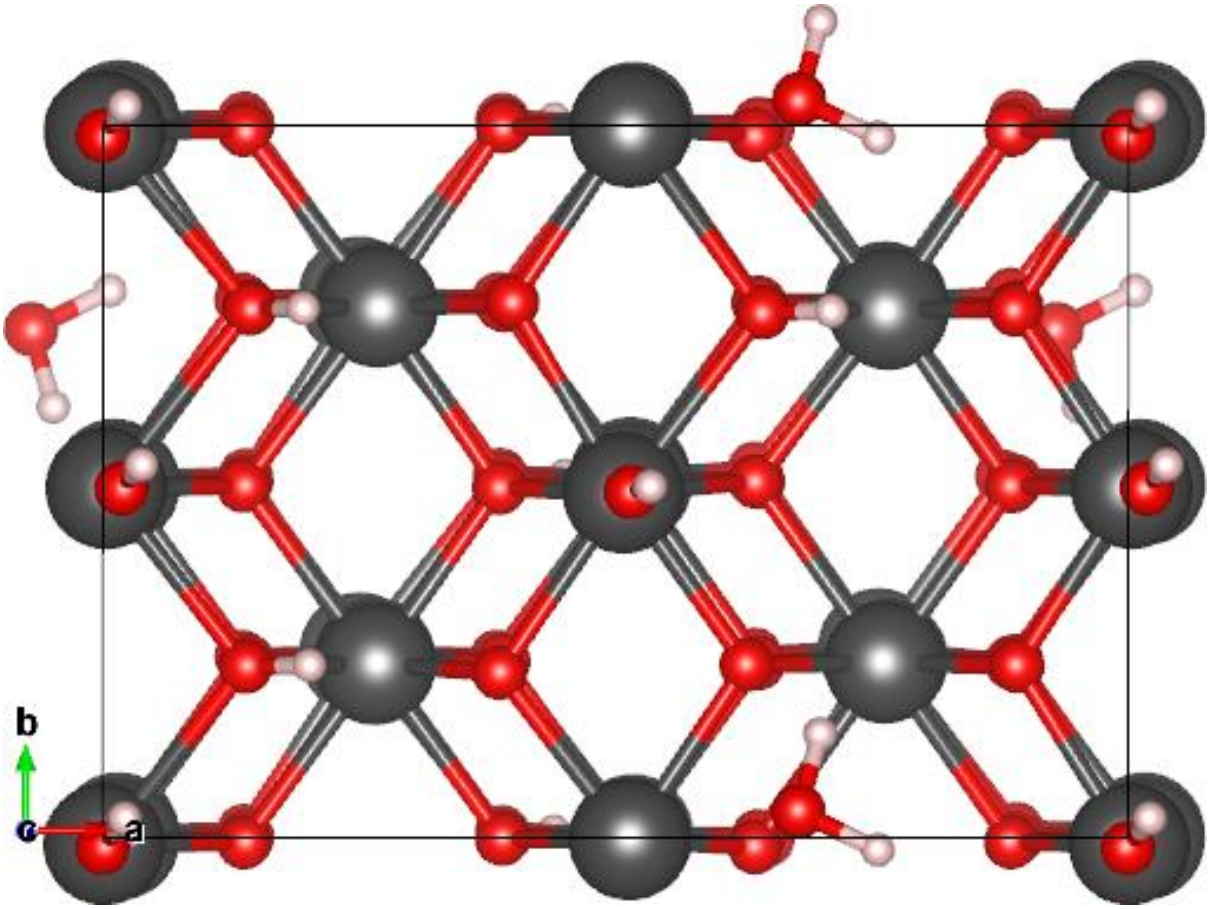

Figure S38: Water adsorbed 25% molecularly and 75% dissociatively on the 2 × 2 PuO_2 {110} surface, yielding a total coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

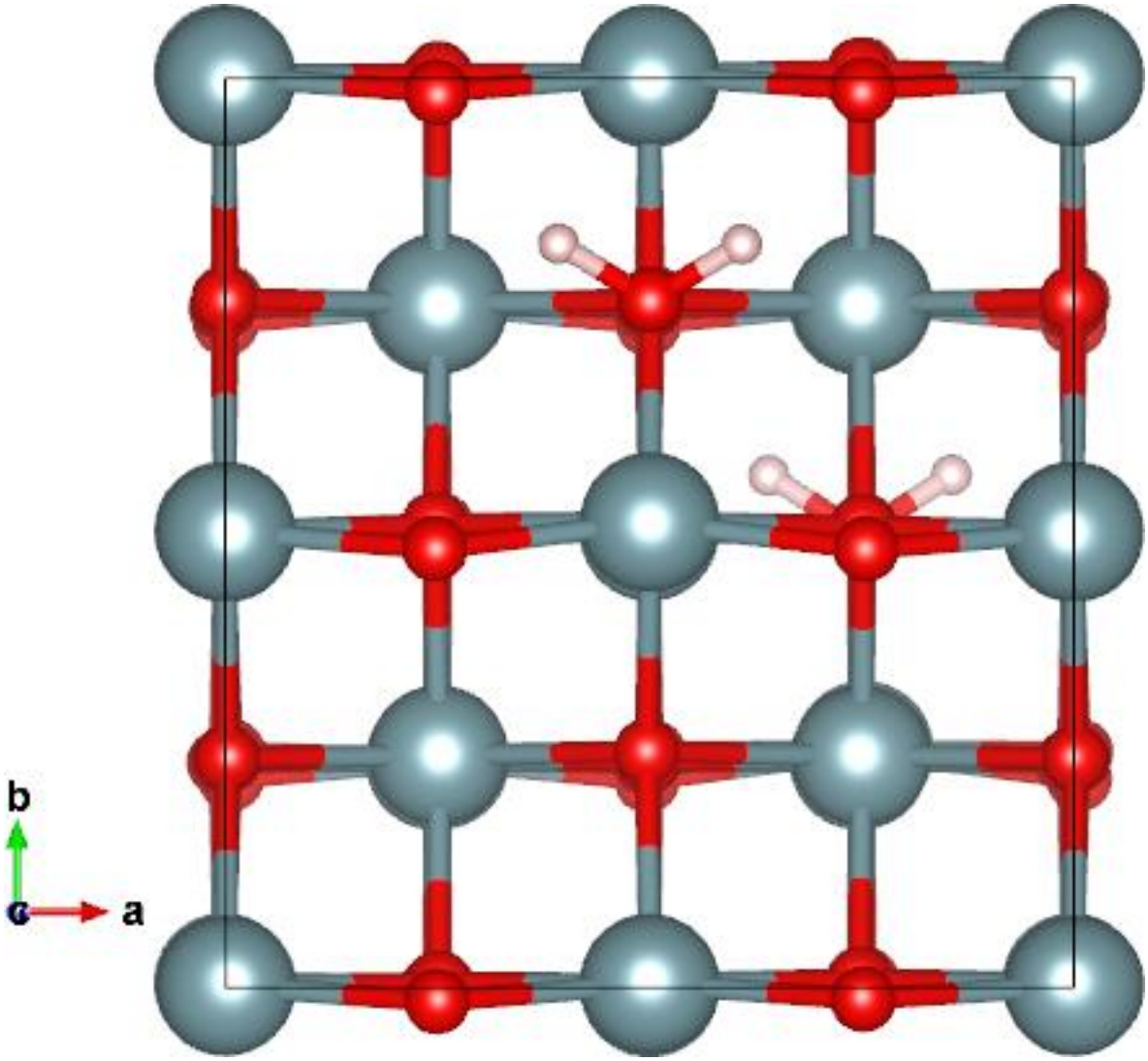

Figure S39: Water adsorbed molecularly on the 2 × 2 UO_2 {100} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

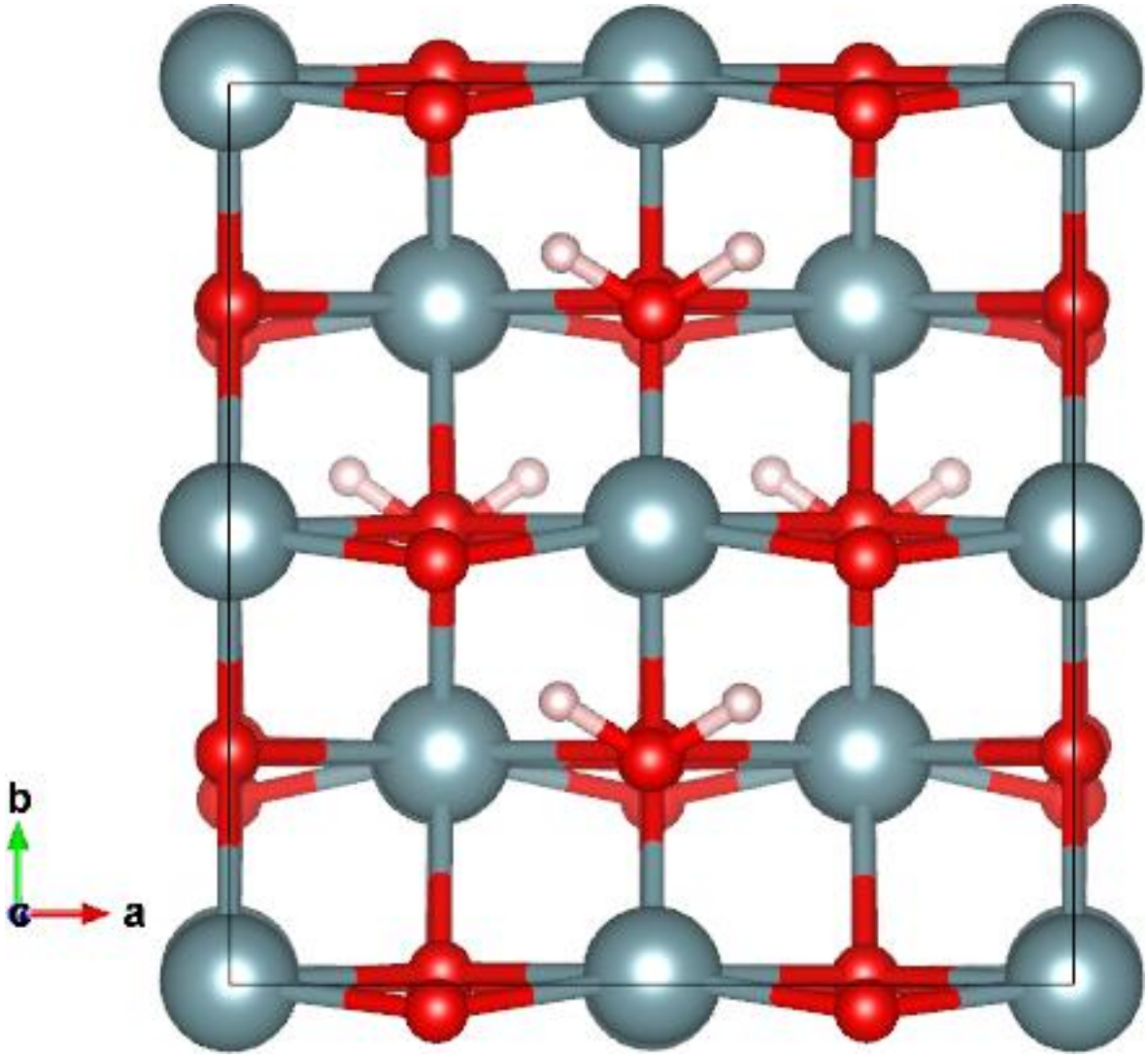

Figure S40: Water adsorbed molecularly on the 2 × 2 UO_2 {100} surface, yielding a coverage of 50%, i.e. half a mono-layer. U atoms in gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

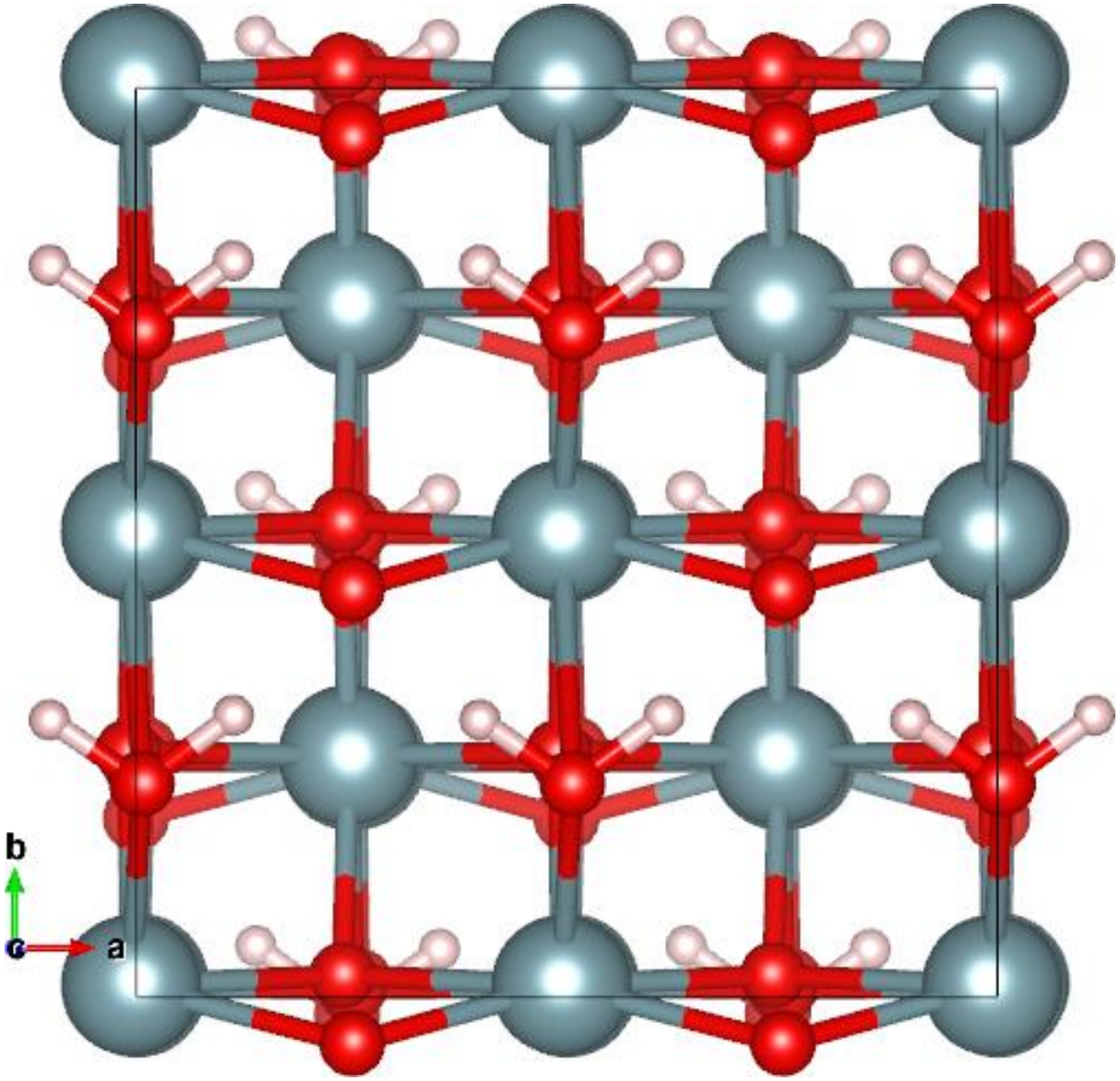

Figure S41: Water adsorbed molecularly on the 2 × 2 UO_2 {100} surface, yielding a coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

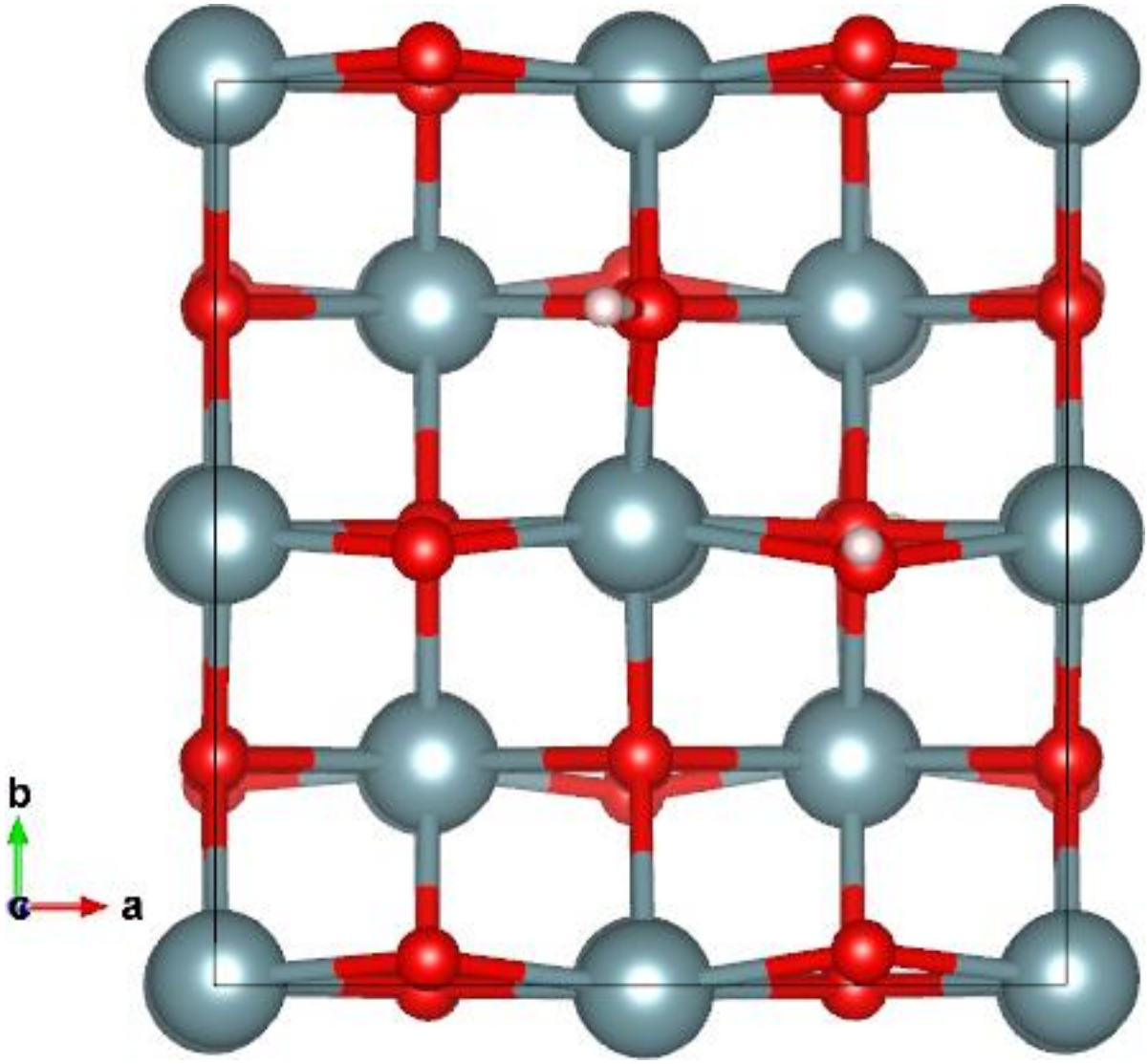

Figure S42: Water adsorbed dissociatively on the 2 × 2 UO_2 {100} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

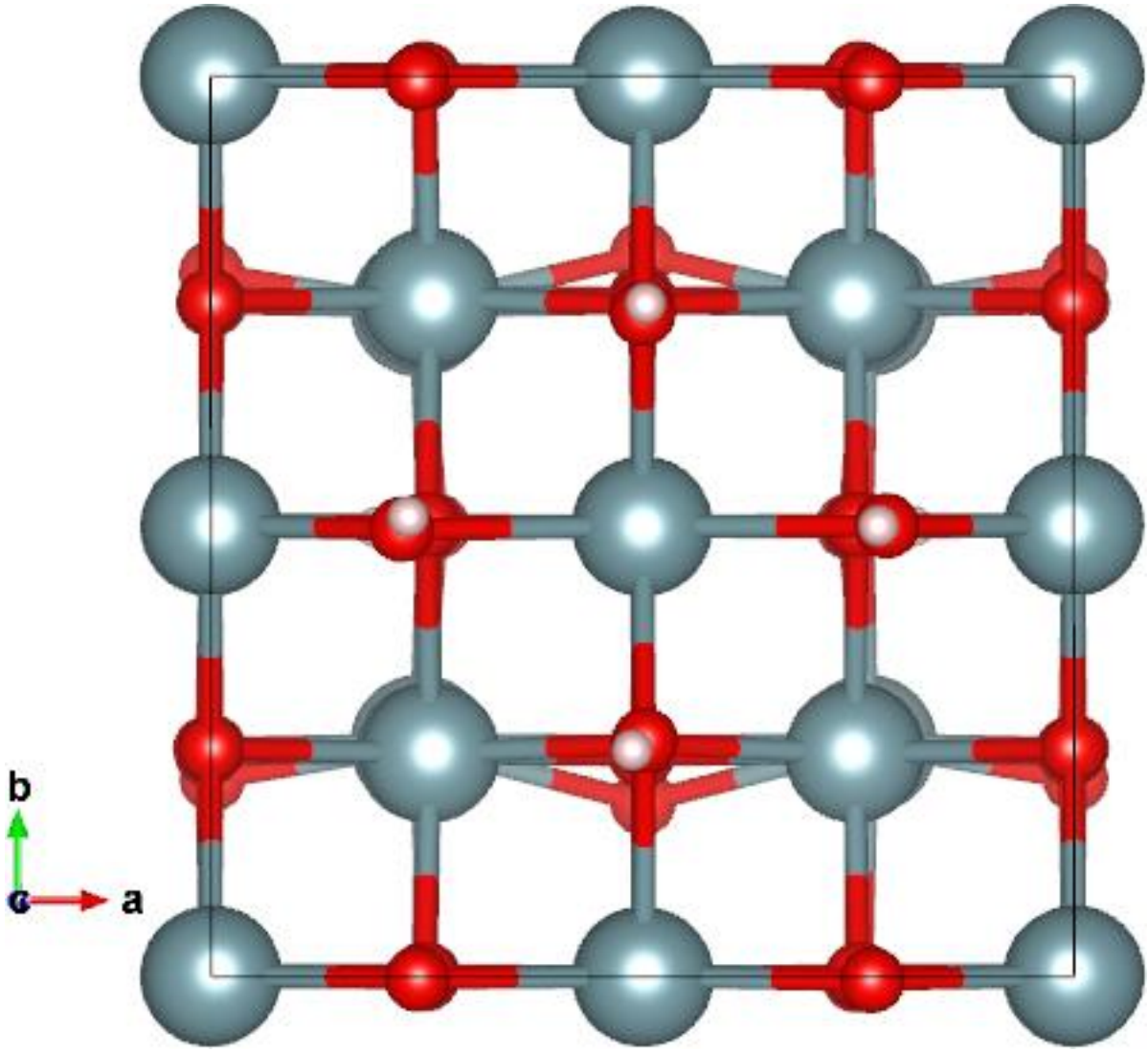

Figure S43: Water adsorbed dissociatively on the 2 × 2 UO_2 {100} surface, yielding a coverage of 50%, i.e. half a mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

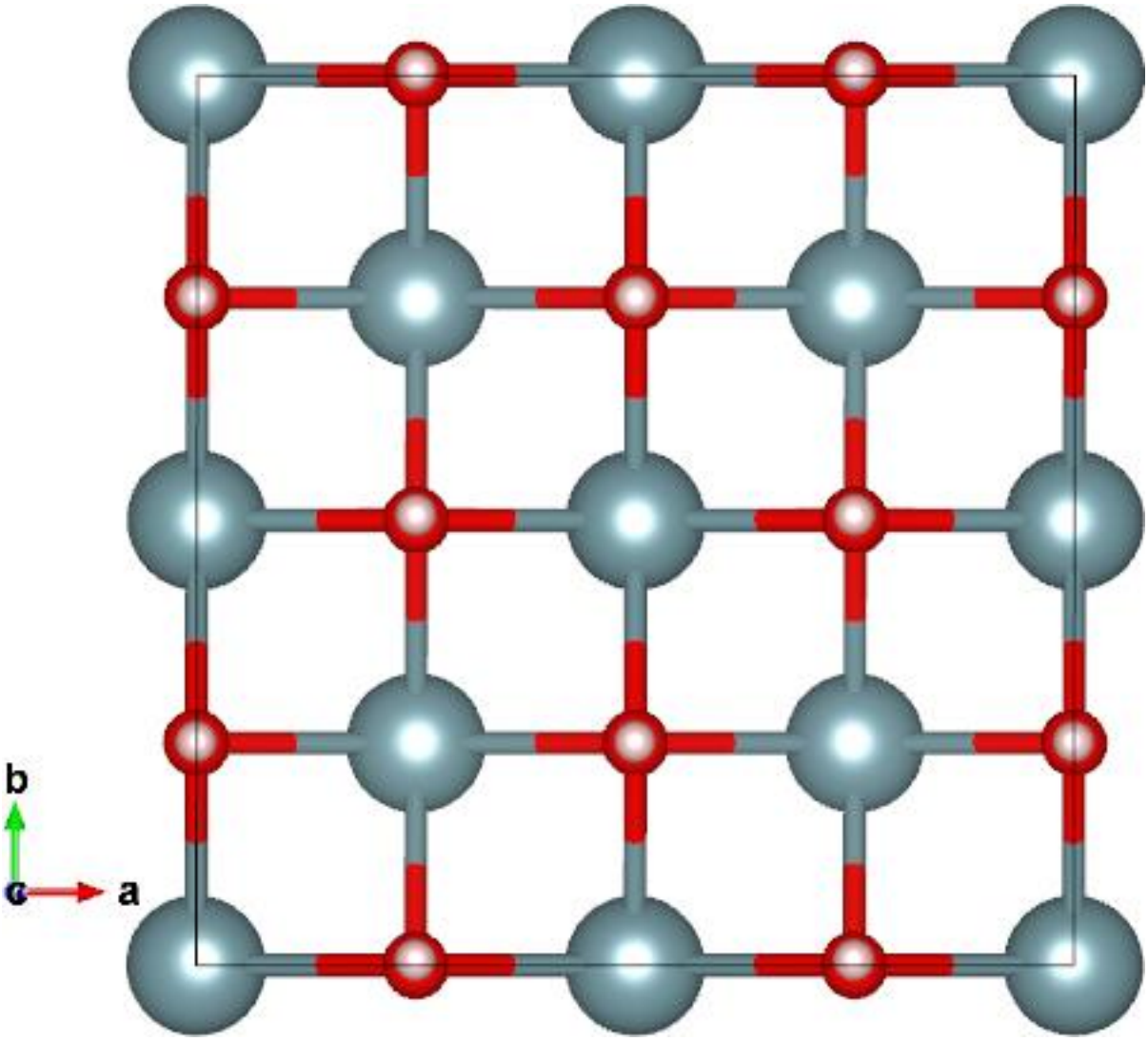

Figure S44: Water adsorbed dissociatively on the 2 × 2 UO_2 {100} surface, yielding a coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

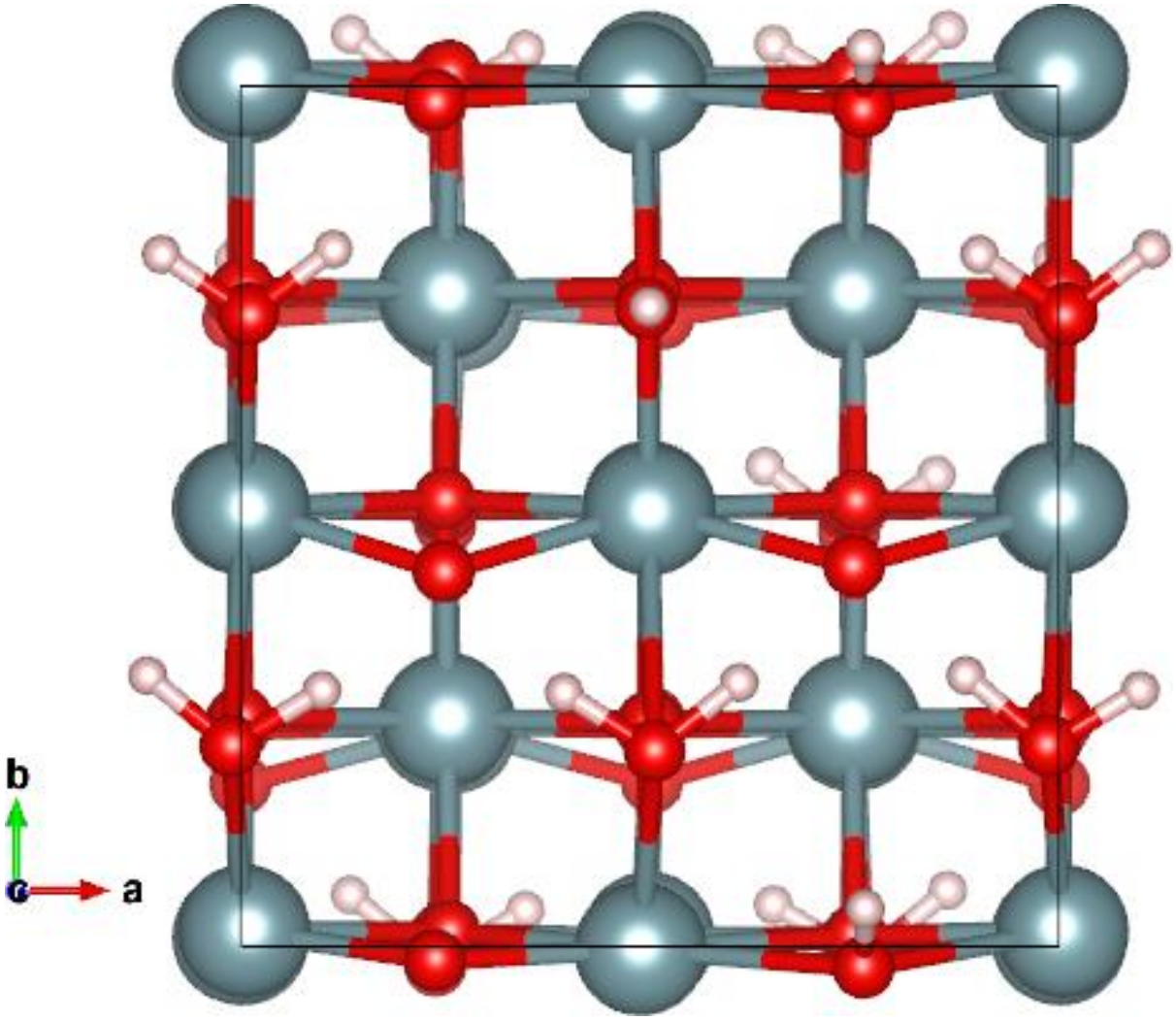

Figure S45: Water adsorbed 75% molecularly and 25% dissociatively on the 2 × 2 UO_2 {100} surface, yielding a total coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

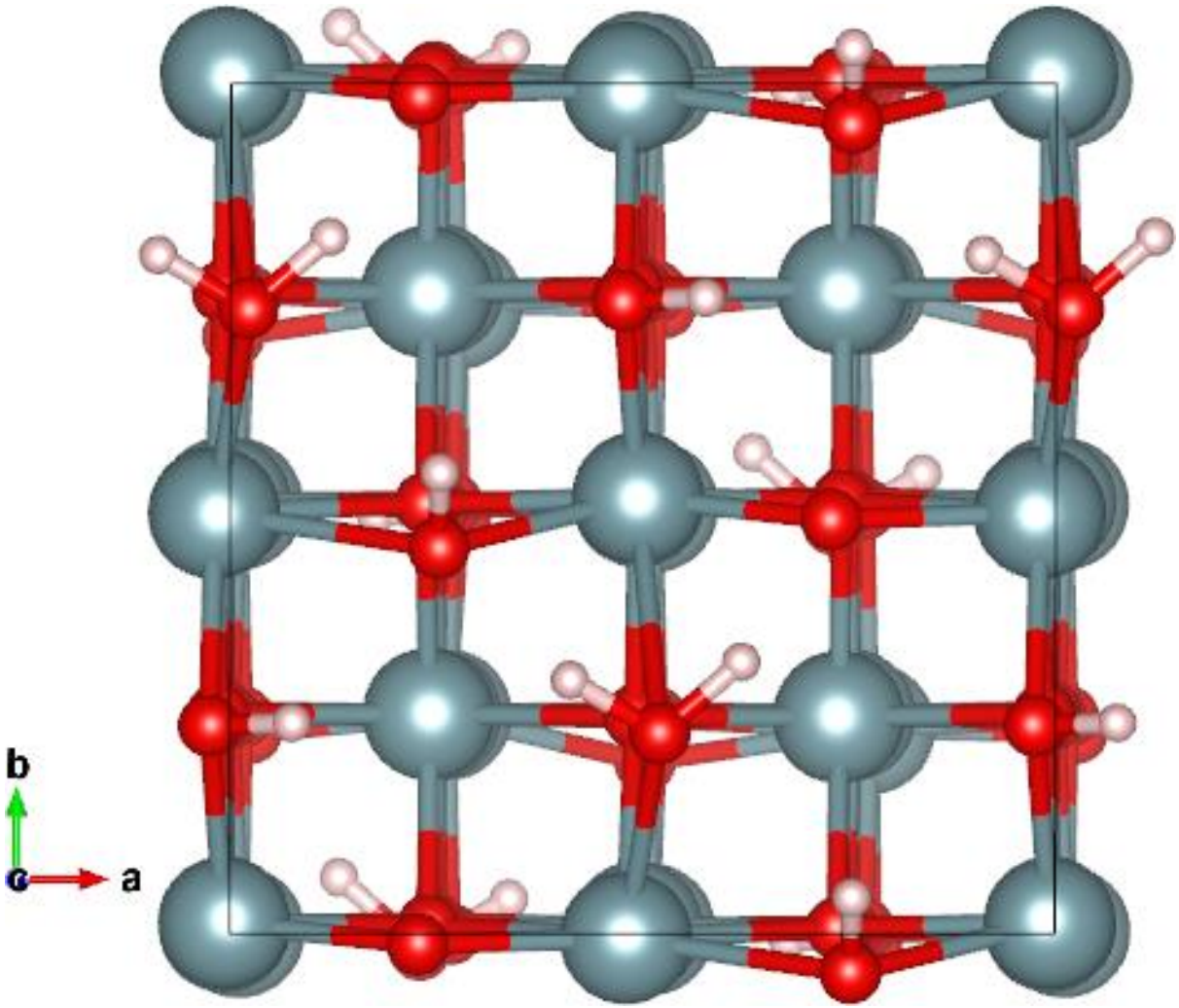

Figure S46: Water adsorbed 50% molecularly and 50% dissociatively on the 2 × 2 UO_2 {100} surface, yielding a total coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

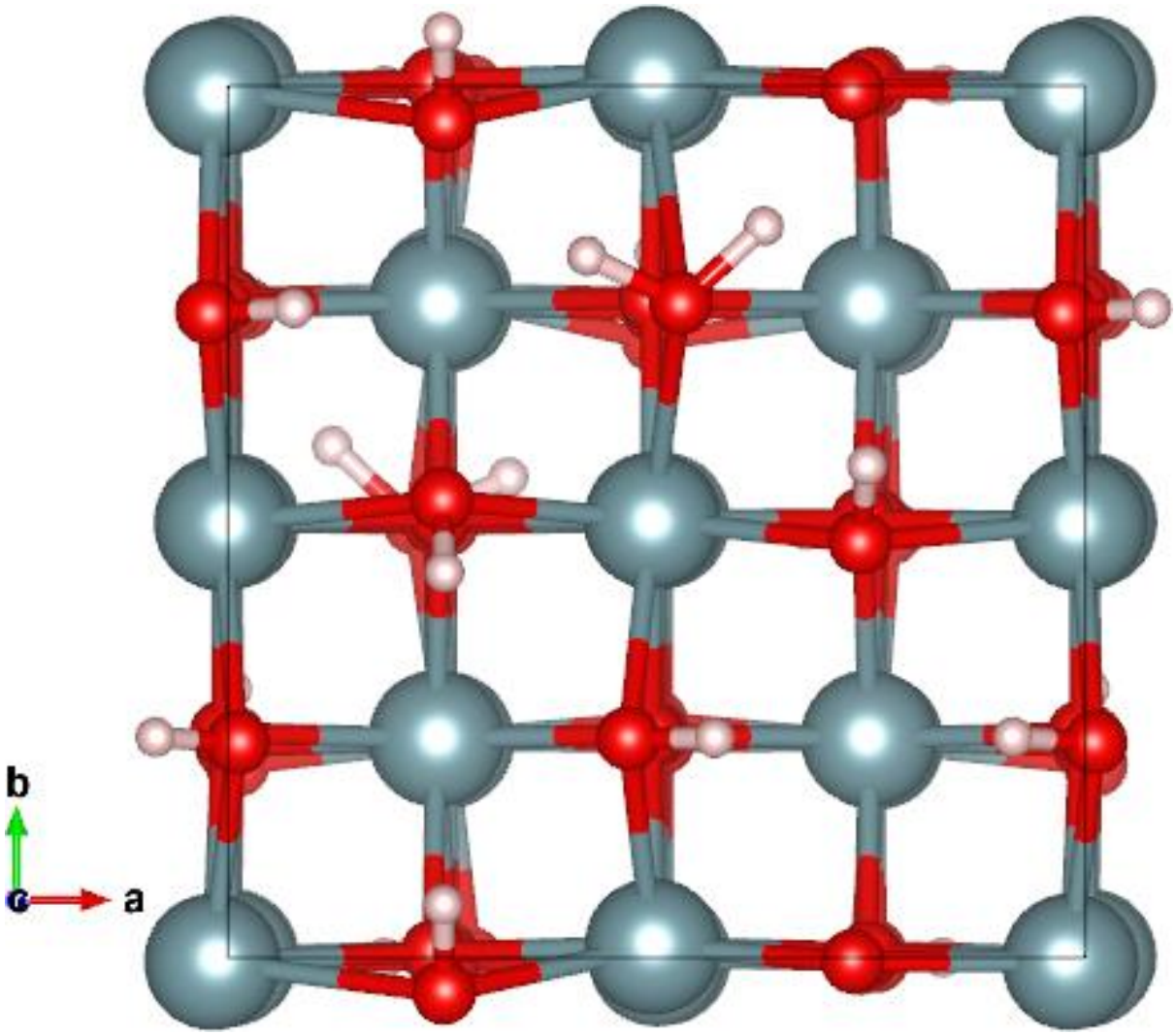

Figure S47*:* Water adsorbed 25% molecularly and 75% dissociatively on the 2 × 2 UO_2 {100} surface, yielding a total coverage of 100%, i.e. one mono-layer. U atoms in gray, oxygen in red and hydrogen in white.

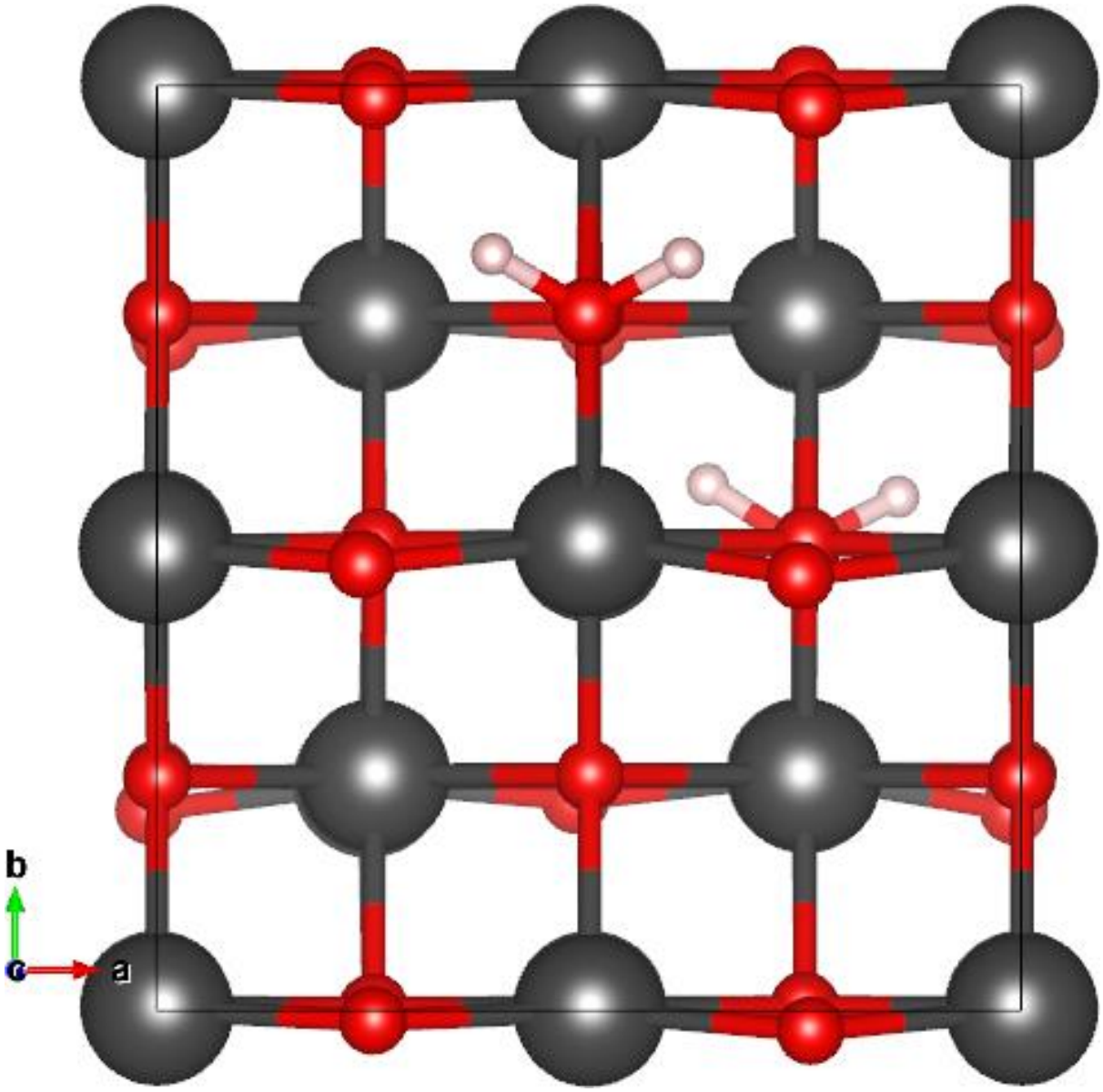

Figure S48: Water adsorbed molecularly on the 2 × 2 PuO_2 {100} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

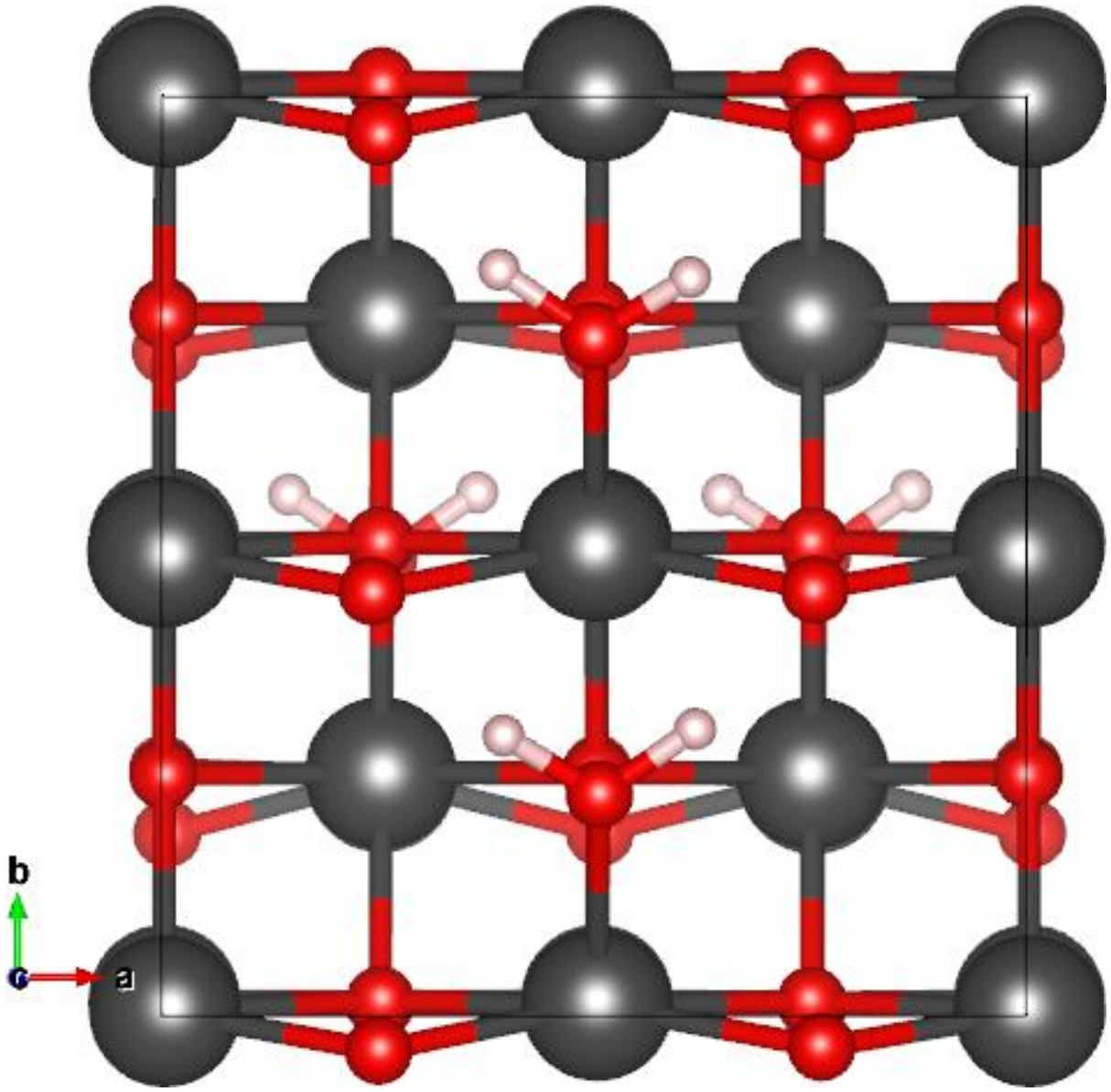

Figure S49: Water adsorbed molecularly on the 2 × 2 PuO_2 {100} surface, yielding a coverage of 50%, i.e. half a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

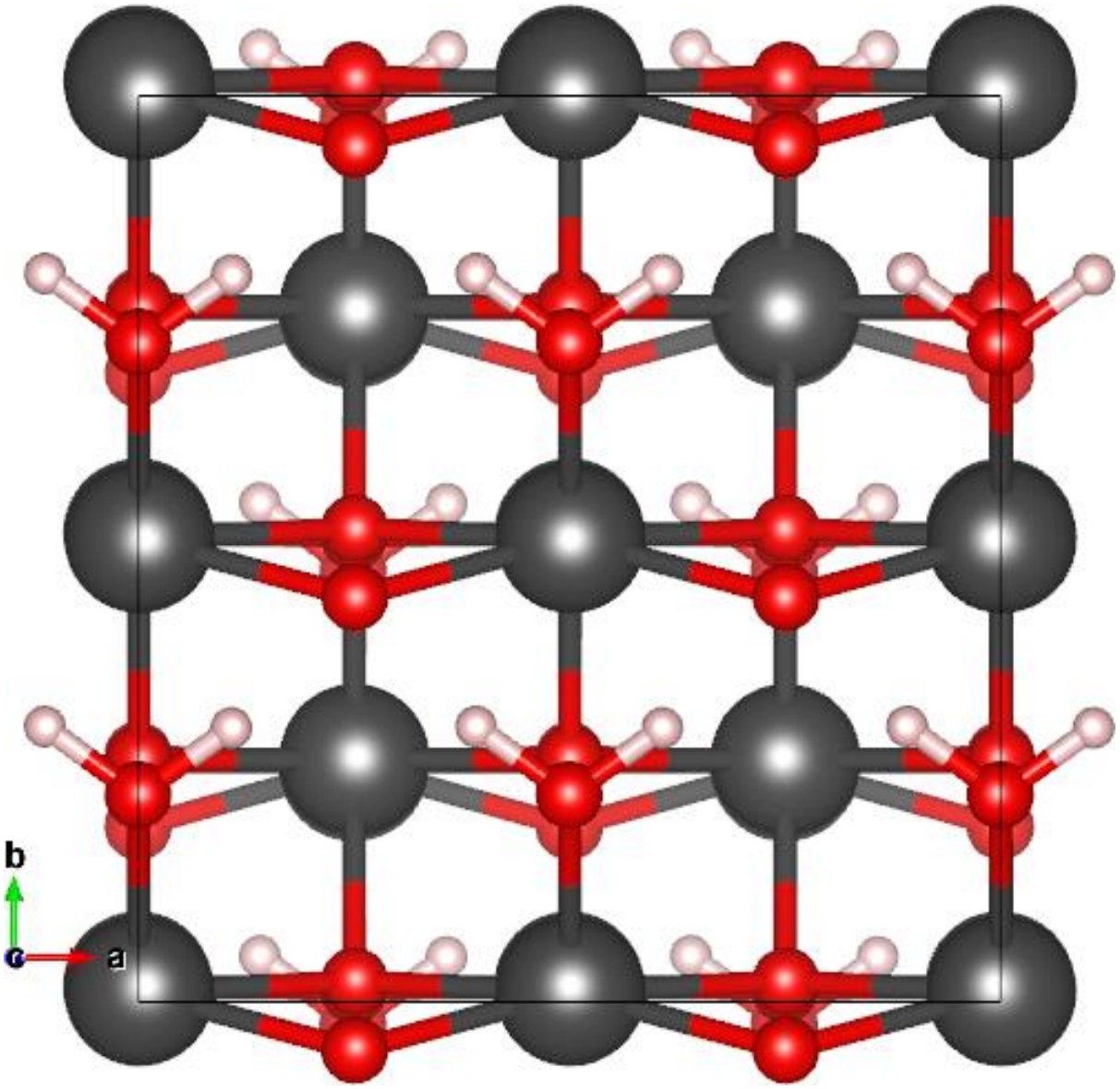

Figure S50: Water adsorbed molecularly on the 2 × 2 PuO_2 {100} surface, yielding a coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white. Adsorption occurs on both sides of the slab and, as the two surfaces have equivalent sites that are offset, we can see both the top and the bottom water molecules.

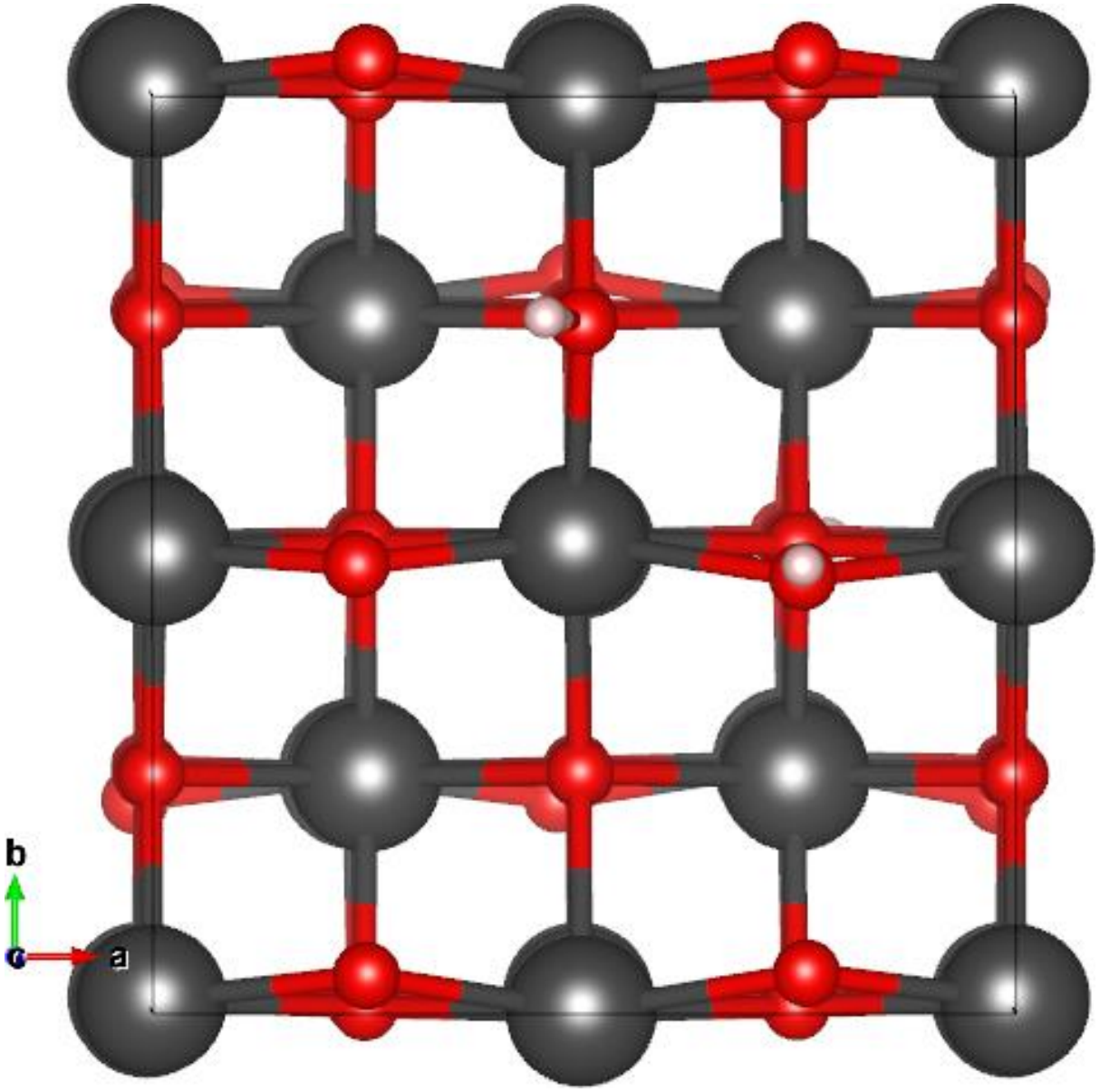

Figure S51: Water adsorbed dissociatively on the 2 × 2 PuO_2 {100} surface, yielding a coverage of 25%, i.e. ¼ of a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

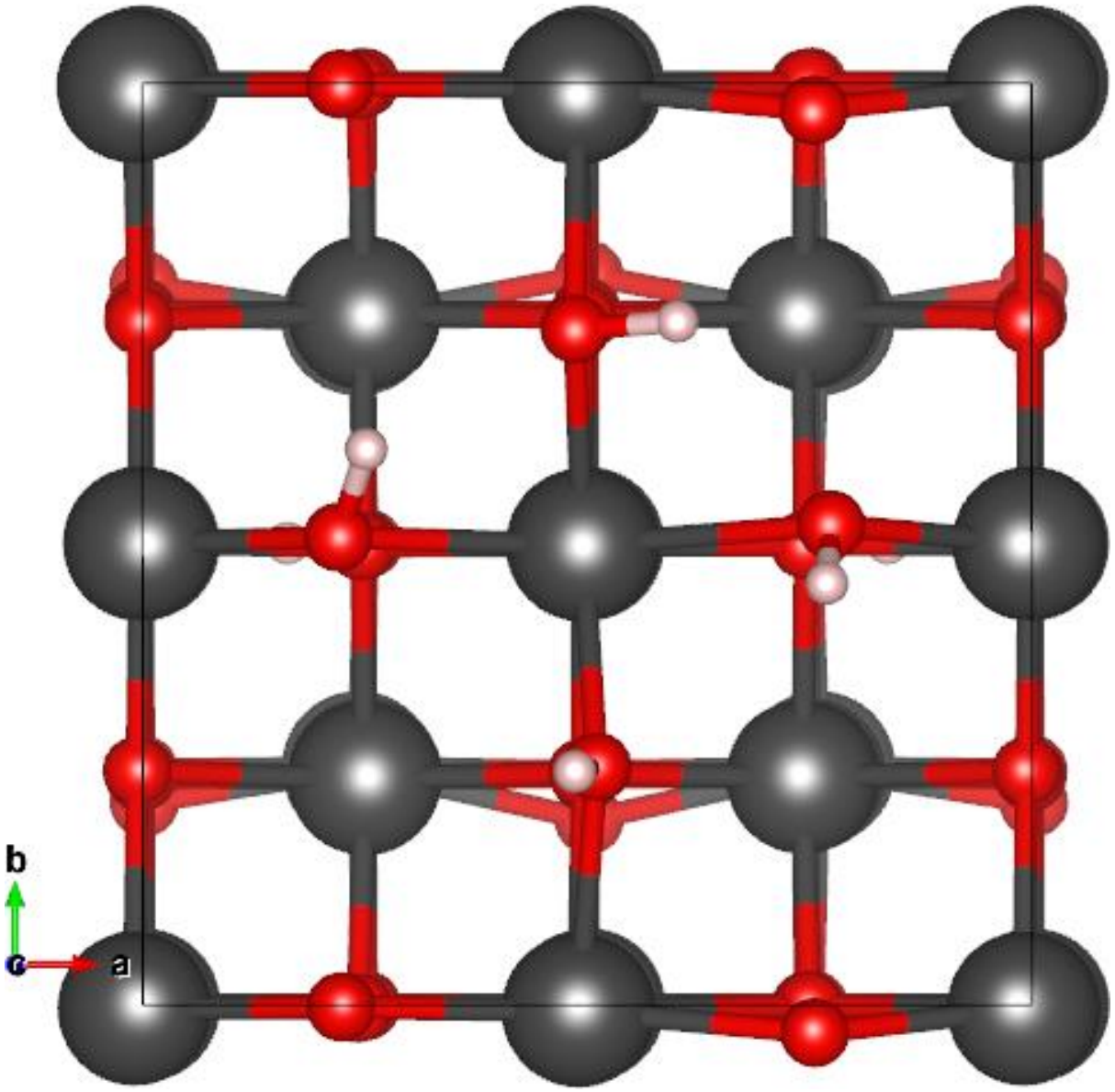

Figure S52: Water adsorbed dissociatively on the 2 × 2 PuO_2 {100} surface, yielding a coverage of 50%, i.e. half a mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

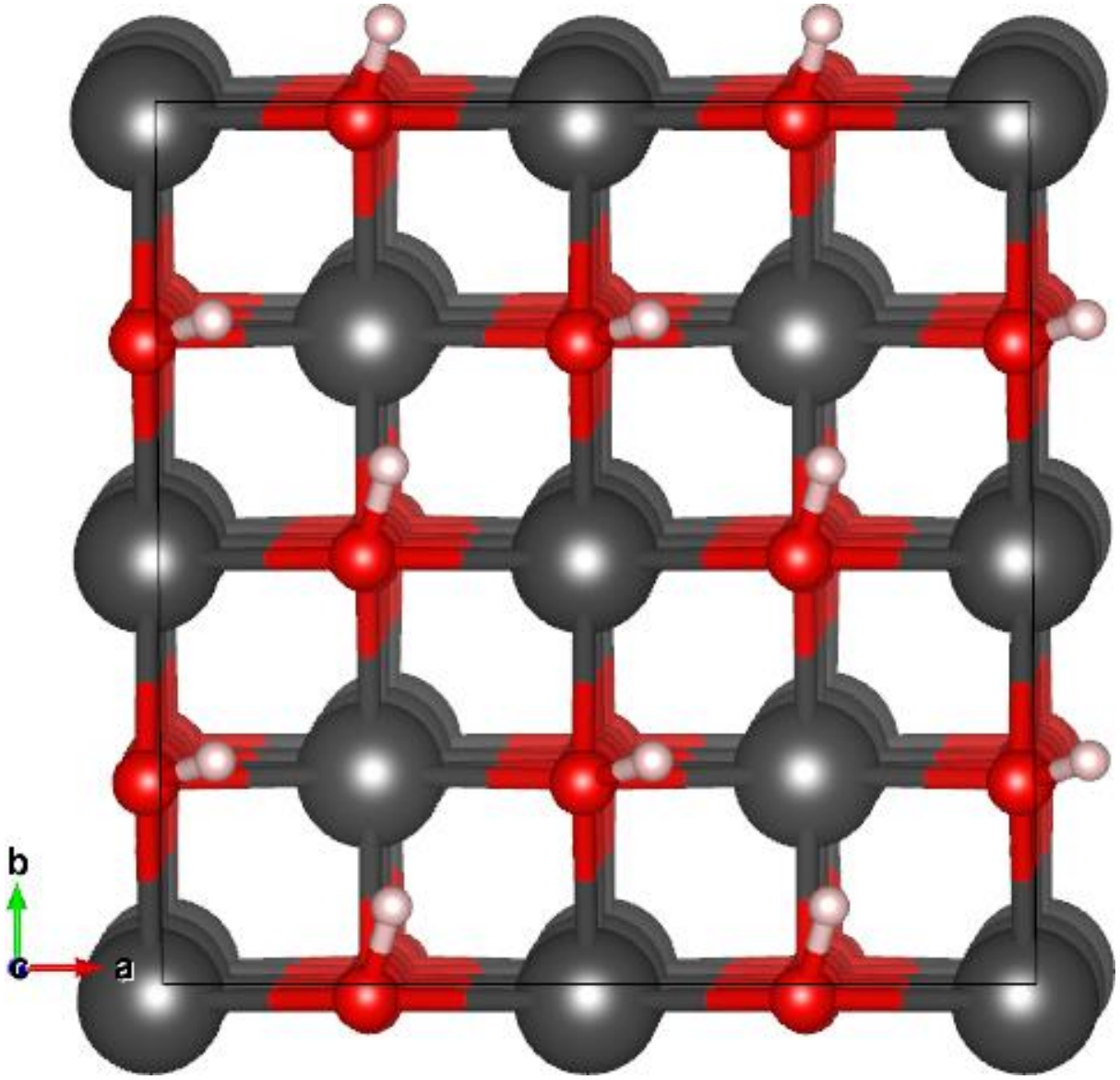

Figure S53: Water adsorbed dissociatively on the 2 × 2 PuO_2 {100} surface, yielding a coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

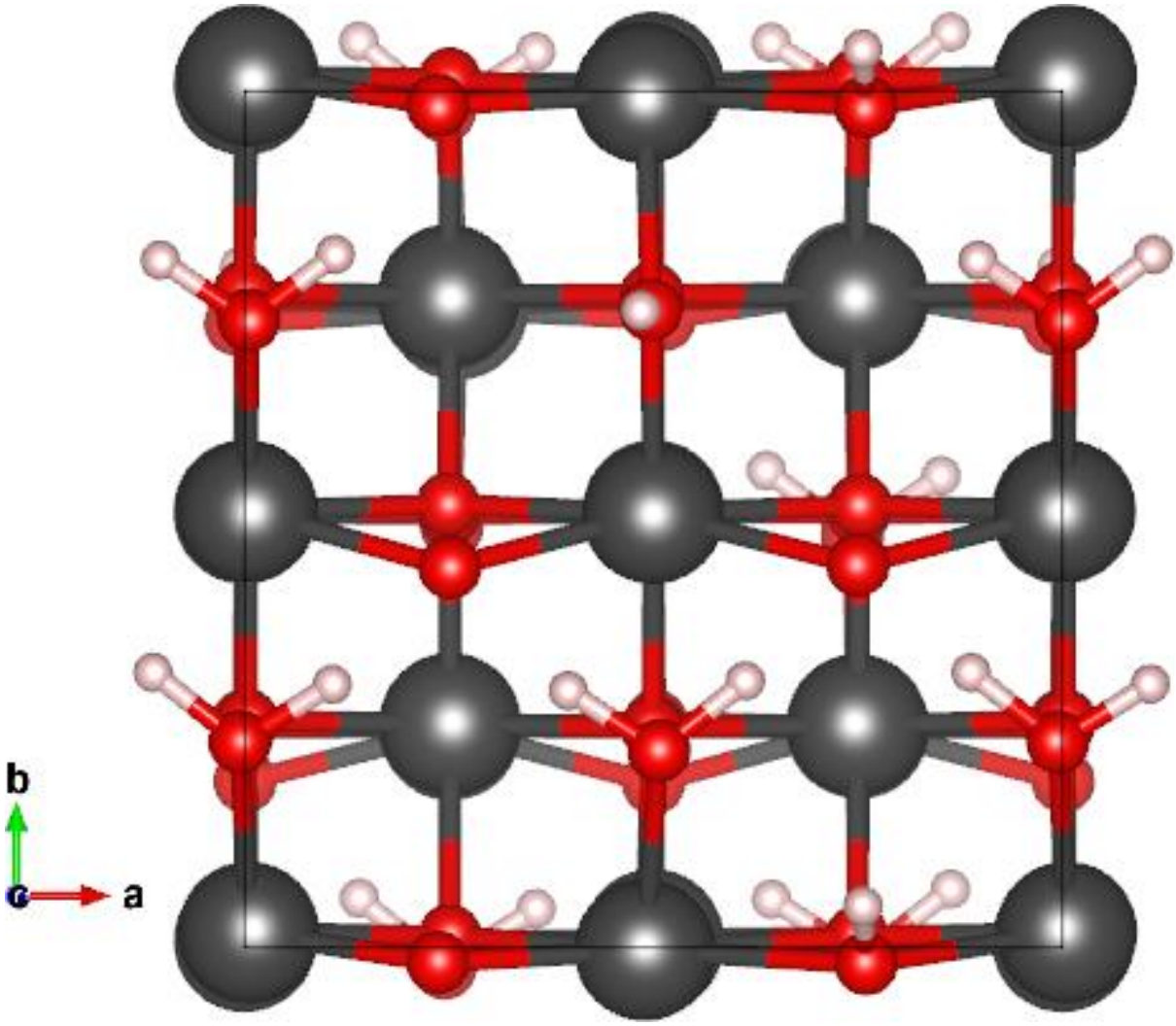

Figure S54: Water adsorbed 75% molecularly and 25% dissociatively on the 2 × 2 PuO_2 {100} surface, yielding a total coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

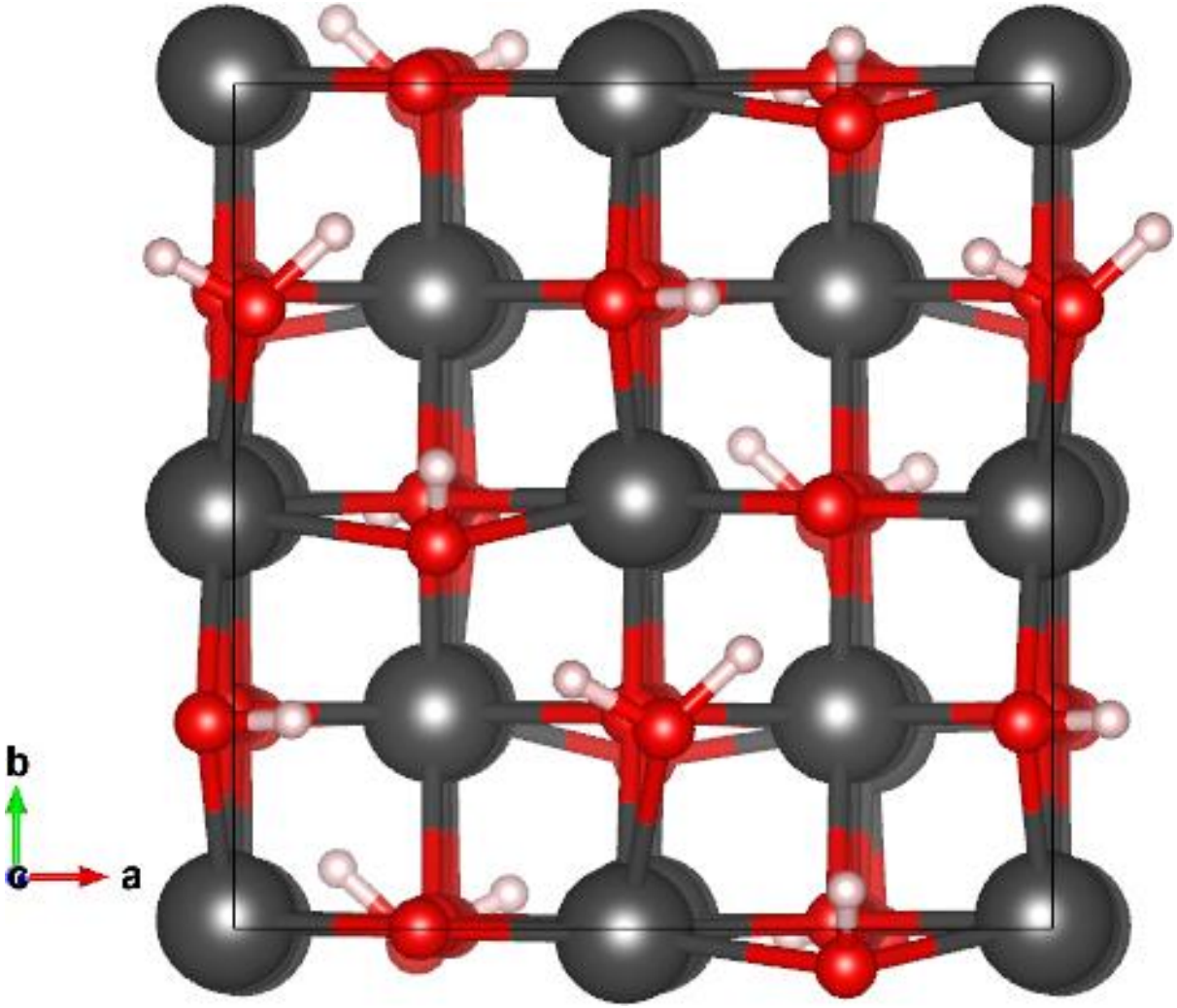

Figure S55: Water adsorbed 50% molecularly and 50% dissociatively on the 2 × 2 PuO_2 {100} surface, yielding a total coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.

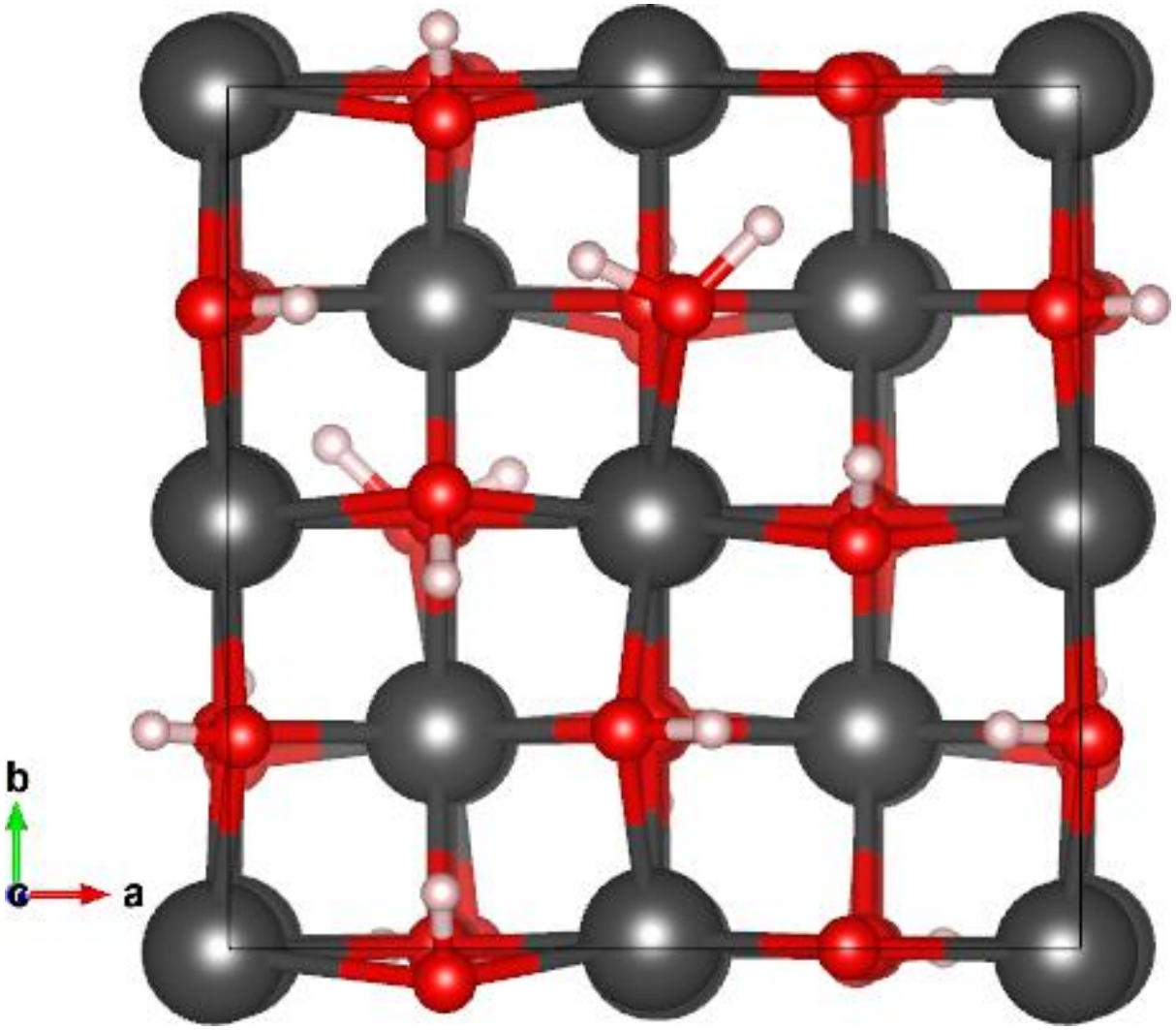

Figure S56: Water adsorbed 25% molecularly and 75% dissociatively on the 2 × 2 PuO_2 {100} surface, yielding a total coverage of 100%, i.e. one mono-layer. Pu atoms in dark gray, oxygen in red and hydrogen in white.