Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information to: Theoretical insight into vibrational spectra of metal-water interfaces from density functional theory based molecular dynamics

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Computational setup

Pt(111) and Au(111) surfaces were modelled by $p(6\times6)$ supercell slabs with 4 atomic layers. The periodic slabs are separated with a 21 Å vacuum region, and thus the size of Pt(111) and Au(111) supercells are $16.869 \times 16.869 \times 27.887$ Å^3 and $17.607 \times 17.607 \times 28.188$ Å^3, respectively. The calculated work functions of Pt(111) and Au(111) are 5.8 and 5.4 eV, which are very close to the experimental values.[1] The Pt(111) and Au(111)-water interfaces were modelled by fully filling the vacuum space in the metal surface models with water, and the density of the bulk region is set ∼1 g/mL. The interface models contain 144 Pt or Au atoms and 151 H_2O molecules in total. The initial configurations of the surface water were computationally optimised to be H-down ice-like bilayer with 2/3 coverage. The rest of the water molecules were pre-equilibrated with classical molecular dynamics (MD) simulations for ∼100 ps. The conditions of these metal-water interfaces correspond to the potentials of zero charge (PZC).

The density functional theory (DFT) implementation in CP2K/Quickstep[2] is based on a hybrid Gaussian plane wave (GPW) scheme, in which orbitals are described by atom centered Gaussian-type basis sets, and auxiliary plane wave basis sets are used to re-expand the electron density in the reciprocal space. A matrix diagonalization procedure was used for the wave function optimisation and the self-consistent field (SCF) convergence was facilitated by Fermi smearing with the electronic temperature of 300 K. The 2s, 2p electrons of O, 5d, 6s electrons of Pt and Au were treated as valence, and the rest core electrons were represented by Goedecker-Teter-Hutter (GTH) pseudopotentials.[3,4] Gaussian basis sets of double-ζ with one set of polarisation functions (DZVP) were used,[5] and the energy cutoff for plane wave expansion was set to 400 Ry. We employed Perdew-Burke-Ernzerhof (PBE) functional[6] to describe the exchange-correlation effects, and the dispersion correction was applied in all calculations with the Grimme D3 method.[7] Born-Oppenheimer molecular dynamics was employed to simulate the interfaces with a time step of 0.5 fs, and the canonical ensemble was imposed by a Nose-Hoover thermostat (NVT) with the temperature target 330 K. The first

3 ps of the simulations were regarded as the equilibration periods, followed by a production period of 5∼10 ps. Note that due to the large size of the interface model, only Γ point was used in all calculations. The vibrational spectra of water were calculated by the Fourier transformation of the hydrogen-hydrogen velocity autocorrelation function.

The adsorption of a water monomer on Pt(111) in gas phase was also calculated for comparison. The optimized structure is water on the top site with the molecular plane almost parallel to the surface. The calculations were carried out using Vienna Ab-initio Simulation Package (VASP).[8–11] PBE functional[6] was used to describe the exchange-correlation effects with the Grimme D3 correction.[7] The plane waves were constructed using projector augmented-wave (PAW) potentials with an energy cutoff of 450 eV.[12,13] The convergence criteria of the geometry optimisation is the maximum force of unconstrained atoms less than 0.05 eV/Å. The finite displacement method was employed to calculate the vibrational frequencies of the optimised structures with the metal atoms fixed.

Table S1: Numbers of surface metal atoms (N), adsorbed water molecules (N_{surf}), watA molecules (N_{watA}) and watB molecules (N_{watB}). γ is the surface water coverage. The results in the table have been reported in our recent work.[14]

Surface	N	N_{surf}	γ / ML	N_{watA}	N_{watB}
Pt(111)	36	27.7	0.77	6.5	21.2
Au(111)	36	29.7	0.82	6.1	23.6

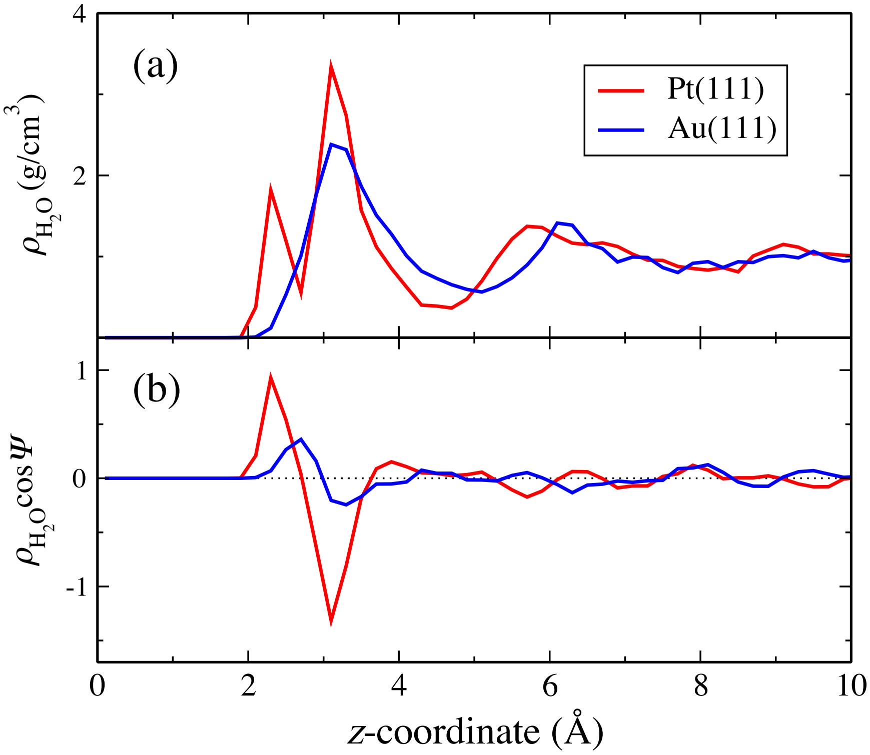

Figure S1: The profiles of water density (ρ_{H_2O}) and dipole orientation ($\rho_{H_2O}\cos\Psi$, where Ψ is the angle between water bisector and surface normal) along the z-coordinate. Red and blue lines represent Pt(111)- and Au(111)-water interfaces, respectively. They are obtained by averaging over the two symmetric interfaces in our models. The zero in z-coordinate indicates the position of the nuclei of the top metal layer. The data was reported in our recent work.[14,15]

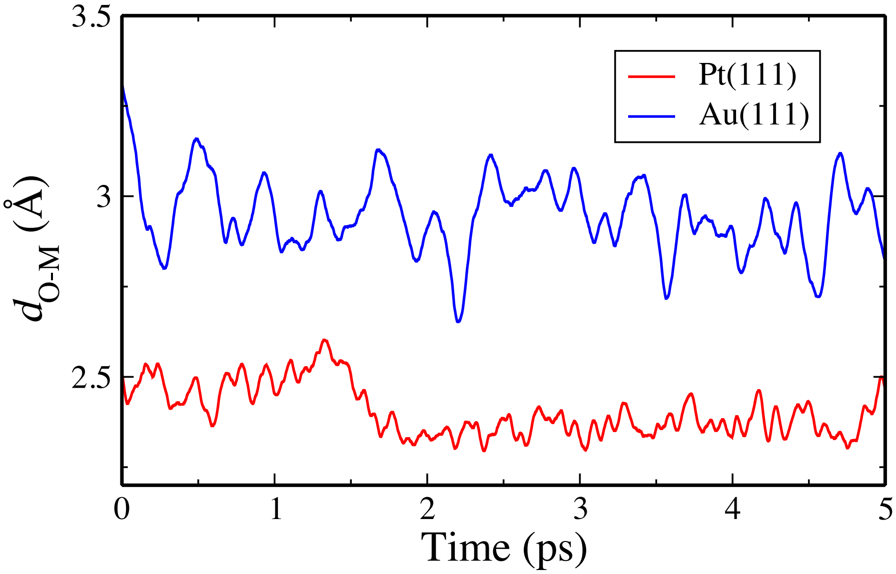

Figure S2: Fluctuation of the distance ($d_{\mathrm{O-M}}$) between the oxygen atoms of watA and their corresponding metal surface along the simulation time.

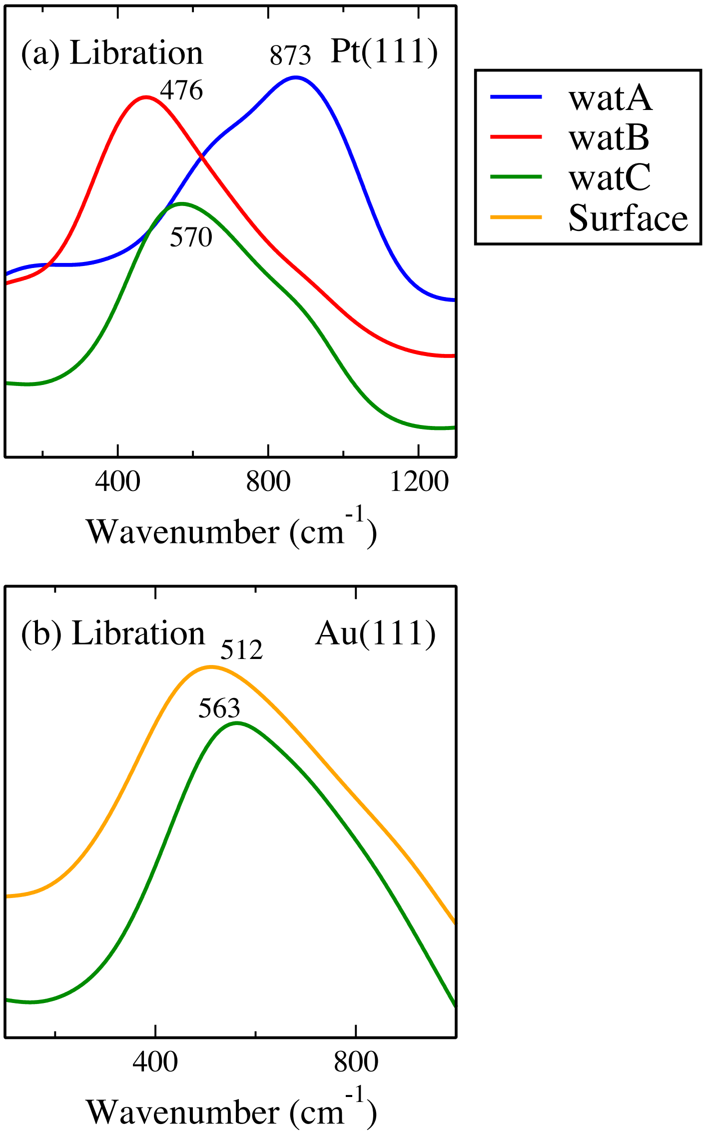

Figure S3: The libration modes of different types of water at the Pt(111)- and Au(111)-water interfaces. The watA, watB and watC and surface water are represented by blue, red, green and orange curves, respectively.

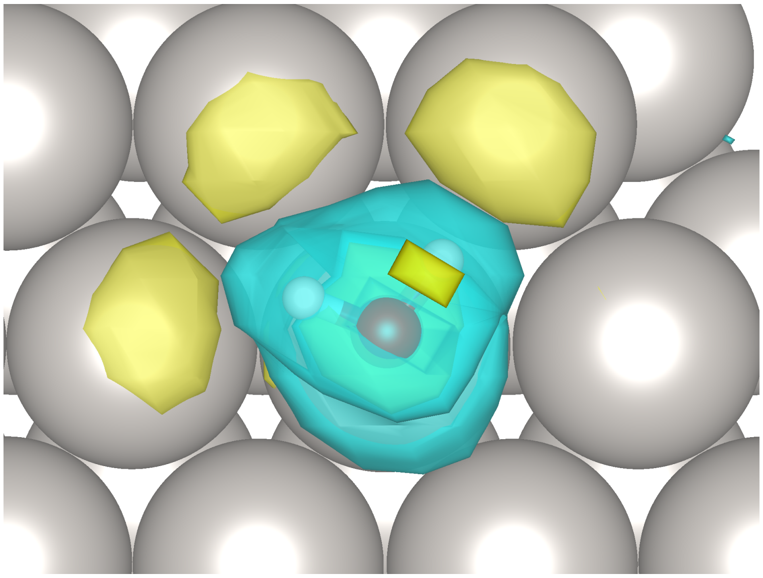

Figure S4: Electron redistribution profile of a water molecule adsorbed on the top site of Pt(111) in gas phase. The isosurfaces represent the electron density difference profile of the interface before and after water interacts with the metal surface electronically, and the regions colored by cyan and yellow indicate electron depletion and accumulation, respectively.

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