Supplementary Information

Self-Diffusion of Individual Adsorbed Water Molecules at Rutile (110) and Anatase (101) TiO$_2$ Interfaces from Molecular Dynamics

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Table S1. Self-diffusivities [x 10^{-9} m^2 s^{-1}] (x,y,z) in adsorbed layer (IHL) and second layer (OHL) from each surface over the first 50 ps of 300 ps sub-intervals. Note that the sum of the different laboratory directions gives the total self-diffusivity. That of bulk water is ~2.23 × 10^{-9} m^2 s^{-1} whilst the experimental bulk-water value is 2.3 × 10^{-9} m^2 s^{-1}.

Table S2. Self-diffusion D (m^2/s) for anatase (101) and rutile (110) at different 50 ps sub-intervals from 100 to 300 ps.

Figure S1. Average hydrogen bonds of different adsorbed layers.

Figure S2. Probability distribution of self-diffusion coefficients of each individual water molecule in the OHL averaged over a 50 ps sub-interval (450 to 500 ps) for (**a**) rutile. (**b**) anatase Diffusivities of the x, y, z directions are shown in blue, red and green dashed lines, respectively. The total diffusivity of individual molecules is represented by the solid black line. Although this sub-interval showed rather unexpected results in the OHL, the other intervals presented distributions similar to those in the 300 ps sub-intervals.

Figure S3. Mean square displacement (MSD) of water molecules in different layers at the water-TiO$_2$ (**a**) anatase (101) and (**b**) rutile (110) interface for the interval of 350 and 400 ps. The self-diffusivity experimental bulk-water value of 2.3 × 10^{-9} m^2 s^{-1} is represented by the grey dotted line for reference.

Figure S4. Velocity auto-correlation function of adsorbed layers of rutile (110).

Figure S5. Probability distribution of self-diffusion coefficients of each individual water molecule averaged over 50 ps sub-intervals for rutile (110) IHL. Water molecules are considerably sluggish in the IHL for all 50 ps sub-intervals

Figure S6. Dissociative adsorption of water on (**a**) anatase (101) and (**b**) rutile (110) surface considering full monolayer coverage. The water molecule on left-side panels consequently split to OH$^-$ that adsorbs on Ti$_{5c}$ and H$^+$ adsorbing on O$_{2c}$/Ob (right-side panels). Titanium atoms are shown in light blue, water hydrogen in white, and oxygen atoms from both TiO$_2$ and water in red. The dashed blue lines represent hydrogen bonds.
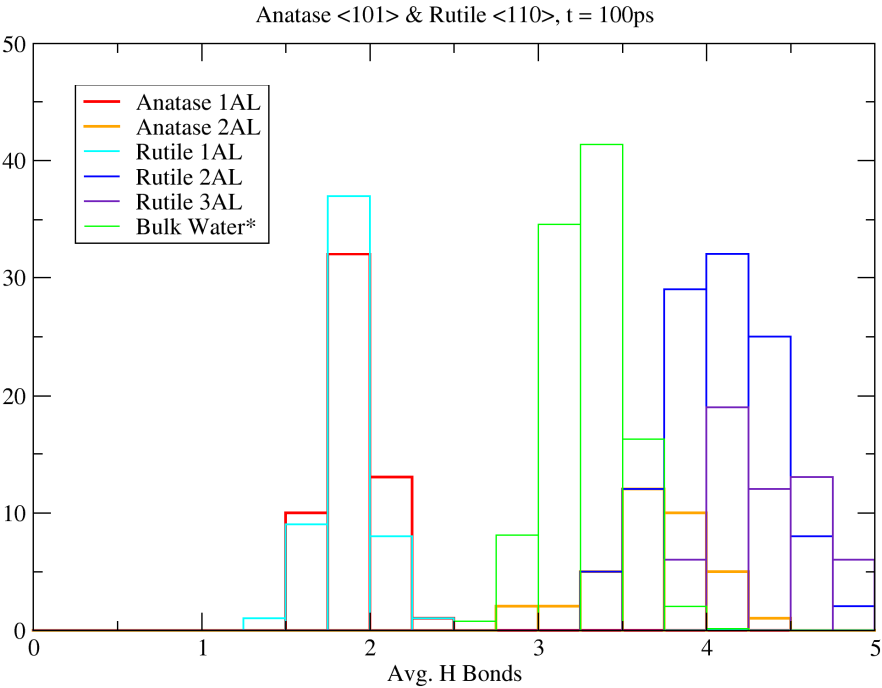
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Surface	IHL	OHL
Rutile (110)	0.0360, 0.0334, 0.0158	1.092, 0.904, 0.935
Anatase (101)	0.398, 0.361, 0.184	0.497, 0.374, 0.323

Table S2. Self-diffusion D (m^2/s) for anatase (101) and rutile (110) at different 50 ps sub-intervals from 100 to 300 ps.

Surface	100 ps	150 ps	200 ps	250 ps	300 ps
Anatase IHL	5.33 × 10^{-10}	3.34 × 10^{-10}	4.94 × 10^{-10}	5.85 × 10^{-10}	4.41 × 10^{-10}
Rutile IHL	1.86 × 10^{-11}	1.69 × 10^{-11}	1.38 × 10^{-11}	1.39 × 10^{-11}	1.36 × 10^{-11}
Anatase OHL	1.83 × 10^{-9}	1.54 × 10^{-9}	1.47 × 10^{-9}	1.48 × 10^{-9}	1.94 × 10^{-9}
Rutile OHL	2.25 × 10^{-9}	6.52 × 10^{-10}	7.83 × 10^{-10}	3.03 × 10^{-9}	9.78 × 10^{-10}

* Bulk water run for 5 ps and normalised.

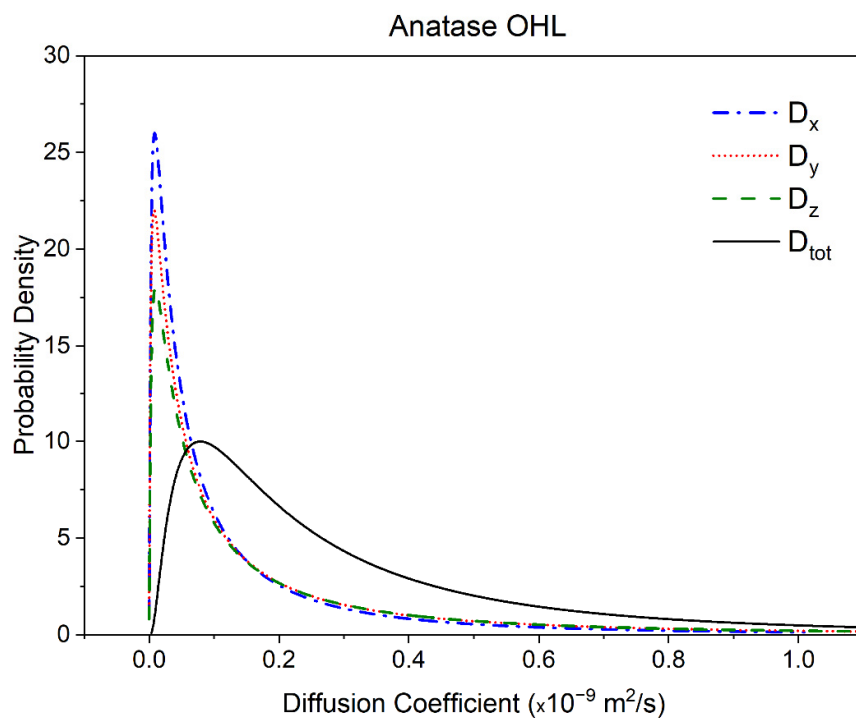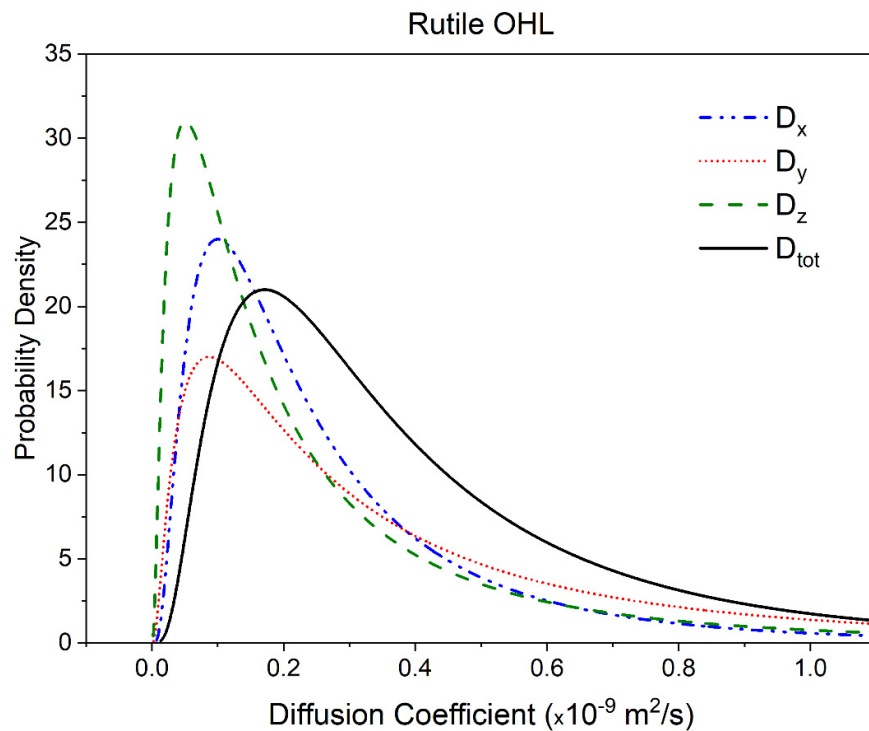**Figure S1.** Average hydrogen bonds of different adsorbed layers.

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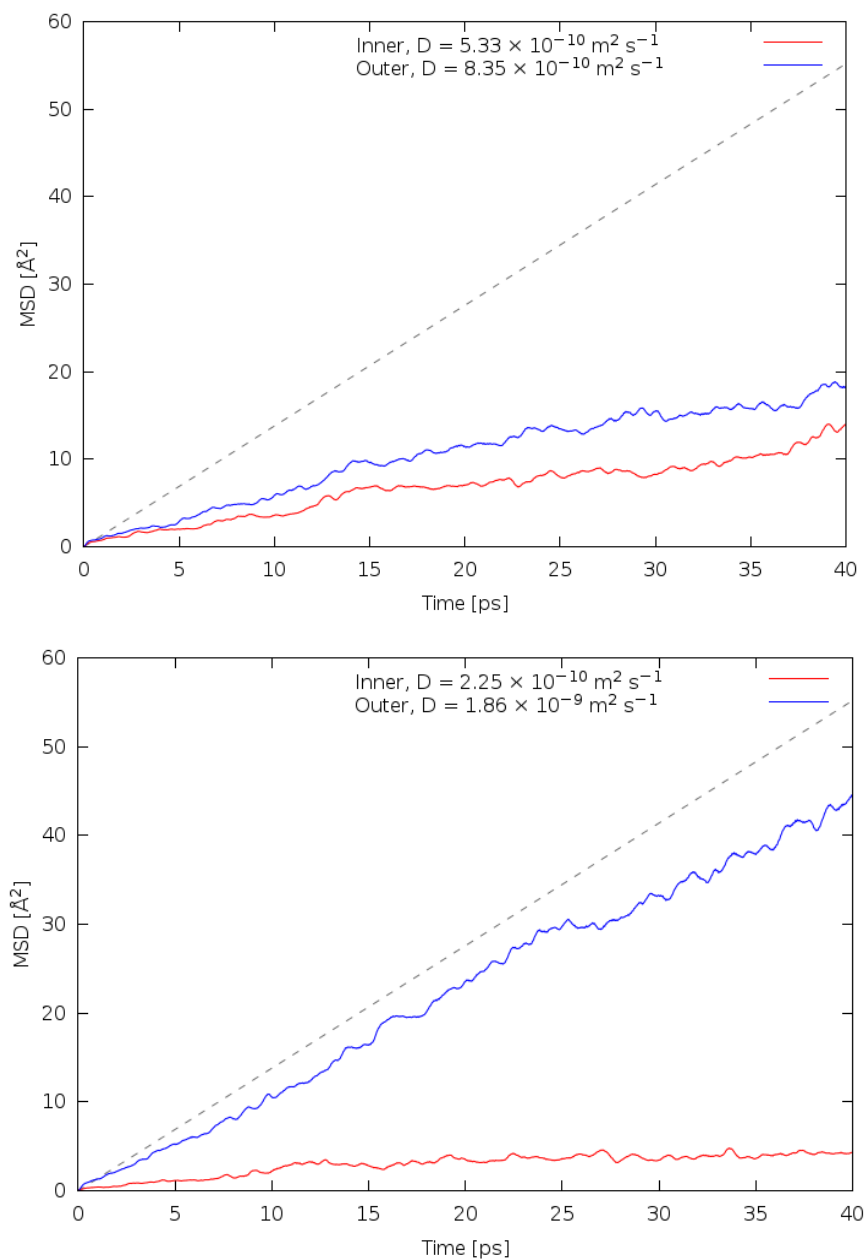
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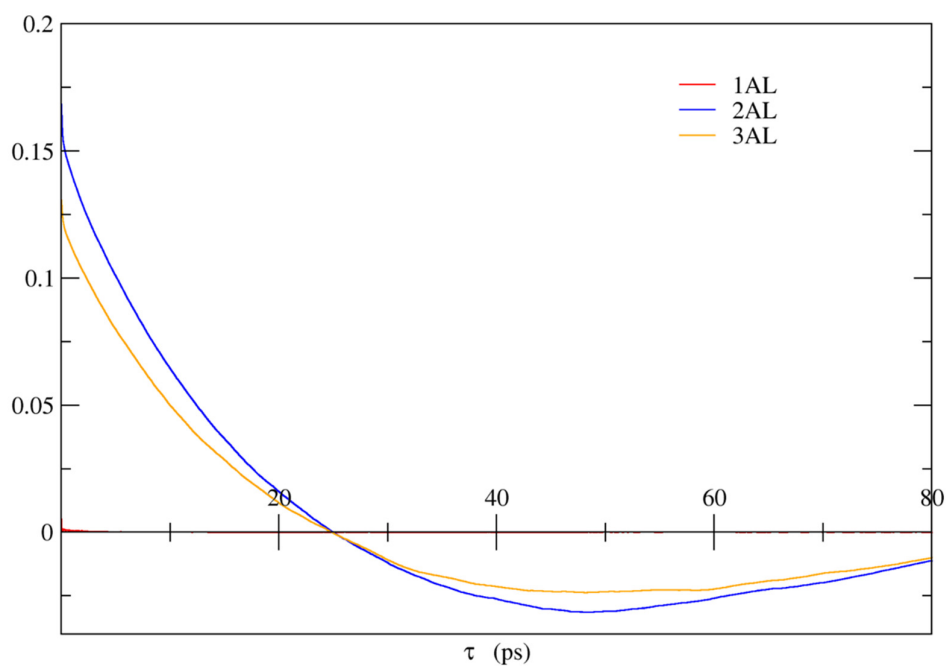
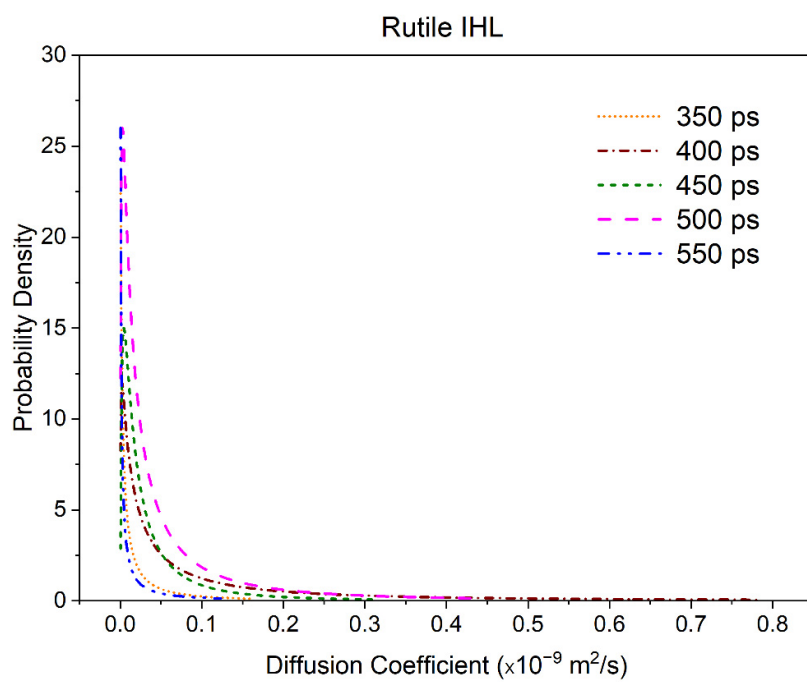**Figure S4.** Velocity auto-correlation function of adsorbed layers of rutile (110).

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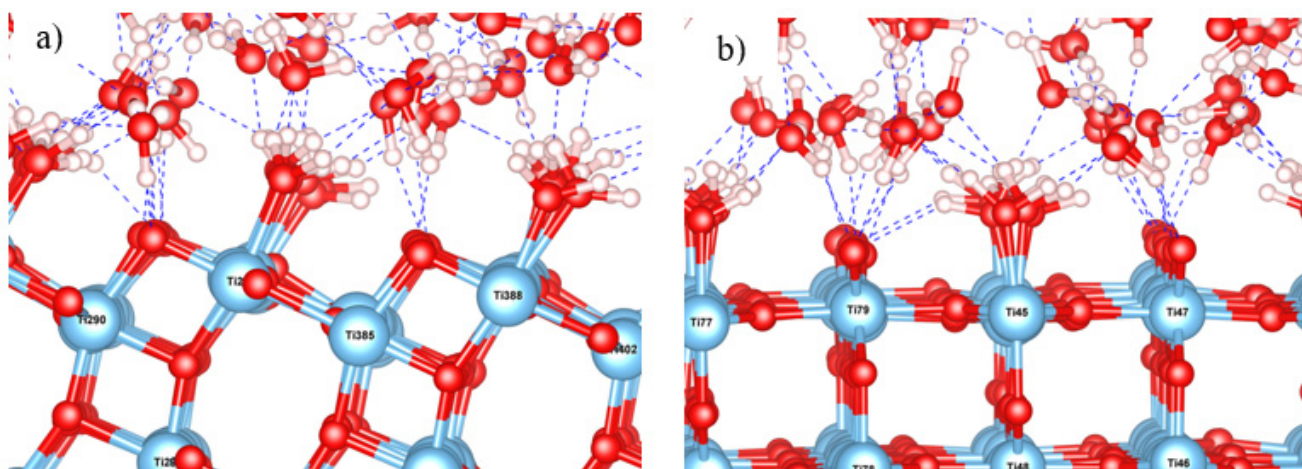
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