Electronic Supplementary Information

Coverage Dependent Water Dissociative Adsorption on Fe(110) from DFT Computation

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Atomistic thermodynamics:

Atomistic thermodynamics[1,2] is a convenient tool to study reactions under specific conditions[3-4]. According to the literature, we take H_2O desorption on Fe(110) surface, $H_2O/Fe \rightarrow Fe + H_2O(g)$, as an example; and the change of Gibbs free energy (ΔG) for this reaction can be described as equation S1.

$$\Delta G = G[Fe(110)] + G_{gas}(H_2O) - G[\{H_2O\}/Fe(110)] \quad \text{(S1)}$$

In this equation, $G[Fe(110)]$ is the Gibbs free energy of the clean Fe(110) surface, while $G[\{H_2O\}/Fe(110)]$ is the Gibbs free energy of the Fe surface with adsorbed H_2O molecule. Because of the large mass differences, the contribution of vibration to the solid surfaces is negligible.[5] Thus, we use the DFT calculated total energy to substitute the Gibbs free energy of the solid surfaces and the $G_{gas}(H_2O)$ equals $\mu(H_2O)$. Such approximations were also widely applied in both early[6] and most recent[7] work related to atomistic thermodynamics methods. The chemical potential of H_2O ($\mu(H_2O)$) can be described as

$$\mu_{H_2O}(T,P) = E^{total}_{H_2O} + \%_{H_2O}(T,P^0) + k_B T ln(P_{H_2O}/P^0)$$

$E^{total}_{H_2O}$ stands for the DFT calculated energy of the isolated H_2O gas phase molecule (including zero point vibrations), and $\%_{H_2O}(T,P^0)$ is the chemical potential at different temperatures, which can be found in thermodynamic tables. The last term $k_B T ln(P_{H_2O}/P^0)$ is the contribution of the temperature and H_2O partial pressure to the chemical potential. Therefore, equation 6 can be rewritten as

$$\Delta G = E[Fe(110)] - E[\{H_2O\}/Fe(110)] + E^{total}_{H_2O} + \%_{H_2O}(T,P^0) + k_B T ln(P_{H_2O}/P^0) \quad \text{(7)}$$

Table S1. Adsorption energies (eV) and desorption temperature (K) of H_2O and H_2 under some different conditions on Fe(110) surface from theory and experiment.

	E_{ads}/eV (PBE/PBE-D2)	PBE/PBE-D2	Experiment
$H_2O(s) \rightarrow H_2O(g)$	0.38/0.62	232K/285 K	
$2OH(s) \rightarrow O(s) + H_2O(g)$	0.84/1.14	333K/400 K	315K[8]
$2H(s) \rightarrow H_2(g)$	1.52/1.69	411K/455 K	
$O(s) + 2H(s) \rightarrow O(s) + H_2(g)$	1.39	380K	
$2O(s) + 2H(s) \rightarrow 2O(s) + H_2(g)$	0.99	275K	
$3O(s) + 2H(s) \rightarrow 3O(s) + H_2(g)$	0.94	263K	
$4O(s) + 2H(s) \rightarrow 4O(s) + H_2(g)$	0.91	255K	
$5O(s) + 2H(s) \rightarrow 5O(s) + H_2(g)$	1.04	290K	
$6O(s) + 2H(s) \rightarrow 6O(s) + H_2(g)$	0.84	240K	
$7O(s) + 2H(s) \rightarrow 7O(s) + H_2(g)$	0.66	190K	
$8O(s) + 2H(s) \rightarrow 8O(s) + H_2(g)$	0.49	148K	
$9O(s) + 2H(s) \rightarrow 9O(s) + H_2(g)$	-0.39		
$O(s) + H_2O(s) \rightarrow O(s) + H_2O(g)$	0.45	248K	
$2O(s) + H_2O(s) \rightarrow 2O(s) + H_2O(g)$	0.31	217K	
$3O(s) + H_2O(s) \rightarrow 3O(s) + H_2O(g)$	0.48	254K	
$4O(s) + H_2O(s) \rightarrow 4O(s) + H_2O(g)$	0.49	258K	
$5O(s) + H_2O(s) \rightarrow 5O(s) + H_2O(g)$	0.49	258K	
$6O(s) + H_2O(s) \rightarrow 6O(s) + H_2O(g)$	0.59	280K	
$7O(s) + H_2O(s) \rightarrow 7O(s) + H_2O(g)$	0.72	308K	
$8O(s) + H_2O(s) \rightarrow 8O(s) + H_2O(g)$	0.33	222K	

Table S2. Model test for Fe(110) surface on H_2O adsorption. ST represents slab thickness, kp represents k-points, VLT (Å) represents vacuum layer thickness, E_{ads} (eV) represents the adsorption energy of H_2O. mLnR represents a m-layer model with n layers were relaxed.

size	ST	kp	VLT	E_{ads}
P(4×4)	3L1R	3×3×1	15	-0.34
	3L1R	5×5×1	15	-0.34
	3L2R	3×3×1	15	-0.35
	3L2R	5×5×1	15	-0.35
	4L2R	3×3×1	15	-0.38

Table S3. Computed adsorption energies (E_{ads}, eV), distances (d, Å) between surface Fe atom to the adsorbed O, H, OH and H_2O as well as the O-H distance and HOH angle θ_{HOH} (°) in the optimized water

	T-site	**LB**-site	**SB**-site	**3FH**-site
			H	
E_{ads}		-0.71	-0.59	-0.76
$d_{H\text{-}Fe}$		1.748;1.748	1.692;1.695	1.787;1.790;1.792
			O	
E_{ads}	-1.77	-3.43	-2.94	-3.43
$d_{O\text{-}Fe}$	1.650	1.846;1.846;2.166;2.221	1.790;1.790	1.851; 1.851; 2.007; 2.455
			OH	
E_{ads}	-3.45 (-3.30)[a]		-3.95 (-3.95)[a]	-4.28
$d_{O\text{-}Fe}$	1.807 (1.779)[a]		1.942;1.952 (1.933;1.938)[a]	2.002;2.006;2.151; 2.647
$d_{O\text{-}H}$	0.976 (0.967)[a]		0.973 (0.972)[a]	0.975
			H_2O	
E_{ads}	-0.38		-0.28[a]	
$d_{O\text{-}Fe}$	2.183		2.363;2.378[a]	
$d_{O\text{-}H}$	0.980		0.979;0.979[a]	
ϑ_{HOH}	106.01		109.08[a]	

(a) For perpendicular configuration to the surface in parenthesis

Table S4: Adsorption energies (E_{ads}, eV), Fe-O ($d_{O\text{-}Fe}$, Å) and H-bonding distances ($d_{H\text{-}bond}$, Å) of $(H_2O)_n$ clusters on Fe(110) surface

	E_{ads}	$d_{Fe\text{-}O}$	$d_{H\text{-}bond}$
$(H_2O)_1$	-0.38	2.183	
$(H_2O)_2$	-0.98	2.080; 3.088	1.639
$(H_2O)_3$	-1.53	2.019; 3.037; 3.059	1.693; 1.697
$(H_2O)_4$	-2.12	2.106; 2.152; 3.032; 3.054	1.665; 1.669; 1.692
$(H_2O)_{5\text{-}t1}$	-2.65	2.064; 2.154; 3.134; 3.319; 3.324	1.637; 1.710; 1.754; 1.772; 2.001
$(H_2O)_{5\text{-}t2}$	-2.60	2.008; 2.305; 3.133; 3.255; 3.391	1.676; 1.669; 1.771; 1.896; 1.970
$(H_2O)_{5\text{-}t3}$	-2.57	2.189; 2.263; 2.341; 3.089; 3.161	1.569; 1.592; 1.840; 1.867; 1.920
$(H_2O)_{6\text{-}t1}$	-3.10	2.136; 2.169; 2.244; 3.206; 3.386; 3.410	1.630; 1.659; 1.744; 1.787; 1.900; 1.913
$(H_2O)_{6\text{-}t2}$	-3.16	2.136; 2.137; 2.313; 3.147; 3.304; 3.573	1.624; 1.654; 1.773; 1.688; 1.910; 1.915
$(H_2O)_{6\text{-}t3}$	-3.23	2.174; 2.183; 2.199; 3.064; 3.082; 3.137	1.554; 1.569; 1.591; 1.820; 1.855; 1.856
$(H_2O)_7$	-3.80	2.156; 2.168; 2.186; 3.056; 3.075; 3.088; 3.456	1.547; 1.591; 1.625; 1.850; 1.856; 1.888; 2.052
$(H_2O)_8$	-4.35	2.108; 2.192; 2.203; 3.073; 3.092; 3.099; 3.535; 4.076	1.540; 1.653; 1.662; 1.742; 1.828; 1.868; 1.868; 1.932
$(H_2O)_{9\text{-}t1}$	-4.77	2.085; 2.182; 2.198; 2.856; 3.019; 3.063; 3.075; 3.575; 4.105	1.567; 1.582; 1.658; 1.678; 1.732; 1.798; 1.800; 1.832; 2.163
$(H_2O)_{9\text{-}t2}$	-4.92	2.083; 2.163; 2.258; 3.140; 3.144; 3.179; 3.400; 3.875; 3.979	1.581; 1.611; 1.746; 1.747; 1.811; 1.838; 1.858; 1.866; 1.895; 1.950

Table S5: Adsorption energies E_{ads} (eV) and bond distances (d, Å) of the IS and FS for H_2O direct dissociation and $2H_2O$ dissociation on Fe(110) surface.

	E_{ads}	d_{Fe-O}	d_{Fe-H}
		H_2O direct dissociation	
H_2O	-0.38	2.183	
OH + H	-1.66	1.995; 2.010; 2.181	1.757; 1.796; 1.817
O+2H	-2.23	1.860; 1.860; 1.954	1.756; 1.787; 1.804; 1.756; 1.787; 1.804
		$2H_2O$ dissociation	
$H_2O + H_2O$	-0.98	2.080; 3.088	
$1H_2O$ + OH + H	-1.87	2.006; 2.046; 2.178; 2.209	1.764; 1.795; 1.811
$1H_2O$ + O + 2H	-2.73	1.881; 1.909; 1.919; 2.176	1.762; 1.786; 1.800; 1.764; 1.788; 1.797
2OH + 2H	-2.98	1.979; 2.053; 2.177; 2.022; 2.057; 2.062	1.716; 1.778; 1.843; 1.742; 1.758; 1.839

Table S6: The barriers E_a (eV) and reaction energies E_r (eV), bond distances (*d*, Å) and the breaking O-H bond distances (Å) of the TS for H_2O and $2H_2O$ dissociation on Fe(110) surface.

	E_a	E_r	d_{Fe-O}	d_{Fe-H}	d_{O-H}
$H_2O \rightarrow OH+H$ (TS1); $OH+H \rightarrow O + 2H$ (TS2)					
TS1	0.68	-1.28	1.959	1.871	1.401
TS2	0.90	-0.57	1.903; 1.995; 2.053	1.762; 1.778; 1.806; 1.804; 1.883	1.273
$2H_2O \rightarrow OH + H + H_2O$ (TS3); $OH + H + H_2O \rightarrow O + 2H + H_2O$ (TS4); $OH + H + H_2O \rightarrow 2OH + 2H$ (TS5)					
TS3	0.61	-0.89	1.986; 2.142	1.843	1.360
TS4	0.57	-0.86	1.989; 2.038; 2.209; 1.975	1.754; 1.797; 1.811; 1.865	1.403
TS5	0.64	-1.11	1.910; 2.001; 2.242; 2.146	1.761; 1.782; 1.801; 1.839; 2.013	1.291

Table S7. Adsorption energies E_{ads} (eV) and bond distances (Å) of the IS and FS for *n*O-assisted H_2O dissociation on Fe(110) surface.

	E_{ads}	d_{Fe-O}	d_{Fe-H}
		1O-assisted H_2O dissociation	
O + H_2O	-1.35	1.886; 1.891; 1.943; 2.196	
2OH	-1.73	2.007; 2.039; 2.104; 2.014; 2.050; 2.063	
O + H + OH	-2.30	1.842; 1.875; 2.098; 2.002; 2.004; 2.099	1.735; 1.786; 1.828
2O + 2H	-2.59	1.825; 1.874; 2.170; 2.254; 1.800; 1.884; 1.918	1.724; 1.798; 1.825; 1.691; 1.743
		2O-assisted H_2O dissociation	
2O + H_2O	-1.92	1.814; 1.859; 1.907; 1.863; 1.897; 1.996; 2.211	
O + 2OH	-2.40	1.853; 1.855; 1.960; 2.002; 2.009; 2.000; 2.018; 2.123	
2O + H + OH	-2.86	1.835; 1.839; 1.981; 1.856; 1.858; 2.151; 2.271	1.747; 1.751; 1.843
3O + 2H	-3.08	1.819; 1.847; 1.909; 1.839; 1.858; 2.002; 1.828; 1.879; 1.907	1.695; 1.743; 1.725; 1.752; 1.849
		3O-assisted H_2O dissociation	
3O + H_2O	-2.63	1.819; 1.853; 1.893; 1.850; 1.871; 1.928; 1.864; 1.895; 1.930; 2.179	
2O + 2OH	-2.87	1.816; 1.857; 1.895; 1.868; 1.871; 1.946; 1.963; 2.081; 2.140; 1.990; 2.002; 2.143	
3O + H + OH	-3.13	1.813; 1.857; 1.889; 1.858; 1.867; 1.894; 1.847; 1.903; 1.939; 1.964; 1.989; 2.157	1.684; 1.755
4O + 2H	-3.50	1.802; 1.874; 1.881; 1.859; 1.864; 1.912; 1.837; 1.880; 1.916; 1.829; 1.838; 1.910	1.689; 1.755; 1.699; 1.790; 1.793
		4O-assisted H_2O dissociation	
4O + H_2O	-3.07	1.810; 1.859; 1.894; 1.840; 1.876; 1.920; 1.865; 1.870; 1.906; 1.856; 1.856; 1.981; 2.160	
3O + 2OH	-3.35	1.814; 1.855; 1.889; 1.846; 1.881; 1.923; 1.970; 1.899; 1.900; 1.986; 1.988; 2.180; 1.985; 2.041; 2.173	
4O + H + OH	-3.62	1.828; 1.875; 2.082; 1.839; 1.870; 1.920; 1.825; 1.882; 1.928; 1.833; 1.845; 1.878; 1.973; 1.983; 2.156	1.737; 1.746; 1.833
5O + 2H	-3.99	1.830; 1.845; 1.885; 1.838; 1.874; 1.942; 1.833; 1.884; 1.902; 1.855; 1.860; 1.899; 1.809; 1.860; 1.892	1.747; 1.750; 1.815; 1.719; 1.742; 1.832
		5O-assisted H_2O dissociation[a]	
5O + H_2O	-3.50	1.820; 1.897; 1.909; 2.199	
4O + 2OH	-3.70	1.985;; 1.989; 2.135; 1.922; 2.041	
5O + H + OH	-3.96	1.818; 1.833; 1.913; 1.947; 2.005; 1.096	1.712; 1.785; 1.816
5O + H + OH-t2	-4.07	1.955; 2.000; 2.116; 1.825; 1.952; 1.913	1.751; 1.767; 1.802
6O + 2H	-4.24	1.784; 1.879; 1.887; 1.819; 1.847; 1.909	1.764; 1.767; 1.782; 1.710; 1.743; 1.811
		6O-assisted H_2O dissociation[a]	
6O + H_2O	-3.99	1.830; 1.873; 1.911; 2.233	
5O + 2OH	-4.02	1.980; 2.034; 2.198; 1.982; 2.004; 2.111	
6O + H + OH	-4.06	1.982; 1.992; 2.079; 1.836; 1.888; 2.098; 2.248	1.738; 1.742; 1.778
7O + 2H	-4.21	1.849; 1.873; 1.891; 1.853; 1.861; 1.881	1.691; 1.759; 1.802; 1.690; 1.698; 1.941
		7O-assisted H_2O dissociation[a]	
7O + H_2O	-4.27	1.855; 1.867; 1.932; 2.163	
6O + 2OH	-4.29	1.989; 2.020; 2.129; 1.988; 2.023; 2.126	
7O + H + OH	-4.10	1.799; 1.869; 1.885; 1.989; 2.020; 2.047	1.693; 1.739; 1.821
8O + 2H	-4.17	1.796; 1.870; 1.881; 1.849; 1.853; 1.890	1.698; 1.741; 1.801; 1.665; 1.782; 1.836
		8O-assisted H_2O dissociation[a]	
8O + H_2O	-4.01	1.831; 1.853; 1.981; 2.338	
7O + 2OH	-3.58	1.972; 2.050; 2.085; 2.013; 2.028; 2.049	
8O + H + OH	-3.81	1.784; 1.889; 1.897; 2.005; 2.024; 2.229	1.650; 1.771; 1.843
9O + 2H	-2.75	1.837; 1.842; 1.863; 1.805; 1.846; 1.861	1.668; 1.737; 1.832; 1.672; 1.747; 1.784

[a]After n>5, we do not give the information of the former O atoms because of the same site with the systems of (*n-1)*O+H_2O

Table S8. The barriers E_a (eV) and reaction energies E_r (eV) of nO-assisted H_2O dissociation on Fe(110) surface, and the bond distances (Å) of the transition states.

	E_a	E_r	d_{Fe-O}	d_{Fe-H}	d_{O-H}
1O + H_2O → 2OH (TS6); 2OH → OH + O + H (TS7); OH + O + H →2O + 2H (TS8)					
TS6	0.40	-0.38	1.970; 2.006; 2.007; 1.936		1.350
TS7	0.90	-0.57	2.013; 2.039; 2.049; 1.964; 1.987; 2.048	1.811; 1.877	1.295
TS8	0.95	-0.29	1.839; 1.887; 1.965; 1.914; 1.981; 2.024	1.722; 1.785; 1.827; 1.700; 1.935	1.326
2O + H_2O → O + 2OH (TS9); O + 2OH → OH + 2O + H (TS10); OH + 2O + H →3O + 2H (TS11)					
TS9	0.41	-0.48	1.815; 1.853; 1.938; 1.944; 1.976; 2.142; 1.935		1.384
TS10	1.01	-0.46	1.819; 1.853; 1.925; 1.940; 1.987; 2.151; 1.999; 2.024; 2.074	1.793; 1.861	1.300
TS11	1.02	-0.22	1.815; 1.844; 1.920; 1.848; 1.862; 2.037; 1.913; 1.993; 2.006	1.740; 1.743; 1.843; 1.695; 1.932	1.329
3O + H_2O → 2O + 2OH (TS12); 2O + 2OH → OH + 3O + H (TS13); OH + 3O + H →4O + 2H (TS14)					
TS12	0.34	-0.24	1.822; 1.848; 1.891; 1.847; 1.869; 1.940; 1.934; 2.019; 2.051; 1.965		1.300
TS13	0.93	-0.26	1.813; 1.856; 1.892; 1.861; 1.866; 1.925; 1.930; 2.012; 2.024; 1.976; 2.000; 2.120	1.699; 1.957	1.334
TS14	1.04	-0.37	1.811; 1.863; 1.886; 1.855; 1.866; 1.911; 1.831; 1.891; 1.910; 1.890; 1.965; 2.000	1.694; 1.747	1.320
4O + H_2O → 3O + 2OH (TS15); 3O + 2OH → OH + 4O + H (TS16); OH + 4O + H →5O + 2H (TS17)					
TS15	0.32	-0.28	1.814; 1.854; 1.892; 1.851; 1.870; 1.927; 1.862; 1.877; 1.905; 1.889; 1.924; 1.984		1.140/1.296
TS16	1.01	-0.27	1.814; 1.856; 1.887; 1.838; 1.877; 1.919; 1.857; 1.891; 1.897; 1.965; 1.972; 2.201; 1.942; 1.963; 2.059	1.690; 1.942	1.356
TS17	1.26	-0.37	1.833; 1.845; 1.878; 1.839; 1.870; 1.920; 1.837; 1.883; 1.997; 1.825; 1.882; 1.928; 1.964; 1.975; 2.179	1.737; 1.746; 1.833; 1.626	1.350
5O + H_2O → 4O + 2OH (TS18); 4O + 2OH → OH + 5O + H (TS19); OH + 5O + H →6O + 2H (TS20)					
TS18	0.58	-0.20	1.897; 2.016; 2.054; 1.995		1.301
TS19	1.01	-0.26	1.968; 2.008; 2.094; 1.907; 1.950; 2.035	1.679; 2.029	1.353
TS20	1.04	-0.17	1.818; 1.843; 1.915; 1.875; 1.967; 1.991	1.759; 1.763; 1.792; 1.687; 1.990	1.330
6O + H_2O → 5O + 2OH (TS21); 5O + 2OH → OH + 6O + H (TS22); OH + 6O + H →7O + 2H (TS23)					
TS21	0.57	-0.03	1.884; 1.950; 2.192; 2.098		1.349
TS22	1.14	-0.04	1.983; 1.985; 2.089; 1.906; 2.018; 2.191	1.772; 1.844	1.260
TS23	1.15	-0.15	1.834; 1.889; 1.999; 1.942; 1.958; 2.022	1.721; 1.746; 1.778; 1.828	1.301
7O + H_2O → 6O + 2OH (TS24); 6O + 2OH → OH + 7O + H (TS25); OH +7O + H →8O + 2H (TS26)					
TS24	0.55	-0.02	1.939; 1.883; 1.902		1.250
TS25	1.31	0.19	1.995; 2.027; 2.034; 1.900; 1.959; 1.970	1.683; 1.994	1.354

TS26	1.19	-0.07	1.800; 1.872; 1.877; 1.898; 1.958; 1.965	1.703; 1.737; 1.810; 1.636	1.343
8O + H_2O → 7O + 2OH (TS27); 7O + 2OH → OH + 8O + H (TS28); OH +8O + H →9O + 2H (TS29)					
TS27	0.79	0.43	1.953; 1.972; 1.962		1.679
TS28	1.28	-0.23	1.991; 2.025; 2..037; 1.961; 1.971; 1.996	1.747; 1.917	1.361
TS29	2.09	1.06	1.842; 1.866; 1.869; 1.896; 1.916; 1.966	1.678; 1.716; 1.842; 1.684; 1.914	1.352

After n>5, we do not give the information of the former O atoms because of the same site with the systems of (*n-1)*O+H_2O

Figure S1: The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of $2H_2O$ dissociation (iron/blue; oxygen/red; hydrogen/yellow)

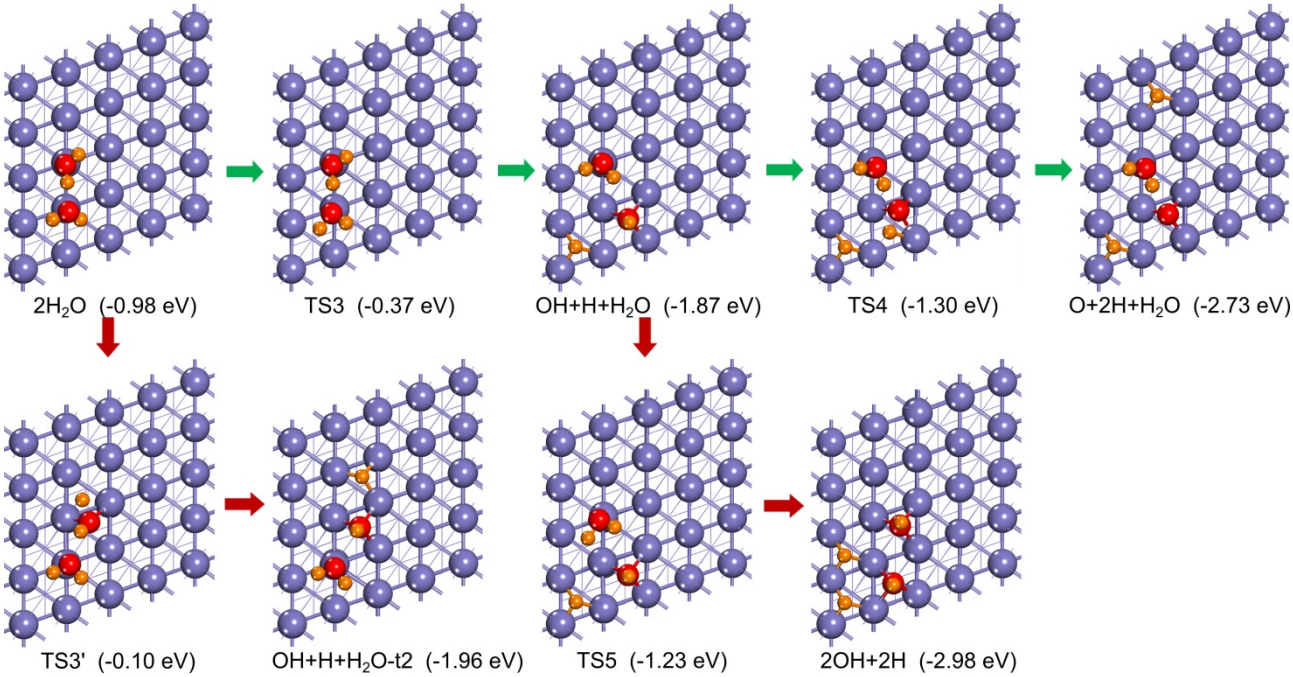


Figure S2. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

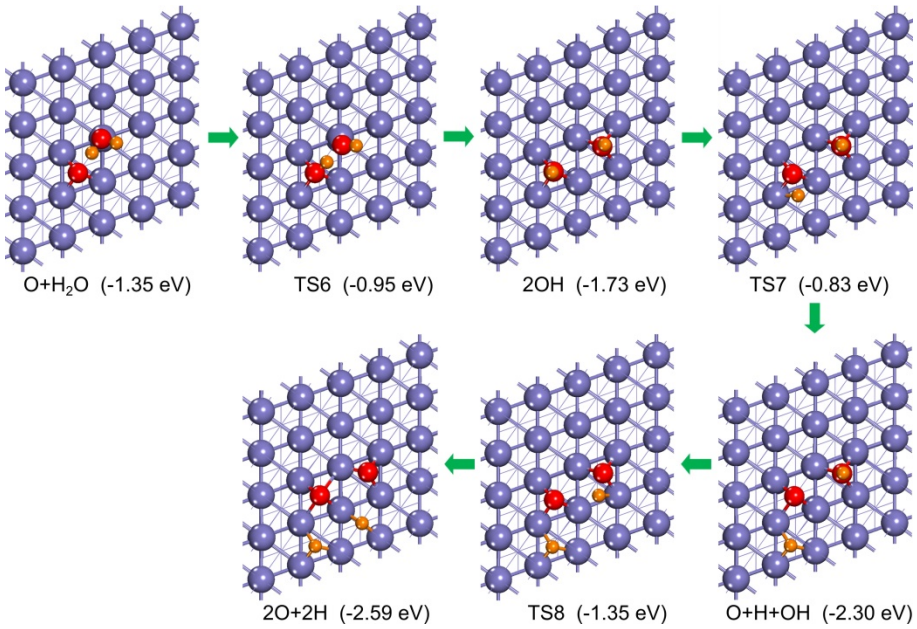


Figure S3. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 2O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

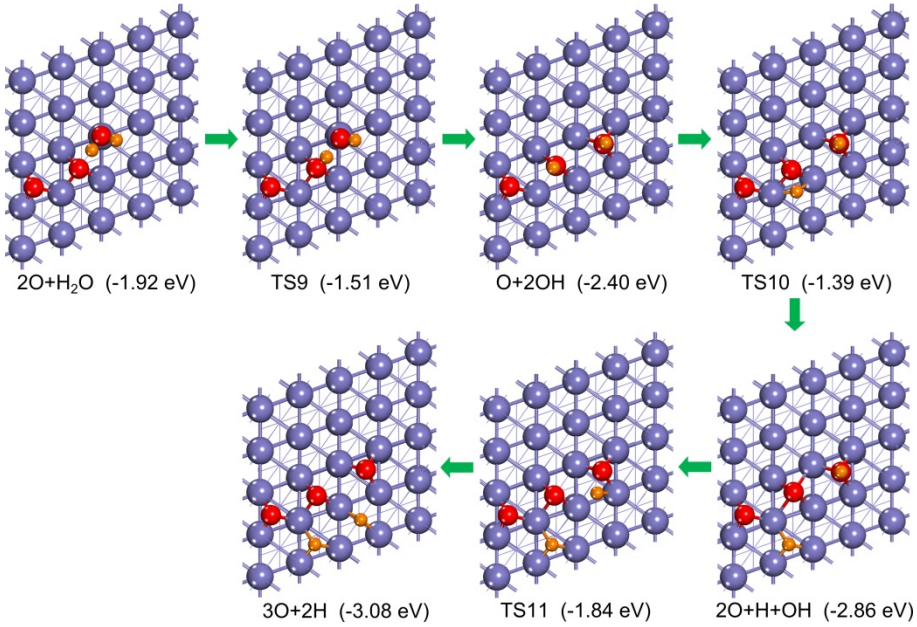


Figure S4. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 3O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

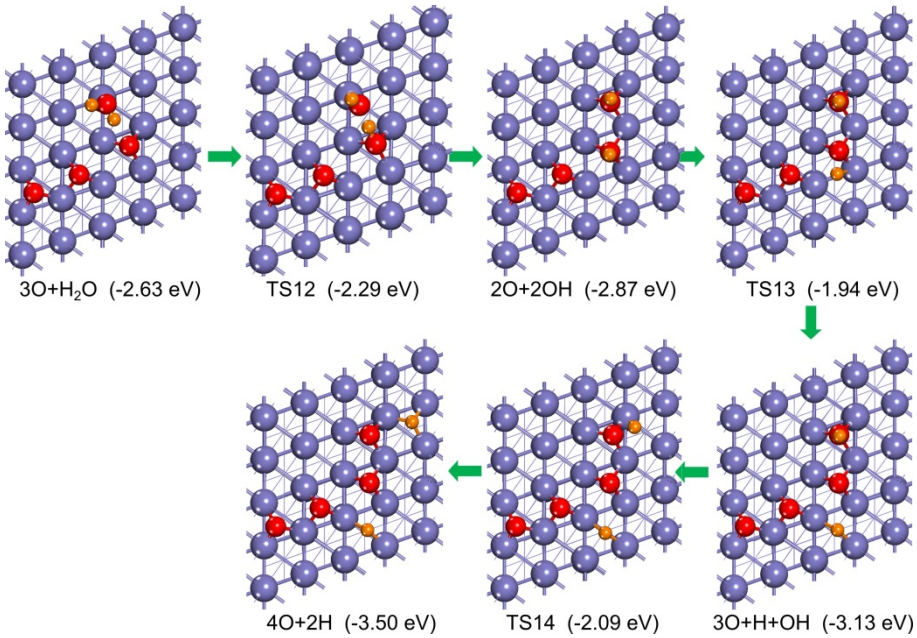


Figure S5. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 4O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

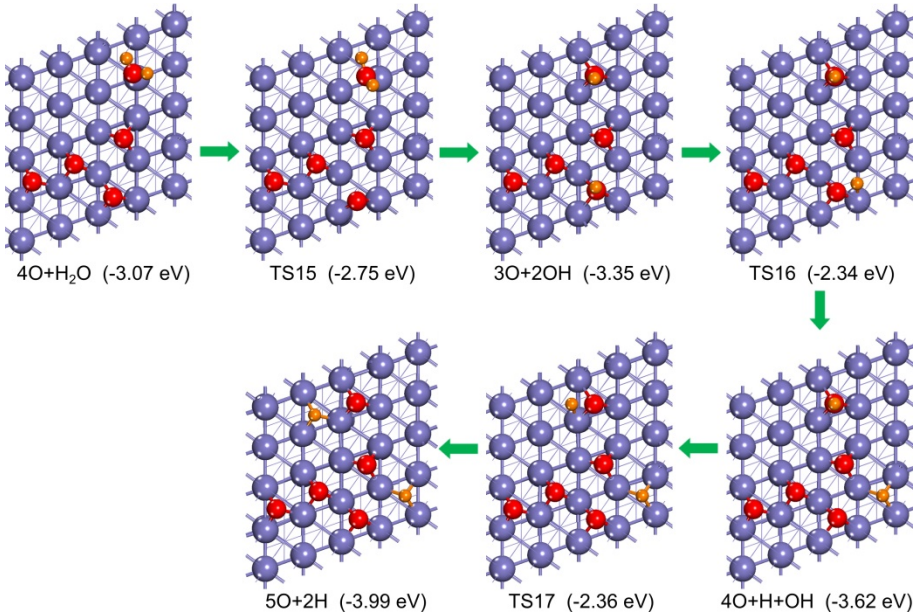


Figure S6. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 5O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

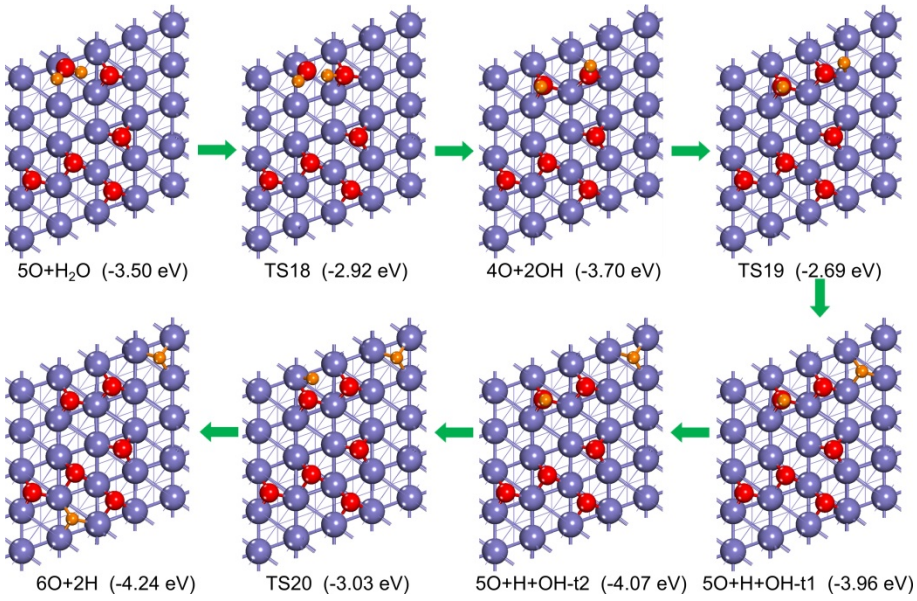


Figure S7. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 6O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

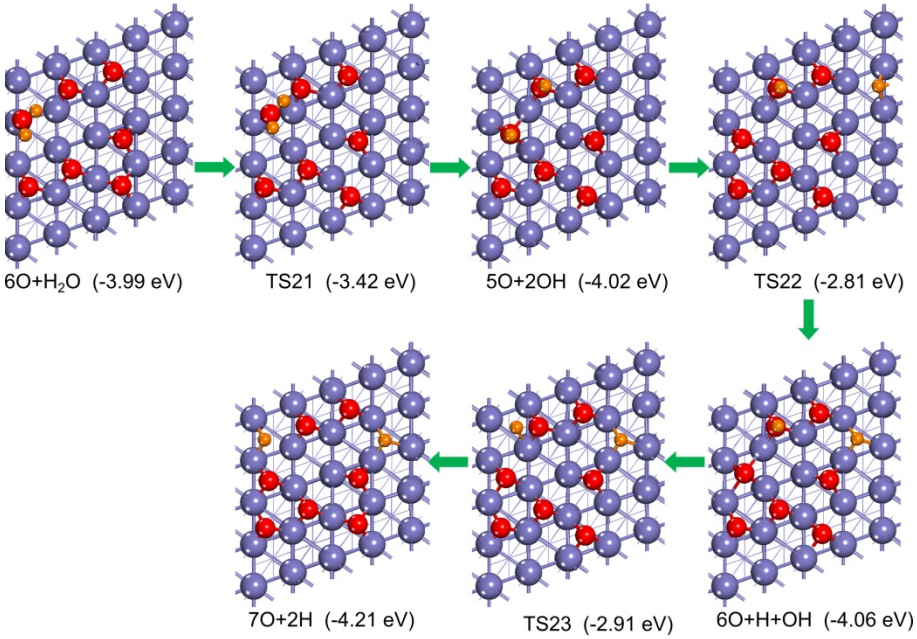


Figure S8. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 7O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

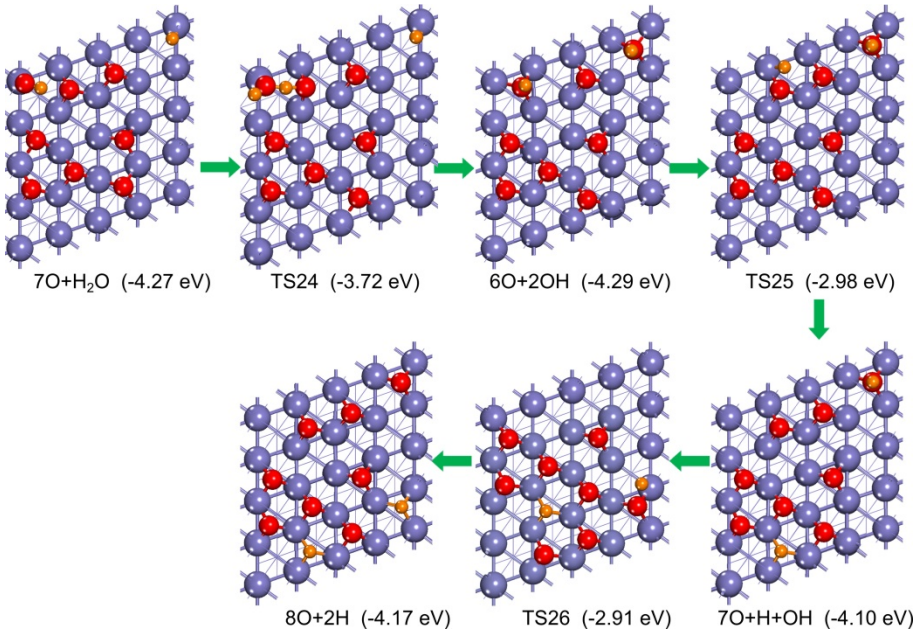


Figure S9. The optimized geometries and the adsorption energy (eV) for the stationary points in the reaction of H_2O dissociation on 8O pre-covered surface (iron/blue; oxygen/red; hydrogen/yellow)

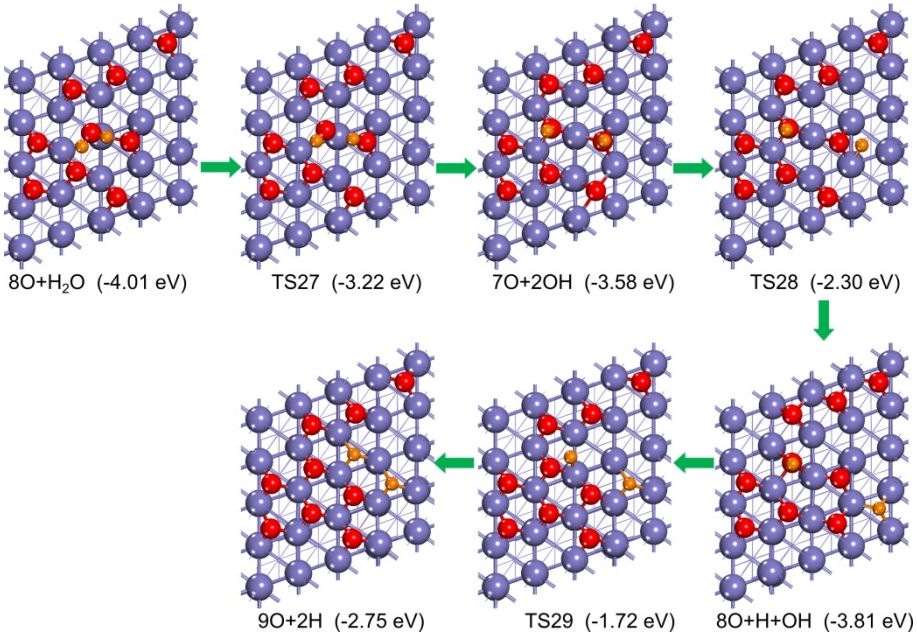
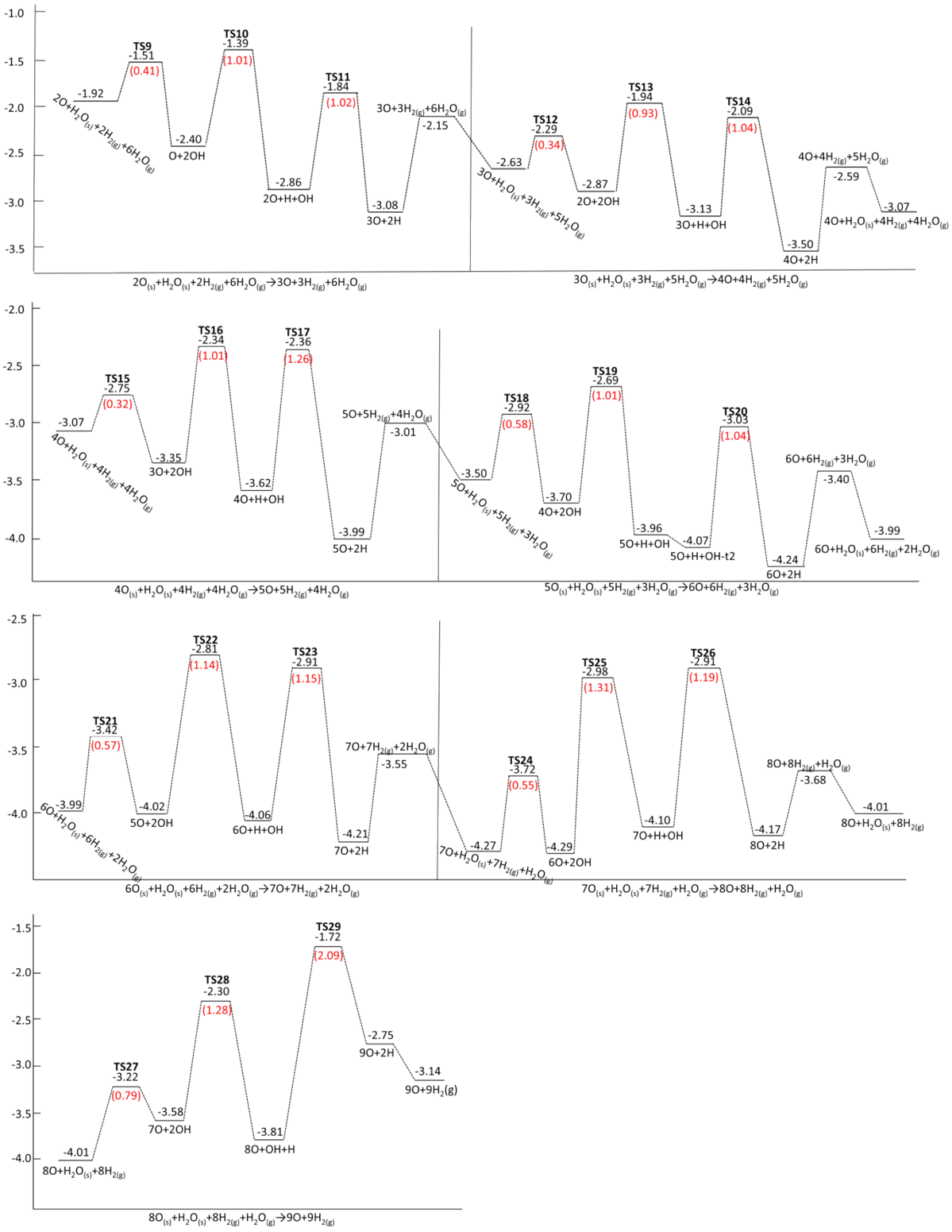


Figure S10: Potential energy surfaces (in eV) for H_2O dissociation on nO(n = 2 - 8) pre-covered Fe(110) surface. The red data in the parentheses are the relevant reaction barriers (s for surface species; and g for gaseous species)



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