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Adsorption and Dissociation of H_2O on the (001) Surface of Uranium Mononitride: Energetics and Mechanism from First-Principles Investigation

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Atomistic thermodynamics method.

The DFT total-energy calculations give energy only at zero temperature T= 0 and zero pressure P= 0. To study the interactions of water molecules with the UN surface referring to real reaction conditions, it is necessary to take into account temperature and water partial pressure. This is achieved by using the "*ab initio* atomic thermodynamics" approach.[1, 2] In this method, the change of Gibbs free energy for the adsorption processes studied here can be described as

$$\Delta G_{UN}^{ads}(T, p, nH_2O) = G[nH_2O/UN] - G[UN] - nG(H_2O), \quad \text{(S1)}$$

where $G[nH_2O/UN]$ is the Gibbs free energy of the UN(001) surface with n H_2O molecules, while $G[UN]$ and $G[H_2O]$ are those of the clean UN(001) surface and a single water, respectively.

The Gibbs free energy is associated with the Helmholtz free energy, F, via

$$G(T, p) = F(T, p) + pV(T, p) \quad \text{(S2)}$$

Also F can be written as

$$F(T, p) = E_{DFT}^{total}(V) + F^{vib}(T, V) \quad \text{(S3)}$$

In the present situation, the volume effect and the vibration contribution to the Gibbs free energy of the solid surfaces are small[2] and thus are neglected in our calculations. Therefore, the Gibbs free energy can be replaced by the total energy (E^{total}) calculated by VASP, and Equation (S1) can be described as:

$$\Delta G_{UN}^{ads}(T, p, nH_2O) = E[nH_2O/UN] - E[UN] - nG(H_2O), \quad \text{(S4)}$$

where *E*[nH_2O/UN] and *E*[*UN*] are the total energies of the corresponding systems. The *G*(H_2O) term equals to $\mu_{H2O}(T,p)$. Then, the H_2O chemical potential[2] can be described as

$$\mu_{H2O}(T,p) = E_{H2O}^{\text{total}} + \tilde{\mu}_{H2O}(T,p^0) + k_B T \ln(p_{H2O}/p^0), \quad \text{(S5)}$$

where E_{H2O}^{total} is the total energy of a water molecule. The $\tilde{\mu}_{\text{H2O}}(T,p^0)$ term includes the contributions from vibration and rotation of a H_2O molecule. It can be got from the thermodynamic tables as Sun et al. did[3]. The last term of the formula is the contributions of temperature and H_2O partial pressure.

Finally, the change in the Gibbs free energy of the UN(001) surface after adsorption of n H_2O molecules can be described as

$$\Delta G_{UN}^{ads}(T,p,nH_2O) = E[nH_2O/UN] - E[UN] - nE_{H2O}^{total} - n\bar{\mu}_{H2O}(T,p^0) - nk_B T \ln(p_{H2O}/p^0). \quad \text{(S6)}$$

Adsorption of H, O, OH on UN (001) Surface.

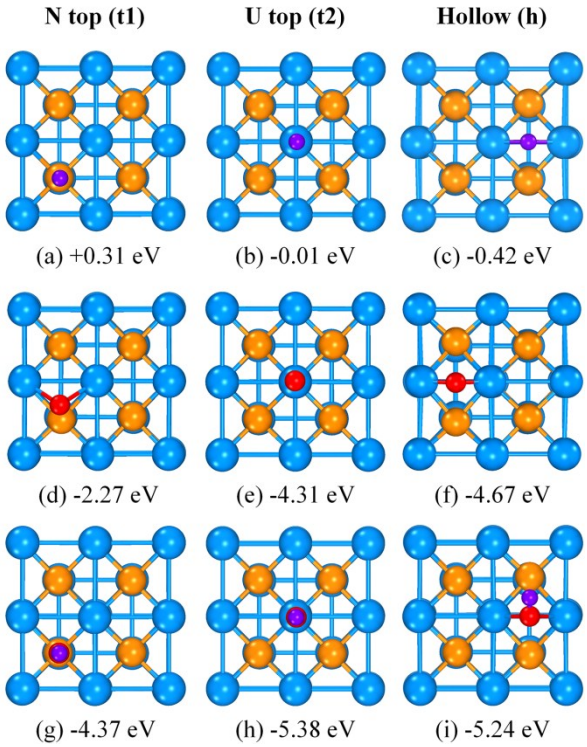

Fig. S1. Top views of the optimized adsorption structures of (a, b, c) H, (d, e, f) O, and (g, h, i) OH on the UN (001) surface. The nitrogen and hydrogen atoms are plotted in yellow and purple, respectively, while the oxygen and uranium atoms are red and blue, respectively.

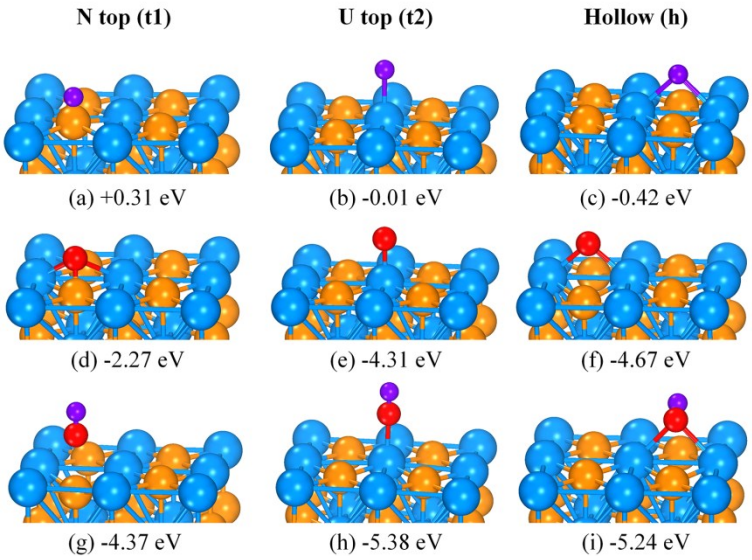

Fig. S2. Side views of the optimized adsorption structures of (a, b, c) H, (d, e, f) O, and (g, h, i) OH on the UN (001) surface. Color code as in Fig. S1.

Table S1. Adsorption energies (E_{ads}, eV) and structural parameters (length in Å) of H, O, and OH adsorption on the UN (001) surface[a].

	E_{ads}	$d_{N\text{-}H}$	$d_{U\text{-}H}$	$d_{O\text{-}N}$	$d_{O\text{-}U}$	$d_{H\text{-}O}$
(a)	+0.31	1.05				
(b)	-0.01		2.14			
(c)	-0.42		2.33/2.32			
(d)	-2.27			1.51	2.38/2.44	
(e)	-4.31				1.88	
(f)	-4.67				2.18/2.18	
(g)	-4.37			2.40		0.98
(h)	-5.38				2.16	0.97
(i)	-5.24				2.47/2.47	0.98

[a] $d_{H\text{-}N}$ denotes the distance between the H atom and the surface N atom. $d_{H\text{-}U}$ denotes the distance between the H atom and the surface U atom. $d_{O\text{-}N}$ denotes the distance between the O atom and the surface N atom. $d_{O\text{-}U}$ denotes the distance between the O atom and the surface U atom. $d_{H\text{-}O}$ denotes the distance between the H atom and the O atom.

In this section, we studied the adsorption structures and energies of the H, O, and OH species on the UN(001) surface by considering the nitrogen top (t1), uranium top (t2), and hollow (h) sites with different initial configurations. Fig. S1 illustrates

the top views of all the relatively stable adsorption configurations of the studied species, and the corresponding side views are given in Fig. S2. The detailed adsorption energies and structure parameters for these adsorption configurations are shown in Table S1.

Fig. S1a and b present the adsorption configurations of a single H atom at the nitrogen top and uranium top sites, and the adsorption energies of +0.31 and -0.01 eV were obtained with the predicted N-H and U-H bond lengths of 1.05 and 2.14 Å, respectively. The most stable adsorption configuration is at the hollow site with the H atom coordinating to two surface U atoms as shown in Fig. S1c. The corresponding U-H bond lengths are 2.33/2.32 Å, which are a little bit longer than that at the uranium top site. The adsorption energy for this configuration is -0.42 eV, which is much lower than those of the first two cases. For one O atom at the nitrogen top site (Fig. S1d), the obtained adsorption energy is about -2.27 eV. Here, the O atom coordinates to the nearest N atom and two U atoms, and the O-N and O-U bond lengths are about 1.51 and 2.38/2.44 Å here, respectively. Fig. S1e and f gives the adsorption configurations of a single O atom at the uranium top and hollow sites, where the O atom coordinates to one and two surface U atoms with the O-U bond lengths of 1.88 and 2.18/2.18 Å, respectively. The adsorption energies are about -4.31 and -4.67 eV for the above two cases, respectively, i.e. the hollow site still becomes the most favorite one among these sites. Bocharov et al.[4] have reported the oxygen adsorption energies of -4.80 and -2.88 eV at the uranium top and nitrogen top sites, respectively, which are lower than the values obtained here. At the nitrogen top and uranium top sites, the adsorbed OH species is perpendicular to the surface with the hydrogen atom pointing outwards (Fig. S1g and h). The obtained O-N and O-U bond lengths are 2.40 and 2.16 Å, respectively. Adsorption of the OH group at the hollow site (Fig. S1i) is characterized by coordination to two surface U atoms, where the O-U bond lengths are about 2.47/2.47 Å. The adsorption energy of the OH group at the uranium top reaches -5.38 eV, which is more negative than the other two cases (t1, -4.37 eV; h, -5.24 eV).

Table S2. Adsorption energies (E_{ads}, eV) and structural parameters (Å) of H_2O adsorption on the UN(001) surface[a].

	E_{ads}	$d_{U\text{-}O}$	$d_{U\text{-}H}$	$d_{H\text{-}bond}$	$d_{H\text{-}H}$	$d_{N\text{-}H}$
(a)	-1.70	2.81; 2.81				1.71; 1.73
(b)	-3.19	2.59; 2.56/2.55	2.30/2.32	1.55	2.30	
(c)	-4.05	2.56/2.28; 2.57/2.28	2.22/2.22; 2.23/2.22		2.19; 2.20	
(d)	-2.44	2.78; 2.75; 2.85		2.51		1.76; 1.76
(e)	-4.30	2.60; 2.37; 2.57	2.35/2.56	1.77; 1.61	1.65	
(f)	-5.34	2.60; 2.46/2.43; 2.39/2.48	2.17/2.23; 2.30/2.26	1.75; 1.91	2.21	
(g)	-5.77	2.36/2.38; 2.36/2.42; 2.39/2.38	2.15/2.12; 2.21/2.21; 2.20/2.12	2.60	2.06; 2.20; 2.02	
(h)	-3.36	2.72; 2.74; 2.72; 2.74		1.90; 1.89; 1.88; 1.92		
(i)	-5.15	2.71; 2.54; 2.49; 2.60	2.35/2.33	2.18; 1.54; 1.42	1.42	
(j)	-6.61	2.58; 2.59; 2.51/2.46; 2.50/2.50	2.23/2.23; 2.24/2.23	1.53; 1.54	2.26; 2.24	
(k)	-6.86	2.34/2.41; 2.52/2.41; 2.33/2.40; 2.77/2.58	2.23/2.23; 2.20/2.20; 2.07/2.07	1.59	2.17; 2.24; 2.19	
(l)	-6.51	2.33/2.35; 2.39/2.30; 2.32/2.38; 2.35/2.33	2.12/2.08; 2.11/2.11; 2.08/2.12; 2.11/2.11		2.16; 2.06; 2.15; 2.10; 2.15; 2.14	

[a] $d_{U\text{-}O}$ is the bond distance from oxygen atoms of water ($d_{U\text{-}O(w)}$) and OH groups ($d_{U\text{-}O(h)}$) to surface U atoms. $d_{H\text{-}bond}$ denotes the formed hydrogen bond length.

Adsorption of two water molecules on the UN (001) surface.

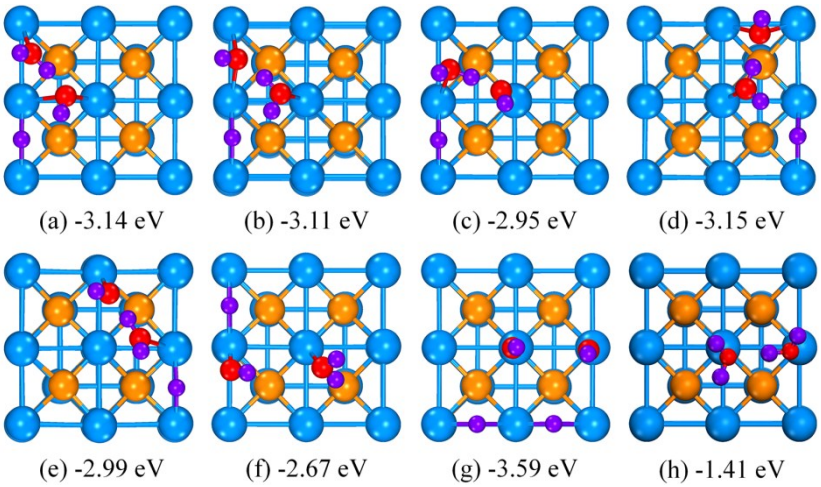

Fig. S3. Optimized adsorption structures of two water molecules on the UN (001) surface. Color code as in Fig. S1.

Table S3. Adsorption energies (E_{ads}, eV) and structural parameters (length in Å) of H_2O adsorption on the UN (001) surface[a].

	E_{ads}	$d_{U\text{-}O}$	$d_{U\text{-}H}$	$d_{H\text{-}bond}$	$d_{H\text{-}H}$
(a)	-3.14	2.63; 2.73/2.46	2.30/2.32	1.47	2.33
(b)	-3.11	2.49/2.66; 2.63	2.31/2.35	1.55	2.41
(c)	-2.95	3.09/2.65; 2.34	2.32/2.31	1.50	
(d)	-3.15	2.60/2.52; 2.63	2.32/2.43	1.63	
(e)	-2.99	2.40; 2.89/2.62	2.34/2.32	1.45	
(f)	-2.67	2.25; 2.68	2.23/2.30		
(g)	-3.59	2.11; 2.11	2.23/2.23; 2.23/2.24		
(h)	-1.41	2.78;2.66		1.88	

[a] $d_{U\text{-}O}$ denotes the distance between the O atom of the adsorbed H_2O and the surface U atom. $d_{U\text{-}H}$ denotes the distance between the H atom and the surface U atom. $d_{H\text{-}bond}$ denotes the length of the hydrogen bond. $d_{H\text{-}H}$ denotes the distance between the two interactional H atoms.

Adsorption of three water molecules on the UN (001) surface.

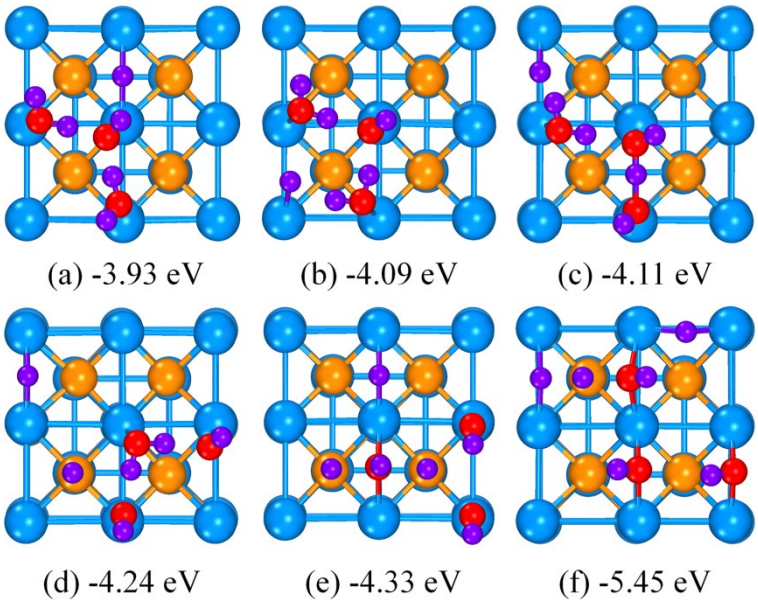

Fig. S4. Optimized adsorption structures of three water molecules on the UN (001) surface. Color code as in Fig. S1.

Table S4. Adsorption energies (E_{ads}, eV) and structural parameters (length in Å) of H_2O adsorption on the UN (001) surface[a].

	E_{ads}	$d_{U\text{-}O}$	$d_{U\text{-}H}$	$d_{H\text{-}bond}$	$d_{H\text{-}H}$	$d_{H\text{-}N}$
(a)	-3.93	2.54; 2.50; 2.51	2.21/2.22	1.47; 1.46	2.23	
(b)	-4.09	2.63; 2.37; 2.58	2.60/2.24	1.69; 1.65	1.93	
(c)	-4.11	2.62; 2.59; 2.35	2.31/2.48	1.86; 1.33	1.51	
(d)	-4.24	2.56; 2.28; 2.22	2.19/2.25	1.71; 1.72		1.04
(e)	-4.33	2.44/2.55; 2.16; 2.16	2.23/2.22			1.05; 1.04
(f)	-5.45	2.44/2.44; 2.35/2.47; 2.36/2.45	2.29/2.30; 2.16/2.14	2.68	1.70; 2.42	1.06

[a] $d_{U\text{-}O}$ denotes the distance between the O atom of the adsorbed H_2O and the surface U atom. $d_{U\text{-}H}$ denotes the distance between the H atom and the surface U atom. $d_{H\text{-}bond}$ denotes the length of the hydrogen bond. $d_{H\text{-}H}$ denotes the distance between the two interactional H atoms. $D_{H\text{-}N}$ denotes the distance between the H atom and the surface N atom.

Adsorption of four water molecules on the UN (001) surface.

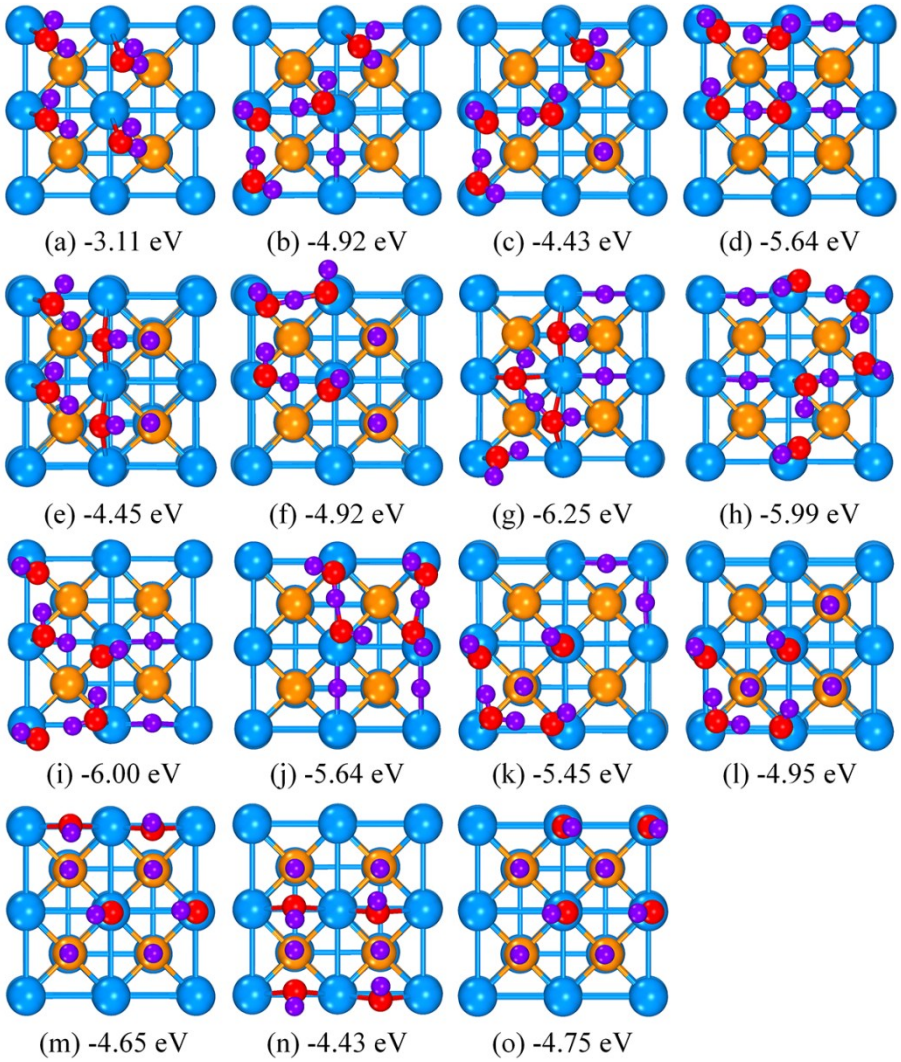

Fig. S5. Optimized adsorption structures of four water molecules on the UN (001) surface. Color code as in Fig. S1.

Table S5. Adsorption energies (E_{ads}, eV) and structural parameters (length in Å) of H_2O adsorption on the UN (001) surface[a].

	E_{ads}	$d_{U\text{-}O}$	$d_{U\text{-}H}$	$d_{H\text{-bond}}$	$d_{H\text{-}H}$	$d_{H\text{-}N}$
(a)	-3.11	2.86; 2.97; 2.80; 2.82		2.34; 2.19		1.70; 1.72
(b)	-4.92	2.74; 2.42; 2.62; 2.64	2.25/2.18	1.97; 1.79; 1.50		
(c)	-4.43	2.90; 2.49; 2.60; 2.67		2.04; 1.68; 1.50		1.04
(d)	-5.64	2.33; 2.54; 2.27; 2.49	2.17/2.17; 2.12/2.12	1.41; 1.45		
(e)	-4.45	2.63; 2.67/2.63; 2.68; 2.73/2.68		1.58; 1.59	2.26; 2.34	1.04; 1.04
(f)	-4.92	2.63; 2.34; 2.58; 2.35		1.36; 1.91; 1.66		1.04; 1.04
(g)	-6.25	2.41/2.48; 2.43/2.73; 2.90/2.64; 2.66	2.22/2.22; 2.27/2.26	1.80; 1.35; 1.93	2.13; 2.27	
(h)	-5.99	2.36; 2.46; 2.46; 2.36	2.14/2.14; 2.16/2.14	1.59; 1.67; 1.59; 1.67	2.15	
(i)	-6.00	2.36; 2.45; 2.36; 2.46	2.15/2.13; 2.14/2.15	1.68; 1.59; 1.68; 1.59		
(j)	-5.64	2.46; 2.52; 2.27; 2.35	2.11/2.12; 2.17/2.17	1.41; 1.42	2.30	
(k)	-5.45	2.23; 2.13; 2.45; 2.23	2.10/2.09; 2.09/2.10	1.58; 1.57		1.05
(l)	-4.95	2.27; 2.18; 2.54; 2.26		1.73; 1.71		1.04; 1.04; 1.04
(m)	-4.65	2.54/2.47; 2.48/2.52; 2.18; 2.17				1.04; 1.05; 1.05; 1.04
(n)	-4.43	2.51/2.58; 2.49/2.59; 2.51/2.52; 2.52/2.49				1.05; 1.05; 1.05; 1.05
(o)	-4.75	2.13; 2.14; 2.16; 2.16				1.04; 1.04; 1.04; 1.04

[a] $d_{U\text{-}O}$ denotes the distance between the O atom of the adsorbed H_2O and the surface U atom. $d_{U\text{-}H}$ denotes the distance between the H atom and the surface U atom. $d_{H\text{-bond}}$ denotes the length of the hydrogen bond. $d_{H\text{-}H}$ denotes the distance between the two interactional H atoms. $D_{H\text{-}N}$ denotes the distance between the H atom and the surface N atom.

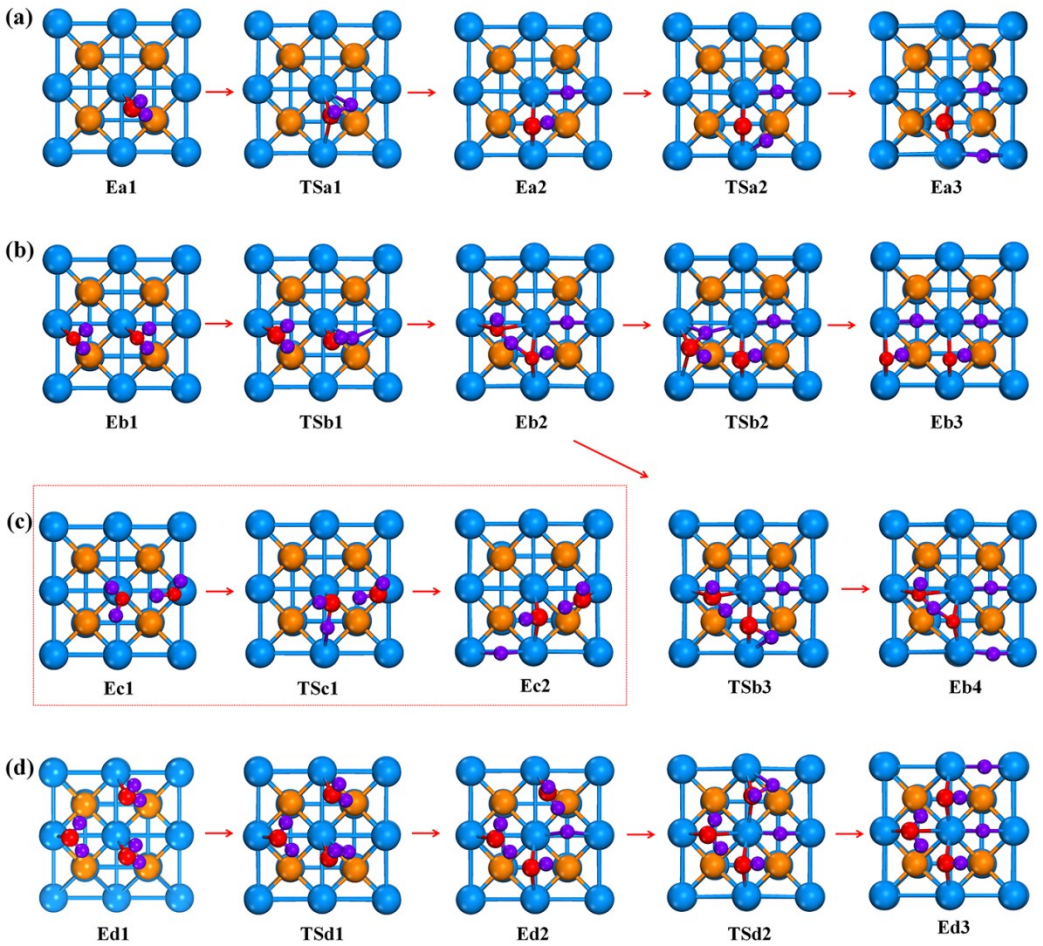

Fig. S6. Optimized geometries of all the transition states and intermediates for H_2O dissociation at different coverages. Color code as in Fig. S1.

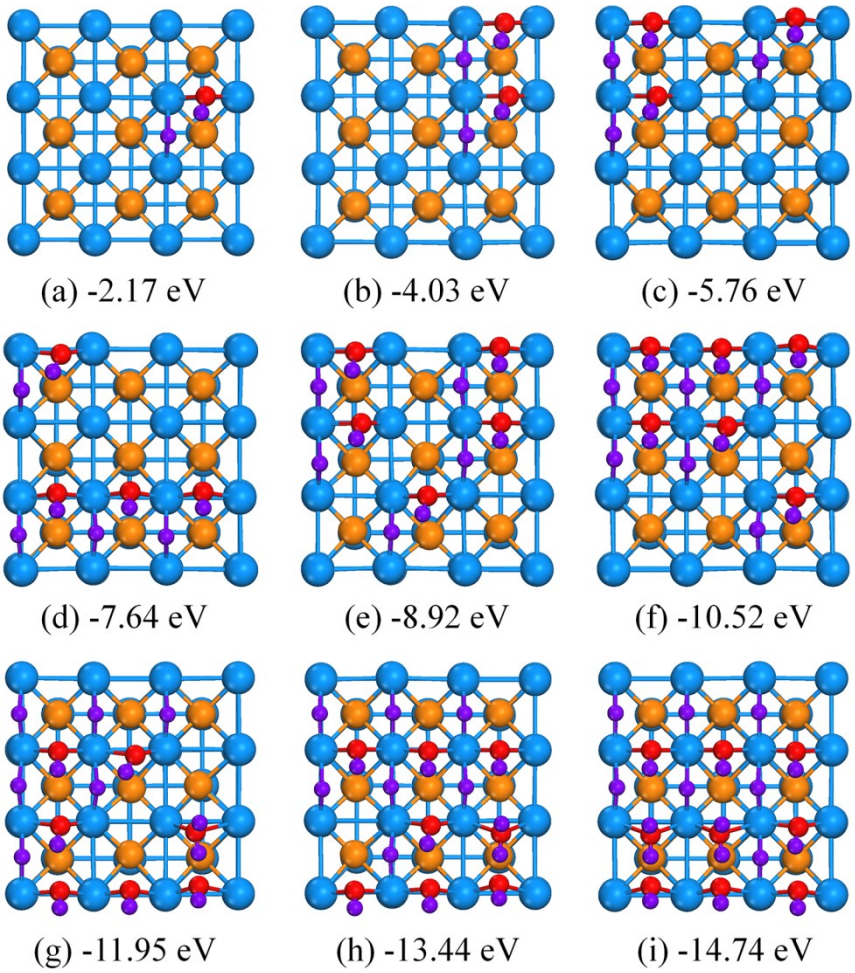

Fig. S7. Optimized adsorption structures of one to nine water molecules on the p(3×3) surface. Color code as in Fig. S1.

Reference

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