Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for:

Hydrogen adsorption on MoS$_2$-surfaces: A DFT study on preferential sites and the effect of sulfur and hydrogen coverage

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Adsorption free energy. The free energy of adsorption is estimated by assuming constant zero-point energy and entropic contributions in accordance with the method introduced by Hinnemann *et al.* [1].

$$\Delta G_{\mathrm{H}} = \Delta E_{\mathrm{H}} + \underbrace{\Delta E_{\mathrm{ZPE}} - T\Delta S_{\mathrm{H}}}_{\approx \text{ constant}} \tag{1}$$

Here, the vibrational and configurational entropies of the adsorbed H*-intermediate are assumed to be negligible, and thus the entropy difference is simply $\Delta S_{\mathrm{H}} \approx -1/2 S^{\circ}_{\mathrm{H}_2} = -0.7\,\mathrm{meV\,K^{-1}}$ [2]. The zero-point energy of a studied system is defined as the sum over all ground state vibrational modes in accordance with Eq. (2).

$$E_{\mathrm{ZPE}} = \frac{hc}{2} \sum_{i}^{\text{modes}} \tilde{\nu}_i \tag{2}$$

In their article, Hinnemann *et al.* report coverage independent vibrational frequencies of $2535\,\mathrm{cm^{-1}}$, $594\,\mathrm{cm^{-1}}$ and $474\,\mathrm{cm^{-1}}$ for the H* intermediate adsorbed to the MoS$_2$-surface. The ground state vibrational frequency of the gas phase H$_2$ is obtained from the literature as $4400\,\mathrm{cm^{-1}}$ [2]. Hence, the ZPE-contribution to the free energy of adsorption is $\Delta E_{\mathrm{ZPE}} = E^{\mathrm{H}}_{\mathrm{ZPE}} - 1/2 E^{\mathrm{H_2}}_{\mathrm{ZPE}} \approx 0.09\,\mathrm{eV}$. Evaluating the entropic term at a temperature of 298 K gives $-T\Delta S_{\mathrm{H}} \approx 0.2\,\mathrm{eV}$, and therefore the constant correction to the free energy of adsorption is determined as approx. 0.29 eV.

Lattice parameters. The lattice parameters were optimized by generating a set of trial structures with varying Mo-Mo (a), S-S (t) and interlayer ($c/2$) separations, and computing the respective total energies. The behavior of the energy as a function of the changing lattice parameters is displayed in Figure S1. The optimized values were hence obtained as $a \approx 3.14\,\text{Å}$, $t \approx 3.15\,\text{Å}$ and $c/2 \approx 6.06\,\text{Å}$, in good agreement with experiments [3, 4].

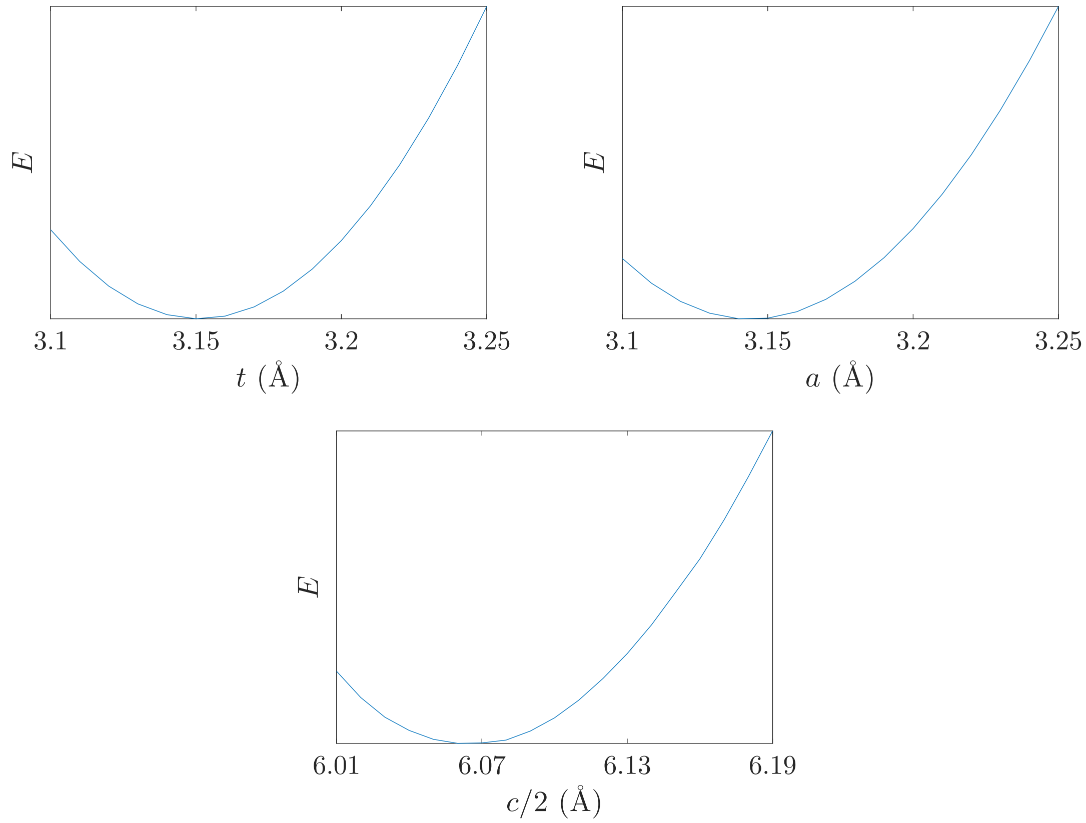


Figure S1: Total energy plots of 2H-MoS_2 from the lattice parameter optimization. t, a and $c/2$ correspond to the S-S, Mo-Mo and interlayer distances, respectively.

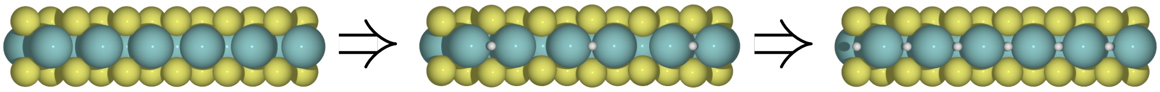
Reference systems. The calculated reference energies used in evaluating the energies of adsorption and formation are given in Table S1. These total energies were calculated for fully relaxed systems using the same methods and parameters as described in the main article, Section 2.1.

Surface rearrangements. The adsorption-induced structural response of the studied edge-configurations is illustrated in Figure S2 (minor reconstruction) and Figure S3 (major reconstruction) for hydrogen coverages of 50 % and 100 %. The main unifying feature of the

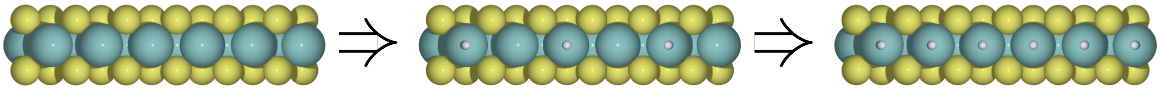
Table S1: Computed total energies for reference systems/molecules.

System	E_{DFT} (Ha)	Notes
H_2	-1.162	
H_2S	-11.384	
2H-MoS_2	-6393.006	$Mo_{72}S_{144}$, basal pl.

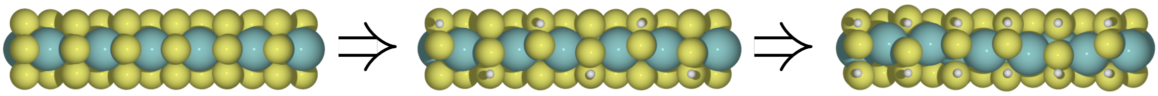
major reorganizations is the splitting of the terminal S_2-dimers, which is coupled with a decreasing ΔG_{H} vs. θ_{H} behavior for all concerned configurations (Mo-100, top/bridge; S-75, top/hollow).



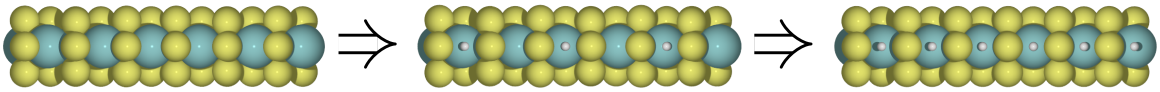
Mo-0, bridge: $\theta_\mathrm{H} = 0\,\%$ Mo-0, bridge: $\theta_\mathrm{H} = 50\,\%$ Mo-0, bridge: $\theta_\mathrm{H} = 100\,\%$



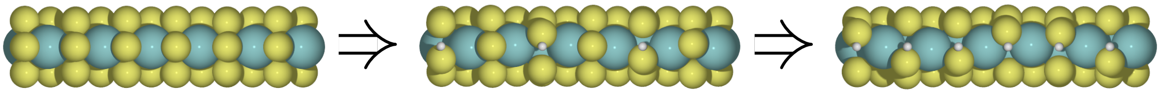
Mo-0, top: $\theta_\mathrm{H} = 0\,\%$ Mo-0, top: $\theta_\mathrm{H} = 50\,\%$ Mo-0, top: $\theta_\mathrm{H} = 100\,\%$



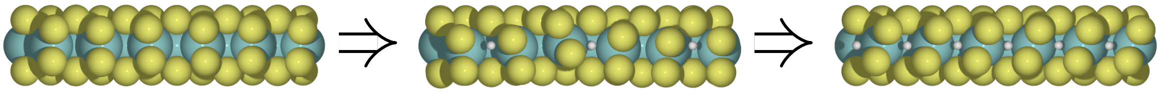
Mo-50, bridge$_1$: $\theta_\mathrm{H} = 0\,\%$ Mo-50, bridge$_1$: $\theta_\mathrm{H} = 50\,\%$ Mo-50, bridge$_1$: $\theta_\mathrm{H} = 100\,\%$



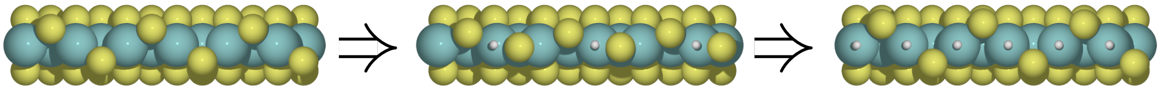
Mo-50, bridge$_2$: $\theta_\mathrm{H} = 0\,\%$ Mo-50, bridge$_2$: $\theta_\mathrm{H} = 50\,\%$ Mo-50, bridge$_2$: $\theta_\mathrm{H} = 100\,\%$



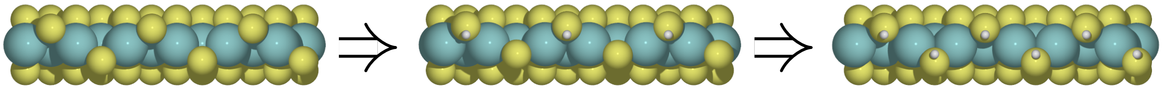
Mo-50, top: $\theta_\mathrm{H} = 0\,\%$ Mo-50, top: $\theta_\mathrm{H} = 50\,\%$ Mo-50, top: $\theta_\mathrm{H} = 100\,\%$



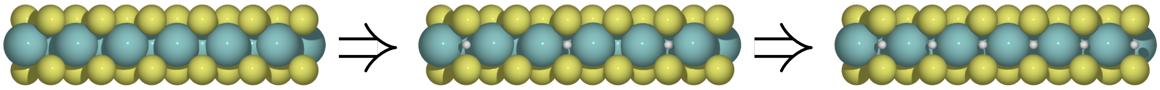
Mo-100, hollow: $\theta_\mathrm{H} = 0\,\%$ Mo-100, hollow: $\theta_\mathrm{H} = 50\,\%$ Mo-100, hollow: $\theta_\mathrm{H} = 100\,\%$



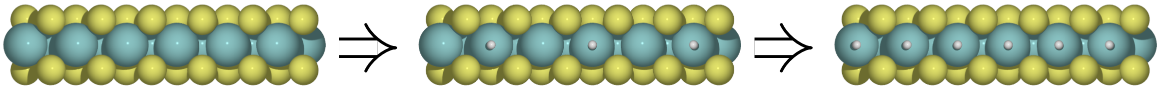
S-50, bridge: $\theta_\mathrm{H} = 0\,\%$ S-50, bridge: $\theta_\mathrm{H} = 50\,\%$ S-50, bridge: $\theta_\mathrm{H} = 100\,\%$



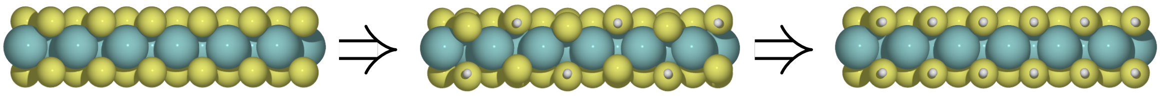
S-50, top: $\theta_\mathrm{H} = 0\,\%$ S-50, top: $\theta_\mathrm{H} = 50\,\%$ S-50, top: $\theta_\mathrm{H} = 100\,\%$



S-100, bridge: $\theta_\mathrm{H} = 0\,\%$ S-100, bridge: $\theta_\mathrm{H} = 50\,\%$ S-100, bridge: $\theta_\mathrm{H} = 100\,\%$

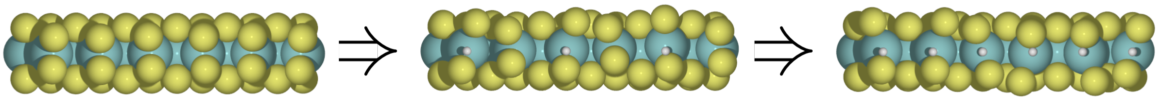


S-100, hollow: $\theta_\mathrm{H} = 0\,\%$ S-100, hollow: $\theta_\mathrm{H} = 50\,\%$ S-100, hollow: $\theta_\mathrm{H} = 100\,\%$

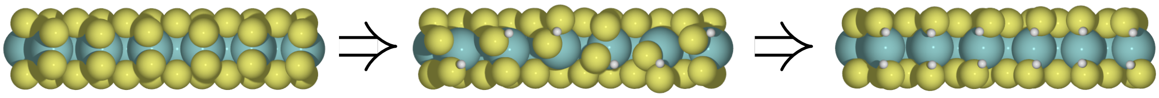


S-100, top: $\theta_\mathrm{H} = 0\,\%$ S-100, top: $\theta_\mathrm{H} = 50\,\%$ S-100, top: $\theta_\mathrm{H} = 100\,\%$

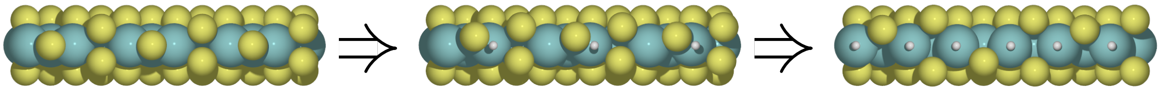
Figure S2: Minor surface rearrangements induced by H-adsorption. For all configurations, the free energy of adsorption was seen to be roughly constant or increase as a function of θ_H.



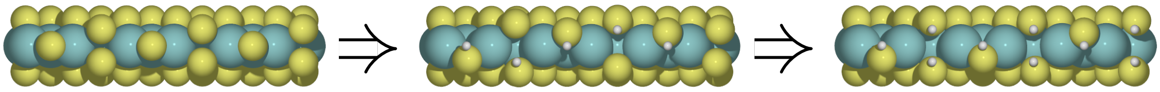
Mo-100, bridge: $\theta_{\mathrm{H}} = 0\,\%$ Mo-100, bridge: $\theta_{\mathrm{H}} = 50\,\%$ Mo-100, bridge: $\theta_{\mathrm{H}} = 100\,\%$



Mo-100, top: $\theta_{\mathrm{H}} = 0\,\%$ Mo-100, top: $\theta_{\mathrm{H}} = 50\,\%$ Mo-100, top: $\theta_{\mathrm{H}} = 100\,\%$



S-75, hollow: $\theta_{\mathrm{H}} = 0\,\%$ S-75, hollow: $\theta_{\mathrm{H}} = 50\,\%$ S-75, hollow: $\theta_{\mathrm{H}} = 100\,\%$



S-75, top: $\theta_{\mathrm{H}} = 0\,\%$ S-75, top: $\theta_{\mathrm{H}} = 50\,\%$ S-75, top: $\theta_{\mathrm{H}} = 100\,\%$

Figure S3: Major surface rearrangements induced by H-adsorption. The main unifying feature of pictured rearrangements is the splitting of the terminal disulfide bridges upon H-adsorption. In addition, significant shifting of S-atoms can be observed. A decreasing trend in the adsorption free energy (strengthened binding) with increasing H-coverage is seen for these systems.

References

[1] Hinnemann, B.; Moses, P. G.; Bonde, J.; Jørgensen, K. P.; Nielsen, J. H.; Horch, S.; Chorkendorff, I.; Nørskov, J. K. *J. Am. Chem. Soc.* **2005**, *127*(15), 5308–5309.

[2] Atkins, P. W.; De Paula, J. *Physical Chemistry;* Oxford University Press: New York, 6th ed., 1998.

[3] Dickinson, R. G.; Pauling, L. *J. Am. Chem. Soc.* **1923**, *45*(6), 1466–1471.

[4] Helveg, S.; Lauritsen, J. V.; Lægsgaard, E.; Stensgaard, I.; Nørskov, J. K.; Clausen, B.; Topsøe, H.; Besenbacher, F. *Phys. Rev. Lett.* **2000**, *84*(5), 951.