pH and Alkali Cation Effects on the Pt Cyclic Voltammogram Explained Using Density Functional Theory: Supplementary Information

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Table S1: Adsorption site analysis for K* and H* at 1/9 ML on Pt(111), Pt(100), and Pt(110).

Table S2: Aqueous free energy of $K^+_{(aq)}$ and $H^+_{(aq)}$ calculated using the experimental solvation energy method and the computational hydrogen electrode method (with the equivalent method for potassium, using its standard dissolution potential).

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Table S5: Charge on K* as evaluated by a Bader charge analysis as a function of coverage on Pt(111), Pt(100), and Pt(110).

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Table S9: Gibbs free energy of interaction between K* and H* as a function of coverage on Pt(111), Pt(100), and Pt(110).

Table S10: Charge on hydrogen when co-adsorbed at 1 ML with K* as a function of K* coverage on Pt(111), Pt(100), and Pt(110).

Table S11: Adsorption potential of 1/9 ML OH* on Pt(111), Pt(100), and Pt(110) in the absence and presence of 1/9 ML K*.

Table S12: Adsorption potential of 1/9 ML K* into H_2O and $OH+H_2O^*$ structures on Pt(111) (100) and (110).

Simulating Cyclic Voltammograms (Comments)

Figure S13: Simulated cyclic voltammograms for hydrogen adsorption/desorption on (H*, black line), hydroxide adsorption/desorption (OH*, blue line), and their sum (H*+OH*, red line) for adsorption on Pt(100).

Figure S14: Simulated cyclic voltammogram for the sum of hydrogen adsorption/desorption and hydroxide adsorption/desorption (dark red line) for adsorption on Pt(100), from Figure S13. The background gives the experimentally measured cyclic voltammogram for hydrogen and hydroxide adsorption onto a Pt(100) single crystal electrode in a 0.1 M $HClO_4$ electrolyte solution (faint red line) as adapted from N. Garcia-Araez[1].

Images of adsorbed minimum energy structures for H_2O^* and $OH+H_2O^*$ on Pt(111), Pt(100), and Pt(110).

a)

Pt(111) K* Adsorption Site	Energy (eV)
Atop	-210.230
Bridge	-210.306
HCP	**-210.317**
FCC	-210.312

b)

Pt(100) K* Adsorption Site	Energy (eV)
Atop	-205.243
Bridge	-205.331
3-fold	**-205.432**

c)

Pt(110) K* Adsorption Site	Energy (eV)
Atop	-197.676
Short bridge	-197.765
FCC	**-198.084**
Long bridge	-198.018

d)

Pt(111) H* Adsorption Site	Energy (eV)
Atop	-211.021
Bridge	-211.019
HCP	-211.007
FCC	**-211.057**

e)

Pt(100) H* Adsorption Site	Energy (eV)
Atop	-206.080
Bridge	**-206.259**
3-fold	-205.897

f)

Pt(110) H* Adsorption Site	Energy (eV)
Atop	-198.769
Short bridge	**-198.852**
FCC	-198.280
Long bridge	

Table S1: Adsorption site analysis for K* (**a-c**) and H* (**d-f**) at 1/9 ML on Pt(111), Pt(100), and Pt(110).

	Exp. Solvation Energy $G_{C^+_{(gas)}} + \Delta G^{exp}_{solv}$	Comp. Hydrogen Electrode $\frac{1}{2}G_{H_{2\,(g)}} + 4.6$ $G_{K_{(s)}} + E^{exp}_{diss} + 4.6$
H⁺(aq)	0.842	1.147
K⁺(aq)	0.780	0.655

Table S2: Aqueous free energy of $K^+_{(aq)}$ and $H^+_{(aq)}$ calculated using the experimental solvation energy method and the computational hydrogen electrode method (with the equivalent method for potassium, using its standard dissolution potential).

	Free energy (eV)
H₂ (g) 1 atm	-6.906
H₂O (aq)	-14.278
OH⁻ (aq) 1 M	-9.997

Table S3: Free energy H₂, H₂O$_{(aq)}$, and OH⁻$_{(aq)}$.

Pt(111) K* Coverage	Dipole moment (eÅ)
Bare 3x3	0.012
Bare 2x2	0.005
1/9 ML	-1.060
1/4 ML	-0.650
1/3 ML	-1.274
1/2 ML	-0.481
3/4 ML	-0.496
1 ML	-0.793

Pt(100) K* Coverage	Dipole moment (eÅ)
Bare 3x3	0.003
Bare 2x2	0.001
1/9 ML	-1.027
1/4 ML	-0.737
1/2 ML	-0.614
3/4 ML	-0.496
1 ML	-0.440

Pt(110) K* Coverage	Dipole moment (eÅ)
Bare 3x3	-0.033
Bare 2x2	-0.014
1/9 ML	-0.926
1/4 ML	-0.743
1/2 ML	-0.979
3/4 ML	-0.873
1 ML	-0.784

Table S4: Dipole moments for K* on Pt(111), Pt(100), and Pt(110) as a function of coverage.

Pt(111) K* Coverage	Average Bader Charge
1/9 ML	+ 0.834
1/4 ML	+ 0.723
1/3 ML	+ 0.621
1/2 ML	+ 0.550
3/4 ML	+ 0.335
1 ML	+ 0.252

Pt(100) K* Coverage	Average Bader Charge
1/9 ML	+ 0.832
1/4 ML	+ 0.751
1/2 ML	+ 0.560
3/4 ML	+ 0.472
1 ML	+ 0.435

Pt(110) K* Coverage	Average Bader Charge
1/9 ML	+ 0.835
1/4 ML	+ 0.792
1/2 ML	+ 0.708
3/4 ML	+ 0.604
1 ML	+ 0.563

Table S5: Charge on K* as evaluated by a Bader charge analysis as a function of coverage on Pt(111), Pt(100), and Pt(110).
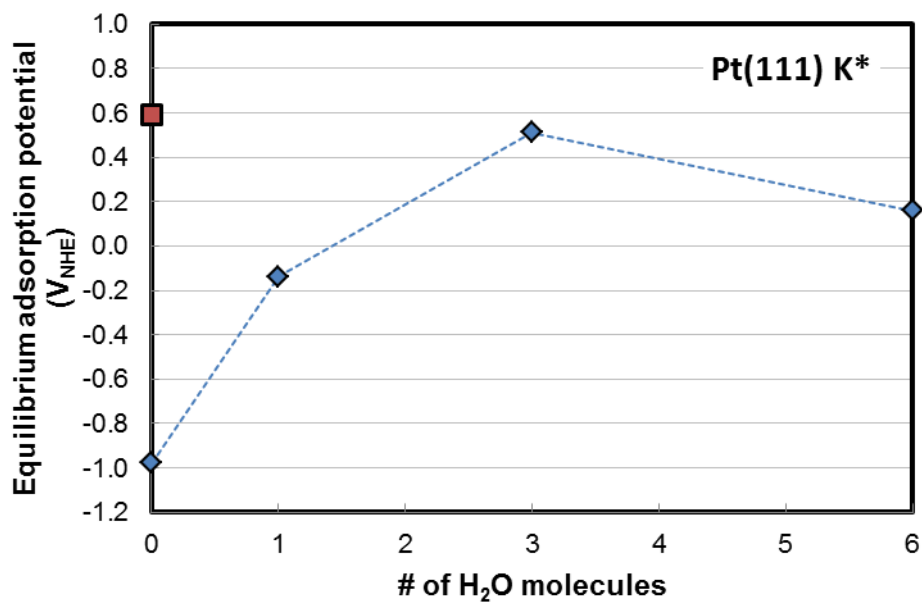
Figure S6: Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode, on the favorability to specifically adsorb potassium on Pt(111), as given by its equilibrium adsorption potential (V_{NHE}).
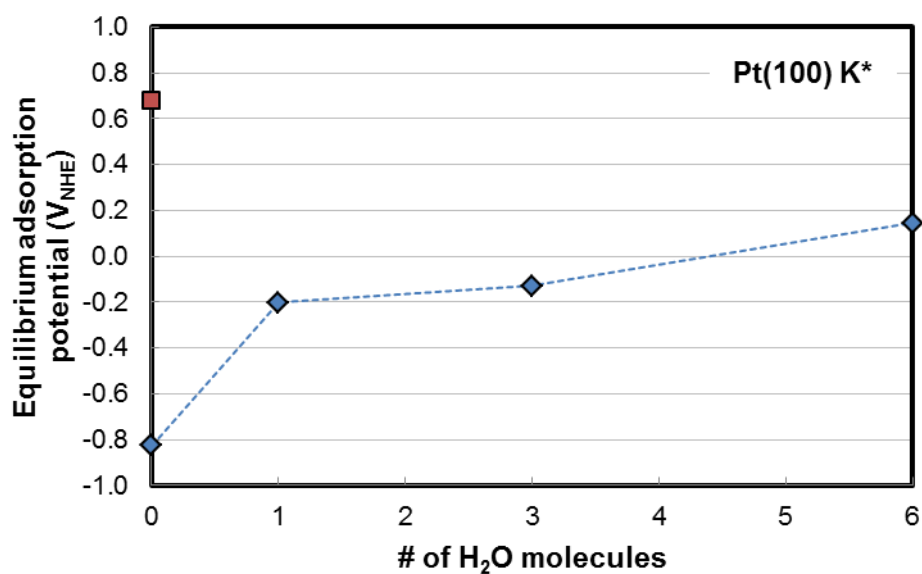
Figure S7: Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamond) or by implicit solvation (red square), on the favorability to specifically adsorb potassium on Pt(100), as given by its equilibrium adsorption potential (V_{NHE}).
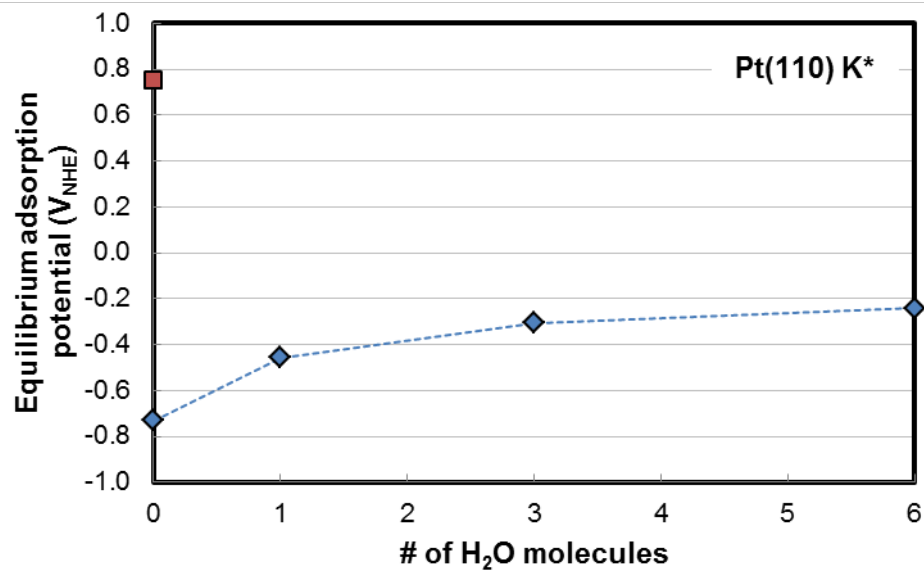
Figure S8: Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamonds) or by implicit solvation (red square), on the favorability to specifically adsorb potassium on Pt(110), as given by its equilibrium adsorption potential (V_{NHE}).

Pt(111)	ΔG_{K-H} interaction (eV) (per H*)
K* 1/9 ML H* 1 ML	0.094
K* 1/4 ML H* 1ML	0.197

Pt(100)	ΔG_{K-H} interaction (eV) (per H*)
K* 1/9 ML H* 1 ML	0.044
K* 1/4 ML H* 1ML	-0.094

Pt(110)	ΔG_{K-H} interaction (eV) (per H*)
K* 1/9 ML H* 1 ML	-0.005
K* 1/4 ML H* 1ML	0.002

Table S9: Gibbs free energy of interaction between K* and H* as a function of coverage on Pt(111), Pt(100), and Pt(110).

Pt(111)	Average H* Bader charge
H* 1ML	0.045
K* 1/9 ML H* 1 ML	0.079
K* 1/4 ML H* 1ML	0.105

Pt(100)	Average H* Bader charge
H* 1ML	0.091
K* 1/9 ML H* 1 ML	0.122
K* 1/4 ML H* 1ML	0.179

Pt(110)	Average H* Bader charge
H* 1ML	0.065
K* 1/9 ML H* 1 ML	0.124
K* 1/4 ML H* 1ML	0.173

Table S10: Charge on hydrogen when co-adsorbed at 1 ML with K* as a function of K* coverage on Pt(111), Pt(100), and Pt(110).

OH⁻(aq) adsorption potential (V_{NHE})	OH* (1/9 ML)	K* + OH* (1/9 ML)
Pt(111)	1.209	-
Pt(100)	0.548	-
Pt(110)	0.780	0.331

Table S11: Adsorption potential of 1/9 ML OH* on Pt(111), Pt(100), and Pt(110) in the absence and for OH* on Pt(110) in the presence of 1/9 ML K*.

	K⁺(aq) Adsorption potential (V_{NHE})
Pt(111) 1/9 ML K* 1/3 ML OH* 1/3 ML H₂O*	-0.491
Pt(100) 1/9 ML K* 1/3 ML OH* 1/3 ML H₂O*	-0.834
Pt(110) 1/4 ML K* 1/2 ML OH* 1/2 ML H₂O*	-1.017

Table S12: Equilibrium adsorption potential of 1/9 ML K* into H_2O and OH+H_2O* structures on Pt(111) (100) and (110). Calculated using the potassium dissolution potential method. Includes dipole correction.

Simulating Cyclic Voltammograms

As can be seen in Figure 4, the simulated cyclic voltammograms for the H/OH phase change reaction on Pt(100) and Pt(110) match experiment well, in terms of the general location (potential) and the size of the adsorption/desorption peak (in both acid and base (Figure 8)). The simulated cyclic voltammograms do not capture the finer details in the shape of both the adsorption peaks on Pt(100) and on Pt(110). This is due our neglecting three important points in the phase change model, as a computational simplification, which, if they were to be captured accurately with DFT, may reproduce all of the details of the experimentally measured cyclic voltammograms. Namely, in the phase change reaction simulated voltammograms, we have neglected the explicit coverage dependence of hydrogen, the coverage dependence of hydroxide, and the fact that they could compete for the same sites on each surface and could co-adsorb (though the interaction between adsorbed hydrogen and hydroxide should be small).

As a simple example, consider Figures S13 and S14, where we have modeled the adsorption of H* and OH* on Pt(100) separately (not as a phase change reaction). While we still neglect competitive adsorption in this case, Figure S14 shows that this yields a much broader peak, removing some of the disagreement with experiment.
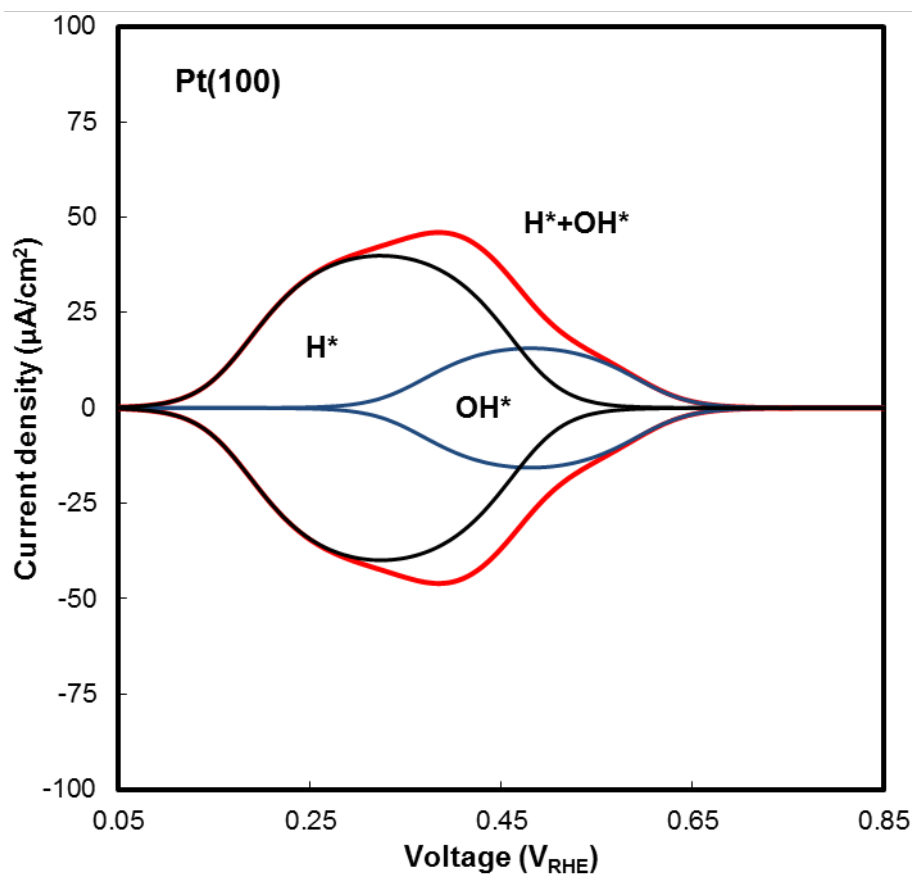
Figure S13: Simulated cyclic voltammograms for hydrogen adsorption/desorption on (H*, black line), hydroxide adsorption/desorption (OH*, blue line), and their sum (H*+OH*, red line) for adsorption on Pt(100). The sum does not include competitive adsorption. The hydrogen adsorption/desorption cyclic voltammogram includes the coverage dependence calculated with DFT and configurational entropy, while hydroxide adsorption/desorption only includes the effect of the configurational entropy on the coverage dependence of hydroxide adsorption. Maximum hydrogen coverage is 1 ML while that of hydroxide is 1/3 ML in the minimum energy hydroxide+water structure (1/3 ML OH* 1/3 ML H_2O*). The scan rate is 50 mV/s, the temperature 300K, and adsorption occurs from a pH=0 electrolyte.
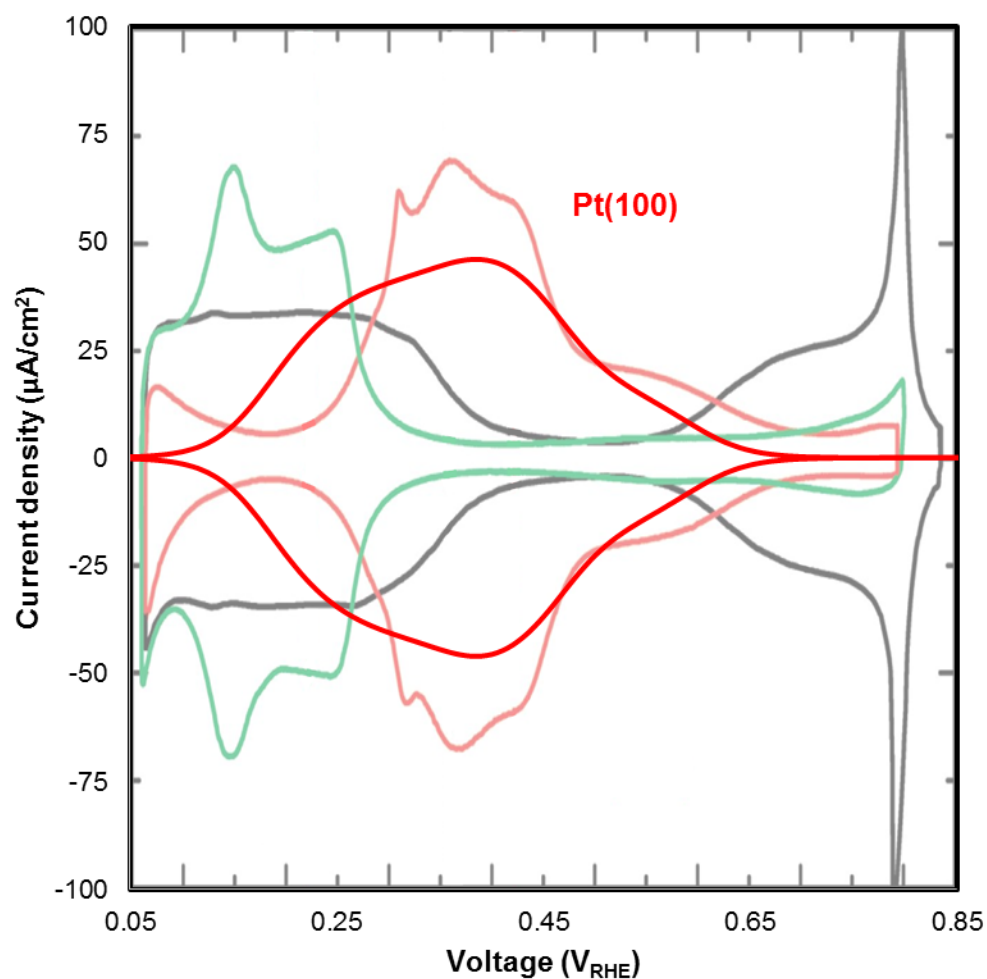
Figure S14: Simulated cyclic voltammogram for the sum of hydrogen adsorption/desorption and hydroxide adsorption/desorption (dark red line) for adsorption on Pt(100), from Figure S13. The background gives the experimentally measured cyclic voltammogram for hydrogen and hydroxide adsorption onto a Pt(100) single crystal electrode in a 0.1 M HClO$_4$ electrolyte solution (faint red line) as adapted from N. Garcia-Araez[1]. The simulated cyclic voltammogram shown here (and in Figure S13) does not include a phase change reaction or competitive adsorption of hydrogen and hydroxide.

Images of adsorbed minimum energy structures for H_2O* and $OH+H_2O$* on Pt(111), Pt(100), and Pt(110).
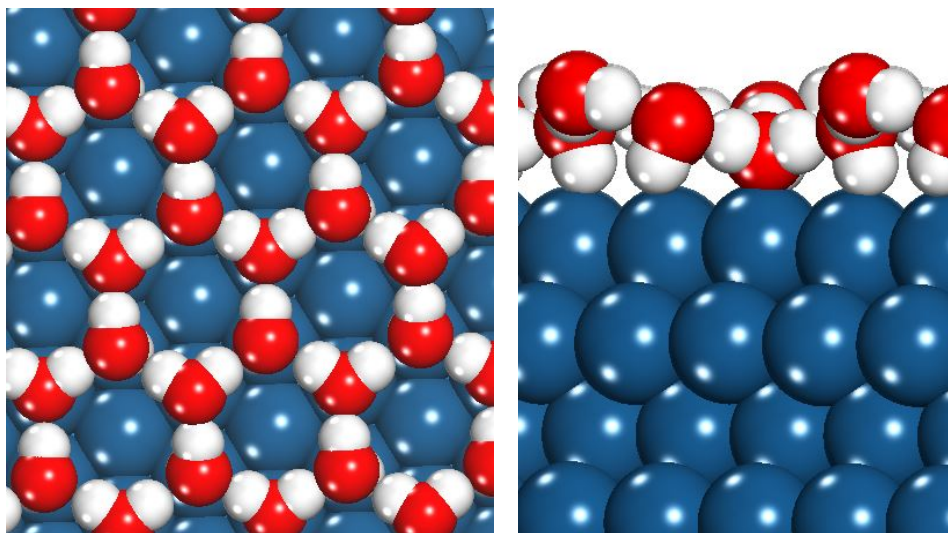
Pt(111)

Pt(111) Minimum energy water structure 6 H_2O* in 3x3 unit cell (6/9 ML H_2O).
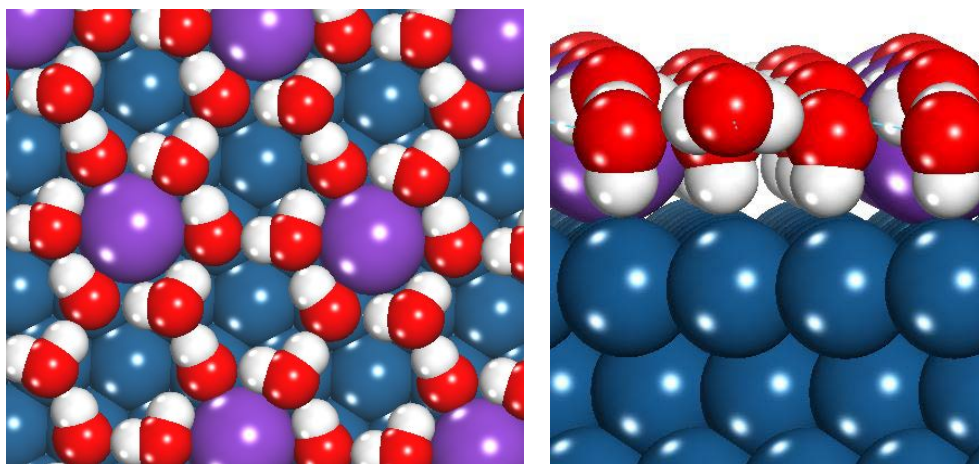
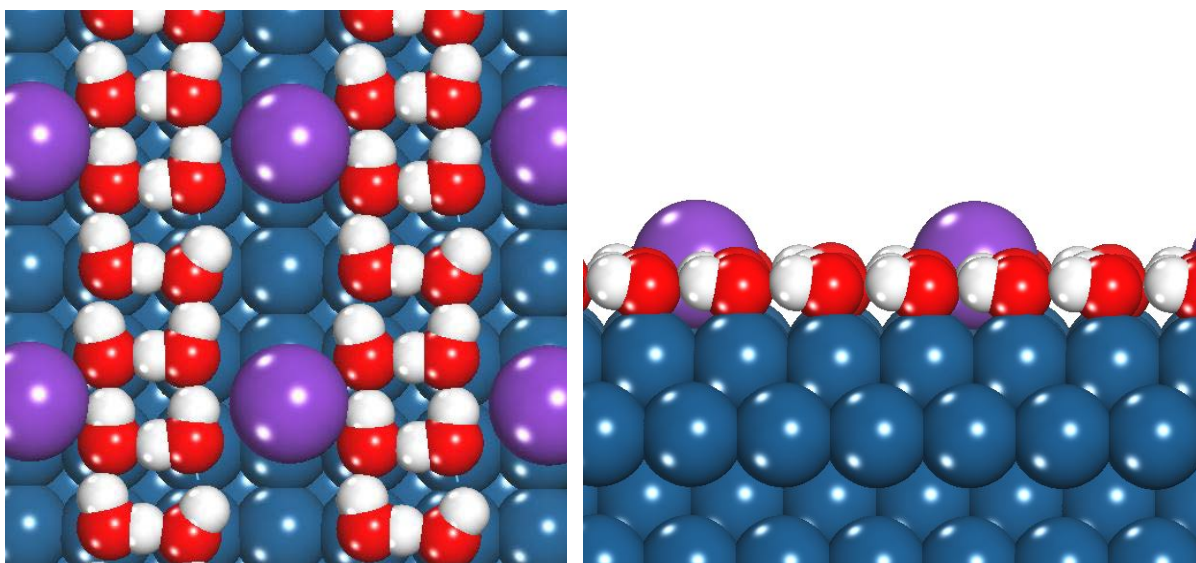
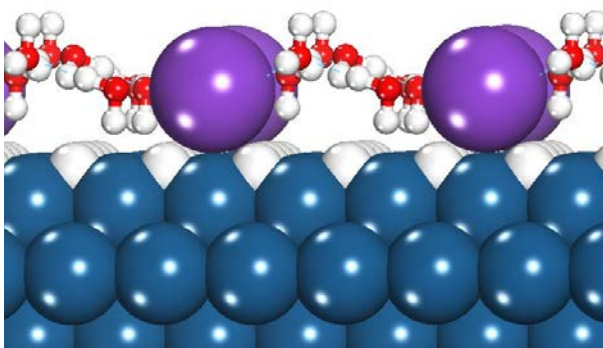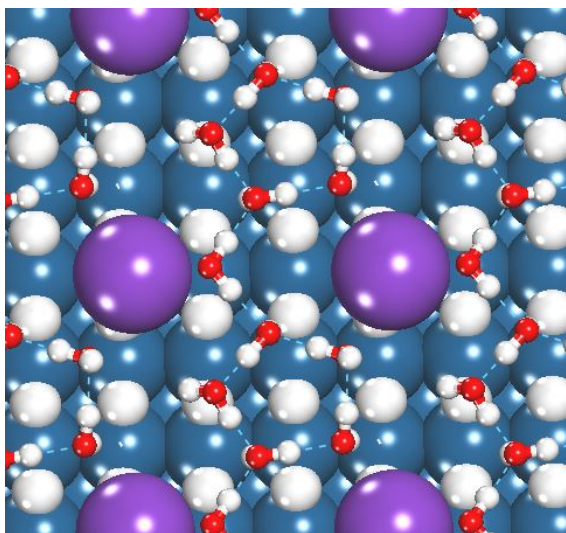Pt(111) Minimum energy water structure 6 H_2O* in 3x3 unit cell with 1/9 ML K*.
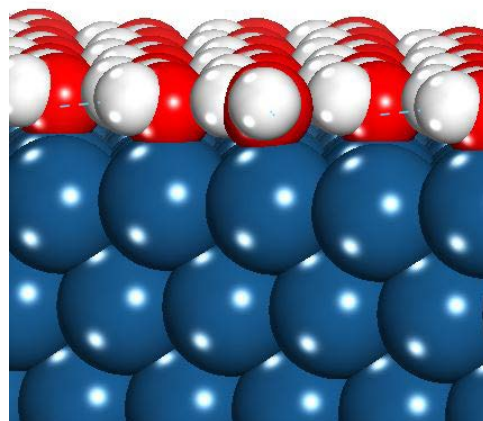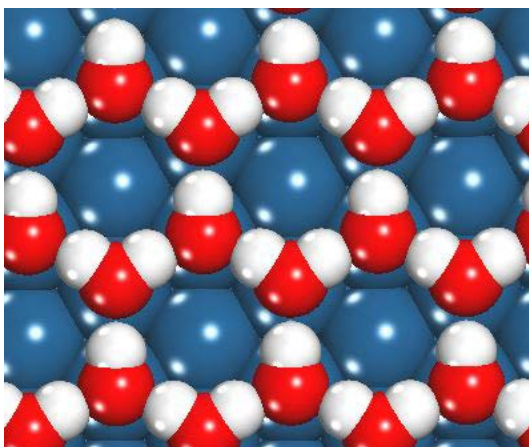
Pt(111) Minimum energy hydroxide+water structure 3OH*+ 3 H_2O* in 3x3 unit cell (3/9 ML OH, 3/9 ML H_2O).
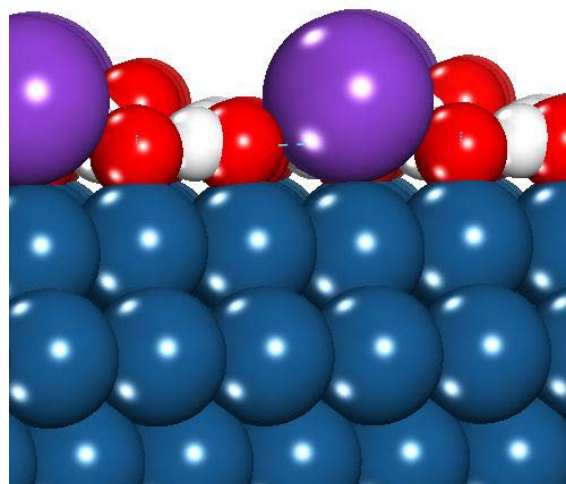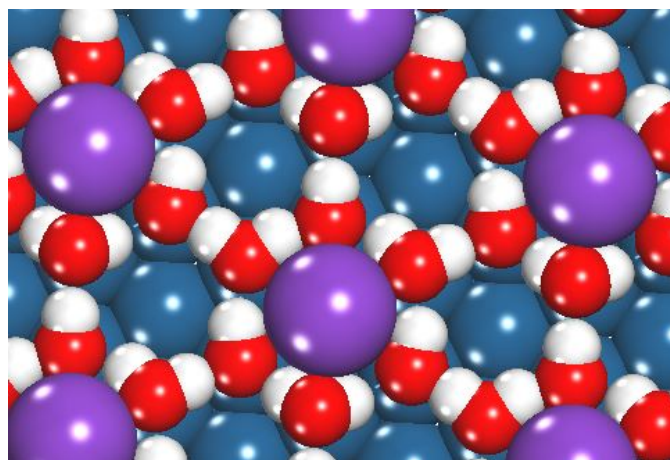
Pt(111) Minimum energy hydroxide+water structure 3OH*+ 3 H_2O* in 3x3 unit cell with K* 1/9 ML (3/9 ML OH, 3/9 ML H_2O, 1/9 ML K*).
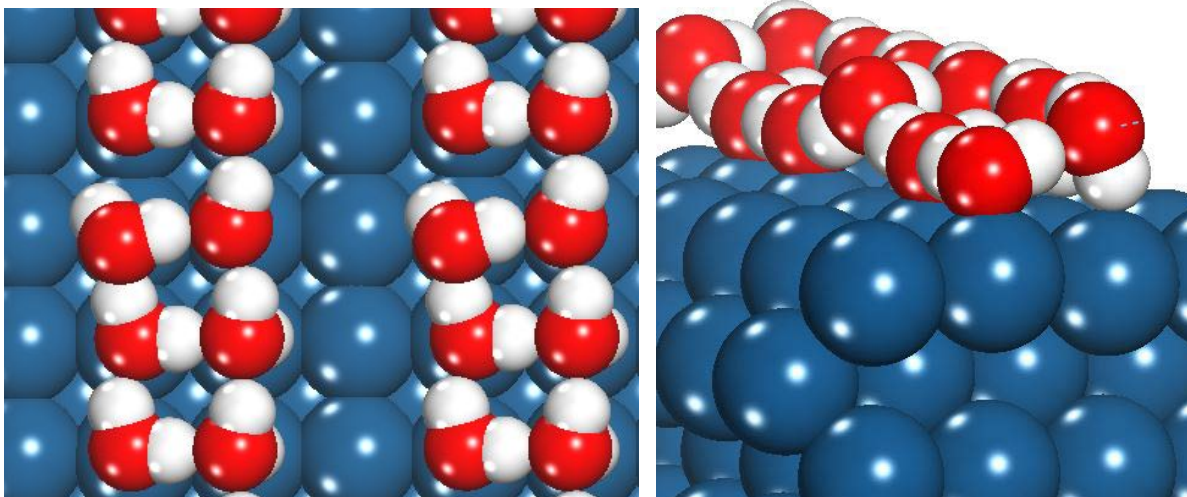
Pt(100)

Pt(100) Minimum energy water structure 6 H_2O* in 3x3 unit cell (6/9 ML H_2O).
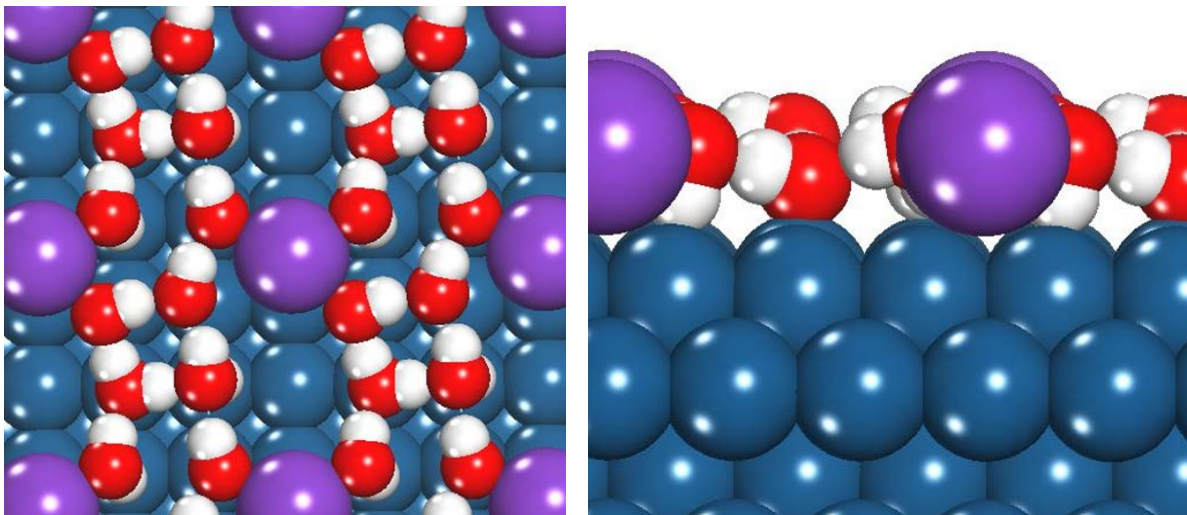
Pt(100) Minimum energy water structure 6 H_2O* in 3x3 unit cell with 1/9 ML K*.
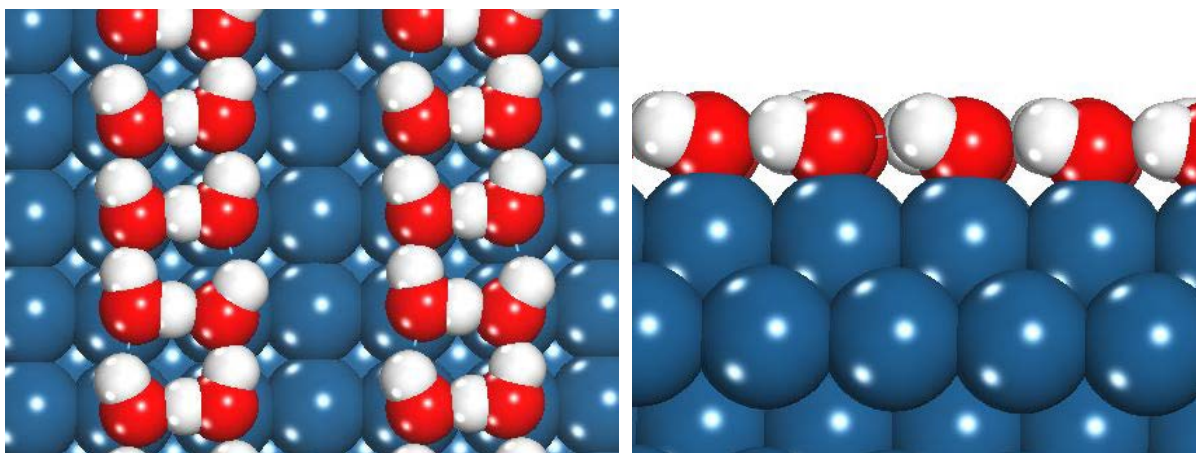
Pt(100) Minimum energy hydroxide+water structure 3OH*+ 3 H_2O* in 3x3 unit cell (3/9 ML OH, 3/9 ML H_2O).

Pt(100) Minimum energy hydroxide+water structure 3OH*+ 3 H_2O* in 3x3 unit cell with K* 1/9 ML (3/9 ML OH, 3/9 ML H_2O, 1/9 ML K*).

Pt(100) Minimum energy water structure with 1 ML H* and 1/9 ML K* in 3x3 unit cell (6/9 ML H$_2$O, 1/9 ML K*, 1 ML H*).
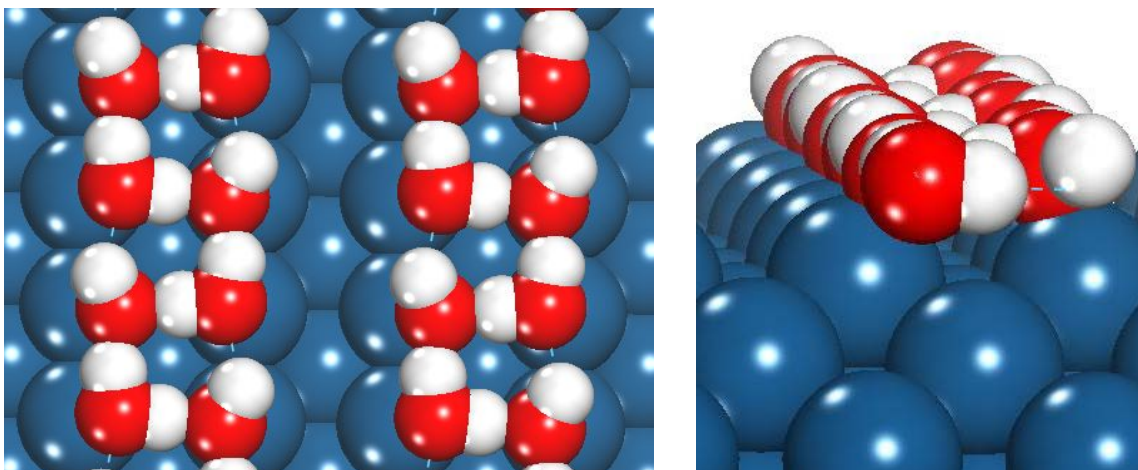
Pt(110)
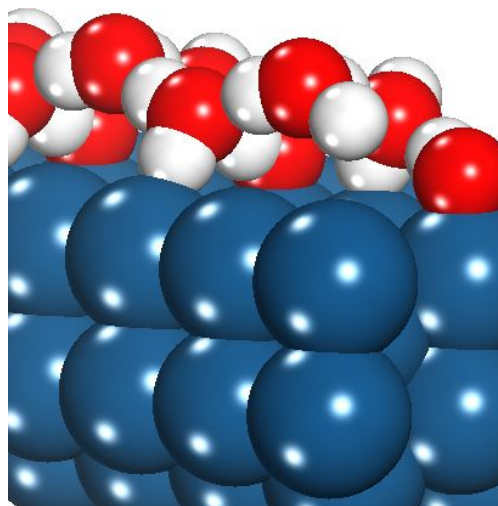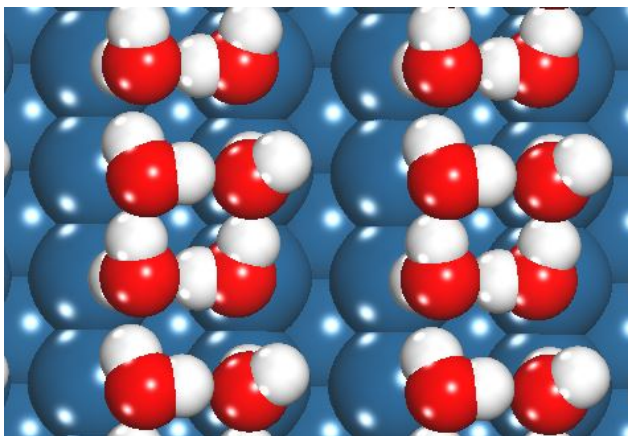
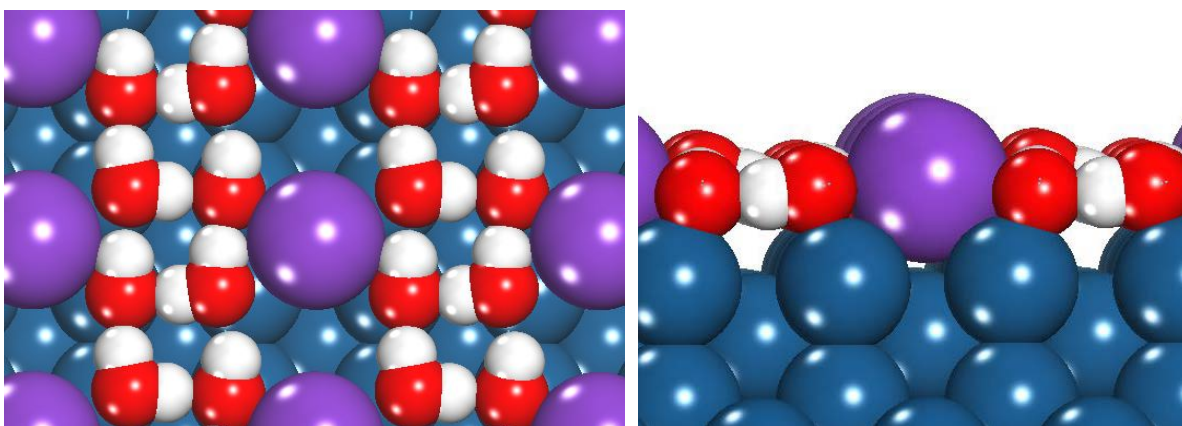Pt(110) Minimum energy water structure 4 H_2O^* in 2x2 unit cell (1 ML H_2O).
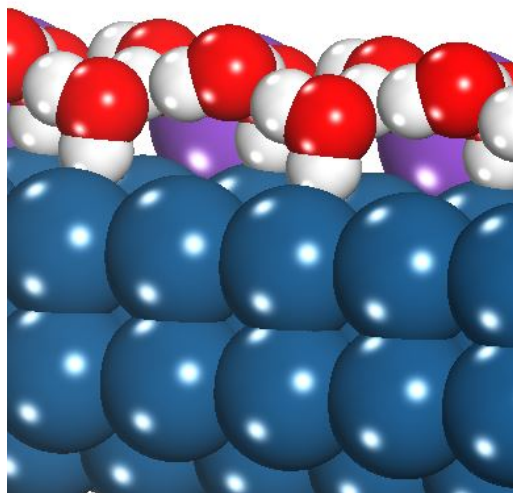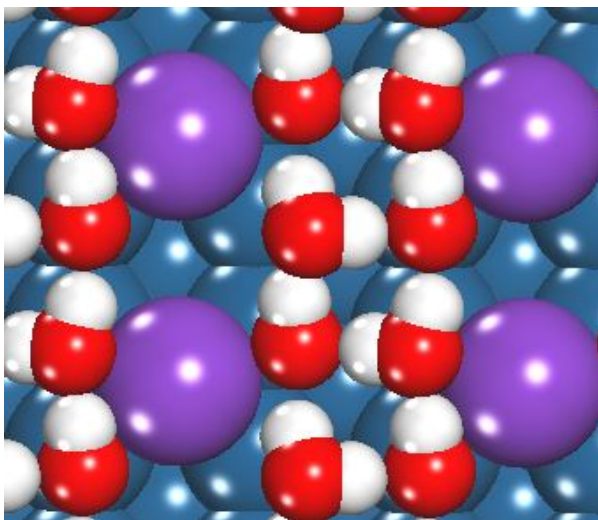
Pt(110) Minimum energy water structure 4 H_2O^* in 2x2 unit cell with 1/4 ML K^*.
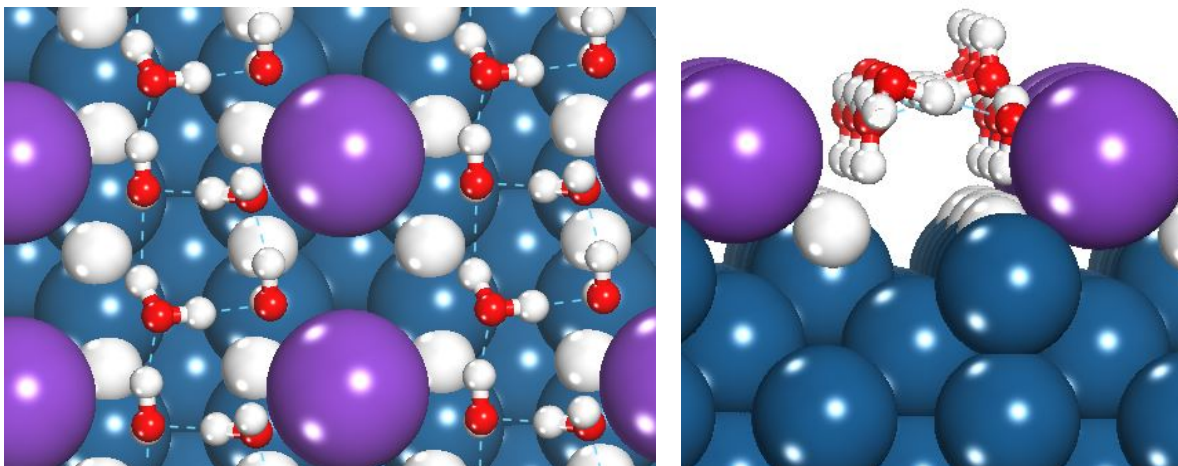
Pt(110) Minimum energy hydroxide+water structure 2OH*+ 2 H_2O* in 2x2 unit cell (1/2 ML OH, 1/2 ML H_2O).

Pt(110) Minimum energy hydroxide+water structure 2OH*+ 2 H_2O* in 2x2 unit cell with 1/4 ML K* (1/2 ML OH, 1/2 ML H_2O, 1/4 ML K*).

Pt(110) Minimum energy water structure with 1 ML H* and 1/4 ML K* in 2x2 unit cell (1 ML H$_2$O, 1/4 ML K*, 1 ML H*).

References

1.   Garcia-Araez, N. Enthalpic and Entropic Effects on Hydrogen and Oh Adsorption on Pt(111), Pt(100), and Pt(110) Electrodes as Evaluated by Gibbs Thermodynamics. *J. Phys. Chem. C* **2011,** *115*, 501-510.