

## **Supplementary Information for “A density functional theory study of the hydrogenation and reduction of the thio-spinel Fe<sub>3</sub>S<sub>4</sub> {111} surface”**

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This file contains a compilation of figures and tables that complement the results and discussion of the main paper.

Content:

- **PRISTINE SURFACE PROPERTIES**

  - Schematic Representation of Fe<sub>3</sub>S<sub>4</sub>

- **Hydrogen on Fe<sub>3</sub>S<sub>4</sub>{111}**

  - Schematic Representation of H<sub>2</sub> evolution on Fe<sub>3</sub>S<sub>4</sub>{111}

  - H<sub>2</sub> Free Energy

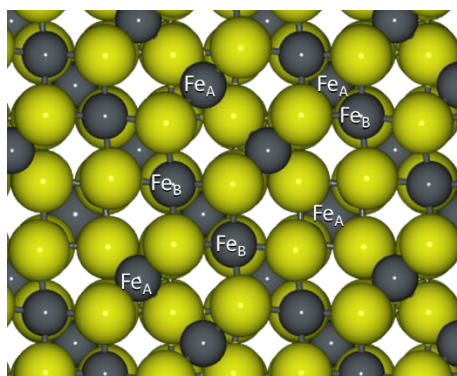
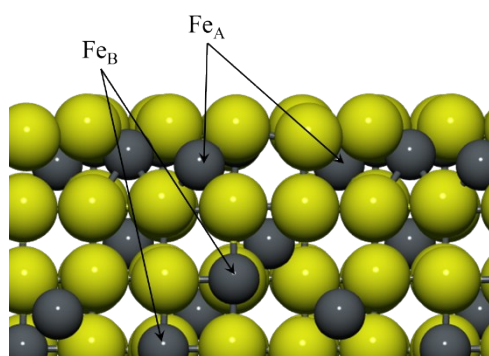
  - H sequestration in Fe<sub>3</sub>S<sub>4</sub>{111}

## Pristine Surface Properties

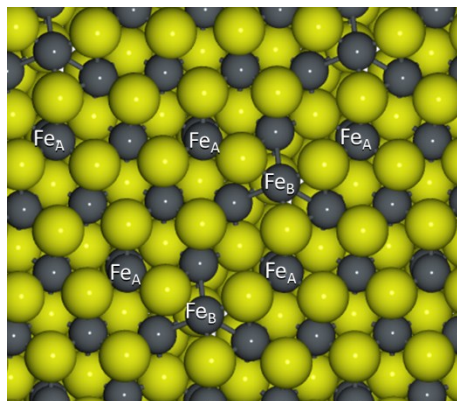
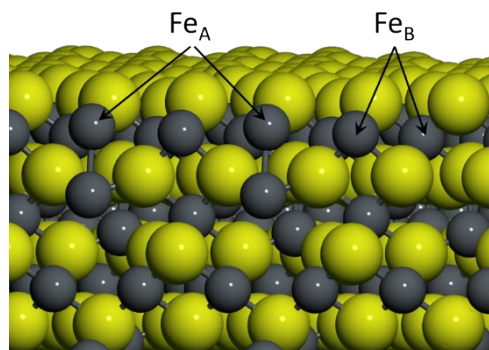
### *Schematic Representation of $Fe_3S_4$*

**Figure S1.** Side (right) and top view (left) of  $Fe_3S_4$  surfaces. Different types of Fe are exposed in the surface with a lower coordination number than in the bulk, labelled as ( $Fe_A$ ) and ( $Fe_B$ ) from the spinel formulation  $Fe_A(Fe_B)_2S_4$ . Grey balls and sticks denote Fe and dark-yellow the S atoms.

$Fe_3S_4\{001\}$

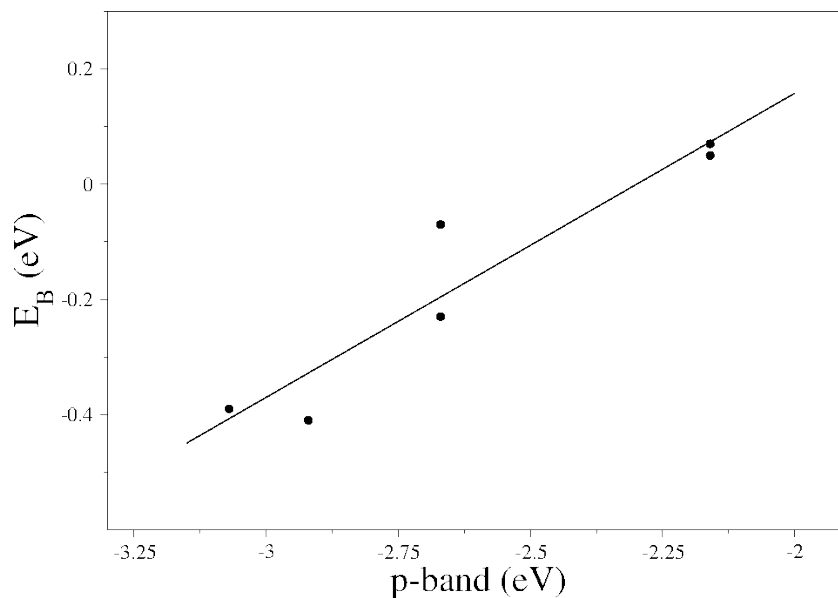


$Fe_3S_4\{111\}$

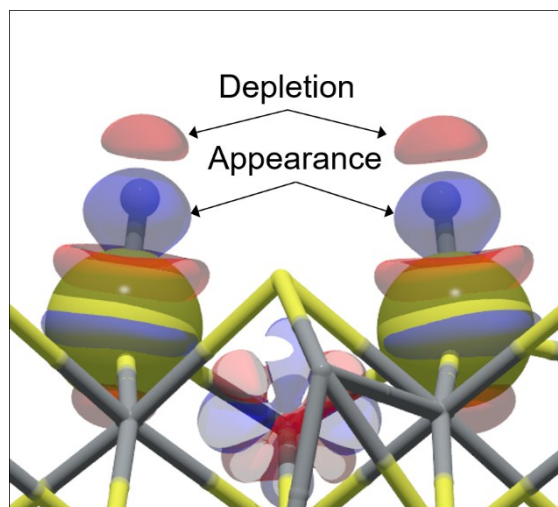


## Hydrogen on Fe<sub>3</sub>S<sub>4</sub>{111}

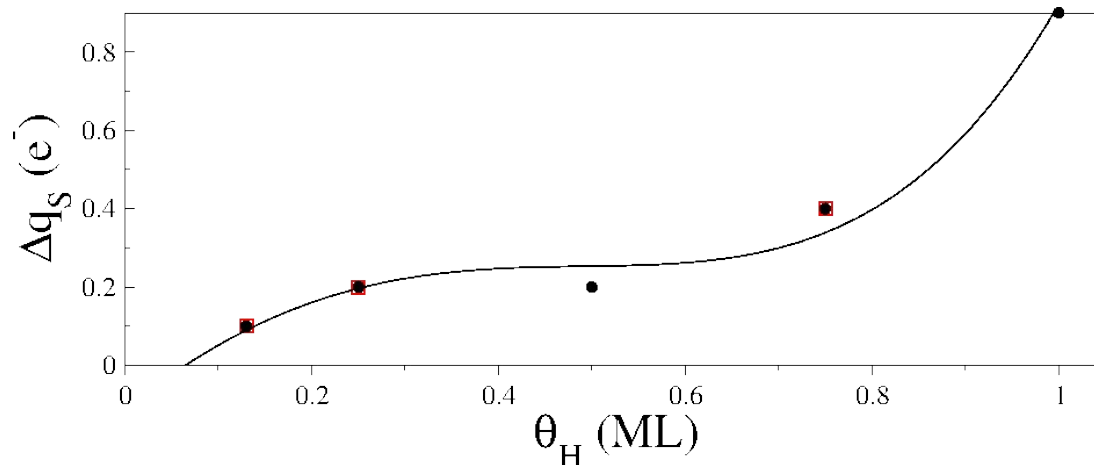
**Figure S2.** Hydrogen binding energy ( $E_B$ ) as a function of the bare S p-band centre. A linear trend was extrapolated from the calculated values on Fe<sub>3</sub>S<sub>4</sub>{111} in black solid dots:  $E_B = 1.214 + 0.528 \cdot E_{p\text{-band}}$ ,  $R^2 = 0.94$ .



**Figure S3.** Side view of a charge density difference flux representation of two atomic H adsorbed on top of S sites in the Fe<sub>3</sub>S<sub>4</sub>{111} surface. Grey denotes Fe, dark-yellow the S atoms and white H atoms (S–H spheres are magnified). Red clouds indicate the charge density depletion and blue its appearance.



**Figure S4.** Surface sulfur main charge difference as a function of H coverage ( $\theta_H$ ) on  $\text{Fe}_3\text{S}_4\{111\}$  and  $\text{Fe}_3\text{S}_4\{001\}$  surfaces, solid circles and red squares respectively. Solid line represents the regression of the solid points:  $\Delta q_S = -0.112 + 1.93 \cdot \theta_H + 2.89 \cdot \theta_H^2 + 2.00 \cdot \theta_H^3$ ,  $R=0.99$ .



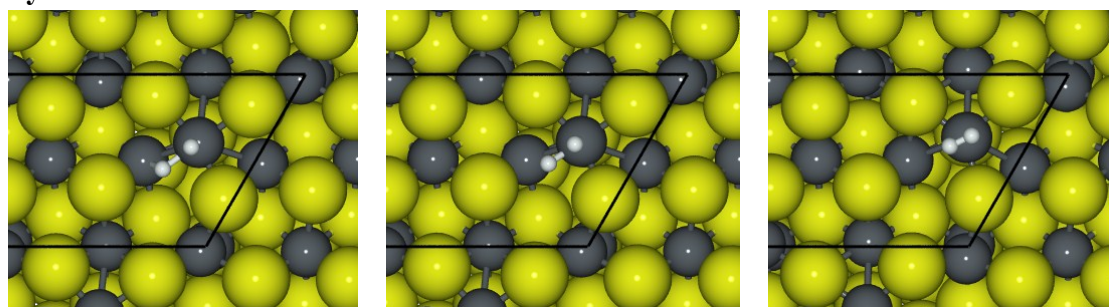
*Schematic Representation of  $\text{H}_2$  evolution on  $\text{Fe}_3\text{S}_4\{111\}$*

**Figure S5.** Top-view schematic representations of the  $\text{H}_2$  evolution structures on  $\text{Fe}_3\text{S}_4\{111\}$ . Note that the final state of the associative processes is the bare surface and an isolated  $\text{H}_2$  molecule. Grey balls and sticks denote Fe cations, dark-yellow S anions and white H atoms.

**Molecular Desorption**

Initial State	TS	Final State (before desorption)
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**System 1**

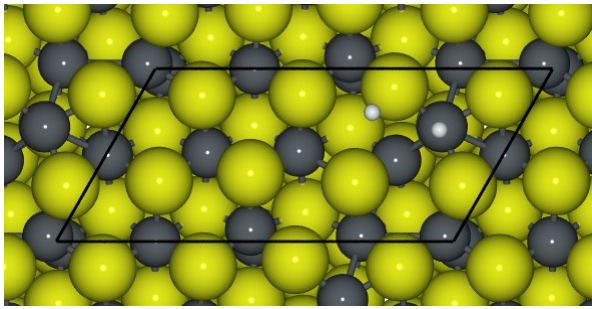


**Associative Desorption**

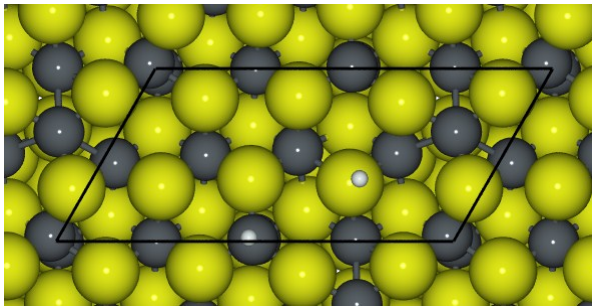
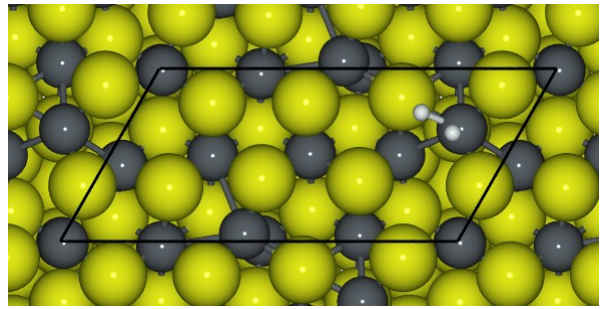
Initial State	TS
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**System 2**

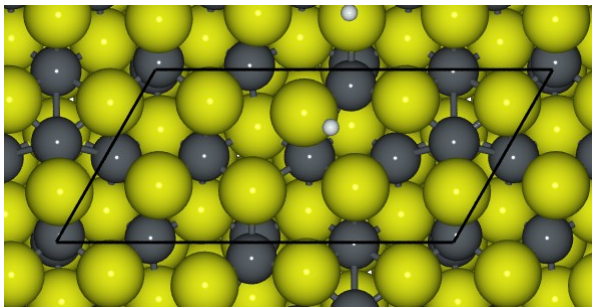
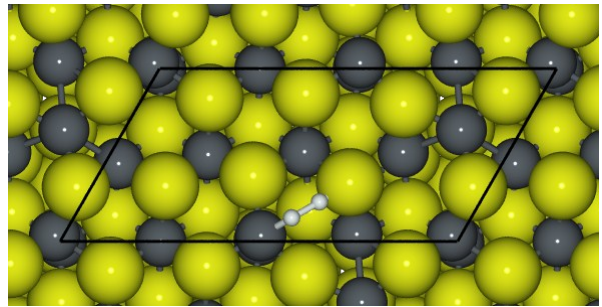




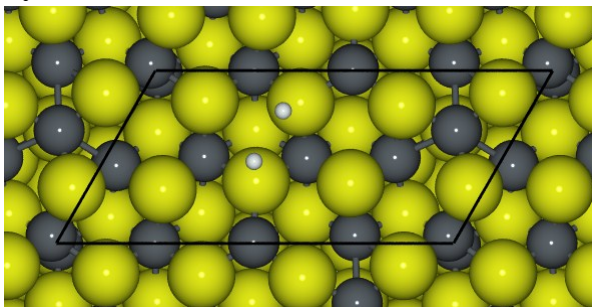
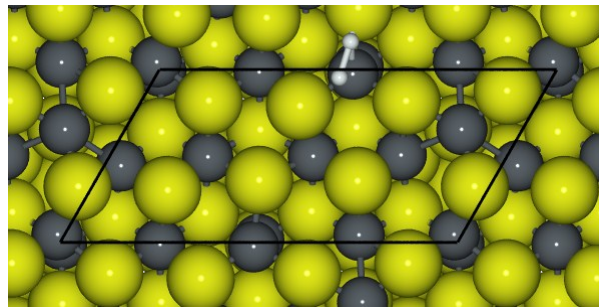
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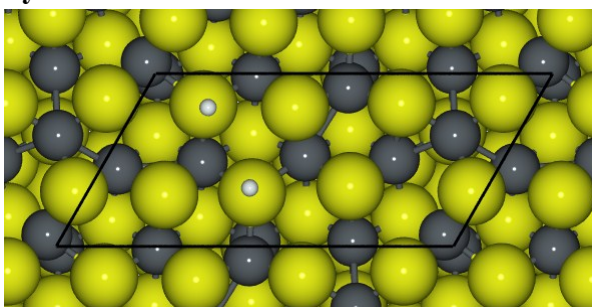
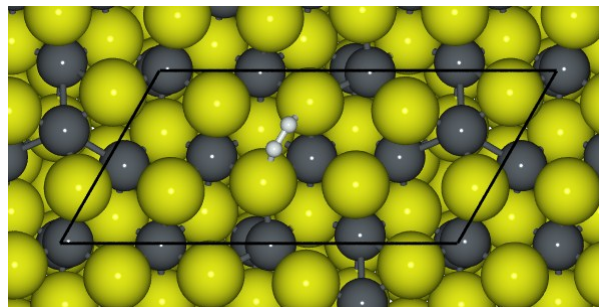
System 4



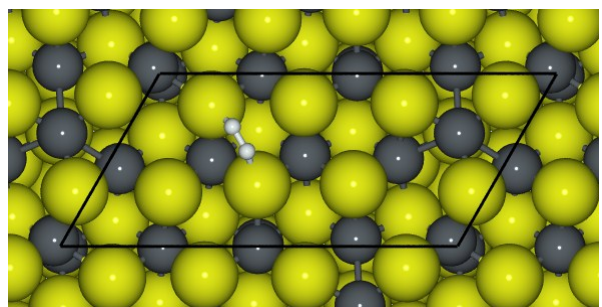
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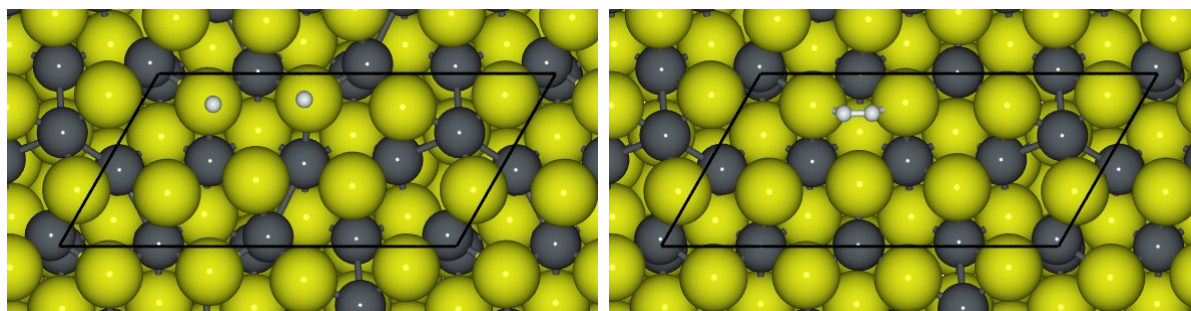


System 6



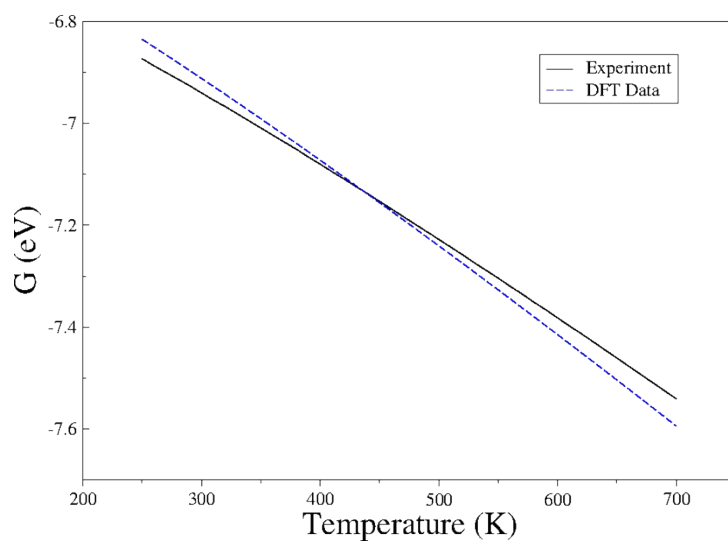
System 7





### *H<sub>2</sub> Free Energy*

**Figure S6.** Experiment (Ref. 69 in the main paper) (solid-black line) and computed (blue-dashed line) free energy ( $G$ ) for H<sub>2</sub> molecule from 250 to 700 K at 1 atm of pressure. The average relative error is 0.09 %.



*H sequestration in  $Fe_3S_4\{111\}$*

**Figure S7.** Side view representation of (A) the initial and (B) the optimized structure of a hydrogen atom incorporated into the  $Fe_3S_4\{111\}$  structure at  $\theta_H = 1$  ML. Grey balls and sticks denote Fe cations, dark-yellow S anions and white H atoms.

