Supporting Information to: Linear Correlation between Water Adsorption Energies and Volta Potential Differences for Metal/water Interfaces

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1. Models

Cu(110) and Ag(110) surfaces are modeled by 3×4 periodic slabs with 6 atomic layers. Cu(100), Zn(0001) and Pb(111) surfaces are modeled by 4×4 periodic slabs with 4 atomic layers. Pd(111) surface is modeled by a 4×4 periodic slab with 5 atomic layers. Cu(111), Ag(111) and Pt(100) surfaces are modeled by 4×4 periodic slab with 6 atomic layers. Pt(111) and Au(111) surfaces are modeled by 6×6 periodic slabs with 4 atomic layers. The sizes of interface models are respectively $11.246 \times 11.246 \times 35.940$ Å³ for Pt(100), $11.059 \times 11.059 \times 30.030$ Å³ for Pd(111), $16.869 \times 16.869 \times 27.887$ Å³ for Pt(111), $10.139 \times 10.139 \times 32.169$ Å³ for Cu(100), $8.854 \times 10.224 \times 40.435$ Å³ for Cu(111), $10.571 \times 10.571 \times 35.884$ Å³ for Zn(0001), $11.568 \times 11.568 \times 32.807$ Å³ for Ag(111), $17.607 \times 17.607 \times 28.188$ Å³ for Au(111) and $14.142 \times 14.142 \times 33.574$ Å³ for Pb(111), $12.257 \times 11.556 \times 37.223$ Å³ for Ag(110), $10.754 \times 10.139 \times 36.069$ Å³ for Cu(110).

The water adsorption energies (E_{ads}) are calculated on metal surfaces by using different k-point sampling, e.g. 1x1x1, 3x3x1 or 4x4x1, as listed in Table S2. Since we use rather large cells, the computed E_{ads} converge quickly with k-point sampling. The optimized structures of water on surfaces are all shown in Figure S1. Note that on three open surfaces, i.e. Cu(110), Au(110) and Ag(110), water has two different adsorption configurations with similar adsorption energies, as seen in Figure S2. Considering at interface the chemisorbed water tends to form hydrogen bonds with neighbouring water, we take the water configuration with O-H bonds tilted up for this study. To be consistent, we use E_{ads} calculated with 1x1x1k-point sampling in Figure 3 in the main text because the interface models are computed at the Γ point only. Differently, we use E_{ads} calculated with larger k-point sampling for the correlation with $\Delta\Phi$ from experimental values (Figure 1 in the main text), because they have higher accuracy.

The metal/water interfaces are built by fully filling the vacuum space between the metallic slabs and their periodic images, and the numbers of water molecules are chosen such that the density of water in the bulk region is kept $\sim 1 \text{ g/cm}^3$ (see Table S3). Note that each model

shown in Figure S3 contains two symmetrical metal/ H_2O interfaces, and they correspond to the condition of potential of zero charge (PZC) in experiment.

2. Computational setup

All the calculations are performed with CP2K¹ in this work. The density functional theory (DFT) implemented in CP2K is based on a hybrid Gaussian plane wave (GPW) scheme that the orbitals are described by an atom centered Gaussian-type basis set, and an auxiliary plane wave basis set is used to re-expand the electron density in the reciprocal space. The 2s, 2p electrons of O, 3d, 4s electrons of Cu, 3d, 4s electrons of Zn, 4s, 4p, 4d, 5s electrons of Pd, 4d, 5s electrons of Ag, 5d, 6s electrons of Pt, 5d, 6s electrons of Au, 6s, 6p electrons of Pb, 4d, 5s electrons of Cd, 5s, 5p electrons of Sb and In, 6s, 6p electrons of Bi, 4s, 4p, 4d, 5s electrons of Rh, and 5s, 5p, 5d, 6s electrons of Ir are treated as valence, and the rest core electrons are represented by Goedecker-Teter-Hutter (GTH) pseudopotentials.^{2,3} The Gaussian basis set is double- ζ with one set of polarisation functions (DZVP),⁴ and the energy cutoff for density expansion is set to 400 Ry. The Perdew-Burke-Ernzerhof (PBE)⁵ functional is used to describe the exchange-correlation energies, and the dispersion correction is applied in all calculations with the Grimme D3 method.⁶

BFGS minimizer is used for optimizing structures, and during the geometry optimization process, the bottom two atomic layers are fixed for all the surface models. For ab initio molecular dynamics simulations (AIMD), Born-Oppenheimer MD is used for modeling Pt(111)/water, Ag(111)/water and Au(111)/water interfaces. The canonical ensemble condition is imposed by a Nose-Hoover thermostat (NVT) with a target temperature of 330 K, and the time step is set to 0.5 fs. Part of results of Pt(111)/water, Ag(111)/water and Au(111)/water interfaces have been published in our previous work.⁷ For other interface models, we use the second generation Car-Parrinello molecular dynamics (SGCPMD)⁸ for sampling configurations. The target temperature is set to 330 K. The correction step is obtained by 5 iterations of the orbital transformation (OT) optimization,⁹ and the integration time for each step is 0.5 fs. The Langevin friction coefficient (γ_L) is set to 0.001 fs⁻¹, and the intrinsic friction coefficients (γ_D) are 2.2 × 10⁴ fs⁻¹ for H₂O, 9 × 10⁵ fs⁻¹ for Ag, 5 × 10⁵ fs⁻¹ for Pt, Pd and Cu, respectively. The time evolution of total energy of interfaces are plot for assessing the stability of SGCPMD runs, as shown in Figure S11. For each AIMD simulation, an initial ~5 ps (~10000 steps) of MD trajectory is used to equilibrate the system, and then followed by a production period of 5~25 ps. Due to the large size of the cells, only the Γ point in the reciprocal space is used for all the AIMD simulations.

3. Determination of PZC for metal/water interfaces

The PZC (U_{PZC}) of metal/water interfaces are calculated with the computational standard hydrogen electrode (cSHE) method.⁷ The original formula of the cSHE method is

$$e_0 U_{\rm PZC} = -E_{\rm F}^{(i)} + \Delta_{\rm dp} A_{\rm H_3O^+}^{(i)} - \mu_{\rm H^+}^{g,\circ} - \Delta E_{\rm zp}, \tag{1}$$

in which $E_{\rm F}^{(i)}$ denotes for the Fermi level of the interface. $\Delta_{\rm dp}A_{\rm H_3O^+}^{(i)}$ represents the deprotonation free energy of a H₃O⁺(aq) ion in the bulk water of the interface model, and it is the key to converting the potential into the SHE scale. $\mu_{\rm H^+}^{g,\circ}$ is the standard chemical potential of the gas phase proton, and $\Delta E_{\rm zp}$ is a correction for the zero-point energy of O-H bond in H₃O⁺(aq). The latter two terms are known constants, 15.81 eV and 0.35 eV, respectively.

It should be mentioned that the calculation of $\Delta_{dp}A_{H_3O^+}^{(i)}$ is time-consuming, and in order to make the electrode potential computation more efficient, the term $\Delta_{dp}A_{H_3O^+}^{(i)}$ is replaced by the deprotonation energy of a H₃O⁺(aq) ion calculated from a bulk water model $(\Delta_{dp}A_{H_3O^+}^{(w)})$. The recommended value of $\Delta_{dp}A_{H_3O^+}^{(w)}$ is 15.35 eV, and it is revealed that $\Delta_{dp}A_{H_3O^+}^{(w)}$ is insensitive to the functional used.¹⁰ Due to the different periodic boundary conditions employed for the interface model and bulk water model, the value of $\Delta_{dp}A_{H_3O^+}^{(i)}$ is differed from $\Delta_{dp}A_{H_3O^+}^{(w)}$ by a term called Hartree potential difference (Δ V). The value of ΔV can not be directly computed, while it is known that ΔV also equals to the difference of the electrostatic potential energy of bulk water calculated from the interface model $(-e_0\phi_{wat}^{(i)})$ and the pure water model $(-e_0\phi_{wat}^{(w)})$. Therefore, we can write

$$\Delta_{\rm dp} A_{\rm H_3O^+}^{(i)} - \Delta_{\rm dp} A_{\rm H_3O^+}^{(w)} = -e_0 \phi_{\rm wat}^{(i)} - (-e_0 \phi_{\rm wat}^{(w)}).$$
(2)

 e_0 is the unit charge, and note that $-e_0\phi_{wat}^{(w)}$ is zero because of the periodic boundary condition. Then, substituting Eqn.(1) with Eqn.(2), we obtain the modified formula of the cSHE method,

$$e_0 U_{\rm PZC} = -E_{\rm F}^{(i)} - e_0 \phi_{\rm wat}^{(i)} + \Delta_{\rm dp} A_{\rm H_3O^+}^{(w)} - \mu_{\rm H^+}^{g,\circ} - \Delta E_{\rm zp}.$$
 (3)

For further details of the cSHE method, readers can refer to References. 7,10

 $E_{\rm F}^{(i)}$ and $\phi_{\rm wat}^{(i)}$ are readily obtained by averaging over AIMD trajectories of the interface models. Both are averaged by taking configurations every 50 MD steps along the AIMD trajectories, and the time accumulative averages are shown in Figure S4 and Figure S5 to check their convergence. The statistical errors of the computed Volta potential difference $(\Delta \Phi)$ and interfacial potential change due to electron redistribution $(\Delta \Phi_{\rm el})$ are estimated by dividing each AIMD trajectory into five evenly-spaced blocks and calculating the standard deviations for the five blocks.



Figure S1: Configurations of water adsorbed on 20 different metal surfaces. Ir, Rh, Pt, Pd, Cu, Ag, Au, Zn, Cd, Pb, In, Sb, Bi, O, and H atoms are colored by cantaloupe, darksalmon, darkgrey, purple, brown, gray, yellow, blue, mediumpurple, iron, magenta, green, cyan, red, and white, respectively.



Figure S2: Two different configurations of water adsorbed on the Cu(110) surface. (a) Water oriented with O-H bonds slightly tilted up; (b) Water oriented with O-H bonds pointing towards metal surface. Cu, O, and H atoms are colored by orange, purple, and white, respectively.



Figure S3: Models of 11 metal/water interfaces at PZC. Pt, Pd, Cu, Zn, Ag, Au, Pb, O and H atoms are colored by darkgrey, purple, brown, turquoise, gray, yellow, iron, red, and white, respectively.



Figure S4: Time accumulative averages of Fermi energies $E_F^{(i)}$ of 11 metal/water interfaces at PZC.



Figure S5: Time accumulative averages of electrostatic potential energies of bulk water $(-e_0\phi_{wat}^{(i)})$ of 11 metal/water interfaces at PZC.



Figure S6: Time accumulative averages of the interface potential change caused by electron redistribution $\Delta \Phi_{\rm el}$ at 11 metal/water interfaces at PZC.



Figure S7: Density of states (DOS) of 11 metal/water interfaces at PZC. The plots are averaged over AIMD trajectories. The DOS of metal surfaces, chemisorbed water, and other water in the models are colored by blue, red, and orange, respectively. The energies of all the states have been referenced to their corresponding Fermi levels.



Figure S8: Probability distribution profiles of angle Ψ of chemisorbed water at 11 metal/water interfaces at PZC. The inset shows Ψ is the angle between the bisector of water and the surface normal.



Figure S9: Time accumulative averages of the surface coverage of chemisorbed water (θ_A) at 11 metal/water interfaces at PZC.



Figure S10: (a) Models of a metal surface with chemisorbed water molecules. The molecular planes of water molecules are controlled to be parallel to the metal surface. Pt, O, and H are represented by gray, purple, and white balls, respectively. The z-coordinate indicates the distance of chemisorbed water from the metal surface. (b) The chemisorption induced dipole (p) of each water at z = 2.4 Å on different metal surfaces. The values of p are very close for most metal surfaces, except that the two Pt surfaces have slightly greater deviation.



Figure S11: Plots of time evolution of total energy of 8 metal/water interfaces computed by the second generation Car-Parinello molecular dynamics.

Surface	PZC/V vs SHE	$\Phi_{ m M}/{ m eV}$	$\Delta \Phi/{ m eV}$
$\operatorname{Ir}(111)$	0.01	5.76	-1.31
Rh(111)	0.05	5.60	-1.11
Pt(100)	0.25	5.75	-1.06
Pd(111)	0.12	5.67	-1.11
Pt(111)	0.29	5.91	-1.18
Cu(110)	-0.75	$4.48 {\sim} 4.87$	-0.81~-1.18
Cu(100)	-0.73	4.56	-0.85
Cu(111)	$-0.73 \sim -0.2$	4.90	$-1.19 \sim -0.7$
Ag(110)	-0.74	4.52	-0.82
Ag(100)	-0.61	4.64	-0.81
Ag(111)	-0.45	4.74	-0.76
Au(100)	0.29	5.22	-0.49
Au(110)	0.19	5.20	-0.57
Au(111)	0.47	5.33	-0.42
Zn(0001)	-0.77	4.40	-0.73
Cd(0001)	-0.72(poly)	4.22(poly)	-0.50
Pb(111)	-0.62(poly)	4.01(poly)	-0.19
$\operatorname{In}(110)$	-0.65(poly)	4.12(poly)	-0.33
Sb(111)	-0.18(poly)	4.55(poly)	-0.29
$\operatorname{Bi}(111)$	-0.41	4.26	-0.23

Table S1: Experimental data^{11–20} of PZC, work functions (Φ_M) and Volta potential differences $(\Delta \Phi)$ for 20 metal surfaces.

model size	k-points	$E_{\rm ads}$
$3 \times 3, 4$ layers	$2 \times 2 \times 1$	-0.565
	$4 \times 4 \times 1$	-0.565
$3 \times 3, 4$ layers	$2 \times 2 \times 1$	-0.550
	$4 \times 4 \times 1$	-0.538
$4 \times 4, 6$ layers	$1 \times 1 \times 1$	-0.546
	$3 \times 3 \times 1$	-0.480
	$4 \times 4 \times 1$	-0.485
4×4 , 5 layers	$1 \times 1 \times 1$	-0.519
	$2 \times 2 \times 1$	-0.455
	$3 \times 3 \times 1$	-0.483
$6 \times 6, 4$ layers	$1 \times 1 \times 1$	-0.495
	$2 \times 2 \times 1$	-0.469
	$3 \times 3 \times 1$	-0.451
$3 \times 4, 6$ layers	$1 \times 1 \times 1$	-0.479
	$2 \times 2 \times 1$	-0.508
	$3 \times 3 \times 1$	-0.517
4×4 , 4 layers	$1 \times 1 \times 1$	-0.436
	$2 \times 2 \times 1$	-0.418
	$3 \times 3 \times 1$	-0.420
$4 \times 4, 6$ layers	$1 \times 1 \times 1$	-0.357
	$2 \times 2 \times 1$	-0.396
	$3 \times 3 \times 1$	-0.388
$3 \times 4, 6$ layers	1×1×1	-0.310
	$3 \times 3 \times 1$	-0.312
	model size 3×3 , 4 layers 3×3 , 4 layers 4×4 , 6 layers 6×6 , 4 layers 3×4 , 6 layers 4×4 , 6 layers 4×4 , 6 layers	model size k-points 3×3, 4 layers 2×2×1 3×3, 4 layers 2×2×1 3×3, 4 layers 2×2×1 4×4, 6 layers 1×1×1 4×4, 5 layers 1×1×1 4×4, 5 layers 1×1×1 4×4, 5 layers 1×1×1 6×6, 4 layers 1×1×1 6×6, 4 layers 1×1×1 3×3×1 3×3×1 4×4, 6 layers 1×1×1 3×3, 1 3×3×1 4×4, 6 layers 1×1×1 4×4, 6 layers 1×1×1 4×4, 6 layers 1×1×1 3×3×1 3×3×1 4×4, 6 layers 1×1×1 3×3×1 3×3×1

Table S2: Calculated water adsorption energies (E_{ads}) on 20 metal surfaces.

Ag(100)	$3 \times 3, 4$ layers	$3 \times 3 \times 1$	-0.279
		$4 \times 4 \times 1$	-0.276
Ag(111)	$4 \times 4, 6$ layers	$1 \times 1 \times 1$	-0.253
		$2 \times 2 \times 1$	-0.294
		$4 \times 4 \times 1$	-0.292
Au(100)	$3 \times 3, 4$ layers	$2 \times 2 \times 1$	-0.293
		$3 \times 3 \times 1$	-0.288
Au(110)	$3 \times 4, 6$ layers	$2 \times 2 \times 1$	-0.306
		$3 \times 3 \times 1$	-0.296
Au(111)	$6 \times 6, 4$ layers	$1 \times 1 \times 1$	-0.245
		$2 \times 2 \times 1$	-0.287
		$3 \times 3 \times 1$	-0.290
$\operatorname{Zn}(0001)$	$4 \times 4, 4$ layers	$1 \times 1 \times 1$	-0.292
		$3 \times 3 \times 1$	-0.267
Cd(0001)	$4 \times 4, 4$ layers	$2 \times 2 \times 1$	-0.220
		$4 \times 4 \times 1$	-0.231
Pb(111)	$4 \times 4, 4$ layers	$1 \times 1 \times 1$	-0.146
		$3 \times 3 \times 1$	-0.145
In(110)	$4 \times 4, 4$ layers	$2 \times 2 \times 1$	-0.146
		$3 \times 3 \times 1$	-0.159
Sb(111)	$4 \times 4, 4$ layers	$1 \times 1 \times 1$	-0.073
		$3 \times 3 \times 1$	-0.071
Bi(111)	$4 \times 4, 4$ layers	$1 \times 1 \times 1$	-0.083
		$3 \times 3 \times 1$	-0.073

Metal surfaces	$ ho_{ m H_{2O}}~(m g/cm^3)$
Pt(111)	0.97
Pt(100)	1.00
Pd(111)	1.05
Cu(111)	1.00
Cu(100)	1.01
$\operatorname{Zn}(0001)$	1.00
Ag(111)	0.98
$\operatorname{Au}(111)$	0.95
Pb(111)	1.00
Cu(110)	1.00
Ag(110)	1.00

Table S3: Densities of water ($ho_{
m H_2O}$) in the bulk regions of metal/water interfaces.

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