# Supporting information for:

# Structural and Electronic Effects at the Interface between Transition Metal Dichalcogenide Monolayers ($MoS_2$, $WSe_2$, and their Lateral Heterojunctions) and Liquid Water

By

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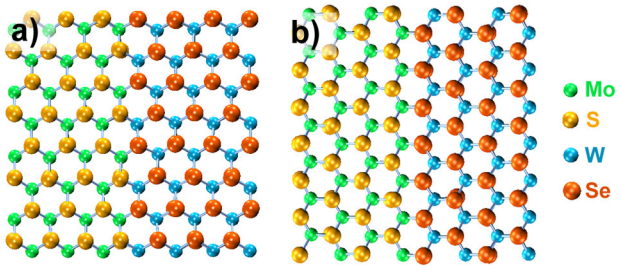



**Figure S1.** (a,b) Schematic view of $MoS_2$-$WSe_2$ armchair and zig-zag prototypical lateral heterojunctions; the figure also demonstrates the size of the TMDC supercells employed in this study.

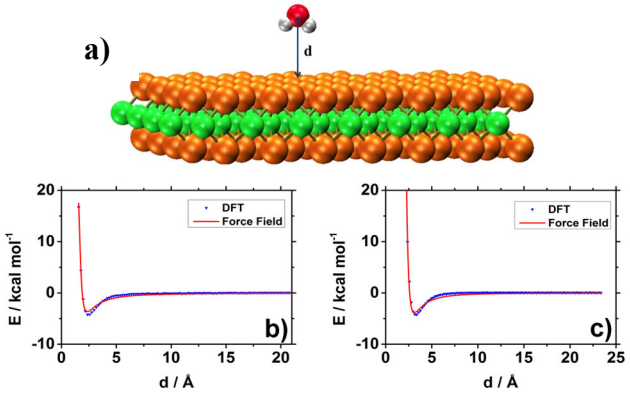



**Figure S2.** (a) Schematic view of the fitting scheme: the water-TMDC interaction energy was scanned as a function of distance between water and TMDCs surface. The comparison between the interaction energy calculated using the empirical parameter and DFT are shown in (b) for water-$MoS_2$ monolayer, and (c) water-$WSe_2$ monolayer, respectively.

**Table S1.** Empirical Parameters for water-TMDCs slabs fitted from the DFT calculations.

| Atom Type | Partial Charge | Pairwise Interaction | $\varepsilon_{ij}$ | Pairwise Interaction | $\sigma_{ij}$ | Pairwise Interaction | $\varepsilon_{ij}$ | Pairwise Interaction | $\sigma_{ij}$ |
|---|---|---|---|---|---|---|---|---|---|
| **Mo** | 0.397 | **Mo-O** | 0.864821 | **Mo-O** | 3.688089 | **Mo-H** | 0.0 | **Mo-H** | / |
| **S** | -0.1985 | **S-O** | 0.17715 | **S-O** | 3.465902 | **S-H** | 0.0 | **S-H** | / |
| **W** | 0.274 | **W-O** | 0.657852 | **W-O** | 3.963807 | **W-H** | 0.0 | **W-H** | / |
| **Se** | -0.137 | **Se-O** | 0.249465 | **Se-O** | 3.752706 | **Se-H** | 0.0 | **Se-H** | / |

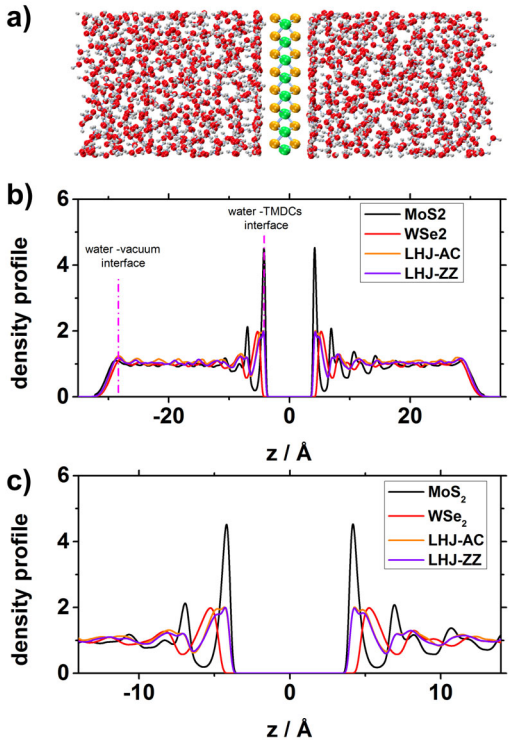



**Figure S3.** (a) Schematic view of large-scale classical MD simulation of TMDC with water. (b) Density profile of TMDC with water obtained from classical MD simulation trajectory: both water-vacuum interfaces and water-TMDCs interfaces are marked. The water-vacuum interface is to help water relax to its bulk density without artificial counting. Both water-vacuum interface (water-hydrophobic interface) and water-TMDCs interface can induce fluctuations reflected as peaks in density profiles. (c) Zoom in of the density profile in (b), demonstrating the water density can relax to 1 (bulk density).

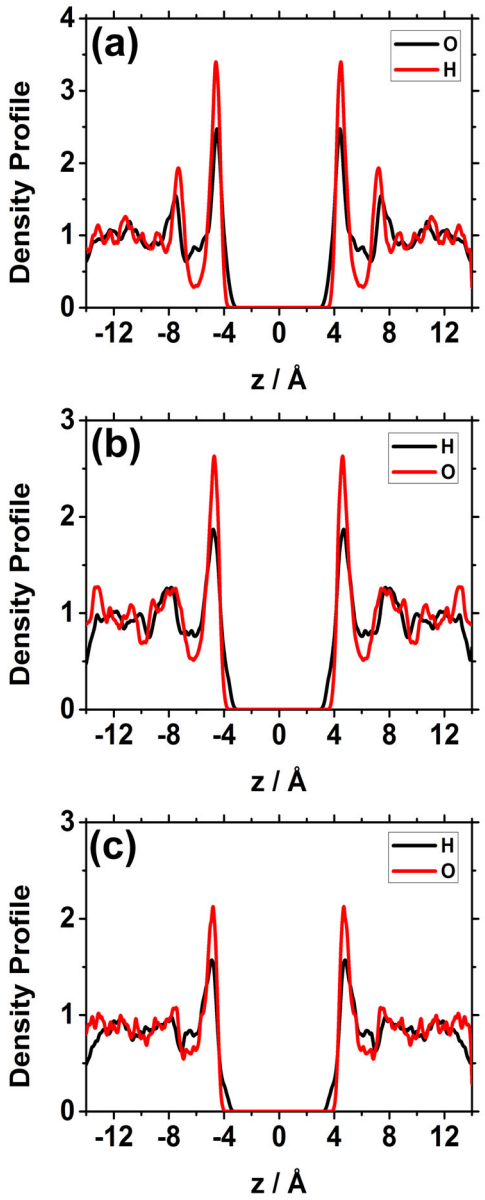



**Figure S4.** Density profile of hydrogen (black line) and oxygen (red line) of water surrounding monolayer $MoS_2$ (a), $WSe_2$ (b), and later heterojunction (c): The first peak is corresponding to the adsorbed water layer, and hydrogen shows a broader peak compared with that of oxygen atoms, indicating a variety of orientations of OH bonds in this layer; in the near-surface region, the density profile for hydrogen is above zero while it is zero for oxygen, indicating hydrogen can be closer to the 2D material surface.

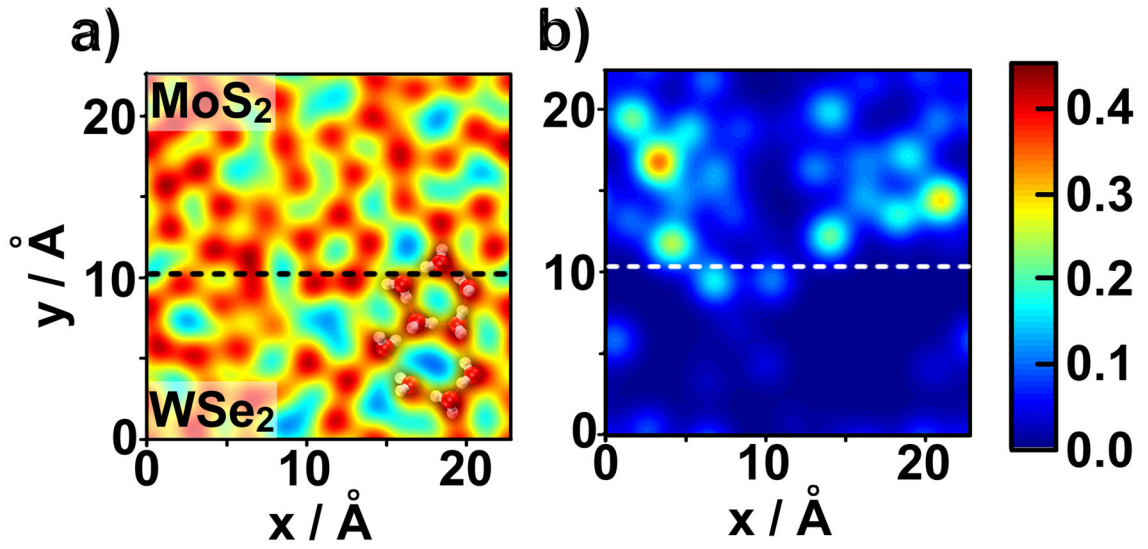



**Figure S5.** Probability maps, $\phi w(x,y)$, for finding ad-layer water molecules on top (a) the armchair LHJ. Ad-layer water molecules correspond to water molecules within the first minima ($|z| \approx 5$ Å) of the water density profiles $\rho_O(z)$, shown in Figure 1. The map on panel (b) is obtained from the map on panel (a) by considering an ad-layer 15% thinner.

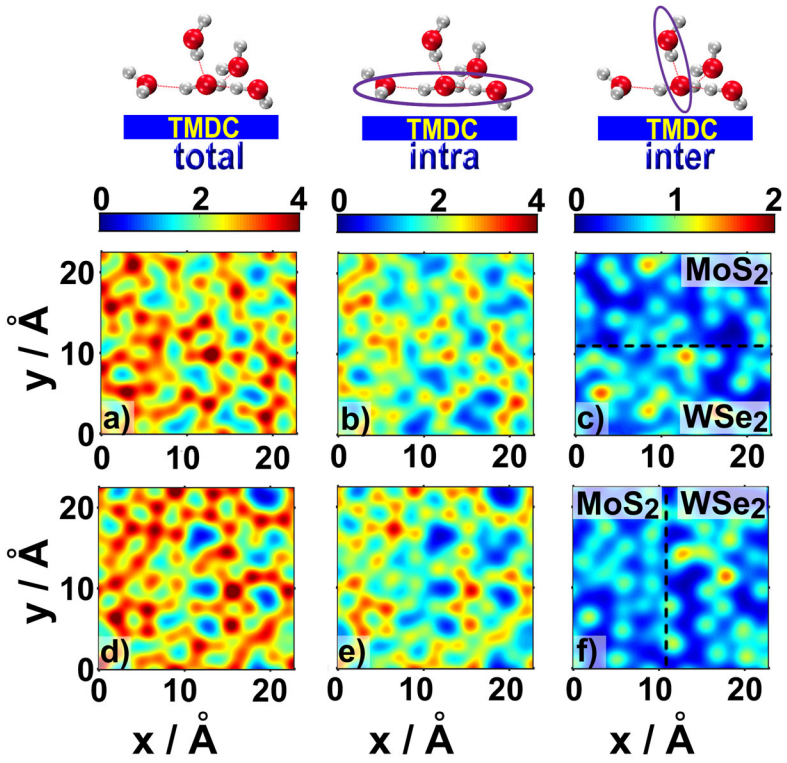



**Figure S6.** Hydrogen bonding network above TMDCs were evaluated in three ways: the total number of H-bonds for ad-layer water molecules, $n_{HB}(x,y)$, above armchair LHJ (a), and zig-zag LHJ (d). The total number of H-bonds were decomposed into H-bonds form by waters within the ad-layer (b), (e), and H-bonds between ad-layer water molecules and water molecules in above layer (c), (f).

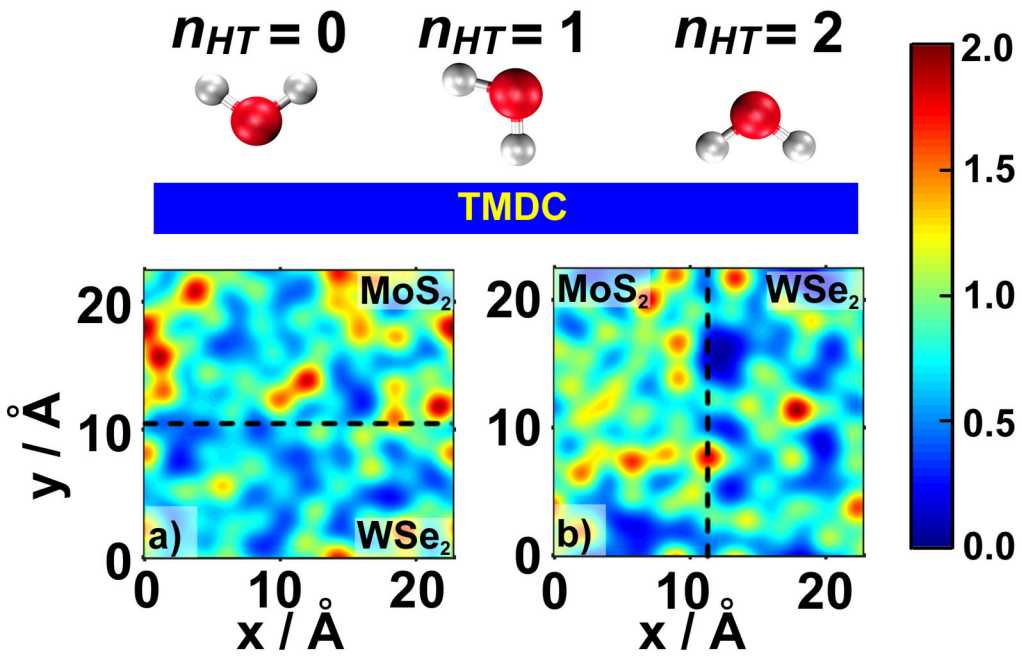



**Figure S7.** Orientation of water molecules above armchair (a) and zig-zag (b) types of LHJs.

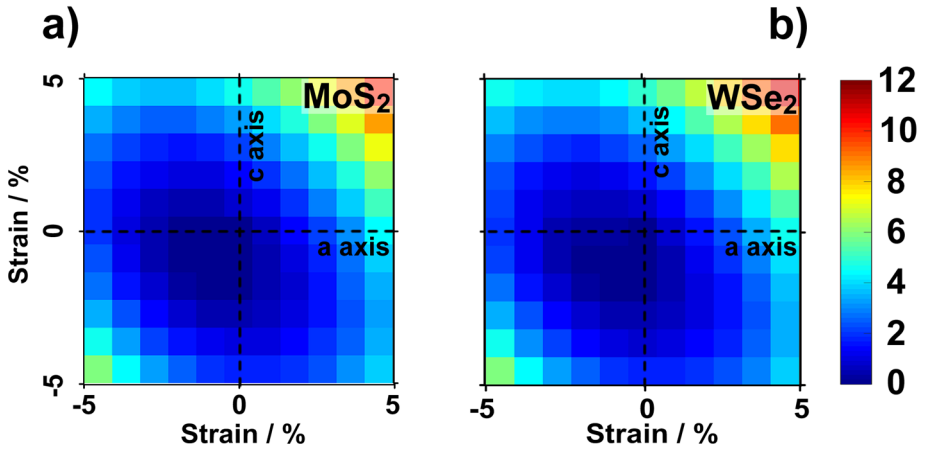



**Figure S8.** Energy map corresponding to the 5% strain of MoS2 (a) and WSe2 (b).

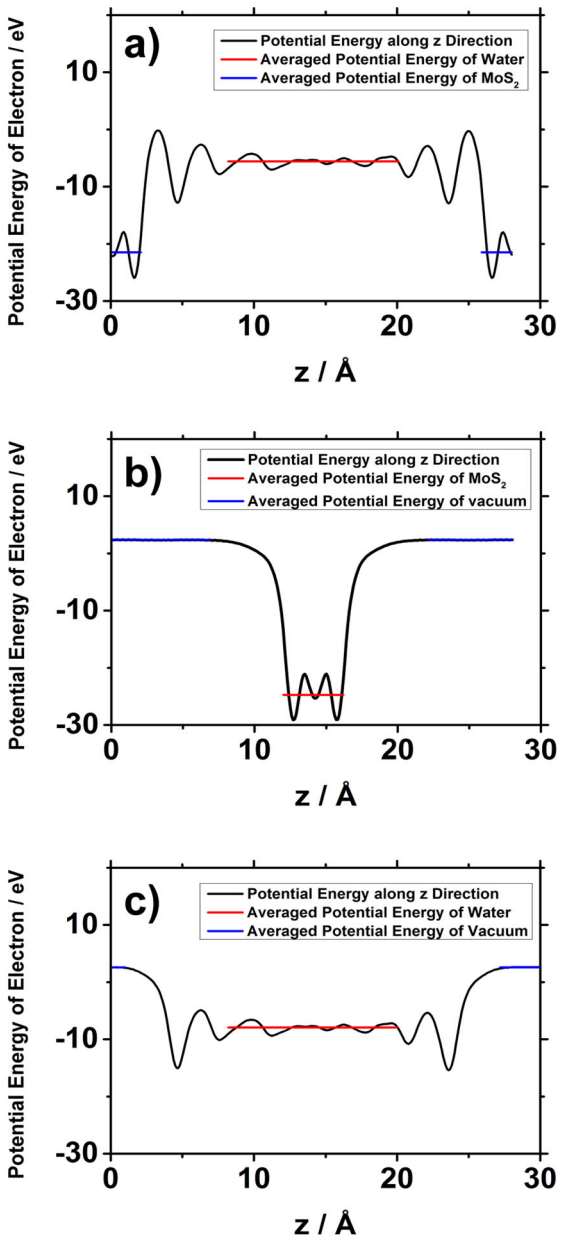



**Figure S9.** Schematic view of electrostatic potential energy presented at different conditions: (a) represents the TMDC monolayer in water; (b) represents the TMDC in vacuum; (c) represents the water in vacuum. The energy difference for different references indicates the band alignment can be achieved through: $\Delta E_{TMDC}^{water} = \Delta E_{TMDC}^{vacuum} - \Delta E_{water}^{vacuum} + \Delta E_{sol}^{eff}$.

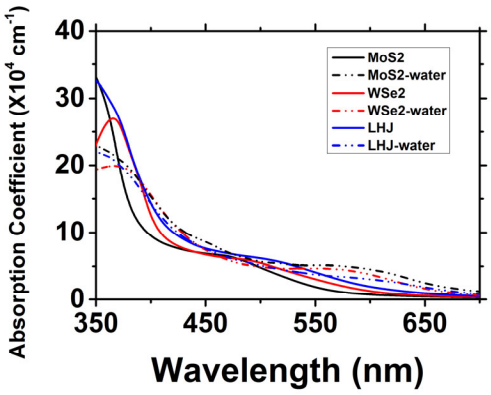



**Figure S10.** Representative solar light absorption spectra for $MoS_2$, $WSe_2$, and LHJs for both optimized structure (solid lines) and structure obtained from the DFT-MD trajectory (dashed lines).

**Structural characterization of the interfacial water molecules.**

*1. Density profiles of the water molecules from the TMDC surface:*

The density profiles of the water oxygen atoms □(O) from the TMDC surface was characterized for water on $MoS_2$, $WSe_2$, and Armchair and Zigzag types of laterial heterojunctions, respectively. These density profiles were weighted by the bulk water density to demonstrate the liquid water at ~14 Å exhibits bulk water property.

*2. Instantaneous liquid surface of the ad-layer water molecules:*

To visualize water fluctuations in the ad-layer, the instantaneous liquid surface, as defined by Willard and Chandler is inserted in Figure 2 as an isosurface of Eq. 1,

$$\phi(r,t) = \sum_{i=1}^{N_{mol}} \frac{1}{\sqrt{2\xi^2\pi}} \exp\left( -\frac{\left(\vec{r}_i(t) - \vec{r}\right)^2}{2\xi^2} \right); \quad (1)$$

where $\vec{r}_i(t)$ is the position of the i-th water oxygen at time t, $\xi$ = 2 Å determines the resolution of the grid used to build the coarse-grained interface.

*3. Locations of the water molecules within the ad-layer*

The structure and mobility of water molecules within the ad-layer is characterized using the water density $\varphi(\vec{a})$, as defined in Eq. 2,

$$\varphi(\vec{a}) = \left\langle \sum_{i=1}^{N_{mol}} \frac{1}{\sqrt{2\xi^2\pi}} \exp\left( -\frac{\left(\vec{a}_i(t) - \vec{a}\right)^2}{2\xi^2} \right) H\left(z_c - z_i(t)\right) \right\rangle ; (2)$$

where $\vec{a}_i$ is the instantaneous position of the $i^{th}$ water oxygen projected onto the TMDC surface, H is the Heaviside step function, which is 1 if the $i^{th}$ water molecule is within the adsorbed layer at time t, i.e. $z_i(t) < z_c$, or 0 otherwise., $\langle\ \rangle$ indicates averaging over the last 4 ps of the DFT-MD trajectory. Here and further, $\xi$ was set to be 1 Å for higher resolution. In turn, the cutoff distance $z_c$ was set to the first

minima, d, of the water density profiles shown in Figure 2, except 0.85*d in Figure 3d.

*4. Hydrogen bonding network (HBN) of the water molecules within the ad-layer*

To characterize the obtained HBN structures, we plot $\psi\left(\vec{a}\right)$ defined in Eq. 3, which provides a tendency of water molecules in the ad-layer to be engaged in H-bonds:

$$\psi\left(\vec{a}\right)=\left\langle \sum_{i=1}^{N_{mol}} \frac{N_i^{HB}(t)}{\sqrt{2\xi^2\pi}} \exp\left(-\frac{\left(\vec{a_i}(t)-\vec{a}\right)^2}{2\xi^2}\right) H\left(z_c-z_i(t)\right)\right\rangle; \qquad (3)$$

where the pre-factor, $N_i^{HB}(t)$, is the number of hydrogen bonds formed by the ith water molecule at time t. The other terms are defined as in Eq. 2.

*5. Detailed orientations of the water molecules within the ad-layer*

To investigate the molecular orientation of adsorbed water molecules we plotted $\rho\left(\vec{a}\right)$ of Eq. 4, which provides a propensity of waters in the ad-layer to interact with the TMDC via H atoms.

$$\rho\left(\vec{a}\right)=\left\langle \sum_{i=1}^{N_{mol}} \frac{n_i(t)}{\sqrt{2\xi^2\pi}} \exp\left(-\frac{\left(\vec{a_i}(t)-\vec{a}\right)^2}{2\xi^2}\right) H\left(z_c-z_i(t)\right)\right\rangle; \qquad (4)$$

where $n_i(t)$ is the number of hydrogen atoms of the ith water molecule staying closer to the TMDCs surface than the oxygen atom in the same water