

Supplementary Materials

Metal-dependent volmer free energies track opposite cation trends on Pt(111) and Au(111) as catalysts for hydrogen evolution

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Supplementary Text

Uncompensated resistance and iR correction. The uncompensated resistance, R_u , was determined under the corresponding measurement conditions. For polycrystalline Pt in 0.1 M LiOH, NaOH, and KOH, the R_u values were 26.22, 23.21, and 25.37 Ω , respectively. For polycrystalline Au in the same electrolytes, the corresponding values were 30.53, 25.05, and 27.56 Ω . Polarization curves were recorded without real-time iR compensation and corrected after measurement using $E_{\text{corrected}} = E_{\text{measured}} - iR_u$, where i is the signed measured current in amperes and R_u is the uncompensated resistance in ohms. The full measured R_u value was used for the correction.

Density functional theory (DFT) calculations. The electrolyte regions of the metal/water interface models were generated with Packmol^[1], and geometry optimizations were performed for the Pt(111) and Au(111) models before AIMD sampling. DFT calculations were carried out with VASP 5.4.4^[2,3] using the PBE exchange-correlation functional^[4] and the D3 dispersion correction^[5]. The plane-wave cutoff was 500 eV. Geometry optimizations were converged to a maximum force of 0.02 eV $\text{\AA}^{-1}$ and a total-energy change of 10^{-6} eV. Periodic boundary conditions were applied. The Pt(111) and Au(111) simulation cells were $11.09 \times 9.60 \times 48.79 \text{ \AA}^3$ and $11.57 \times 10.02 \times 49.09 \text{ \AA}^3$, respectively. Brillouin-zone sampling used the Γ point.

Molecular dynamics (MD) simulations. Brillouin-zone sampling was restricted to the Γ point, symmetry was disabled, and a 1.0 fs time step was used in both constrained and unconstrained AIMD simulations. Unconstrained simulations were performed for 20-30 ps at 298 K in the NVT ensemble using a Nosé-Hoover thermostat. Structural statistics were calculated from the final 5 ps of each full unconstrained trajectory, after the preceding interfacial relaxation. Some trajectories still showed relaxation of the cation-surface distance during the final 10 ps, whereas this behavior was not observed during the final 5 ps. The latter interval was therefore used consistently for structural analysis. Comparisons of the final 5 and 10 ps gave the same cation-dependent trends for the key structural properties examined, including the width of the water-depleted region. This 5 ps analysis window applies only to unconstrained-trajectory statistics.

The constrained slow-growth trajectories retain the separate 10 ps protocol described below. The free-energy profile $W(\xi)$ was obtained by thermodynamic integration of the mean constraint force using the slow-growth approach.^[6]

$$W(\xi_2) - W(\xi_1) = \int_{\xi_1}^{\xi_2} d\xi \left\langle \frac{\partial H}{\partial \xi} \right\rangle_{\xi} = \lim_{g \rightarrow 0} \int_{\xi_1}^{\xi_2} \frac{\partial H}{\partial \xi} \xi dt$$

In the constrained AIMD calculations, the collective variable was $\xi = d(\text{O-H}) - d(\text{M-H})$, where $d(\text{O-H})$ is the breaking water O-H distance and $d(\text{M-H})$ is the distance from the transferring H atom to the target surface metal atom. An interfacial H-down water molecule with the smallest H-to-surface distance was selected as the reactant configuration. Here, $W(\xi)$ is the free energy, H is the Hamiltonian, and $\langle \partial H / \partial \xi \rangle_{\xi}$ is the mean constraint force at fixed ξ . The CV was advanced by 0.0003 Å per 1 fs MD step for 10,000 steps, corresponding to a nominal pulling rate of 0.3 Å ps⁻¹ over 10 ps.

Raman measurements and fitted-area definition. Raman spectra were acquired at -0.05 V vs RHE on polycrystalline Pt and Au in 0.1 M LiOH, NaOH, and KOH. Literature assignments associate the lower- and intermediate-wavenumber O-H components with four- and two-coordinated hydrogen-bonded water, respectively, and the high-wavenumber component with weakly hydrogen-bonded cation-hydrated water.^[7,8] For the present spectra, these are phenomenological assignments within an overlapping envelope, not three uniquely resolved molecular species. The same peak-position settings were used across all spectra. The normalized integrated area of component i is defined below.

$$f_i = \frac{A_i}{A_{strong} + A_{moderate} + A_{weak}}$$

Here, A_i is the integrated area of component i , and the denominator is the sum of the three component areas. The labels strong, moderate, and weak denote the lower-, intermediate-, and high-wavenumber components, respectively. The percentage contribution is 100 times the area fraction. Differences in Raman scattering responses prevent direct conversion of these spectral fractions into molecular population fractions. Because Au exhibits no appreciable HER current at -0.05 V vs RHE, the spectra characterize that fixed-potential interface rather than the more negative potentials used

to compare HER activity.

Water-number profiles and depletion widths. The 20 Å region above the metal surface was partitioned into 1000 uniform bins along the surface normal, giving a bin thickness of 0.02 Å. Water molecules were counted within each bin for each sampled frame and averaged over the final 5 ps of the unconstrained trajectories. Figure 3 plots this average count per bin, not molar density. The lateral areas are $11.09 \times 9.60 = 106.464 \text{ Å}^2$ for Pt(111) and $11.57 \times 10.02 = 115.9314 \text{ Å}^2$ for Au(111). Thus, the bin volumes are 2.12928 and 2.318628 Å³, respectively.

The molar water density is $c(z) = \bar{N}(z)/(N_A V_{\text{bin}} \times 10^{-24})$, where $\bar{N}(z)$ is the mean water count, $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant, V_{bin} is in Å³, and $1 \text{ Å}^3 = 10^{-24} \text{ cm}^3$. Conversely, the count threshold is $N_{\text{bulk}} = c_{\text{bulk}} N_A V_{\text{bin}} \times 10^{-24}$. For $c_{\text{bulk}} = 0.056 \text{ mol cm}^{-3}$, $N_{\text{bulk}} = 0.07181$ for Pt(111) and 0.07819 for Au(111). The local depletion width is the difference between the two surface-normal positions at which the count profile crosses its corresponding threshold around the local minimum. The threshold therefore has the same units as the plotted profile. The bulk concentration is not directly compared with unnormalized counts.

Nearest-water-layer distance. For each trajectory frame, the surface reference is the mean z coordinate of the atoms in the topmost metal layer. Water oxygen atoms lying more than 0 and no more than 5.00 Å above this reference are assigned to the nearest water layer, irrespective of O-down or H-down orientation. Their oxygen-to-reference-plane distances are averaged within each frame, and these frame averages are then averaged over the final 5 ps. Figure 5C reports this mean oxygen position. It is distinct from both the first density-peak position in Figure 3 and the distance of the specific reacting oxygen in Figure 4C,D.

Volmer barrier extraction and uncertainty. The barrier is extracted as the maximum of the constrained free-energy profile before adsorption of the transferring hydrogen atom on the metal surface. The complete profiles are shown in Figure S5, with the near-barrier regions in Figure 4A,B. A small CV increment of 0.0003 Å per 1 fs MD step (nominal pulling rate of 0.3 Å ps^{-1}) was chosen to reduce numerical uncertainty associated with finite increments along the slow-growth path. This setting limits the change in the constraint at each update and provides closely spaced sampling of the

reaction coordinate. The same pulling protocol was used for all eight systems. Table S1 lists the resulting barriers to two decimal places for comparison of the cation-dependent trends. Each barrier is a single-profile estimate. Statistical uncertainty has not been quantified.

Table S1. Volmer activation free-energy estimates for cation-free and single-cation models.

Condition	Pt(111) barrier (eV)	Au(111) barrier (eV)
Cation-free	1.49	1.83
Li ⁺	1.54	1.79
Na ⁺	1.65	1.75
K ⁺	1.70	1.64

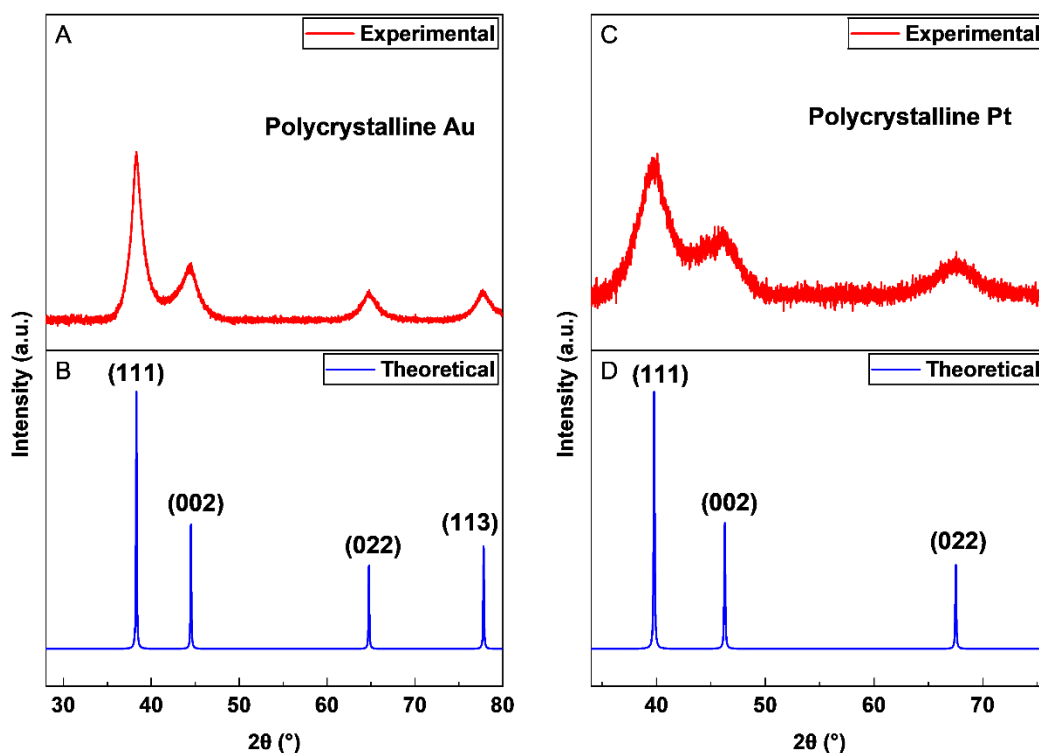


Figure S1. Experimental and calculated reference XRD patterns for polycrystalline Au and Pt. (A,C) Experimental patterns for Au and Pt, respectively. (B,D) Corresponding calculated reference patterns.

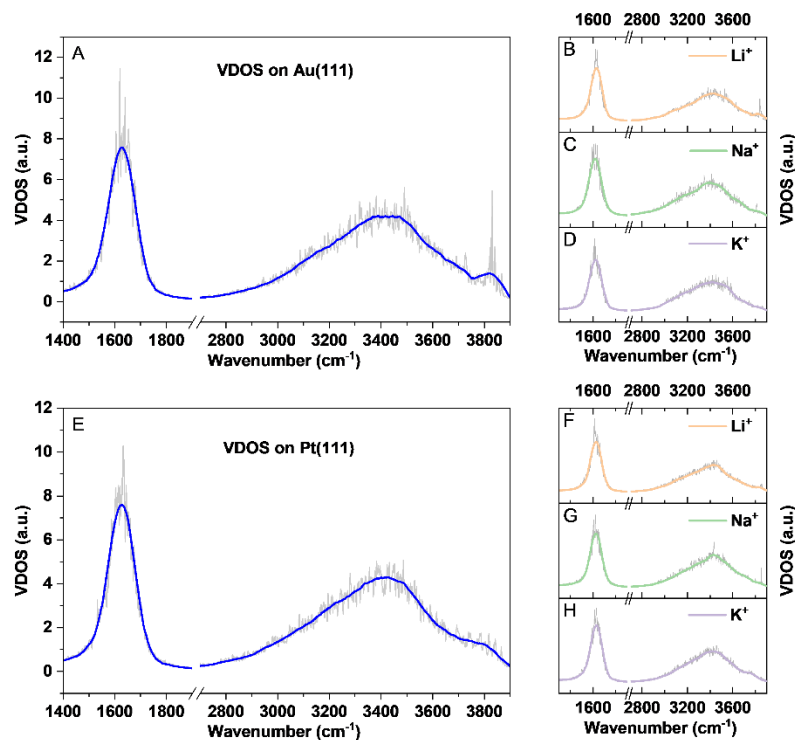


Figure S2. Calculated vibrational density of states (VDOS) of interfacial water. (A) Cation-free Au(111)/water interface. (B-D) Au(111)/water interfaces containing Li^+ , Na^+ , and K^+ , respectively. (E) Cation-free Pt(111)/water interface. (F-H) Pt(111)/water interfaces containing Li^+ , Na^+ , and K^+ , respectively.

On both model surfaces, the VDOS contains an H-O-H bending band near 1620 cm^{-1} and a broad O-H stretching band centered near 3450 cm^{-1} , consistent with the broad vibrational features reported for interfacial water.^[7,8] The relative high-frequency O-H contribution increases from Li^+ to K^+ in the present trajectories, consistent with a greater contribution from weakly hydrogen-bonded water environments at both interfaces.

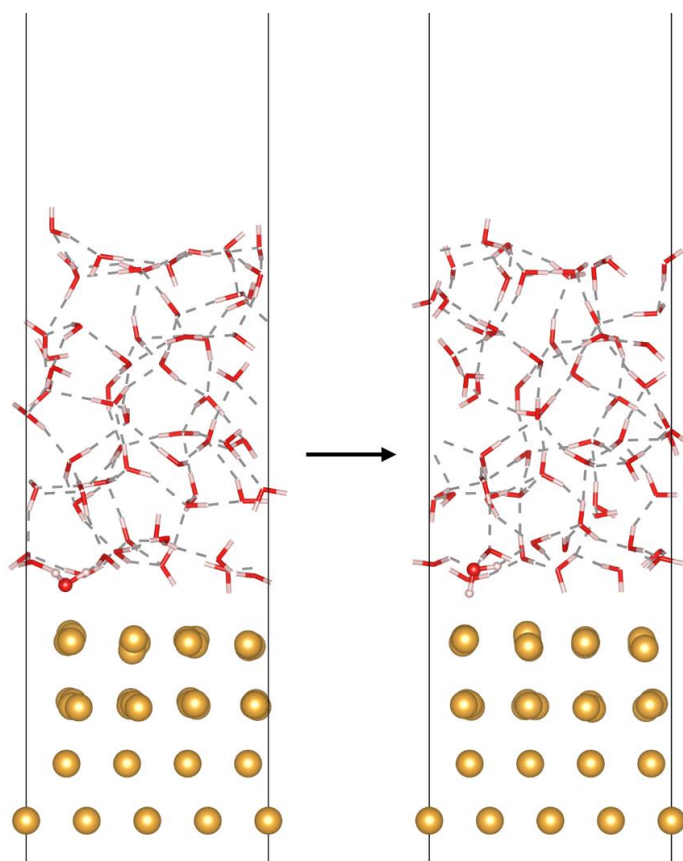


Figure S3. Representative reorientation of an interfacial water molecule from an O-down to an H-down configuration before water dissociation. The structure was rendered using VESTA (version 3.5.8).

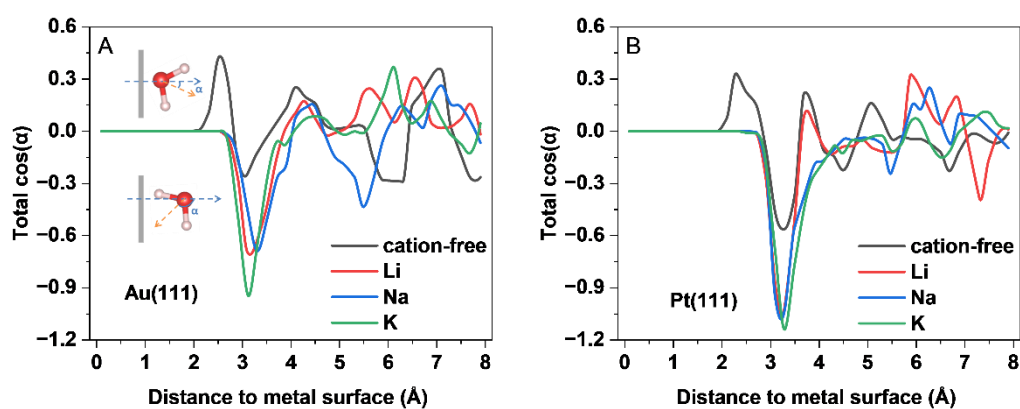


Figure S4. Water-dipole orientation profiles along the surface-normal direction at (A) Au(111)/water and (B) Pt(111)/water interfaces. The insets define the O-down and H-down configurations and the angle α between the water-dipole vector and the outward surface normal. The plotted quantity is $\Sigma \cos(\alpha)$ within each spatial bin and therefore reflects both local water occupancy and orientation.

The water-orientation profiles were obtained by binning water molecules along the surface-normal coordinate and calculating $\Sigma \cos(\alpha)$ within each spatial bin from the AIMD trajectories. In the cation-free models, the first-layer minimum is more negative on Pt(111) than on Au(111), consistent with a larger H-down contribution in the present trajectories. After a cation is introduced, all systems show a negative first-layer minimum near 3.2 Å, indicating preferential H-down orientation in that region. Additional independent trajectories are required to distinguish a concentration effect from finite-sampling variability. Cation-crowded Pt(111) models have shown that cation accumulation can reorganize interfacial water and hydrogen-bond connectivity.^[9]

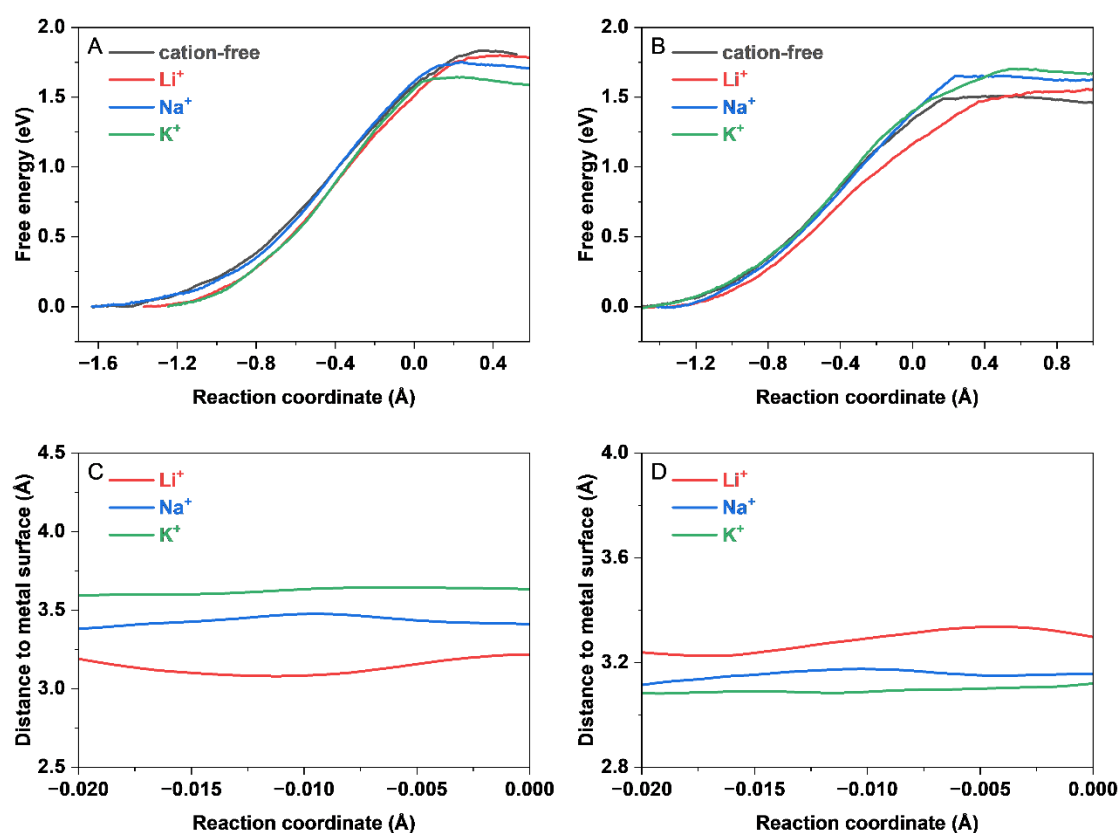


Figure S5. Volmer free-energy profiles on (A) Au(111) and (B) Pt(111) over the full collective-variable range. (C,D) Surface-normal distance of the reacting oxygen from (C) Au(111) and (D) Pt(111) over the displayed CV window. The CV is $d(\text{O-H}) - d(\text{M-H})$, where M denotes the target surface metal atom. The oxygen-metal distances in panels (C,D) refer to the reacting oxygen, consistent with Figure 4C,D in the main text. Table S1 lists all eight barrier estimates.

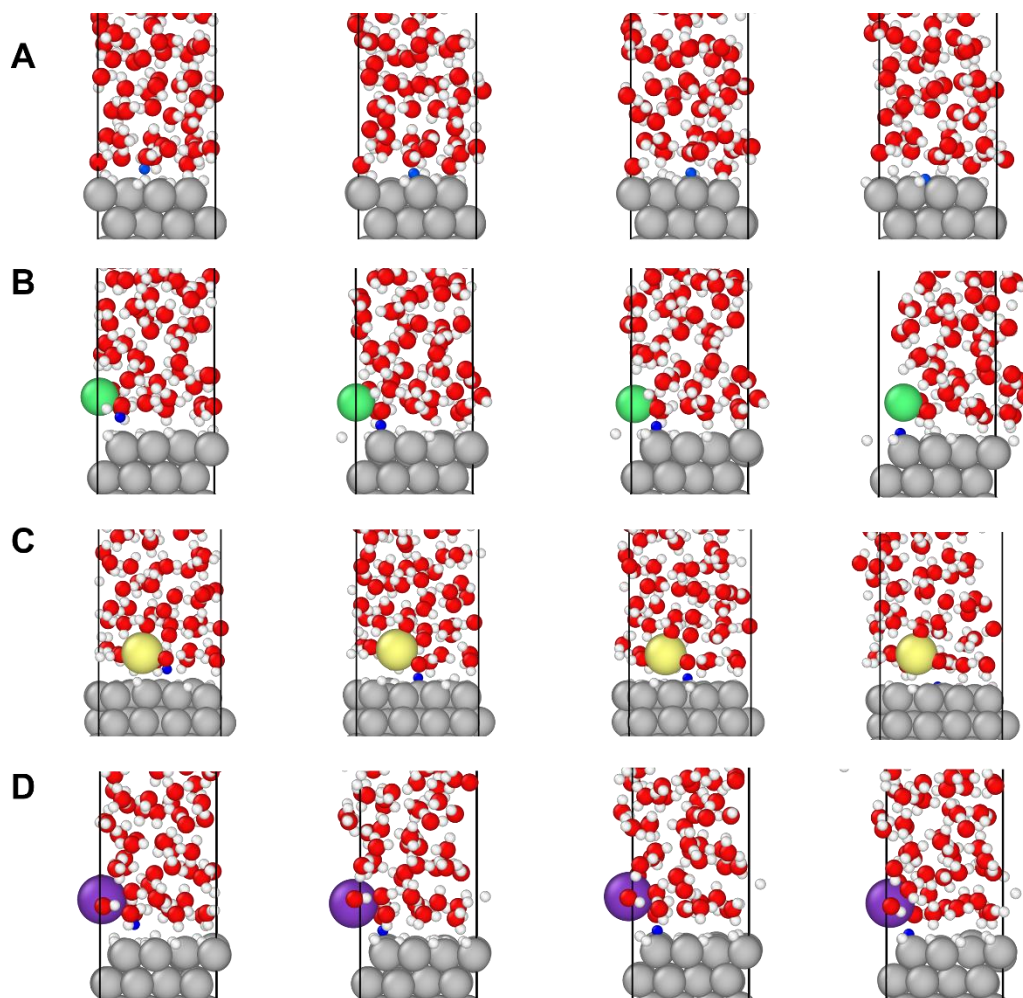


Figure S6. Representative snapshots from unwrapped constrained AIMD trajectories of Volmer water dissociation at Pt(111)/water interfaces. Rows (A-D) show cation-free, Li^+ , Na^+ , and K^+ conditions, respectively. Each row contains selected configurations along the corresponding trajectory. Gray, red, white, and blue spheres denote Pt, O, H, and the transferring H atom. Li^+ , Na^+ , and K^+ are green, yellow, and purple, respectively. The structures were visualized using OVITO Basic 3.15.4. These snapshots correspond to the Pt(111) profiles discussed in Figure 4B,D of the main text.

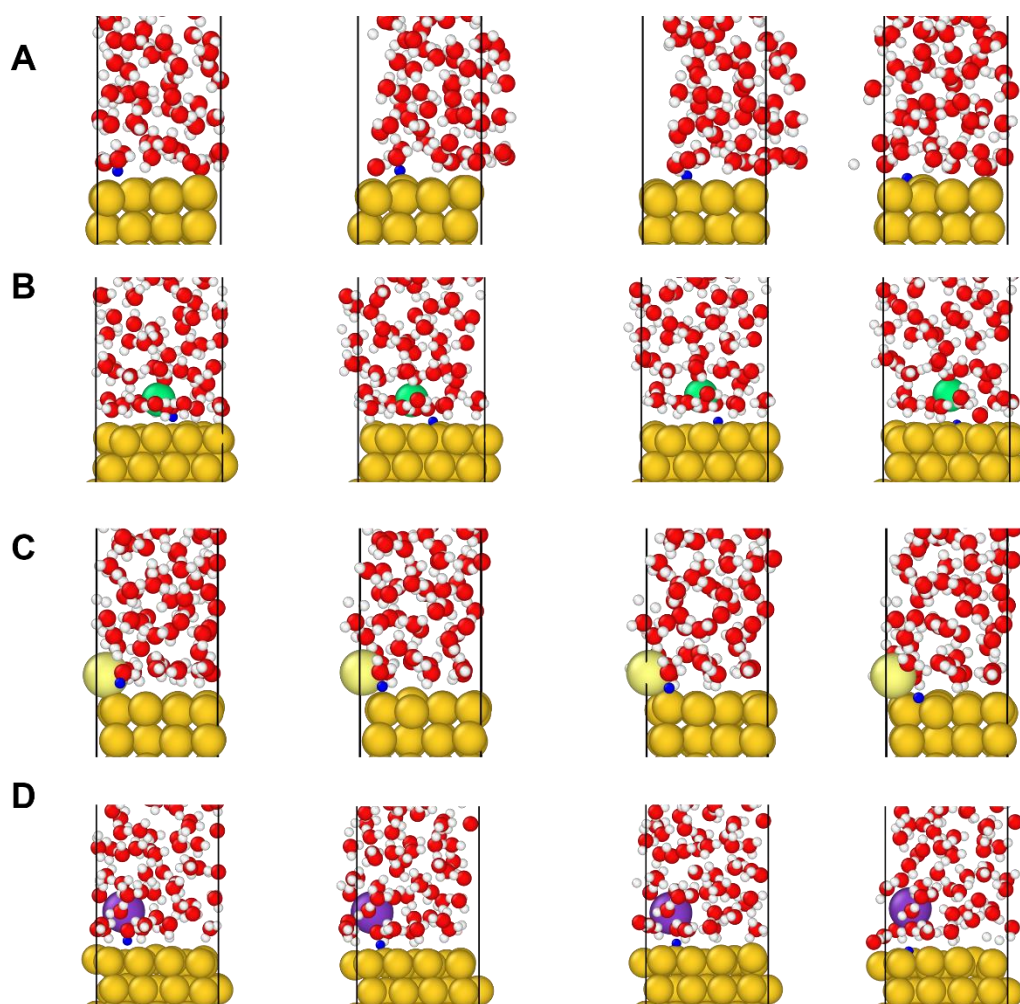


Figure S7. Representative snapshots from unwrapped constrained AIMD trajectories of Volmer water dissociation at Au(111)/water interfaces. Rows (A-D) show cation-free, Li^+ , Na^+ , and K^+ conditions, respectively. Each row contains selected configurations along the corresponding trajectory. Gold, red, white, and blue spheres denote Au, O, H, and the transferring H atom. Li^+ , Na^+ , and K^+ are green, yellow, and purple, respectively. The structures were visualized using OVITO Basic 3.15.4. These snapshots correspond to the Au(111) profiles discussed in Figure 4A,C of the main text.

References

- [1] Martínez, L., Andrade, R., Birgin, E. G., Martínez, J. M. PACKMOL: A package for building initial configurations for molecular dynamics simulations. *J. Comput. Chem.* 2009, 30, 2157-2164. DOI: 10.1002/jcc.21224
- [2] Kresse, G., Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* 1993, 47, 558-561. DOI: 10.1103/PhysRevB.47.558
- [3] Kresse, G., Furthmüller, J. Efficiency of ab-initio total energy calculations for

metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* 1996, 6, 15-50. DOI: 10.1016/0927-0256(96)00008-0

[4] Perdew, J. P., Burke, K., Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 1996, 77, 3865-3868. DOI: 10.1103/PhysRevLett.77.3865

[5] Grimme, S., Antony, J., Ehrlich, S., Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* 2010, 132, 154104. DOI: 10.1063/1.3382344

[6] Sprik, M., Ciccotti, G. Free energy from constrained molecular dynamics. *J. Chem. Phys.* 1998, 109, 7737-7744. DOI: 10.1063/1.477419

[7] You, X., Zhang, D., Zhang, X. G., et al. Exploring the cation regulation mechanism for interfacial water involved in the hydrogen evolution reaction by in situ Raman spectroscopy. *Nano-Micro Lett.* 2024, 16, 53. DOI: 10.1007/s40820-023-01285-1

[8] Wang, Y. H., Zheng, S., Yang, W. M., et al. In situ Raman spectroscopy reveals the structure and dissociation of interfacial water. *Nature* 2021, 600, 81-85. DOI: 10.1038/s41586-021-04068-z

[9] Li, P., Jiang, Y. L., Men, Y., Jiao, Y. Z., Chen, S. Kinetic cation effect in alkaline hydrogen electrocatalysis and double layer proton transfer. *Nat. Commun.* 2025, 16, 1844. DOI: 10.1038/s41467-025-56966-9