

Adsorption and Dissociation of H₂O on Monolayered MoS₂ Edges: Energetics and Mechanism from Ab-Initio Simulations

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KEYWORDS: molybdenum disulfide, density functional theory, metadynamics, activation barrier

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1 MoS₂ Model Structural and Electronic Property Validation

The perfect basal plane monolayer MoS₂ structure was geometrically relaxed to its most energetically stable configuration using the Density Functional Theory (DFT) simulations and the resulting structural parameters were compared to experimentally obtained parameters to gauge the accuracy of the ab-initio simulations. The DFT structural parameters ($a=3.19$ Å, $c=12.14$ Å) closely matched experimentally obtained parameters ($a=3.16$ Å, $c=12.29$ Å),¹ with a difference of only 0.9 % and 1.2 % for each parameter respectively. Furthermore, the density of states (DOS) and projected density of states (PDOS) were calculated for the 1-layer and 2-layer MoS₂. For 2-layer MoS₂ bandgap of 1.64 eV (shown in Figure S1) closely matched experimentally² obtained bandgap of 1.60 eV, although there was a slightly greater difference for a 1-layer MoS₂ with the calculated value being 1.65 eV and experimental value² being 1.91 eV. Nevertheless, there was importantly a clear bandgap, a distinctive feature of monolayer MoS₂, present and within the ballpark of experimental results and this helps to validate our theoretical model.

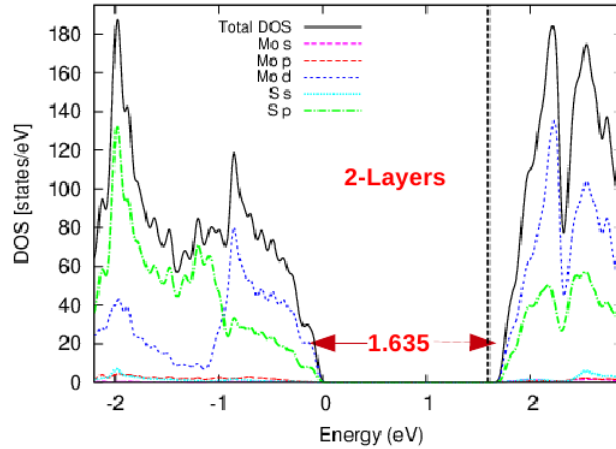


Figure S1: The density of states and projected density of states on the p and d orbitals for 2-layer MoS₂. The Fermi level is set at zero energy value and is represented by the vertical dashed line.

2 Bader Charge Analysis for H₂O Adsorption

The electrostatic repulsions and charge transfer interactions between the H₂O molecule and edge surfaces were investigated by Bader charge analysis. The S and O atoms in all systems had negative effective charges, while the Mo and H atoms had positive effective charges. The free H₂O molecule was found to have effective charges of -1.18e for the O atom and 0.59e for the H atoms, totalling to a charge neutral molecule. For H₂O adsorption on the S50-edge, the effective charges had almost no change, with the O atom now having a charge of -1.17e and the H atoms have charges of 0.53e and 0.58e. The four surface S atoms closest to the H₂O molecule changed from having charges of -0.51e each to charges of -0.47e, -0.50e, -0.47e & -0.49e. This demonstrates the repulsion felt between the O and S atoms as they seem to push charge away from each other, with the O atom transferring charge to the H atoms and the S atoms likely transferring charge to surrounding Mo atoms.

For the S100-edge there was a stronger degree of interaction, expected due to its more favorable binding of the H₂O molecule. The O atom now gains additional negative charge going to an effective charge of -1.22e while the H atoms have charges of 0.59e and 0.60e, producing a small negative overall charge of -0.03e for the H₂O molecule. The four surface S atoms closest to the H₂O molecule changed from having charges of -0.11e and -0.25e to charges of -0.14e, -0.16e, -0.15e & -0.19e, thus going from an average effective charge of -0.18e to -0.16e. The two underlying Mo atoms bonded to these four S atoms go from charges of 1.27e and 1.28e to 1.30e each. All of this suggests there was a charge transfer to the H₂O molecule from the surface S atoms, supported by the fact that charge was not transferred to the underlying Mo atoms from the S atoms as was the case for the S50-edge. It should be also noted that the surface S atoms for S100-edge were less negatively charged than the S50-edge atoms, possibly due to less number of bonds to Mo atoms from which they can draw charge. This helps explain why there is stronger interaction with the H₂O molecule for the S100-edge than S50-edge as there is less repulsion from the overlying negative S atoms and this factor overcomes the geometrical advantages which should make S50-edge more

favorable for interaction (due to more space for the O atom to access underlying Mo atoms).

The Mo-edge displayed the greatest charge redistribution with the H₂O molecule’s O atom possessing an effective charge of -1.30e and the H atoms having charges of 0.68e and 0.62e. The Mo atom closest to the molecule went from a charge of 0.97e to 1.22e. This demonstrates a clear increase in the polarization of the H₂O molecule. There does not seem to be a transfer of charge from Mo to O as the overall charge on the H₂O molecule remains zero. Instead the charge on the Mo atom was likely pushed away further into the surface. The increase in charge redistribution among the edges reflects the trend of more favorable adsorption energies due to greater interaction between the surface and adsorbate molecule. Hence, the adsorption of the H₂O molecule appears to take place through electrostatic attraction.

3 Metadynamics Simulations Details

The metadynamics simulations, run using the PLUMED 2.0 plugin to Quantum Espresso, were simulated using coordination number as the collective variable. A good review of the metadynamics technique is given by Liao and Gervasio.³ The metadynamics algorithm adds a history dependent potential to the Hamiltonian describing the system, where the potential is built from a sum of Gaussians centered along the trajectory of the CVs. The form of the external potential added by the metadynamics algorithm at time t is the following:

$$V_{\mathbf{G}}(S(\mathbf{r}),t)=\omega \sum_{t'=\tau_G, 2\tau_G, \dots \text{ for } t < t'} \exp\left(-\frac{S(\mathbf{r}) - s(t')^2}{2\delta s^2}\right) \quad (1)$$

Here τ_G is the frequency of Gaussian deposition, ω is the Gaussian height and δs is the Gaussian width. We used τ_G =every 15 steps, ω =0.01 eV and δs =0.002 eV for our simulations.

The coordination number between two groups of atoms, A and B, is defined as the following:

$$\sum_{i \in A} \sum_{j \in B} s_{ij} \quad (2)$$

Here, s_{ij} represents contact between two atoms i and j and is a switching function represented by the following expression:

$$s_{ij} = \frac{1 - \left(\frac{\mathbf{r}_{ij} - d_0}{r_0}\right)^n}{1 - \left(\frac{\mathbf{r}_{ij} - d_0}{r_0}\right)^m} \quad (3)$$

Our simulations utilized $r_0=0.9$ Å, $d_0=0.8$ Å, $m=6$ and $n=3$ as parameter values.

4 Frequency Calculations

In order to check the validity of transition states (TSs) obtained from CI-NEB calculation, we optimized the geometries and characterized their stationary point using harmonic vibrational frequency calculations. These calculations were conducted using the PBE density functional in combination with auxiliary SV/J fitting basis set^{4,5} implemented in ORCA quantum chemistry program, version 3.0.⁶ As this calculation is computationally expensive, the size of the models was reduced by removing bottom and side atomic layers, reducing it to 21 atoms cluster. The geometries were fully optimized without any geometrical constraints, taking starting coordinates from the relaxed CI-NEB structures. The resolution-of-the-identity (RI) approximation⁷⁻⁹ technique for the Coulomb integrals was used. The TSs were validated by one imaginary frequency mode obtained in vibrational frequency calculation.

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