Supplementary Information
Modeling pH Effects in the Dynamic Pt(111)/Water Interface Structure on the Atomic Scale.

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The raw data is available in ASE-db format on: http://nano.ku.dk/english/research/theoretical-electrocatalysis/katladb/.
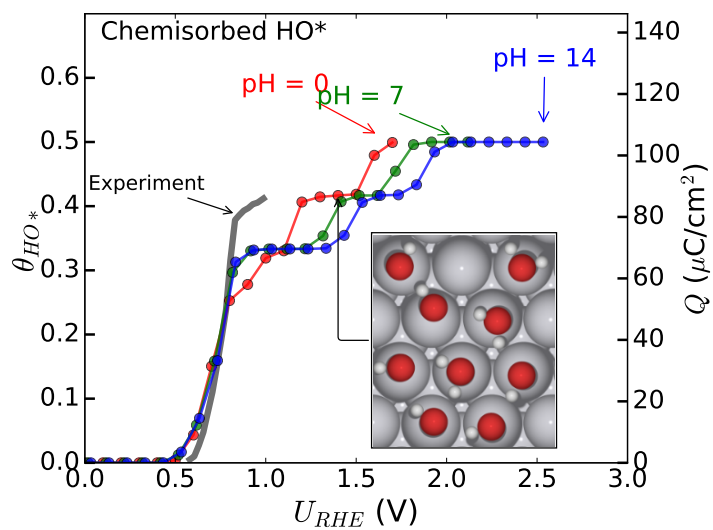
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1 Isotherms

Figure S.1: *HO* coverage isotherm calculated using the GCHE method in the $n < 0$ region from liquid water structures from molecular dynamics. This figure is repeated from Figure 1 in the paper, but also including pH =7, which was omitted in order to not overcrowd Figure 1.*
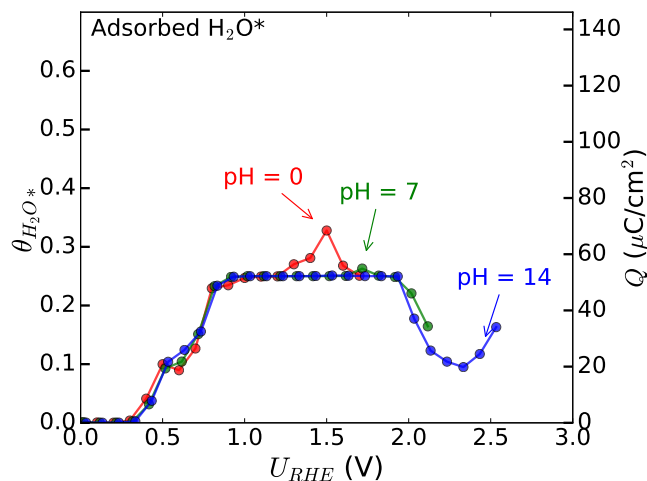
Figure S.2: *Water coverage isotherm calculated using the GCHE method with liquid water structures from molecular dynamics. Water is here defined as adsorbed if the oxygen atom is within 3Å of the surface atoms, and it is only counted for states with $n < 0$.*
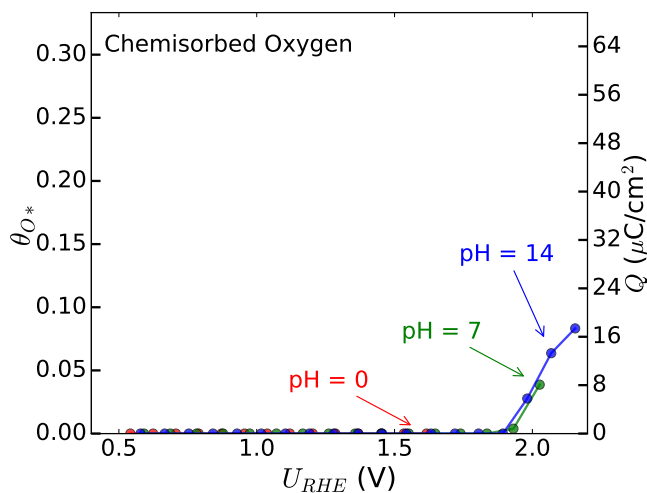

Figure S.3: *Oxygen coverage isotherm calculated using the GCHE method with liquid water structures from molecular dynamics. The green datapoints are at pH = 7 and the blue datapoints are at pH = 14. Note, that the dynamics were not initialized with chemisorbed O*, but at high HO* coverages it spontaneously formed and is thus present in the ensemble at $n \leq -6$.*
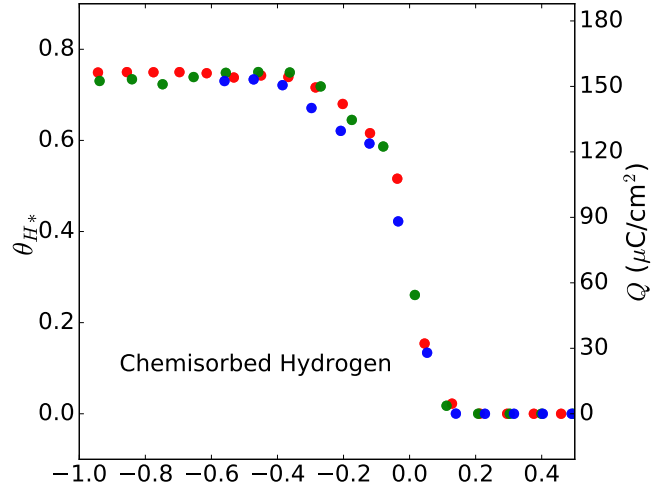
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Figure S.4: θ_H *calculated using the GCHE method with liquid water struc-tures from molecular dynamics. The red datapoints are at pH = 0, the green points are pH = 7 and the blue datapoints are at pH = 14*
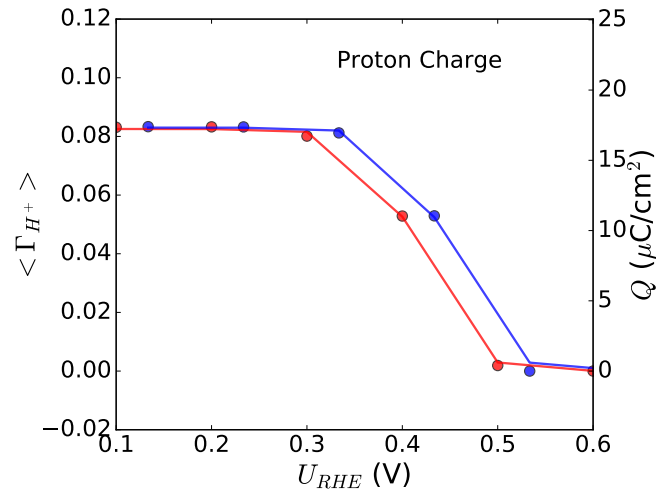

Figure S.5: Γ_{H^+} *calculated using the GCHE method with liquid water struc-tures from molecular dynamics. The red datapoints are at pH = 0 and the blue datapoints are at pH = 14*

2 Relaxed Structures
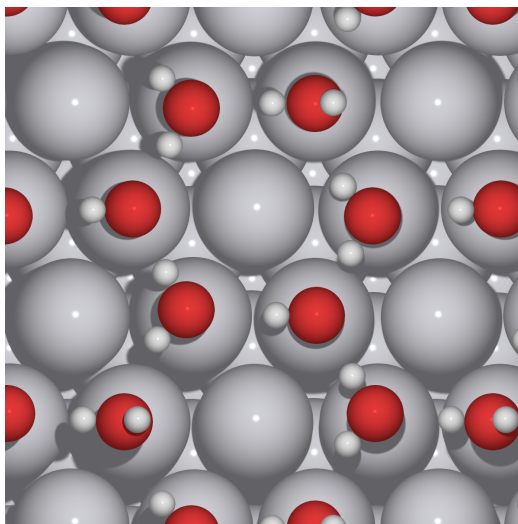

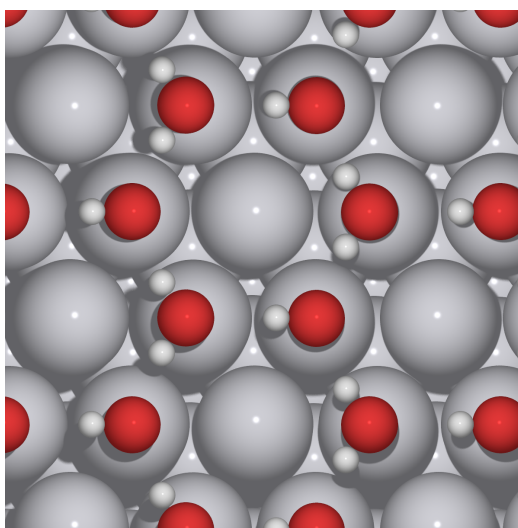Figure S.6: Top view of a relaxed 1/6 ML HO* structure with 1/2 ML water.

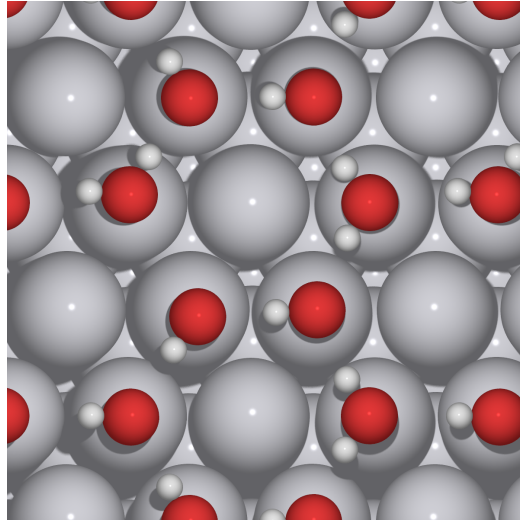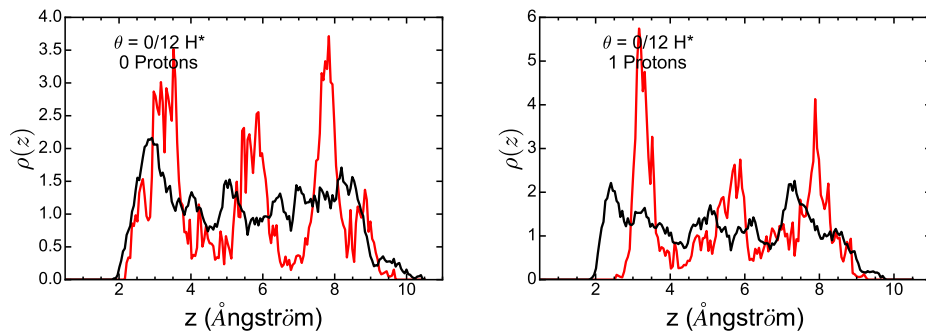Figure S.7: Top view of a relaxed 1/3 ML HO* structure with 1/3 ML water.

Figure S.8: Top view of a relaxed 5/12 ML HO* structure with 3/12 ML water.

3 Structure averages versus proton excess and coverage

(a) The subset where $n = \theta_H = \Gamma_{H^+} = 0$.

(b) The subset where $\theta_H = 0$ and $\Gamma_{H^+} = 1/12$.

Figure S.9: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface.

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(a) $n = \theta_H = \Gamma_{H^+} = 0$.

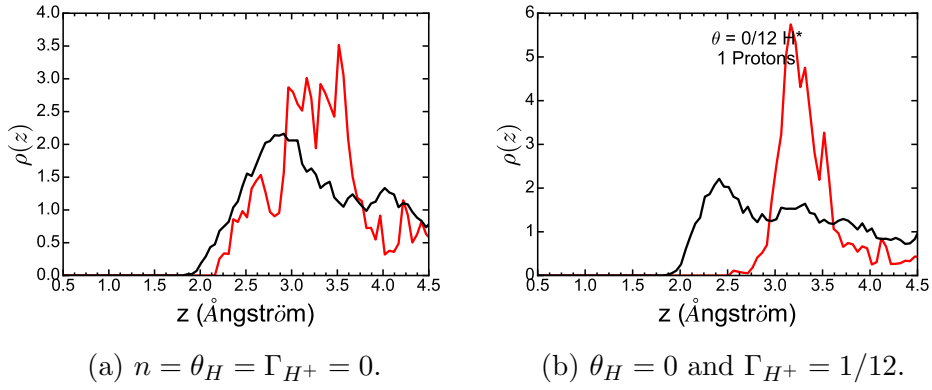(b) $\theta_H = 0$ and $\Gamma_{H^+} = 1/12$.

Figure S.10: Zoomed views of $\rho(z)$. The red lines are the $\rho(z)$ of oxygen and the black lines are the $\rho(z)$ of hydrogen atoms.

(a) The subset where $n = \theta_H = 0 = \Gamma_{H^+} = 0$.

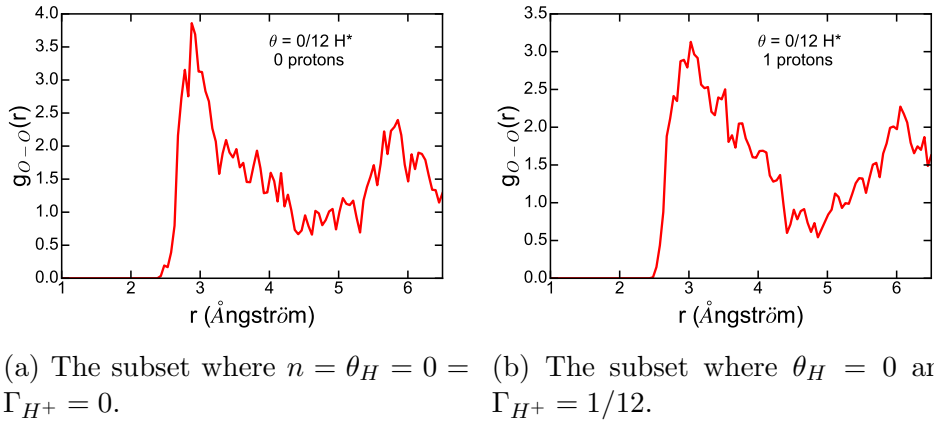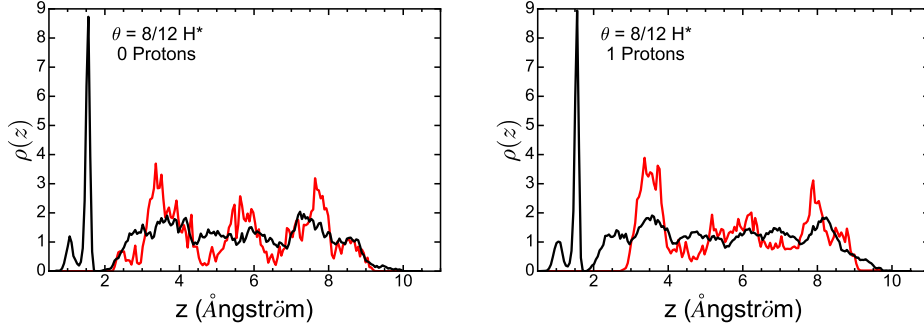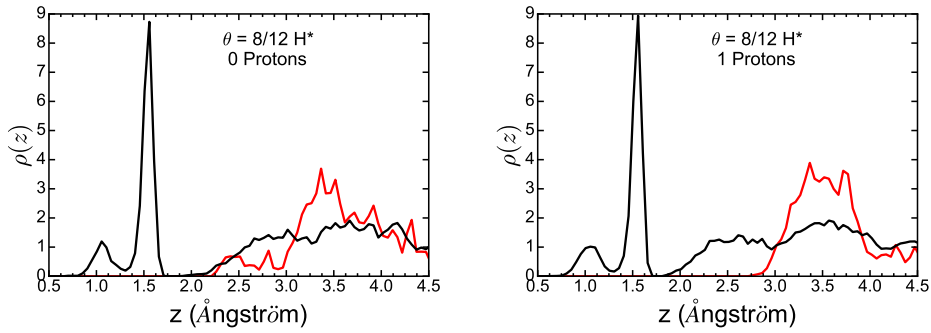(b) The subset where $\theta_H = 0$ and $\Gamma_{H^+} = 1/12$.

Figure S.11: In-plane O-O pair correlation functions around the first layer of water. The cut off planes were at $z = 2.75$ Å and $z = 3.75$ Å from the surface.
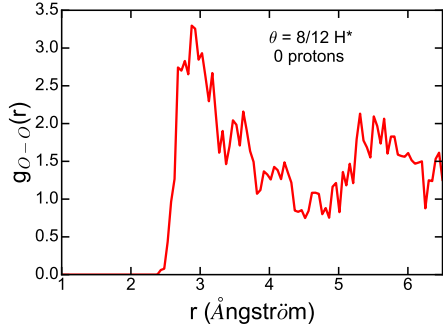
(a) The subset where $\theta_H = 8/12$ and $\Gamma_{H^+} = 0$.

(b) The subset where $\theta_H = 8/12$ and $\Gamma_{H^+} = 1/12$.

Figure S.12: The density, $\rho(z)$, of O atoms (red lines) and H atoms (black lines) versus distance from the surface.
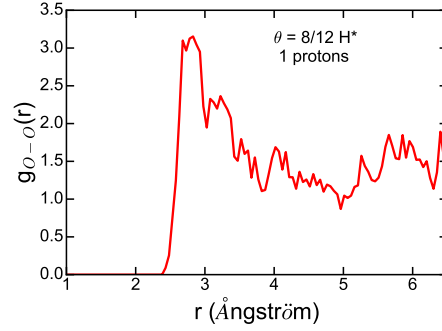

(a) $\theta_H = 8/12$ and $\Gamma_{H^+} = 0$.

(b) $\theta_H = 8/12$ and $\Gamma_{H^+} = 1/12$.

Figure S.13: Zoomed views of $\rho(z)$. The red lines are the $\rho(z)$ of oxygen and the black lines are the $\rho(z)$ of hydrogen atoms.
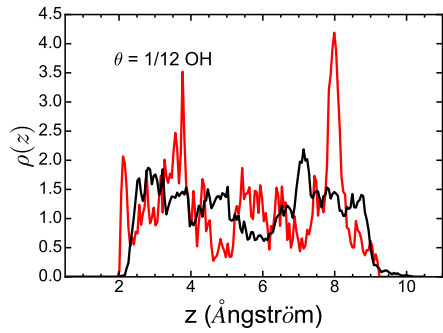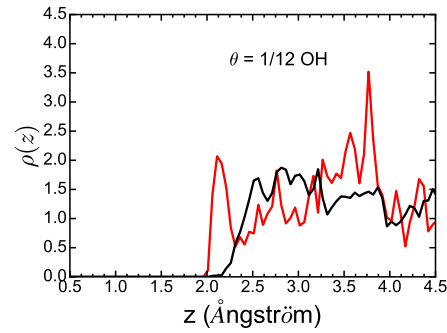
(a) $\theta_H = 8/12$ and $\Gamma_{H^+} = 0$. (b) $\theta_H = 8/12$ and $\Gamma_{H^+} = 1/12$.

Figure S.14: In-plane O-O pair correlation functions around the first layer of water. The cut off planes were at $z = 2.75$ Å and $z = 3.75$ Å from the surface.
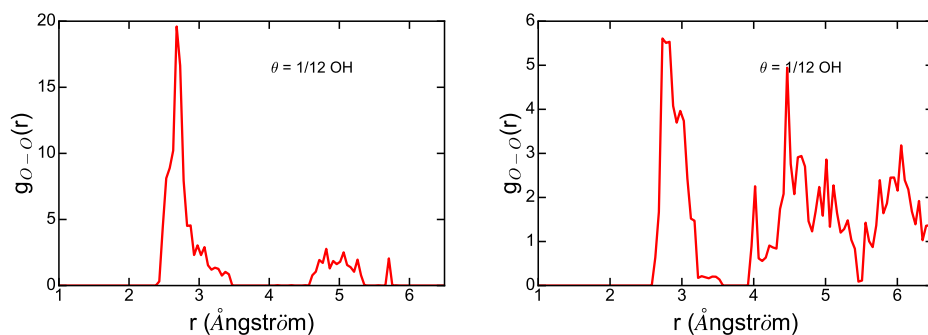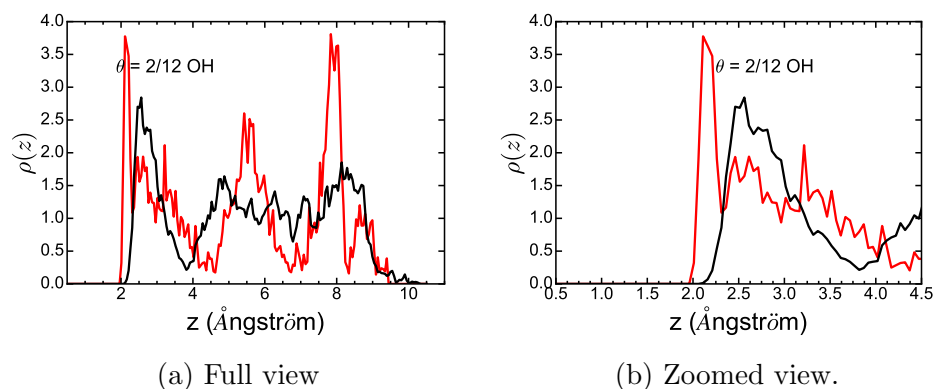

(a) Full view. (b) Zoomed view.

Figure S.15: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface, in the subset where $n = -1$.

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(a) The cut off planes were at $z = 1.8$ Å and $z = 2.6$ Å from the surface.

(b) The cut off planes were at $z = 2.35$ Å and $z = 3.0$ Å from the surface.

Figure S.16: In-plane O-O pair correlation functions around the closest layer of oxygen atoms to the surface (in panel a) and the second closest layer (in panel b).

(a) Full view

(b) Zoomed view.

Figure S.17: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface, in the subset where $n = -2$.
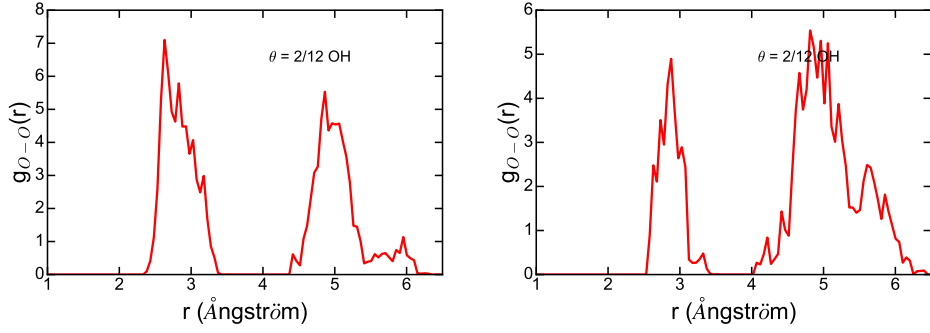
(a) The cut off planes were at $z = 1.8$ Å and $z = 2.6$ Å from the surface.

(b) The cut off planes were at $z = 2.35$ Å and $z = 3.0$ Å from the surface.

Figure S.18: In-plane O-O pair correlation functions around the closest layer of oxygen atoms to the surface (in panel a) and the second closest layer (in panel b).
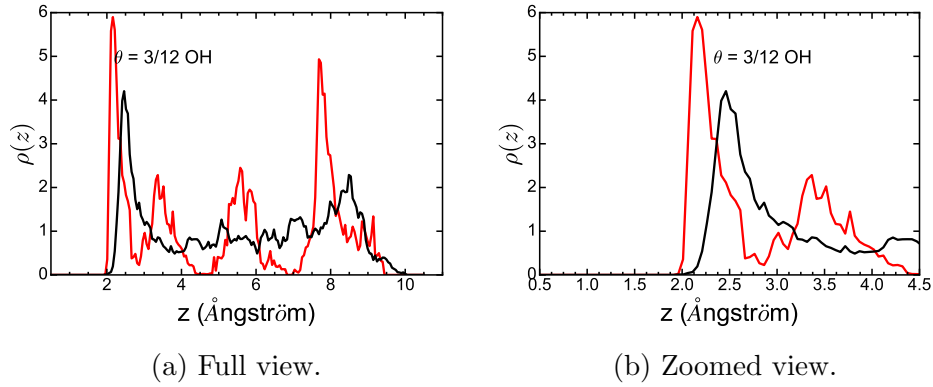

(a) Full view.

(b) Zoomed view.

Figure S.19: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface, in the subset where $n = -3$.

(a) The cut off planes were at $z = 1.8$ Å and $z = 2.6$ Å from the surface.

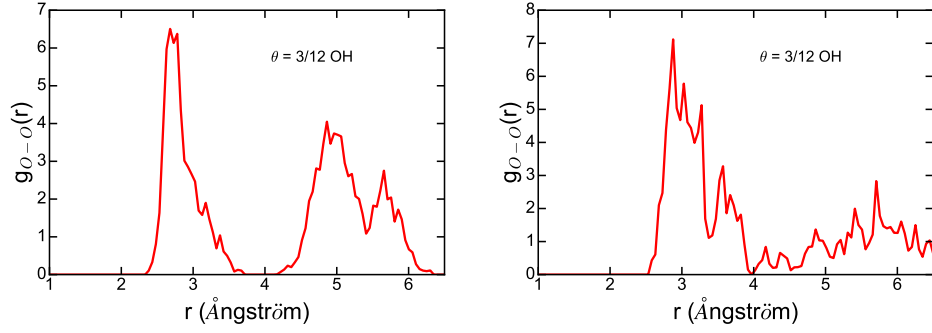(b) The cut off planes were at $z = 3.2$ Å and $z = 3.8$ Å from the surface.

Figure S.20: In-plane O-O pair correlation functions around the closest layer of oxygen atoms to the surface (in panel a) and the second closest layer (in panel b).
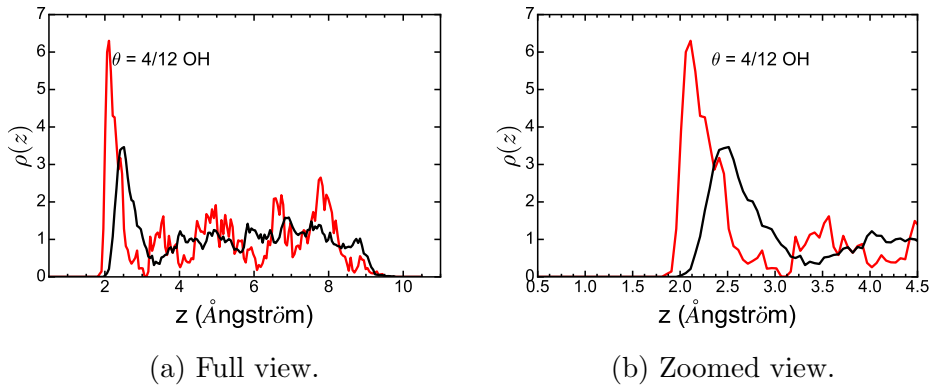

(a) Full view.

(b) Zoomed view.

Figure S.21: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface, in the subset where $n = -3$.

(a) The cut off planes were at $z = 1.8$ Å and $z = 2.6$ Å from the surface.

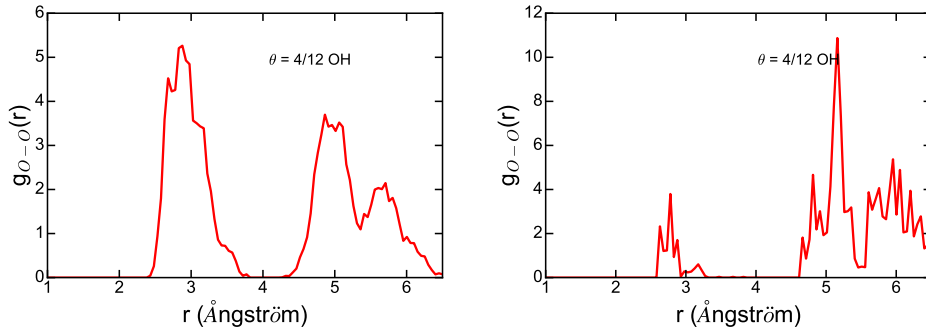(b) The cut off planes were at $z = 3.2$ Å and $z = 3.8$ Å from the surface.

Figure S.22: In-plane O-O pair correlation functions around the closest layer of oxygen atoms to the surface (in panel a) and the second closest layer (in panel b).
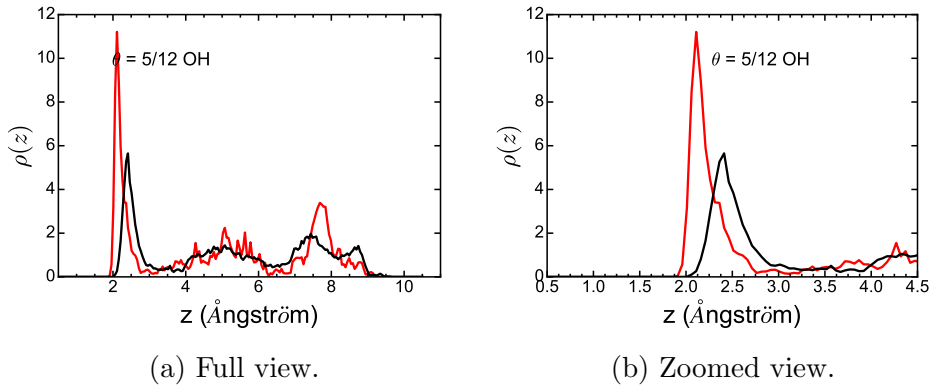

(a) Full view.

(b) Zoomed view.

Figure S.23: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface, in the subset where $n = -5$.

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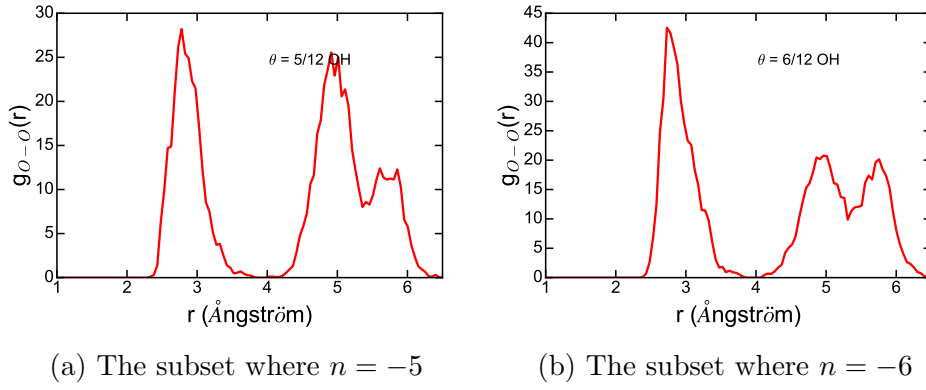(a) The subset where $n = -5$ (b) The subset where $n = -6$

Figure S.24: In-plane O-O pair correlation functions around the closest layer of oxygen atoms to the surface. In both panels, the cut off planes were at $z = 1.8$ Å and $z = 2.6$ Å from the surface.

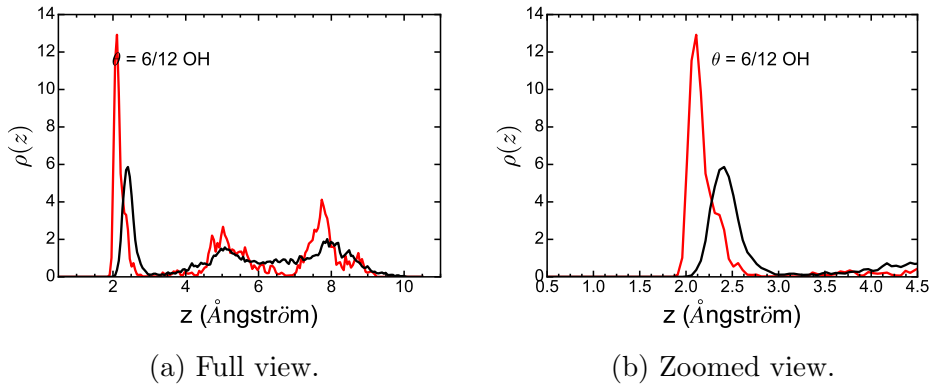

(a) Full view.   (b) Zoomed view.

Figure S.25: The density, $\rho(z)$, of O atoms (red line) and H atoms (black line) versus distance from the surface, in the subset where $n = -6$.
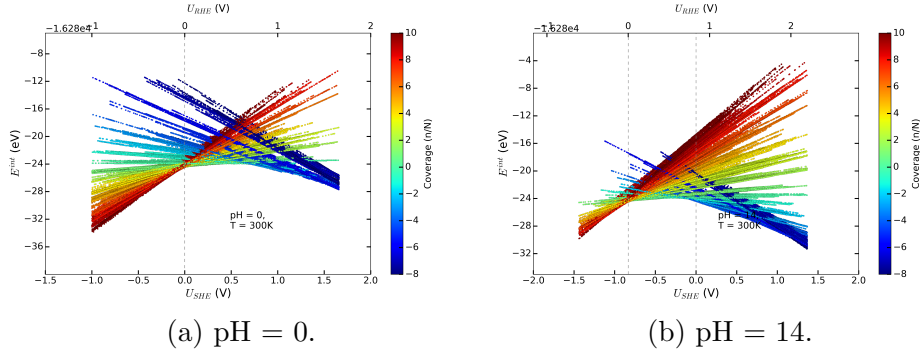
4 Integral Energy Plots

(a) pH = 0.

(b) pH = 14.

Figure S.26: Integral energies of all sampled states versus U_{SHE} and U_{RHE} on the bottom an top axis, respectively.
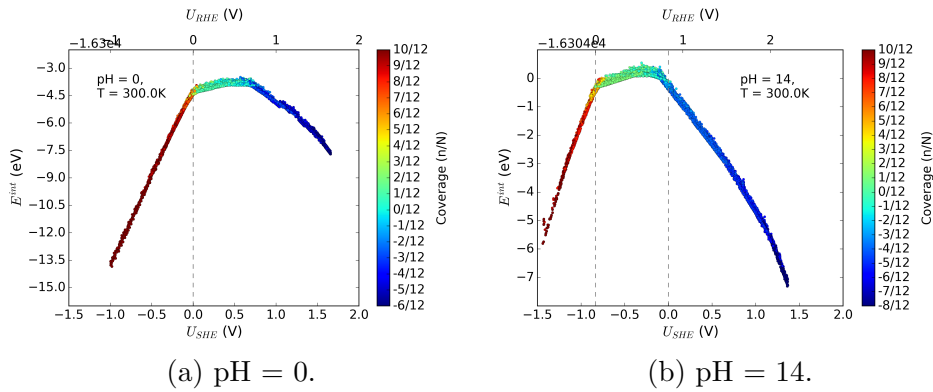

(a) pH = 0.

(b) pH = 14.

Figure S.27: Integral energies of sampled states versus U_{SHE} and U_{RHE} on the bottom an top axis, respectively. These are the ensembles remaining after Monte Carlo annealing at 300 K.

5   Structure convergence.

Below are structural results repeated from Fig. 4-7, compared with results of limiting the sample time to disregard the last 25% of the trajectories.
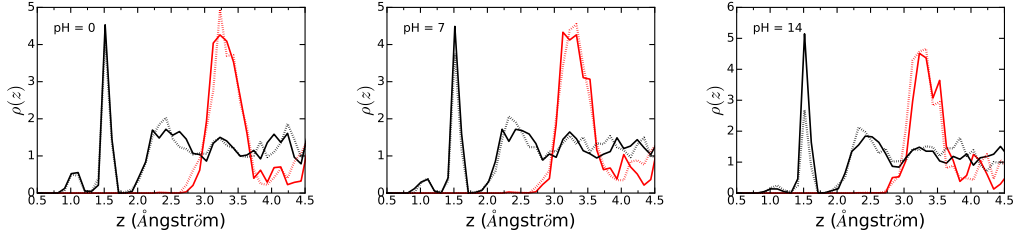

Figure S.28: *Distribution of atomic distances to the surface at 0 V vs. RHE. The red line is for oxygen ions and the black line is for protons. The three panels show the distribution evaluated at various pH. The first two peaks for hydrogen at 1.0 Å and 1.5 Å are attributed to chemisorbed hydrogen in hollow and top sites respectively. The wide third peak from 2 Å to 2.7 Å is due to H-down water. The oxygen function is dominated by a layer around 3 Å to 3.5 Å, which shows the adsorbed water layer. The dashed lines are generated from samples of only 3/4 of the full sample time.*
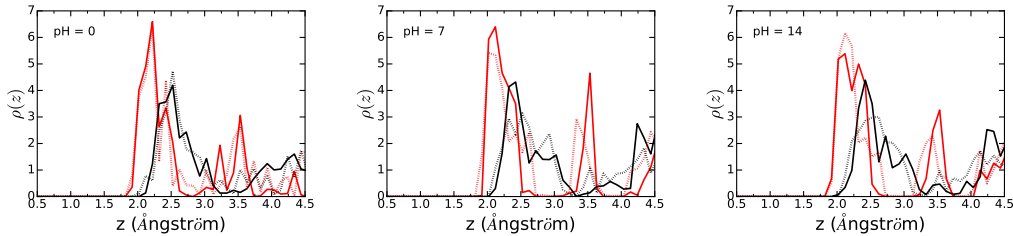

Figure S.29: *Distribution of atomic distances to the surface at 1.0 V vs. RHE. The red line is for oxygen ions and the black line is for protons. The three panels show the distribution evaluated at various pH. The O density is dominated by the first peak at 2.0 Å, which is H_2O^* water and HO^*. No adsorbed hydrogen is visible, but a sharp peak close to the oxygen peak indicates up hydrogen pointing at a shallow angle away from the surface. A second hydrogen peak, distinguishable in the pH = 7 and pH = 14 panels is attributed to down pointing hydrogen from the second layer or up pointing hydrogen from the adsorbed layer. The dashed lines are generated from samples of only 3/4 of the full sample time.*
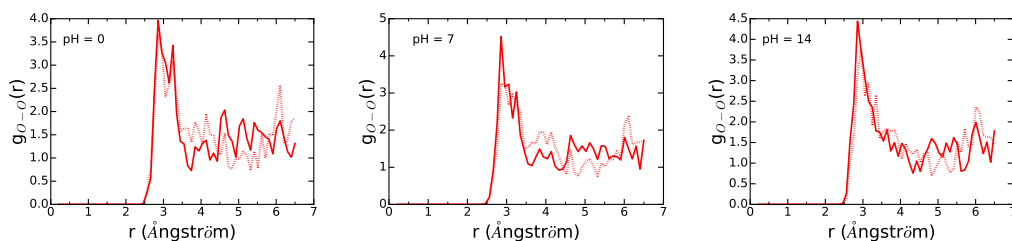
Figure S.30: *O-O pair correlation functions within the first layer of water evaluated at 0.0 V vs. RHE, at various pH. The cut off planes were at z = 2.75 Å and z = 3.75 Å from the surface atoms. The dashed lines are generated from samples of only 3/4 of the full sample time.*
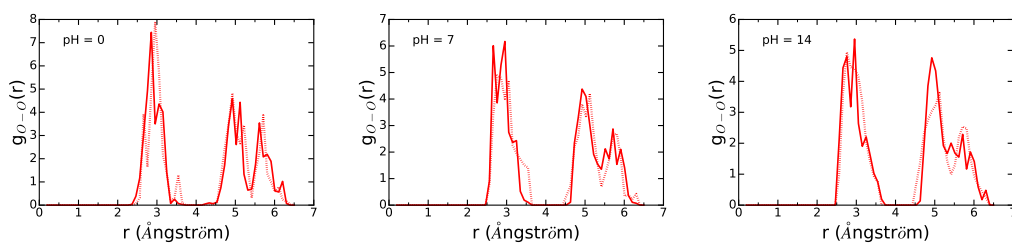

Figure S.31: *O-O pair correlation functions within the first layer of water evaluated at 1.0 V vs. RHE, at various pH. The cut off planes were at z = 1.8 Å and z = 2.6 Å from the surface atoms. The three panels show the functions evaluated at various pH. The dashed lines are generated from samples of only 3/4 of the full sample time.*

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