

Supporting Information:

Interconversion of Hydrated Protons at the Interface between Liquid Water and Platinum

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S1. *Ab Initio* Molecular Dynamics (AIMD) based Umbrella Sampling (US)

To study the interchange of species at the Pt(111)/H_{2n+1}O_n^x interface, MD simulations based on umbrella sampling were used to investigate the desorption and adsorption processes. Such processes can be studied from the changing free energy in terms of a specific collective variable or reaction coordinate. The initial state and final states are located at the local minimum of free energy whilst the transition state resides at the maximum of free energy.

In this particular case, the solvent plays a central role in assisting the treated reaction. A species participating in a liquid phase reaction experience solute-solvent interactions which occur in the tens of femtosecond time scale. To accurately sample the reaction coordinate, a series of Umbrella Sampling (US)^{1,2,3} simulations partially covering the reaction pathways have been carried out. For the free energy calculations, the collective variables (CVs) are the distance between Hydrogen (H) and center of mass of the Pt(111) surface, and the angle between the distance between Pt and H [A(Pt-H)]. The combination of the primitive coordinates is a natural choice for adsorption/desorption processes. In this condition, we found R(O-H) or R(Pt-H) is sufficient for defining a CV, because the subsequent proton transfer reactions can occur in brute-force simulation due to their associated low energy barriers. The umbrella sampling was performed using periodic DFT calculations, and the artificial potential can be established using Gaussian peak modules:

$$\omega(\xi) = h \cdot e^{\left(-\frac{|\xi'(r)-\xi|^2}{2w^2}\right)} \quad (S1)$$

where h and w are the height and width of the Gaussian distribution and ξ is the collective variable (reaction coordinate). As the MD simulations is performed in the canonical ensemble so that the free energy can be related to the probability based on the Boltzmann's distribution through the canonical partition function (Q):

$$Q = \int e^{[-\beta E(r)]} d^N r \quad (S2)$$

where

$E(r)$ – system specific total energy (eV).
 β – thermodynamic beta = $1/k_B T$
 k_b – Boltzmann's constant = 8.617×10^{-5} (eV/K)

The free energy (A) can therefore be expressed using Equation S3:

$$A = -1/\beta \ln Q \quad (S3)$$

Thus, the probability along the set of collective variables can be written as:

$$P(\xi) = \frac{\int \delta[\xi(r) - \xi] e^{-\beta E} d^N r}{\int e^{-\beta E} d^N r} \quad (S4)$$

In each of the individual MD simulations based on umbrella sampling, a fixed artificial potential is introduced, and the potential surface is expressed as:

$$E^b(r) = E^u(r) + \omega_i(\xi) \quad (S5)$$

where

$E^b(r)$ – biased energy potential.
 $E^u(r)$ – unbiased energy potential.
 $\omega_i(\xi)$ – artificial energy potential.

The biased probability distribution, based on biased energy potential can be written as:

$$P_i^b(\xi) = \frac{\int \delta[\xi'(r) - \xi] e^{-\beta(E(r) + \omega_i(\xi(r)))} d^N r}{\int e^{-\beta(E(r) + \omega_i(\xi(r)))} d^N r} \quad (S6)$$

It is essential that we derive a relation between the unbiased probability distribution to the biased energy potential and the artificial potential. Thankfully this can be readily calculated as:

$$P_i^u(\xi) = P_i^b(\xi) e^{-\beta \omega_i(\xi)} \times \frac{\int \delta[\xi(r) - \xi] e^{-\beta \omega_i(\xi(r))} d^N r}{\int e^{-\beta E(r)} d^N r} \quad (S7)$$

The unbiased free energy can therefore be calculated as follows:

$$\begin{aligned}
 A_i^u(\xi) &= -\frac{1}{\beta} \ln P_i^b(\xi) - \omega_i(\xi) + \left(-\frac{1}{\beta} \ln \left[\frac{\int e^{-\beta E(r)} e^{-\beta \omega_i(\xi(r))} d^N r}{\int e^{-\beta E(r)} d^N r} \right] \right) \\
 &= -\frac{1}{\beta} \ln P_i^b(\xi) - \omega_i(\xi) + F_i
 \end{aligned} \quad (S8)$$

Whereby, all the complex terms are contained within F_i , which see a marked simplification for our calculation. The solution of this function can be performed based on the self-consistent theory until the calculation converges to its threshold.

To combine multiple simulations and derive the unbiased probability $P(\delta)$, it is necessary to use methods such as the Weighted Histogram Analysis Method (WHAM)^{4,5}, wherein the likelihood for the observation of a sequence of constrained simulations can be related to the product of the probability of each simulation. A schematic summary of the processes involved in the umbrella sampling methodology is shown in Figure S1.

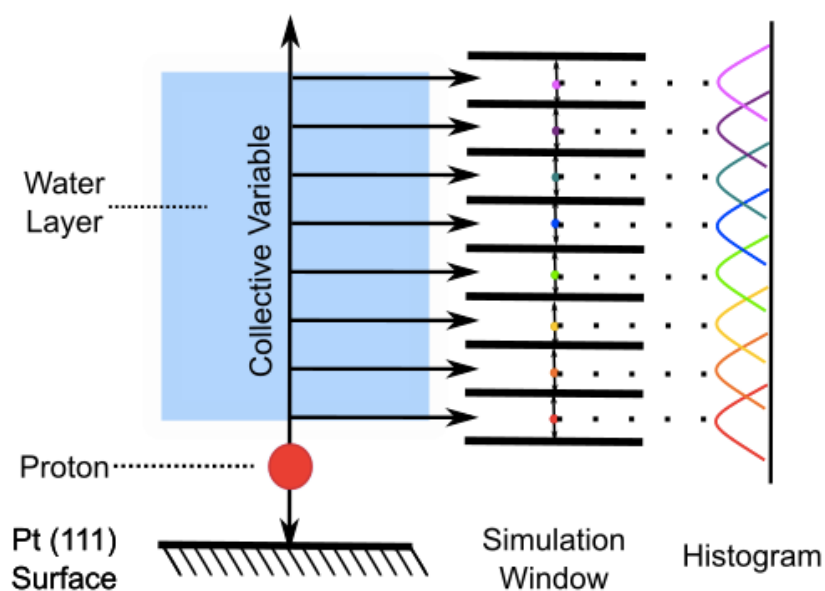


Figure S1 – Schematic representation of the umbrella sampling method for a simple absorption-desorption process between a reactant molecule (red) and a metal surface. Numerous simulations are carried out along a partitioned collective variable divided into simulation windows. The reactant is constrained relative to a sub-surface atom, to drive the system from one thermodynamic state to another e.g. from initial state to final state. Each window provides us with a histogram with a virtual harmonic potential constraint, overlapping windows provide the input for the weighted histogram analysis method (WHAM) which provides free energy profile along the collective variable.

S2. Unit Cell Conversion

All simulations were calculated using either a hexagonal unit cell or an orthorhombic unit cell with equivalent atoms. The hexagonal cell is converted to its corresponding orthorhombic structure via the following matrix transform, which maintains the translation symmetry exhibited by each species in the cell:

$$\begin{aligned} T_{ORTHO} &= \begin{bmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} T_{HEX} \\ &= \begin{bmatrix} 1 & 1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix} \end{aligned} \quad (S9)$$

where

T_{HEX} – primitive lattice vectors of hexagonal unit cell.

T_{ORTHO} – primitive lattice vectors of orthorhombic unit cell.

S3. Atomic Density Profile

$$\rho_{H_2O} = \frac{Nm_{H_2O}}{|\vec{a} \times \vec{b} * ((\bar{z}_{max} - z_{min} * O_{rad})\hat{z})|} \quad (S10)$$

where

N – number of water molecules (11-22).

m_{H_2O} – atomic mass of one water molecule.

$|\vec{a} \times \vec{b}|$ – volume defined by two lattice vectors, a and b .

\bar{z}_{max} – maximum z -coordinate for oxygen, taken as the average over the upper most layer.

z_{min} – minimum z -coordinate for oxygen.

O_{rad} – atomic radius of a single oxygen atom ($\sim 0.6\text{\AA}$).

S4. Radial Pair Distribution Function, ($g(r)$)

The radial pair distribution functions (rpdf) between the atom coordinates in two selections over a 50 ps trajectory were calculated using Equation S11⁶:

$$g(r) = \lim_{dr \rightarrow 0} \frac{\zeta(r)}{4\pi \left(\frac{N_{pairs}}{V}\right) r^2} dr \quad (S11)$$

where

r – distance between an atom pair.

$\zeta(r)$ – the average number of atom pairs found at distance r .

N_{pairs} – number of unique atom pairs, where one atom is from each of the two atom selections.

S5. Coordination Number (CN)

Taking the integral of the radial pair distribution function ($g(r)$), allows us to determine the number of nearest neighbours from a central atom. If we take the integral over the first minimum, we can obtain details about the first hydration sphere / coordination number:

$$CN = \int_0^{r_N} \rho g(r) 4\pi r^2 dr \quad (S12)$$

where

ρ – periodicity constant to account for periodic boundary conditions.

$g(r)$ – radial Pair Distribution Function.

$4\pi r^2$ – area of spherical bin.

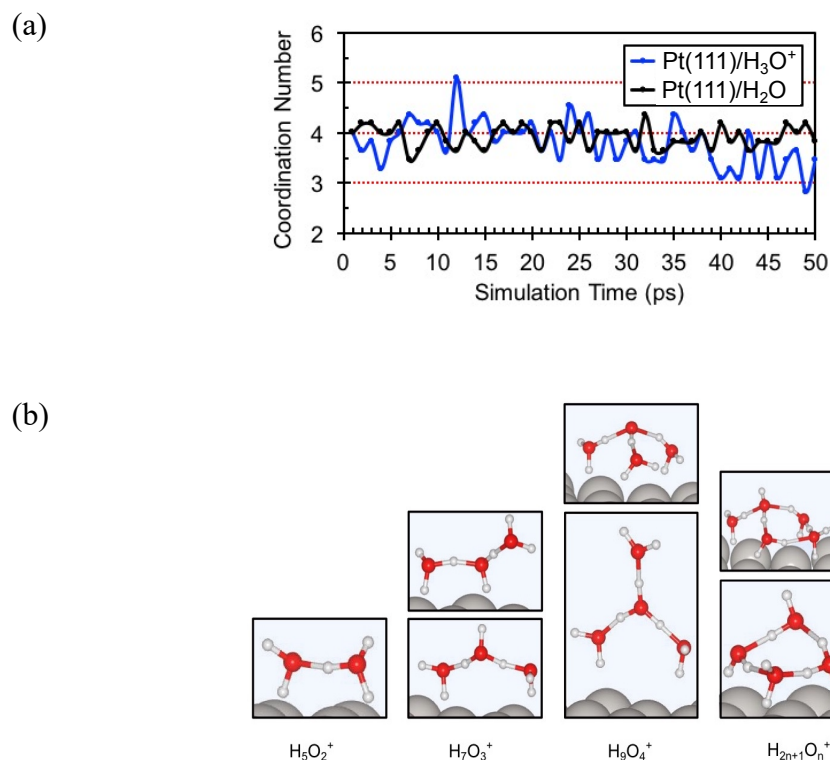


Figure S2 - (a) The static oxygen coordination shell number taken at 1ps intervals for both neutral (system A) and protonated (system B) systems. For clarity, the red dashed lines depicts the integer coordination number of 3, 4 and 5 coordinated species. **(b)** Snapshots of several of the most commonly encountered protonated species observed during the AIMD simulation at the $\text{H}_3\text{O}^+/\text{Pt}(111)$ interface.

S6. Charge Density Difference

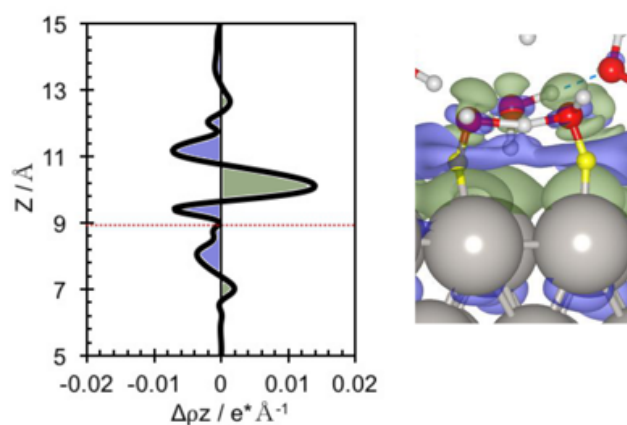
For visualization of bonding we chose to use the charge density difference method. The electron density difference calculated along the z direction was calculated using the following:

$$\Delta\rho(z) = \iint \rho_{diff} dx dy \quad (\text{S13})$$

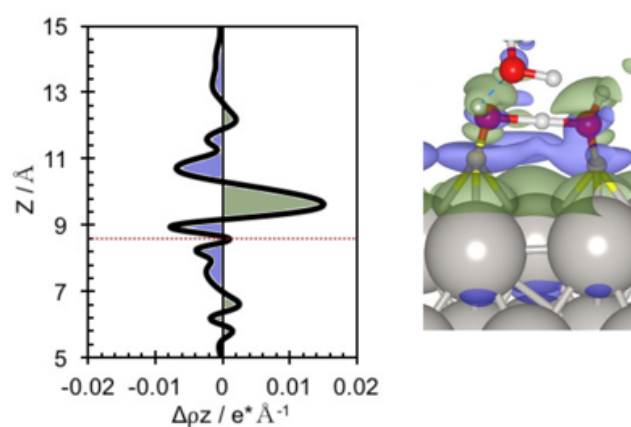
Here, ρ_{diff} is calculated to be the difference between the systems total electron density and the superposition of the isolated species electron densities:

$$\rho_{diff} \left(\frac{e}{\text{\AA}} \right) = \rho_{ABC} - (\rho_A + \rho_B + \rho_C) \quad (\text{S14})$$

(a)



(b)



(c)

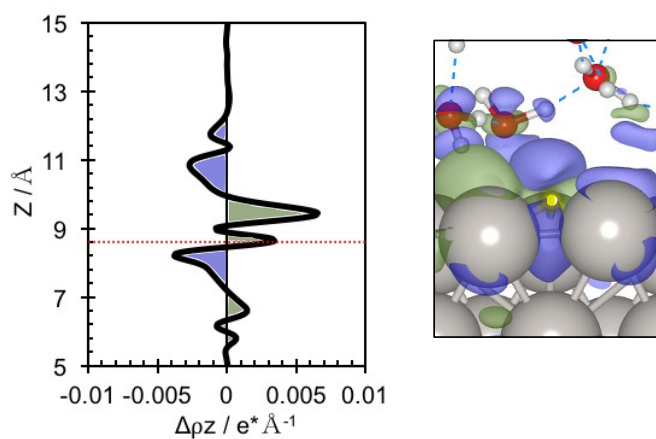


Figure S3(a)-(c) – (left) Planar charge density difference (CDD) and (right) 3D CDD, calculated normal to the Pt(111) surface for the interaction of the water layer and Pt for (a) A hollow site adsorbed cation and (b) A top site adsorbed cation. Obtained from AIMD-US calculations. (c) Hollow site adsorbed hydrogen (Red dashed lines indicate the position of the top most Pt layer, Purple shading represents electron depletion while green shading is electron accumulation). The iso-surface level is set to $0.0015 e/\text{\AA}^3$.

S7. Self-Diffusion Coefficient (D_0)

The self-diffusion coefficient is calculated on adopting the Einstein relation, whereby D_0 can be approximated assuming it is proportional to the mean square displacement (MSD (t)) as a function of time. Equation S15:

$$D_0 = \lim_{t \rightarrow \infty} \left[\frac{MSD(t)}{\omega n \Delta t} \right] \quad (S15)$$

where

$$MSD(t) - \text{time dependant Mean Square Displacement } (\text{\AA}^2) = \frac{\sum_{i=1}^{N_{atoms}} r_i(t_1) - r_i(t_2)}{N_{atoms}}$$

ω – reversibility constant, assuming the diffusion is directionally independent then $\omega = 2$.

n – dimensionality constant, in this case $n = 3$ as we are dealing with diffusion in three-dimensional space.

Δt – simulation time step (ps).

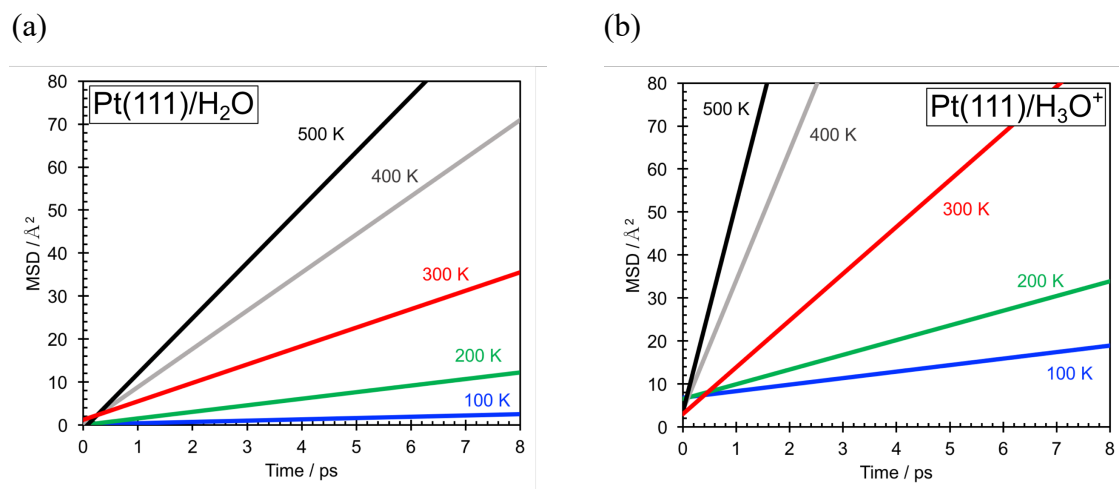


Figure S4(a)-(b) – Plots of the temperature dependant mean square displacement (MSD) as a function of time for oxygen atoms in (a) System A: Pt(111)/H₂O and (b) System B: Pt(111)/H₃O⁺. Calculated as part of Equation S15.

Table 1: Self-diffusion coefficients of water ($D_0(T)$). For comparison, neutron scattering data⁷ for bulk liquid water are reported.

System	T (K)	D_0 ($\text{\AA}^2/\text{ps}$)
H ₂ O/Pt(111)	300	0.702
H ₃ O ⁺ /Pt(111)	300	1.800
Experiment	333	0.502
	368	0.880

S8. Dipole Orientation Analysis

Using the orientation angle θ defined in Figure S5, we have determined the distribution of angles in each layer. With the help of Python and Numpy numerical packages, we firstly extracted all structures in the OUT.ANI file after the MD simulation. For each structure, we could obtain the coordination's of all H and O atoms. Then, we identify H₂O molecules by pairing O with the closest two H, with the restriction that the H-O bond length is between 0.85 and 1.25 \AA and H-O-H angle between 96° and 116°. With the H₂O molecules identified (about 90% of molecules will be identified in the proceeding stage), the orientation angle θ can be calculated by the law of cosines as defined in Figure S5 in the main text.

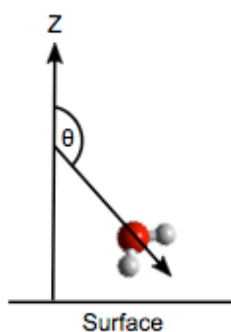


Figure S5 – Definition of the dipole orientation angle (θ), where the z-axis is the vector normal to the Pt(111) surface.

S10. References

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