Supplementary Materials

Intrinsic Origin of Anomalous Double-Layer Capacitance on Pt(111) Revealed by Grand Canonical Density Functional Theory

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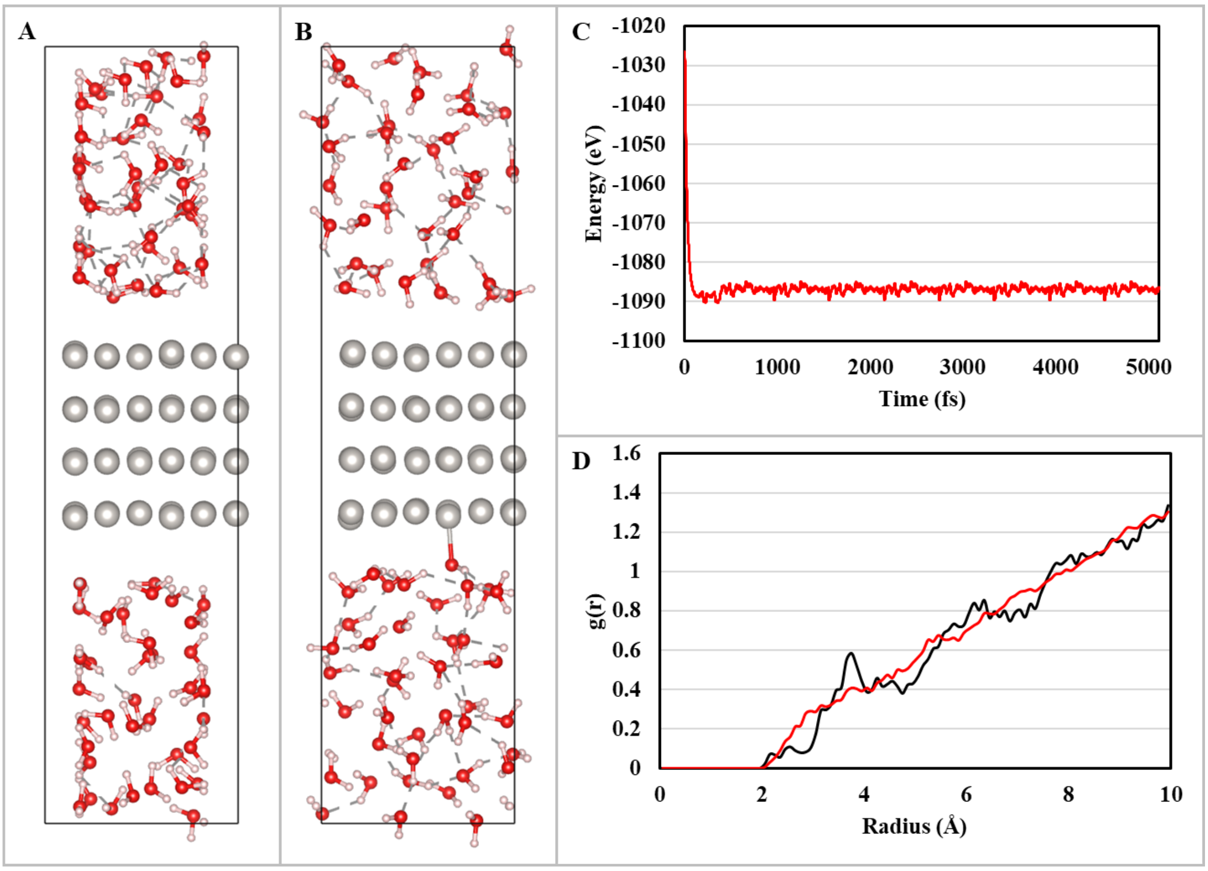
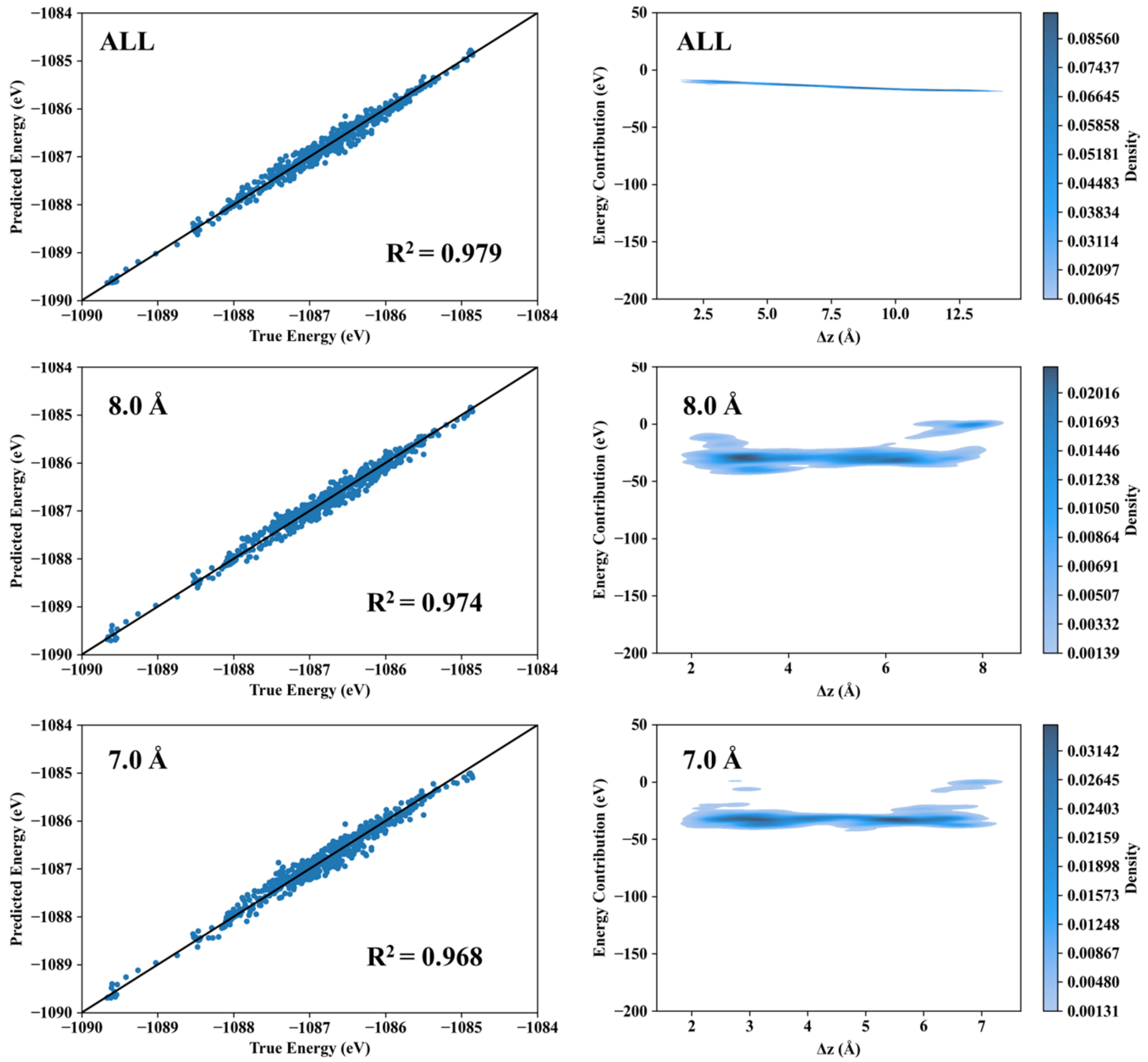


Supplementary 1. (a) Initial atomic pt(111)–water interface structure for the AIMD simulation, (b) one snapshot of atomic pt(111)–water interface structure when the total energy is stabilised during the AIMD simulation, (c) plot of total energy fluctuation of the graphene-water interfaces over timescale of 5.0 ps and (d) radial distribution function (RDF) plot for Pt–O (black) and Pt–H (red). Colour code: gray-Pt, red-O, and pink-H.

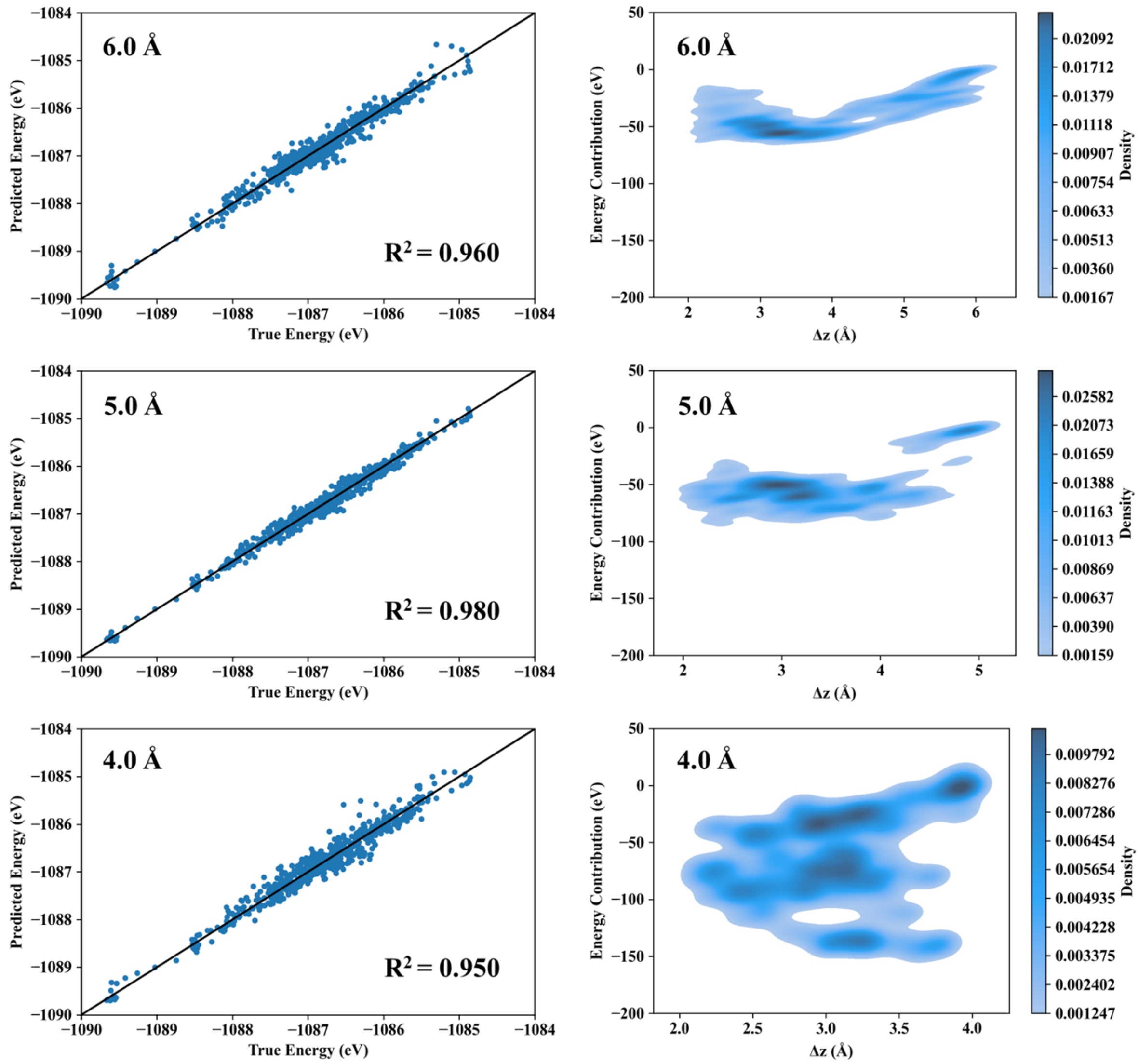
MACHINE LEARNING METHODS

The supervised machine learning model was implemented in PyTorch and trained using the Adam optimiser [23,24]. Input features were constructed from AIMD trajectories, where per-frame oxygen positions relative to the Pt(111) surface were extracted. For each oxygen atom, distances to all Pt atoms and the displacement from the median Pt plane (Δz) were computed. These features were used as inputs to a feed-forward neural network. A Δz cutoff of 4.0–8.0 Å was applied to exclude water molecules beyond the interfacial region. The network consisted of two fully connected hidden layers with 64 neurons each, using the SiLU activation function, and produced per-oxygen energy contributions that were summed to predict the total frame energy. Training labels were obtained from AIMD total energies, hereafter denoted as E_0.

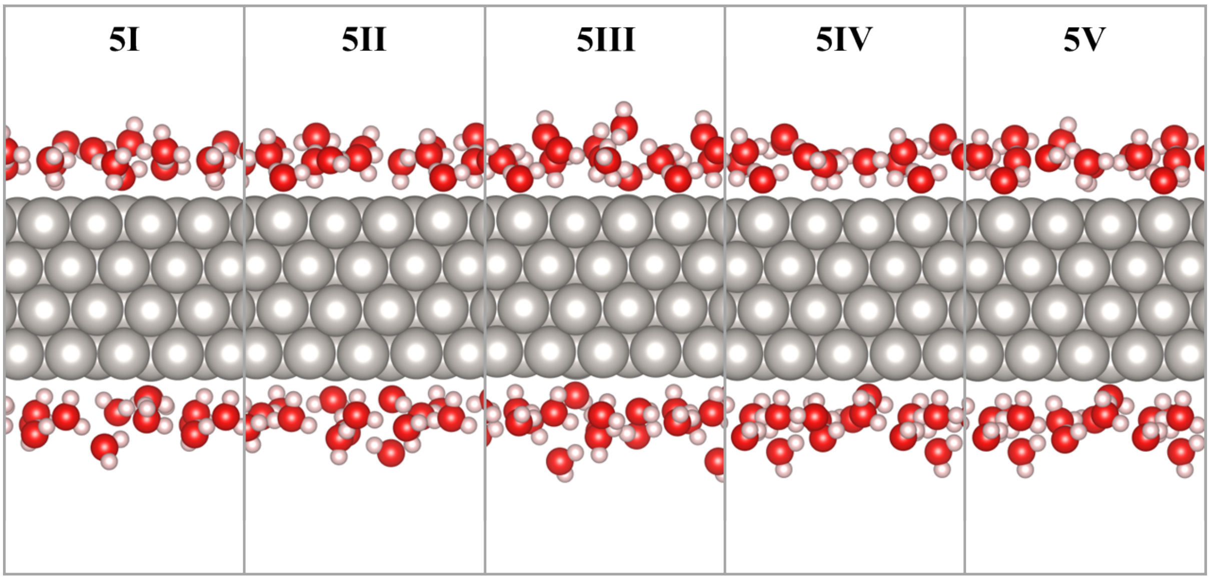
A mean-squared error (MSE) loss function was employed, with an optional stabilisation penalty weighted by Δz. Of the 5200 AIMD frames, the first 200 were discarded due to incomplete energy convergence during initial relaxation. The remaining 5000 frames were randomly split into training (80%) and validation (20%) sets using a fixed seed for reproducibility. Model checkpoints were saved based on improvements in validation loss.



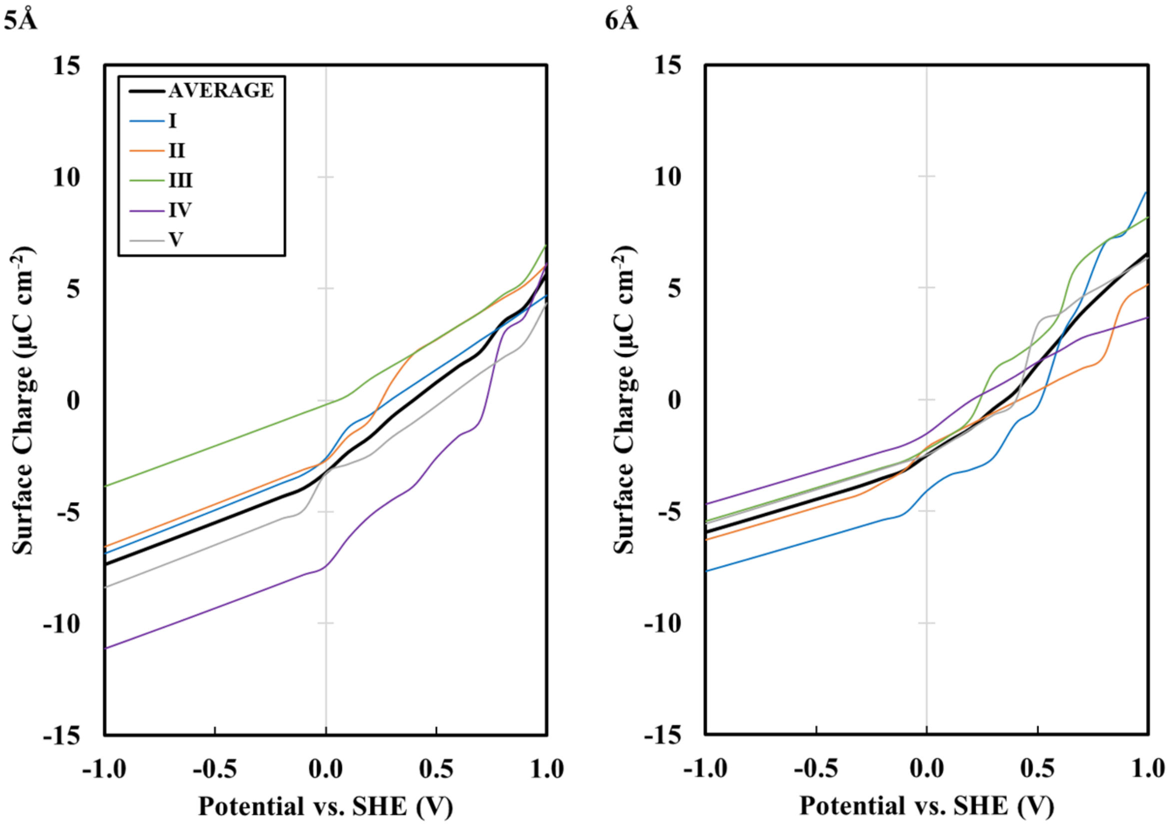
Supplementary 2a. Left: predicted versus true total frame energies (E_0) for the corresponding models using Δz cutoffs of 4–6 Å. Right: kernel density estimates of total energy contributions (eV) versus Δz (Å) for oxygen atoms; colour scale represents the probability density.



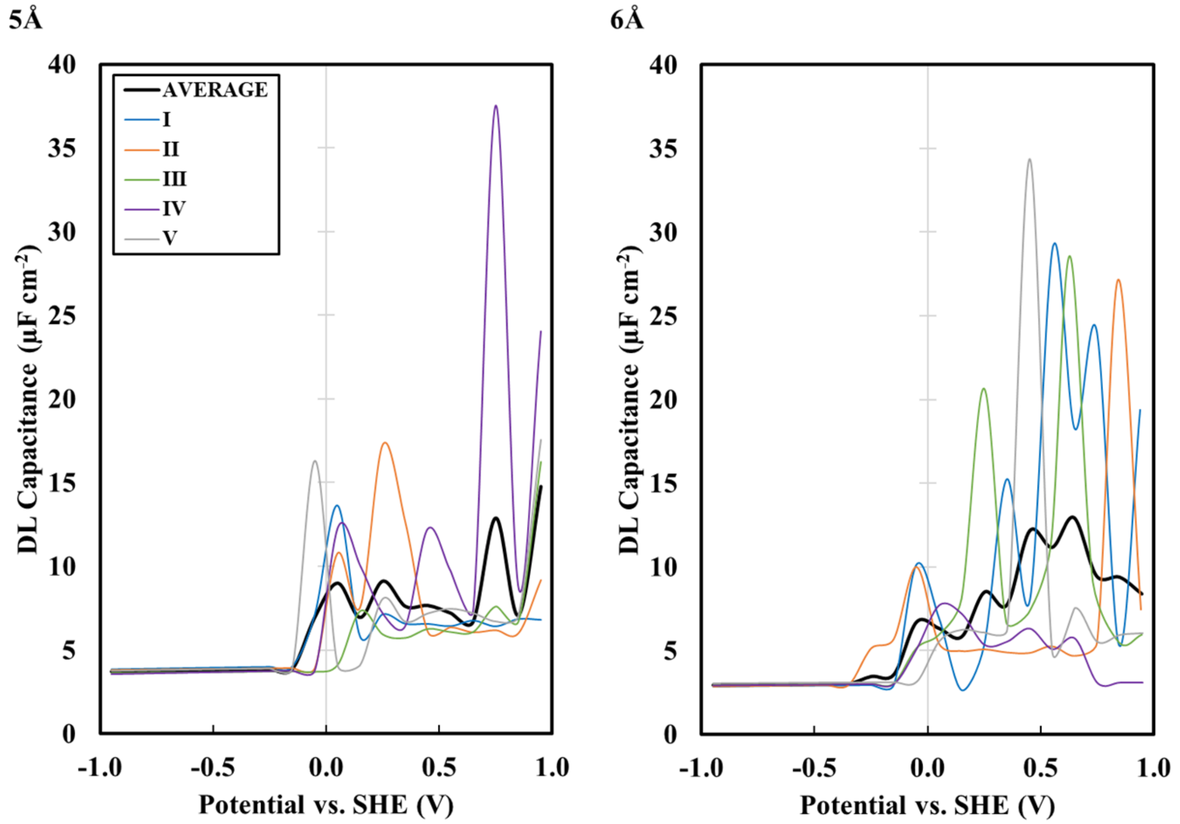
Supplementary 2b. Left: predicted versus true total frame energies (E_0) for the corresponding models using Δz cutoffs of 7–8 Å, plus an all-water (no-cutoff) case. Right: kernel density estimates of total energy contributions (eV) versus Δz (Å) for oxygen atoms; colour scale represents the probability density.



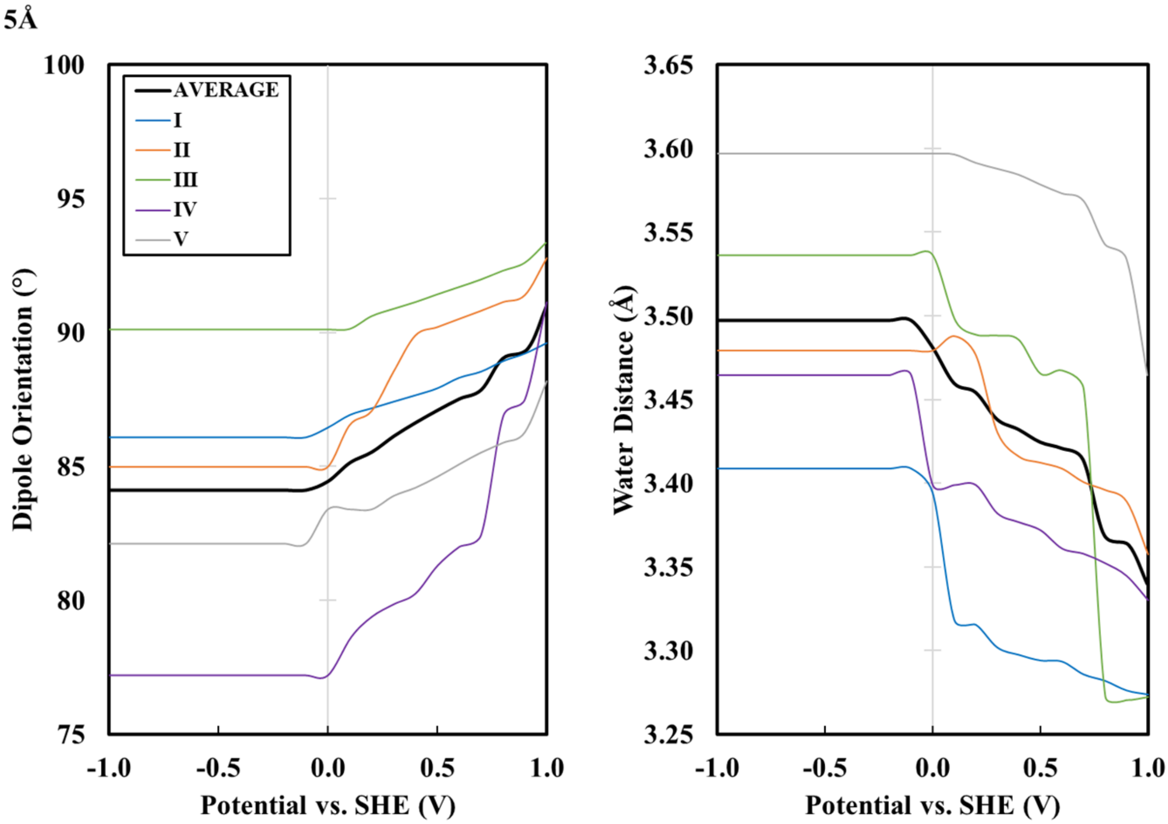
Supplementary 3. Constant-potential GC-DFT relaxed configurations of the Pt(111)–water interface generated from AIMD-sampled structures using a 5.0 Å cutoff distance defined along the surface normal (Δz).



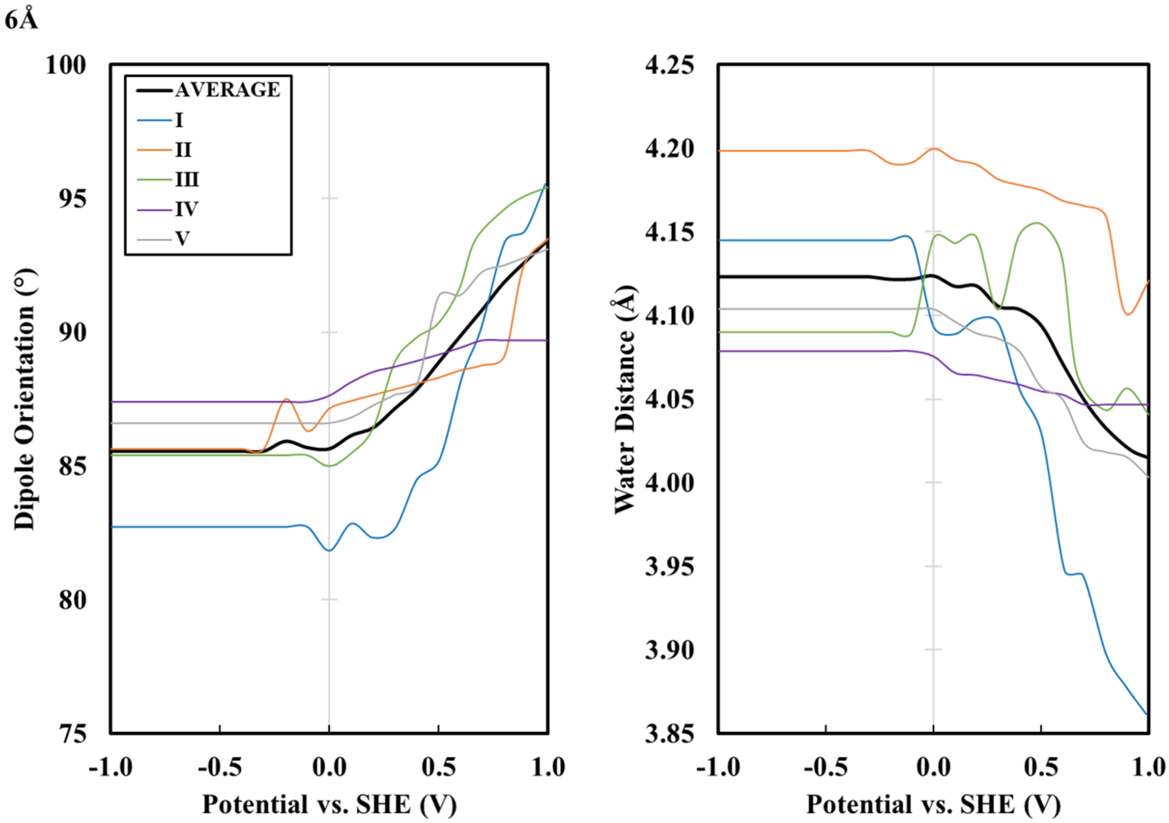
Supplementary 4I. Surface Charge (μC cm⁻²) of the hybrid Pt(111)–water interface as a function of potential (V vs SHE) for the 5 Å and 6 Å cutoffs. Individual hybrid configurations (I–V) are shown together with the averaged response (black).



Supplementary 4II. Electric double-layer capacitance (μF cm⁻²) of the hybrid Pt(111)–water interface as a function of potential (V vs SHE) for the 5 Å and 6 Å cutoffs. Individual hybrid configurations (I–V) are shown together with the averaged response (black).



Supplementary 5I. Individual hybrid configurations for the 5 Å cutoff showing the mean Pt–water distance and first-layer O–H dipole orientation as a function of potential (V vs SHE).



Supplementary 5II. Individual hybrid configurations for the 6 Å cutoff showing the mean Pt–water distance and first-layer O–H dipole orientation as a function of potential (V vs SHE).