

## Supporting Information for: Sulfur-deficient edges as active sites for hydrogen evolution on MoS<sub>2</sub>

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### Water adsorption on the Mo-edge

Test calculations of adsorbed H<sub>2</sub>O on the bare Mo<sub>0</sub> edge found that water molecules adsorb rather strongly, with the favored configuration being the tilted flat orientation on Mo top-sites. As for hydrogen adsorption, the adsorption free energy is defined as

$$\Delta G_{\text{H}_2\text{O}} = \Delta E_{\text{H}_2\text{O}} + \Delta E_{\text{H}_2\text{O}}^{\text{zpe}} - T\Delta S_{\text{H}_2\text{O}}, \quad (1)$$

where the entropy is approximated by  $T\Delta S \approx -TS_{\text{H}_2\text{O}}^\circ = -0.22$  eV.  $E^{\text{zpe}}$  is obtained from the vibrational frequencies. In terms of competition vs. H-adsorption, the dominant surface species will be H-adatoms below  $-0.2$  V, as shown in Figure S1a for coverages of 1/4 and 1 monolayers at pH = 0. In terms of the Boltzmann weight, the probability of a site being occupied by H rather than H<sub>2</sub>O is shown in Figure S1b. The HER onset potential for Mo<sub>0</sub> was found to be around  $-0.25$  V, at which point  $p_{\text{H}} > 0.9$  in the full monolayer case.

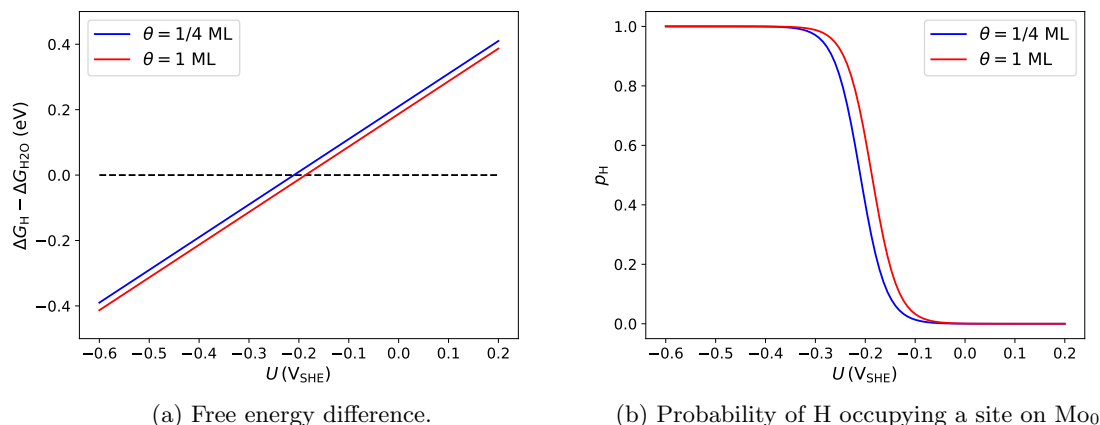


Figure S1: Free energy difference between adsorption of H and H<sub>2</sub>O onto the Mo<sub>0</sub> edge, as a function of electrode potential  $U$ . H-adatom coverage is favored over H<sub>2</sub>O below  $-0.2$  V.

## Implicit solvent cutoff density

In the VASPsol implementation, the dielectric permittivity is modulated by the electron density via a shape function

$$\zeta[n] = \frac{1}{2} \operatorname{erfc} \left( \frac{\log n/n_c}{\sigma\sqrt{2}} \right), \quad (2)$$

where the critical density  $n_c$  defines the point where  $\zeta = \frac{1}{2}$ , i.e. the crossover between solute and solvent, and  $\sigma$  dictates the width of the transition. The default value of  $n_c$  ( $0.0025 \text{ e}/\text{\AA}^3$ ), leads to some small concentration of implicit counter-ions in pockets between MoS<sub>2</sub> layers (which would not be present in the physical system). This has previously been solved by reducing  $n_c$ , where reduction by a factor 10 practically eliminated the interlayer ion concentration [1]. However, it is not immediately clear to which degree the interlayer charge would affect the calculated reaction energetics. Meanwhile, changing  $n_c$  would lead to a significantly altered solvent description also at the water-solid interface. In our tests, lowering  $n_c$  towards 1/10th of the default lowers both the Volmer and Heyrovsky reaction energies, indicating a relative stabilization of the final states relative to the initial states. The effect is quite significant (around 0.3 eV and 0.6 eV for the Volmer and Heyrovsky steps at 0 V, respectively), which seems unlikely to stem from only the interlayer ion concentration. For comparison, tests with a  $4 \times 3 \text{ Pt}_{111}$  system ( $\theta_H = 1.0$ ) show similar (and larger in the Volmer case) dependence of the reaction energy on the  $n_c$  parameter while there naturally is no such interlayer ion charge present, see Figure S2. With this in mind, we proceed with  $n_c = 0.0025 \text{ e}/\text{\AA}^3$ .

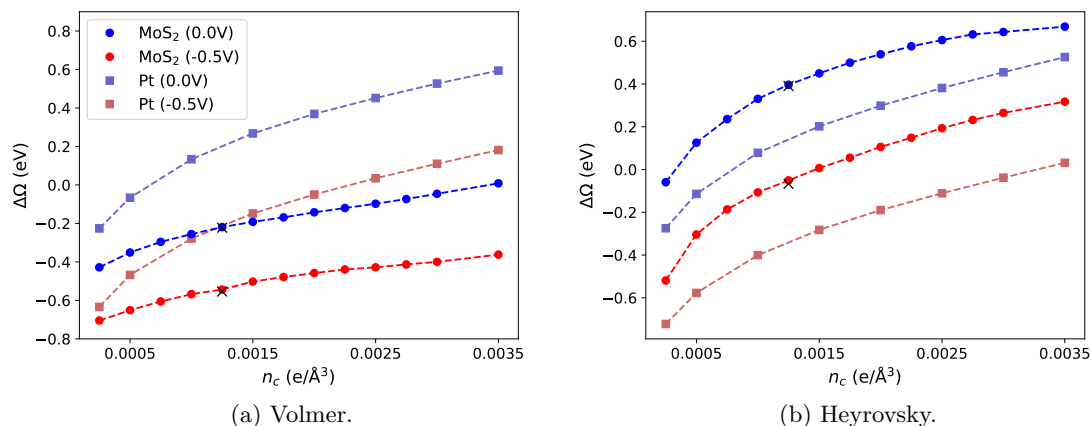


Figure S2: Difference in grand-canonical reaction energy for the Volmer and Heyrovsky steps on the Mo<sub>0</sub> edge and Pt<sub>111</sub> when varying the critical density  $n_c$ . The default value is  $0.0025 \text{ e}/\text{\AA}^3$ , and was used in this work. Crosses denote the energy for geometry-optimized structures, while the rest are from fixed structures (as obtained with default  $n_c$ ). Re-optimizing the geometry only has a small effect on the calculated energy.

## References

- [1] N. Abidi, A. Bonduelle-Skrzypczak and S. N. Steinmann, *ACS Applied Materials & Interfaces*, 2020, **12**, 31401–31410.

## Slab symmetrization

Asymmetric slabs were used in the calculations. We performed tests with point-symmetrized models and found negligible differences in grand-canonical reaction energies for the Volmer and Heyrovsky steps on  $\text{Mo}_0$ , see Figure S3.

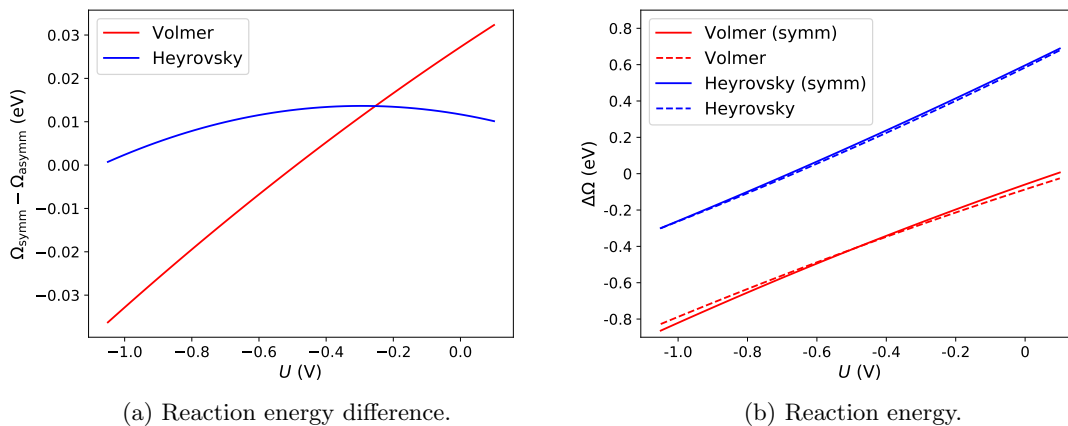


Figure S3: Difference in grand-canonical reaction energy for the Volmer and Heyrovsky steps with symmetric and asymmetric slabs.

## Periodic cation interaction

The artificial interaction between periodic images of the water model was estimated by an isolated Eigen cation in cells of varying lateral dimension  $d$ . The energy due to lateral interaction is less than 0.01 eV for the cell dimensions of  $2 \times 4$   $\text{MoS}_2$ -edge supercells, with respect to the case of  $d = 20$  Å, see Figure S4.

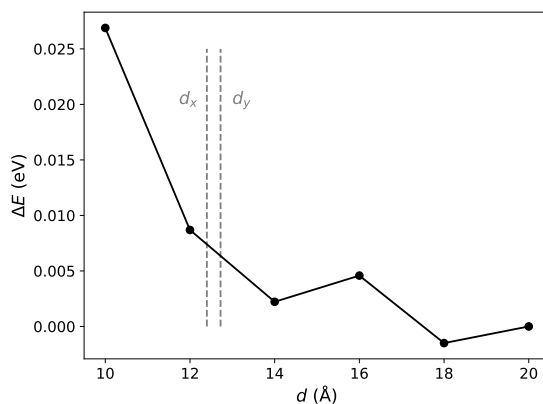


Figure S4: Convergence of the interaction between periodic images of the Eigen cation. Dashed lines represent the dimensions along the  $x$ - and  $y$ -directions of the edge-model supercell.