Supplement to

"Water Adsorption at the Tetrahedral Titania Surface Layer of

$SrTiO_3(110)$-(4 × 1)"

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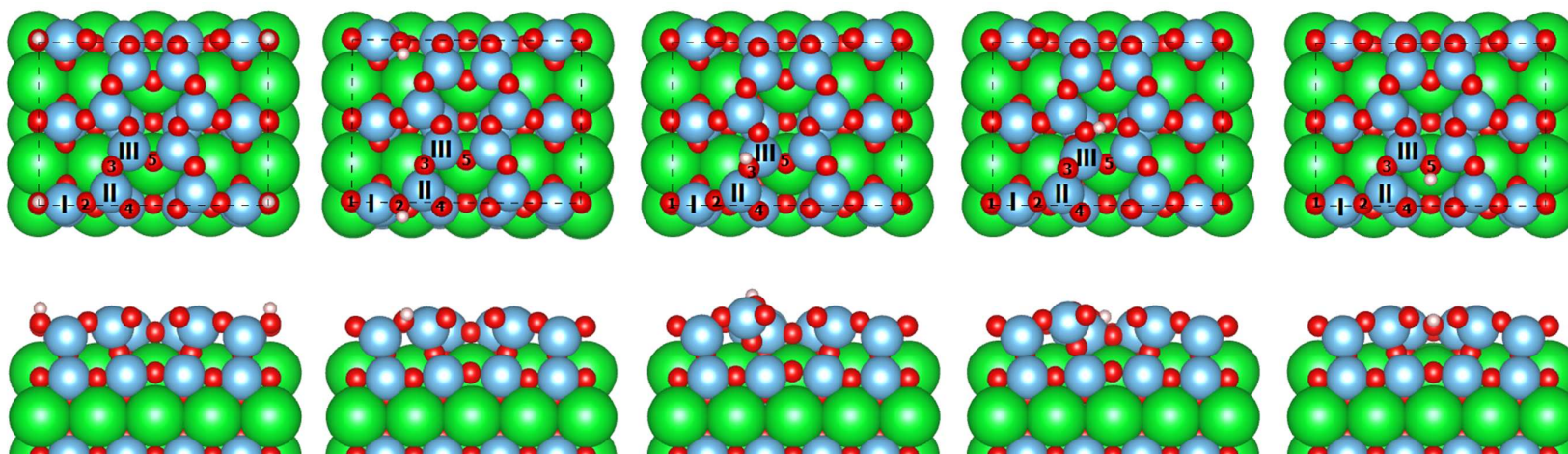# H adsorption on ideal SrTiO₃ (110) (4×1) surface

Figure. S1 Schematic view of atomic H atom adsorbed on SrTiO$_3$ (110) (4×2). The green (large), blue (medium), red (small), and white (smallest) spheres denote Sr, Ti, O, and H atoms, respectively. The configurations from left to right correspond to the hydrogen atom adsorbed on O1 -- O5 atoms as labeled in the figure. Further details are given in the main manuscript, Table 1.

H$_2$O adsorption on ideal SrTiO$_3$ (110) (4×1) surface

Table. S1.Adsorption energies E$_{ads}$ (eV) and bond distances for various molecular adsorption configurations considered with PBE, DFT-D2 and vdW-DFT. O$_w$ denotes the oxygen atom in water, and O$_s$ the oxygen atom located at the surface. M5 is the most stable configuration discussed in the main text.

|	E$_{ads}$ (eV)	Ti--O$_w$ (Å)	H--O$_w$ (Å)	H--O$_s$ (Å)	H--O$_w$--H (°)
DFT-PBE					
M1	-0.376	2.257	0.985,0.986	-	111.70
M2	-0.385	2.387	0.987,0.989	-	106.58
M3	-0.527	2.425,3.010	0.987,0.988	-	107.97
M4	-0.289	-	0.988,0.990	2.074,2.124	103.08
M5	-0.716	2.341	0.987,1.002	2.013	106.16
DFT-D2					
M1	-0.637	2.242	0.986,0.987	-	111.63
M2	-0.598	2.391	0.988,0.989	-	106.40
M3	-0.825	2.418,2.932	0.987,0.988	-	108.31
M4	-0.506	-	0.989,0.990	2.007,2.064	102.90
M5	-1.014	2.325	0.987,1.003	1.978	106.32
vdW-DFT					
M1	-0.721	2.210	0.987,0.987	-	112.49
M2	-0.667	2.348	0.990,0.990	-	106.85
M3	-0.924	2.448,2.552	0.990,0.991	-	109.58
M4	-0.496	-	0.990,0.990	2.087,2.117	103.21
M5	-1.073	2.311	0.989,1.004	2.029	106.38
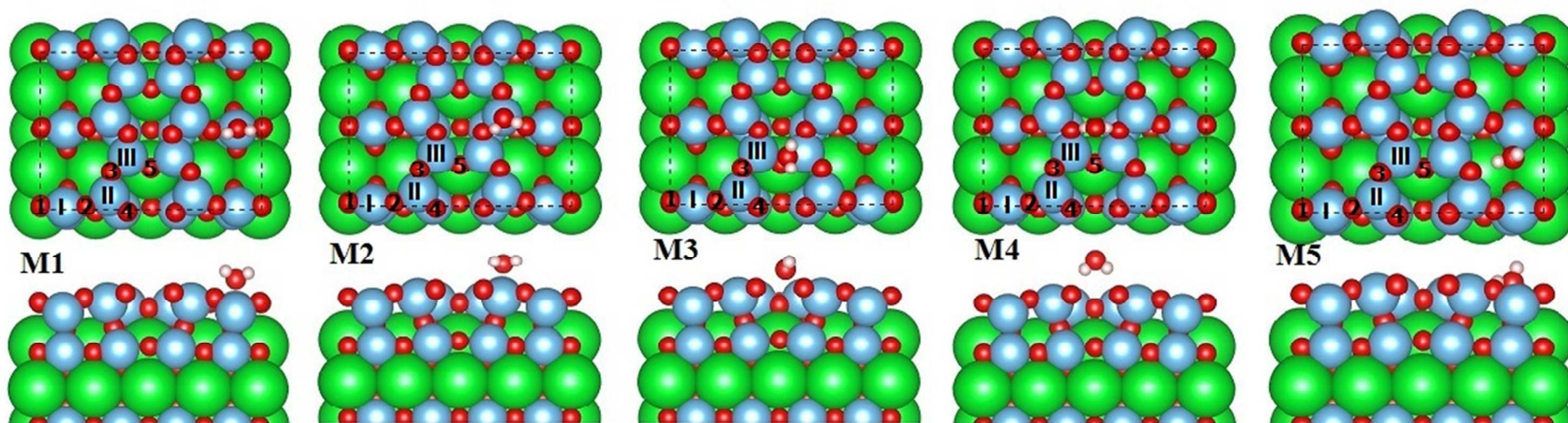
Figure. S2 Schematic view of molecular water adsorbed on SrTiO$_3$ (110) (4×2). The green (large), blue (medium), red (small), and white (smallest) spheres denote Sr, Ti, O, and H atoms, respectively. The configurations from a) to e) correspond to M1 -- M5 listed in the Tab. S1. Only PBE geometries are shown as geometries with other approximation schemes are similar.

Dissociative configurations coadsorption of H and OH

We assumed that OH preferentially adsorbs on a Ti atom, with H on a neighboring/next neighboring surface O atom. Calculations were performed using the PBE scheme only, as DFT-D2 and vdW-DFT increase the adsorption energy, but do not alter the adsorption sequence or geometry. We have identified several local stable configurations as listed in Tab.S2. The geometries of the favorable five configurations are presented in Fig.S3.

Table. S2.Adsorption energies E_{ads} (eV) and bond distances for various dissociative adsorption configurations on non-defective $SrTiO_3$ (110) (4×2) considered within PBE. O_w denotes the oxygen atom in water, and O_s the oxygen atom located on the surface.

	E_{ads} (eV)	Ti--O_w (Å)	H--O_w (Å)	H--O_s (Å)
DFT-PBE				
D1	-0.066	1.953	0.985	1.026
D2	+0.010	1.887	0.990	0.997,2.075
D3	+0.427	1.873	0.986	0.998,2.252
D4	+0.275	1.854	0.986	1.013,1.846
D5	+0.654	1.853	0.986	0.987,2.696
D6	+0.164	1.833	0.984	0.987
D7	-0.779	1.988,2.067	0.990	0.991
D8	+0.720	1.828	0.983	0.993
D9	+0.454	1.826	0.984	0.993
D10	+0.484	1.829	0.984	0.997
D11	-0.168	2.044,2.151	0.990	0.984,2.881
D12	-0.350	2.018,2.019	0.990	0.994

Most of the dissociative adsorption configurations we explored were unstable with positive adsorption energy, while some of them relax to the molecular pattern (not listed in Tab. S2). We found five stable/metastable dissociative configurations with negative/zero adsorption energy, as shown in Fig.S3. The computed adsorption energy for the most stable pattern D7 is -0.779 eV, comparable with the molecular adsorption case. The energy difference between the molecular and dissociative model is just 63 meV, within the computational error. In this configuration, the OH species is anchored at the bridge site between two Ti surface atoms (TiII and TiIII), see Fig. 7b in the main manuscript.
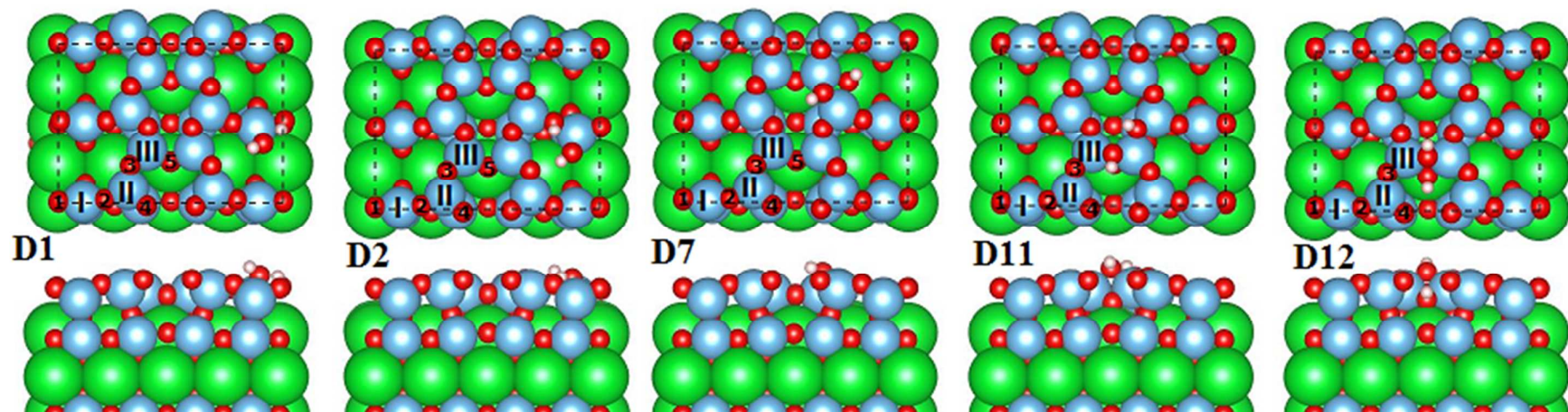
Figure. S3 Schematic view of dissociated water adsorbed patterns on SrTiO$_3$ (110)-(4×2). The green (large), blue (medium), red (small), and white (smallest) spheres denote Sr, Ti, O, and H atoms, respectively. The configurations from left to right correspond to the most favorable configurations D1, D2, D7, D11 and D12 listed in the Tab.S2.

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The energy barrier for the water dissociation processes was determined with the climbing image nudged elastic band (CI-NEB) method to find the minimum energy reaction paths[1] (for details see main text). While the adsorption energy for the D7 configuration is similar to the one for the lowest-energy molecular state, the expected activation barrier is large.

Table. S3. Activation energies E_{act} (eV) and structural characters for various transition state configurations considered within PBE.

	E_{act} (eV)	H--O_w (Å)	H--O_s (Å)
DFT-PBE			
M5-D1	1.72	1.403	1.088
M5-D2	1.80	1.504	1.064
M2-D7	1.72	1.391	1.095
M3-D11	1.57	1.373	1.101
M3-D12	2.16	1.234	1.213
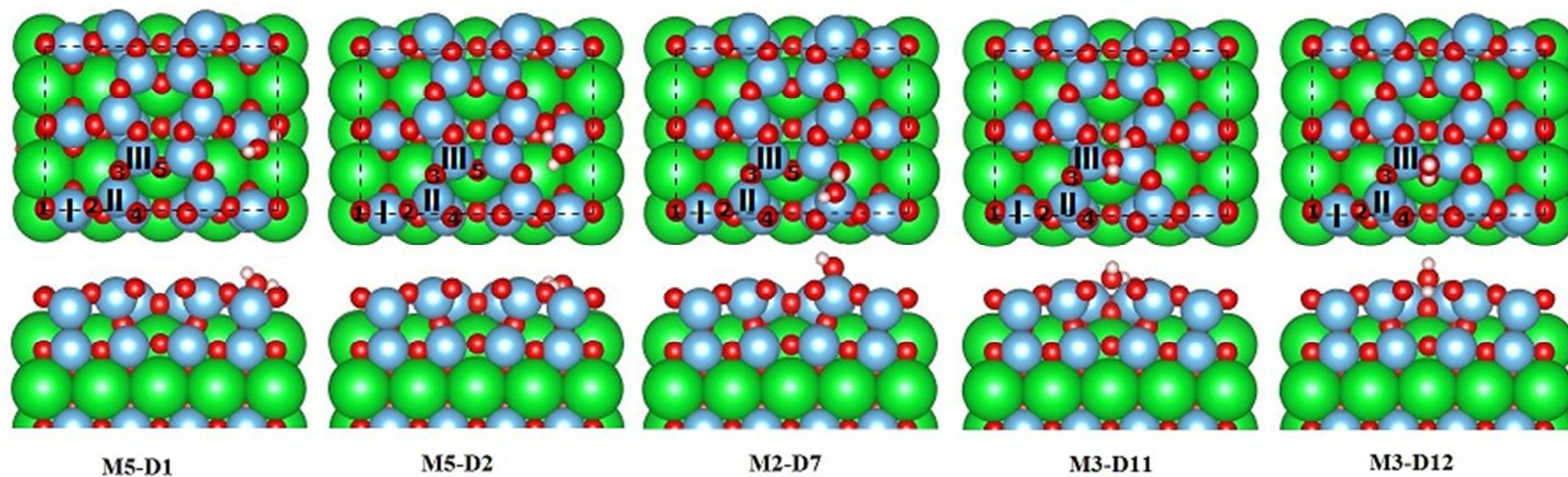
Figure. S4. Schematic view of the water dissociative transition states on the SrTiO$_3$ (110)-(4×2) surface along different reaction paths, the green (large), blue (medium), red (small), and white (smallest) spheres denote Sr, Ti, O, and H atoms, respectively.
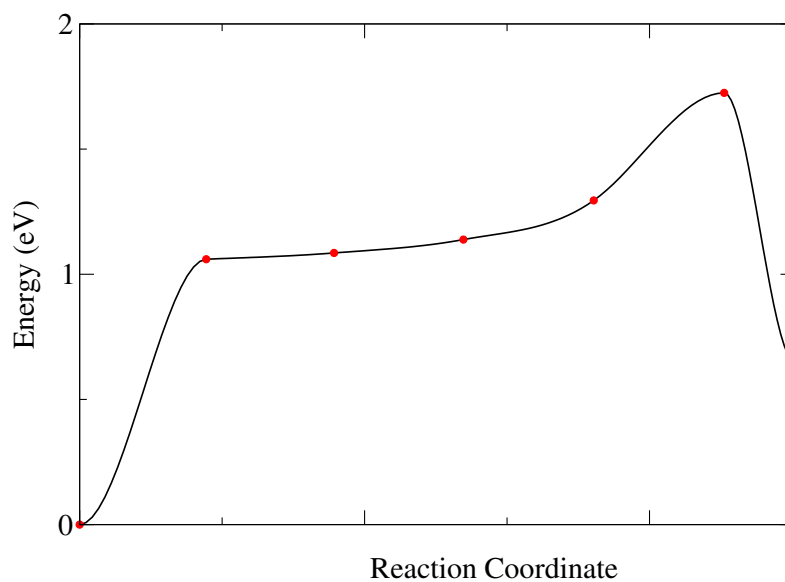
Figure. S5 Energy diagram for dissociation of water on the non-defective SrTiO$_3$ (110)- (4×2) surface along the path from M5 to D1.
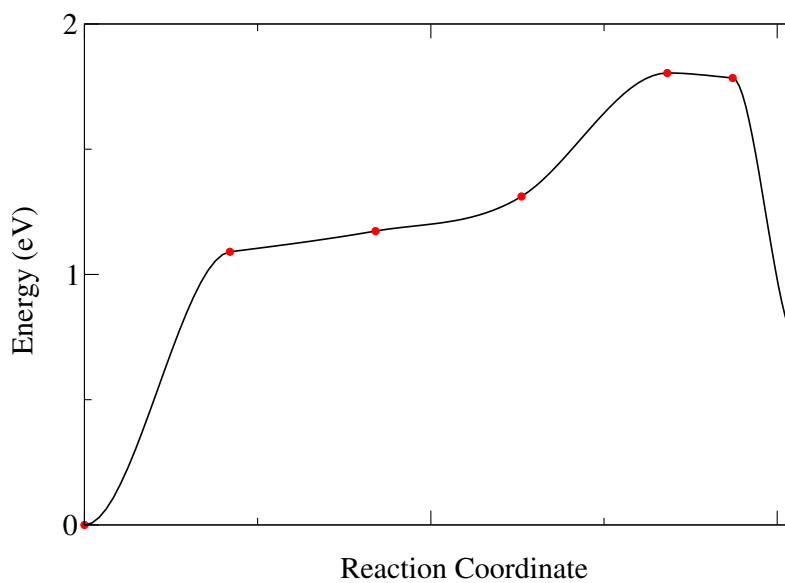

Figure. S6 Energy diagram for dissociation of water on the non-defective SrTiO$_3$ (110)- (4×2) surface along the path from M5 to D2.
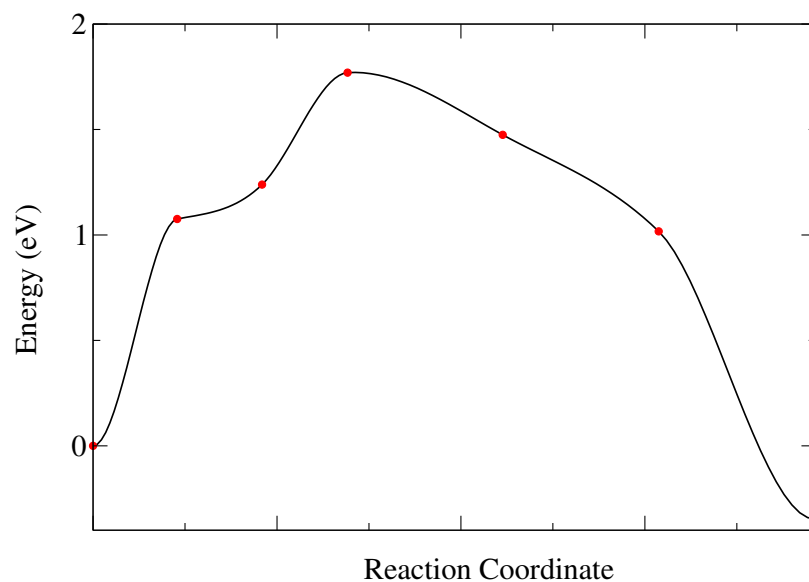
Figure. S7 Energy diagram for dissociation of water on the non-defective SrTiO$_3$ (110)- (4×2) surface along the path from M2 to D7.
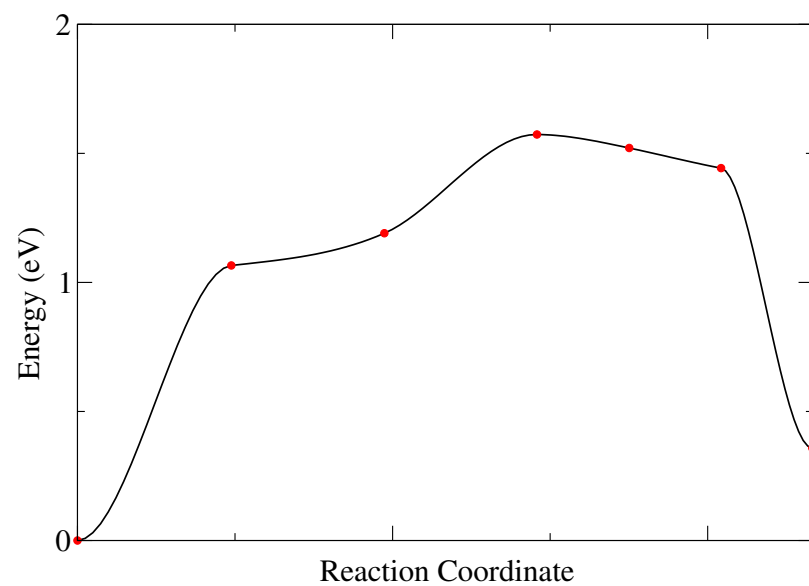

Figure. S8 Energy diagram for dissociation of water on the non-defective SrTiO$_3$ (110)- (4×2) surface along the path from M3 to D11.
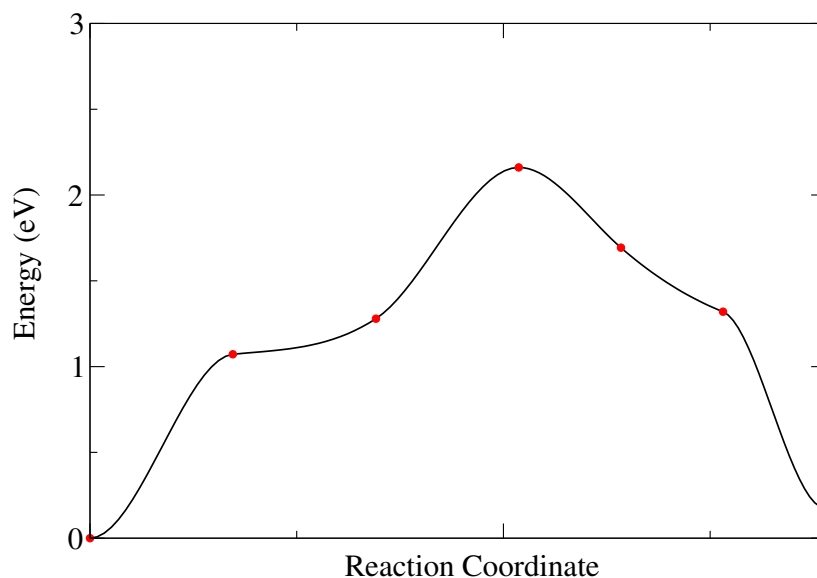
Figure. S9 Energy diagram for dissociation of water on the non-defective SrTiO$_3$ (110)- (4×2) surface along the path from M3 to D12.

Energy profiles that represent the minimum energy path between the initial and final states along the most favorable pathways are presented in Figs.S5-S9. The corresponding transition states geometries and optimized geometrical parameters are shown in Figs.S3 and listed in Tab.S3. In general, the transition state corresponds to geometries where the hydrogen atom is located between the initial and final configuration. The transition barriers for the H$_2$O dissociates on the SrTiO$_3$ (110)- (4×2) surface are rather large (> 1.5 eV), much higher than the adsorption energies, irrespective of the adsorbed pattern: molecular or dissociative, indicating the H$_2$O molecular dissociation should not occur in the absence of an oxygen defect.

References

(1) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901-9904.