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

Supplementary Information

Kinetic model of water adsorption, clustering and dissociation on Fe_3S_4\{001\}

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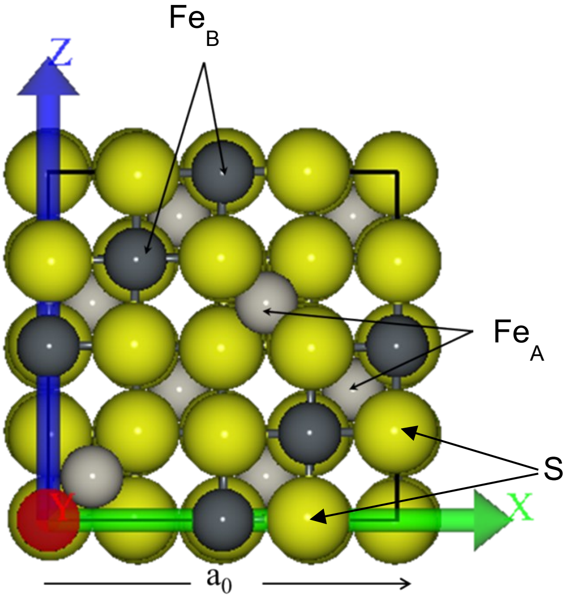
This file contents a compilation of figures and tables that complement the results and discussion in the publication with title **"Kinetic model of water adsorption, clustering and dissociation on Fe_3S_4\{001\}"**.

Content:

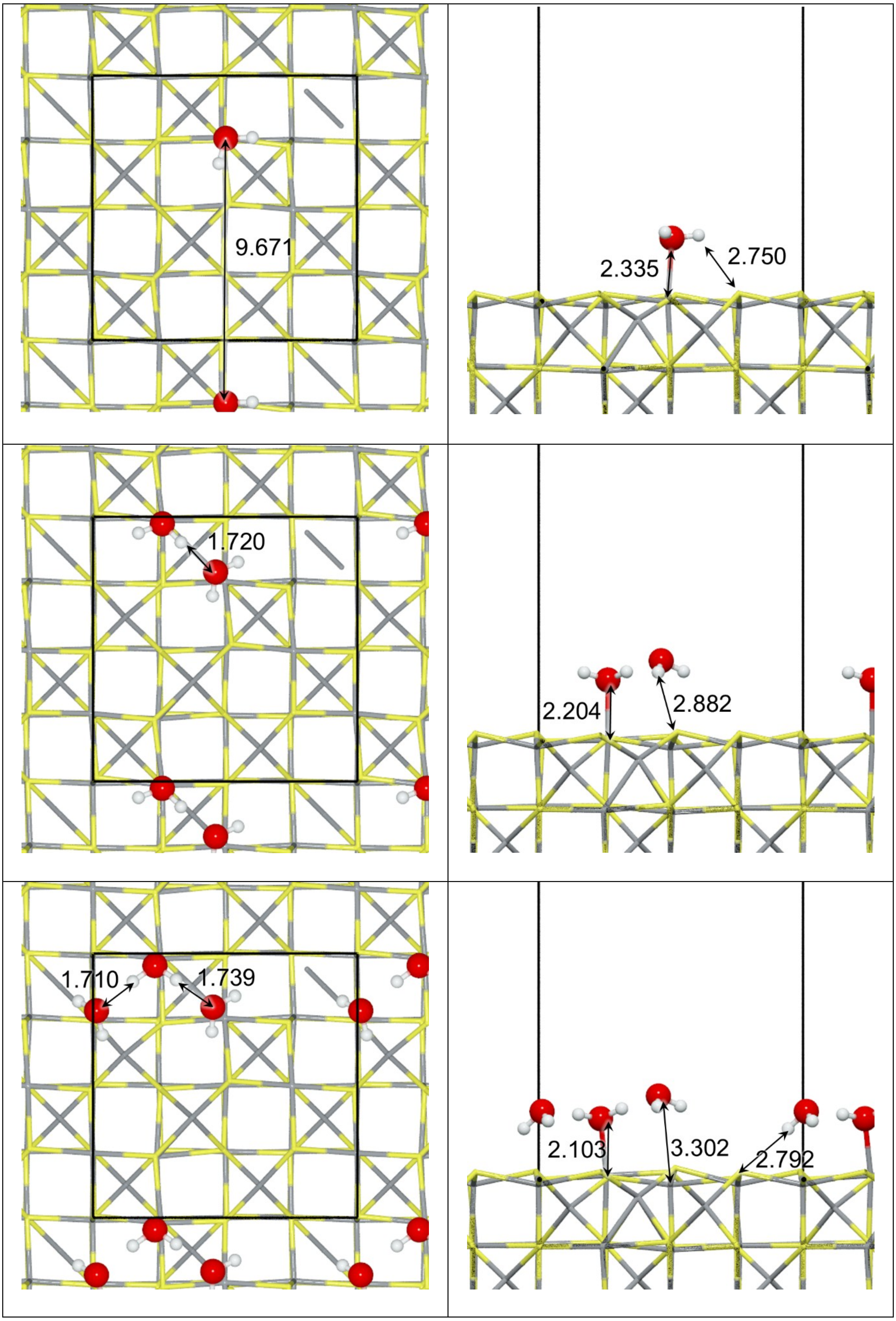
Bulk Structure of greigite

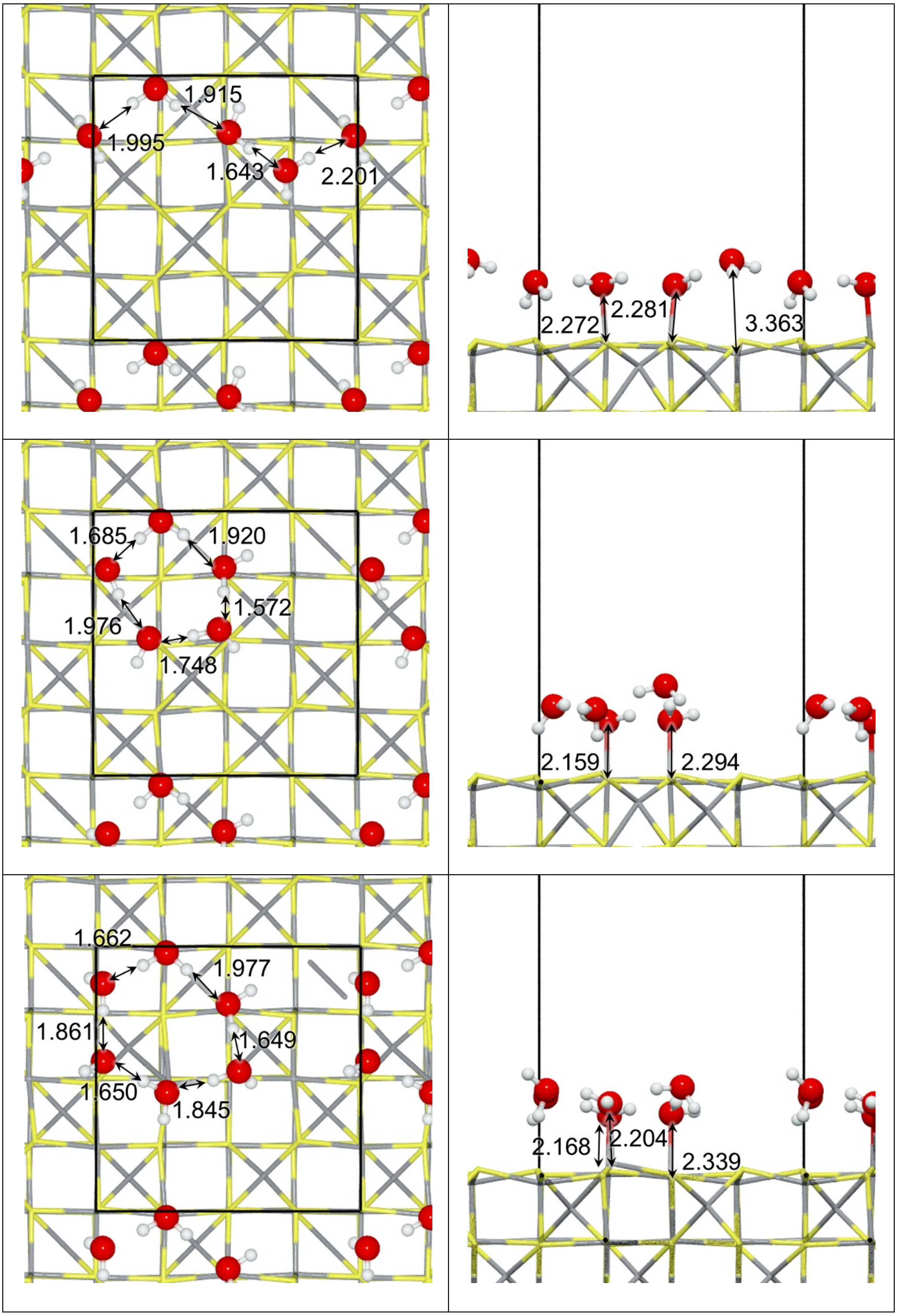
Figure S1. Greigite cubic cell represented by a black square. Tetrahedral (A) and octahedral (B) iron atoms are labelled and represented by light and dark grey spheres, sulfur atoms are yellow spheres. The axes are in green red and blue for x, y, z respectively.



Adsorption Geometries

Figure S2. Top and side view of Fe_3S_4\{001\} surface with $[H_2O]_n$ molecules (n= 1 – 10) forming a monolayer. The color scheme represents O in red and H in white balls and sticks while Fe and S are grey and yellow sticks respectively; black lines delimit the unit cell perimeter. All the distance values are given in Å.


9.671
2.335
2.750
1.720
2.204
2.882
1.710
1.739
2.103
3.302
2.792


1.915
1.995
1.643
2.201
2.272
2.281
3.363
1.685
1.920
1.572
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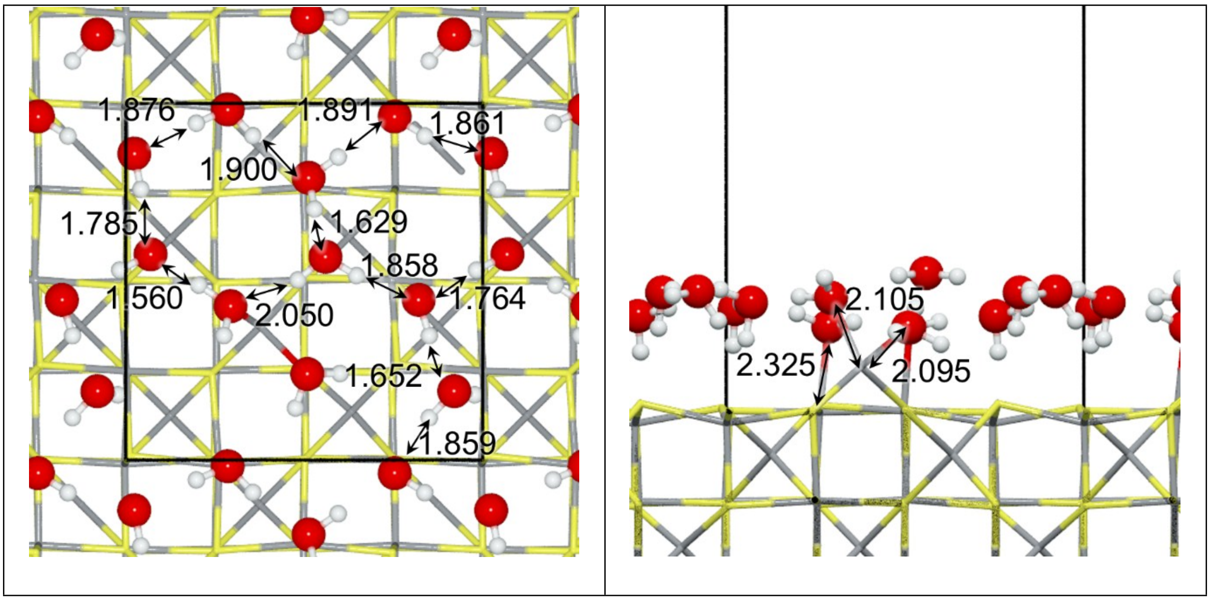
1.662
1.977
1.861
1.649
1.650
1.845
2.168
2.204
2.339


1.876
1.891
1.861
1.900
1.785
1.629
1.858
1.560
2.050
1.764
1.652
1.859
2.105
2.325
2.095

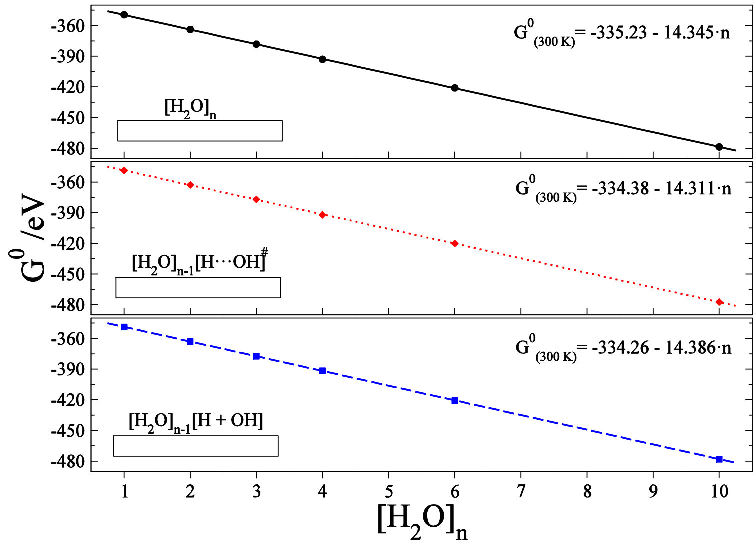
Classical micro-kinetics

We have presented an extensive kinetic model[1-3] for the water cluster formation on the Fe_3S_4\{001\} surfaces on the basis of 20 elementary steps. Additionally, we created an independent model for the formation of clusters considering only molecular diffusion across the surface. No assumptions regarding the mechanism or the rate-limiting step were made, all the processes were bi-directional and all model parameters weer rigorously derived from DFT calculations which we have compared with experimental data collected under realistic conditions, see **Fig S3**. In the frame of Transition State Theory,[4-5] this kinetic models may describe poorly the surface kinetics when local ordering of the surface is important. In this case, computationally expensive approximations can be used, for instance kinetic Monte Carlo (kMC) is capable of accounting for the correct local structure.[6] Unfortunately, such an analysis remains completely impractical for reaction networks as complicated as the one described here. Lateral cluster-cluster interactions can also influence the stability of intermediates.[7] Nevertheless considered the total surface coverage (θ) and interpolated the total energy values for up to a full monolayer, see **Fig S2**. The maximum surface coverage was restricted to 1 ML, and multilayer adsorption was not considered. The energy values are also temperature dependent as explained in the main text.

Interpolation of energies

The absolute energy value of any system was derived from the DFT calculated values following the linear trends in **Figure S2**, which have a correlation of 0.99. This value indicates not only a linear behaviour for the energies within the range of molecules studied but also the accuracy of the calculations and methodology used. These absolute energies correspond to **n** molecule on the surface leading to a difference in energy of not only the interaction but also the contribution of the electronic energy.

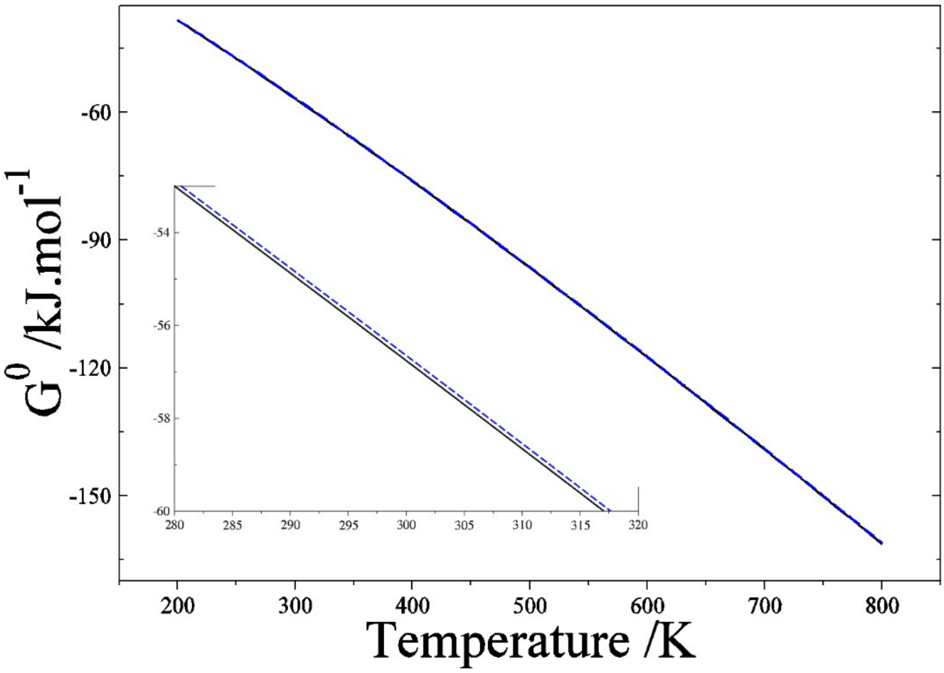
Figure S3. Total free energy (G^0) as a function of n in the $[H_2O]_n$ clusters (n< 11) adsorbed on Fe_3S_4\{001\} at 300 K. Top graph indicates binding energy, middle graph indicates transition estate energies for the H_2O dissociation and bottom graph shows the total energy having a dissociated molecule on the surface. Equations are inserted.



Gas phase molecules

For the micro-kinetic model, we have included ZPE corrections, temperature-dependent heat capacity at constant pressure corrections and entropy contributions, all derived from DFT. Frequencies are calculated using the harmonic oscillator assumption by diagonalization of the mass-weighted Hessian matrix in internal coordinates obtained with a displacement of 0.05 Å. Translational and rotational modes for a gas phase species were defined using its center of mass and principle moments of inertia.

Figure S4. H_2O molecular free energy (G) as a function of the temperature. Solid black line indicates our calculated values and the blue-dashed line indicates the experimental extrapolation from Shomate equations.[8]

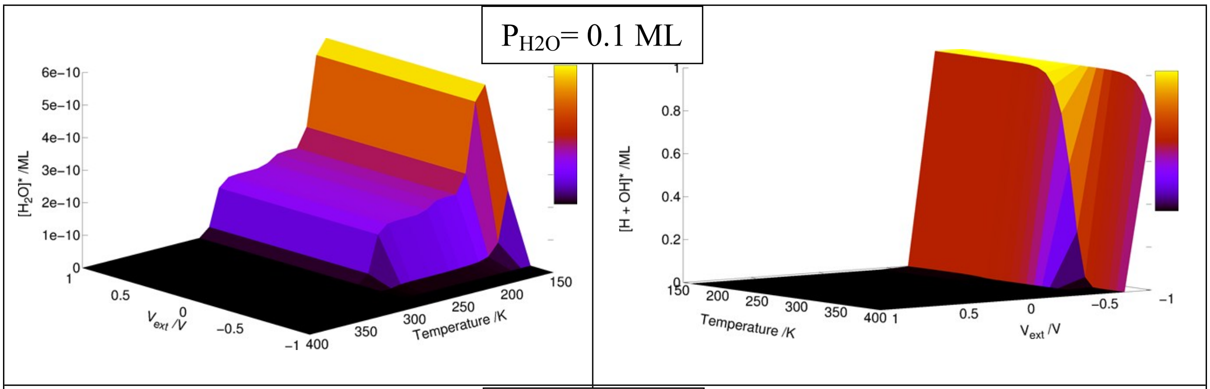


Initial water pressure

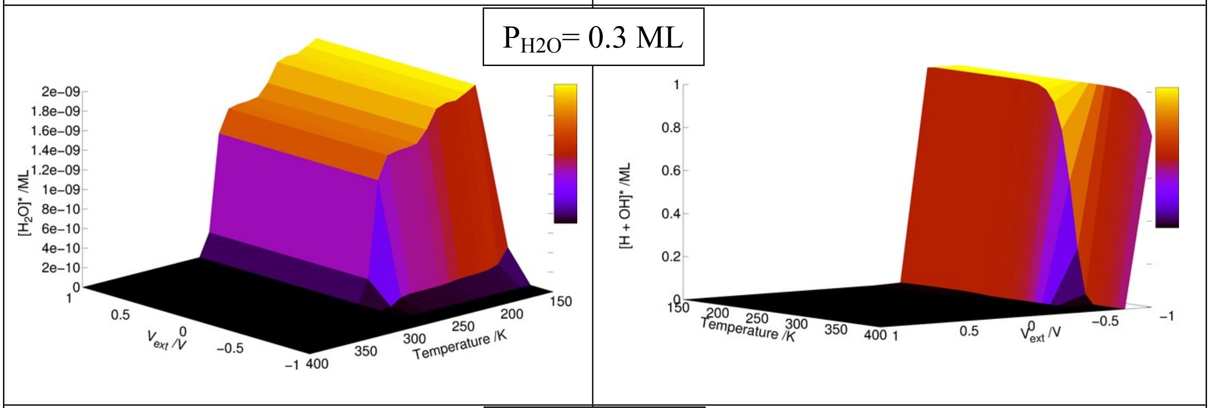
Effect of external potential and temperatures on the adsorption and dissociation of H_2O as a functional of the initial water exposure of the Fe_2S_4{001} surface.

Figure S5. Adsorbed (left) and dissociate (right) water on Fe_3S_4{001} under different conditions on temperature and external potential two seconds after expose the naked surface to different pressures of gas phase water.

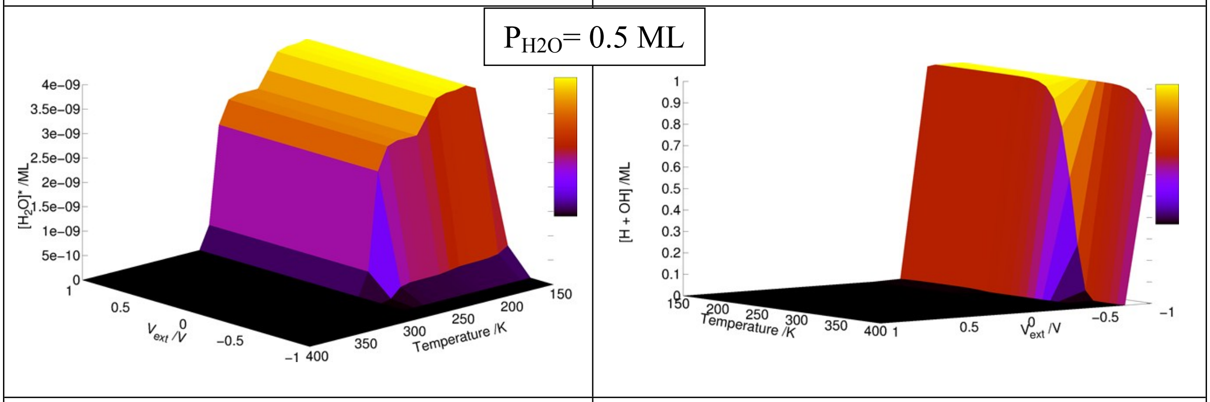
P_{H2O}= 0.1 ML



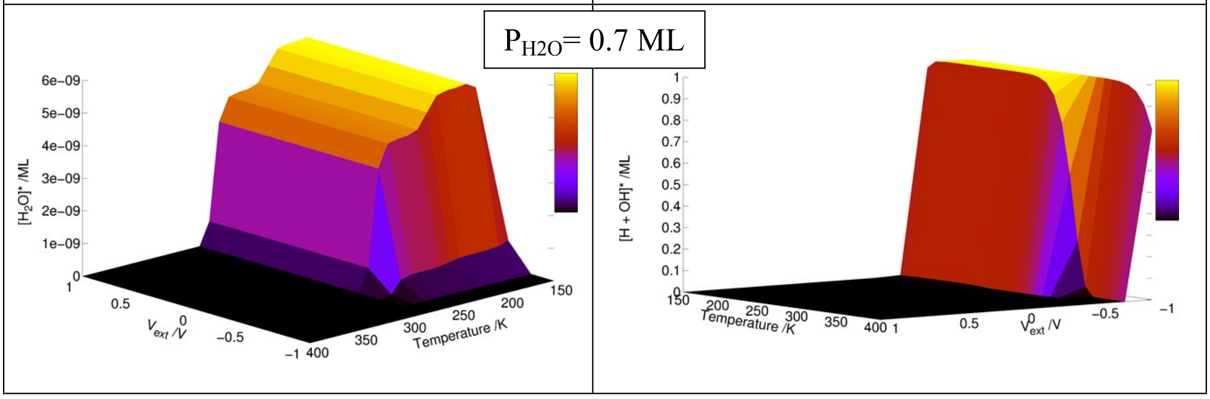
P_{H2O}= 0.3 ML

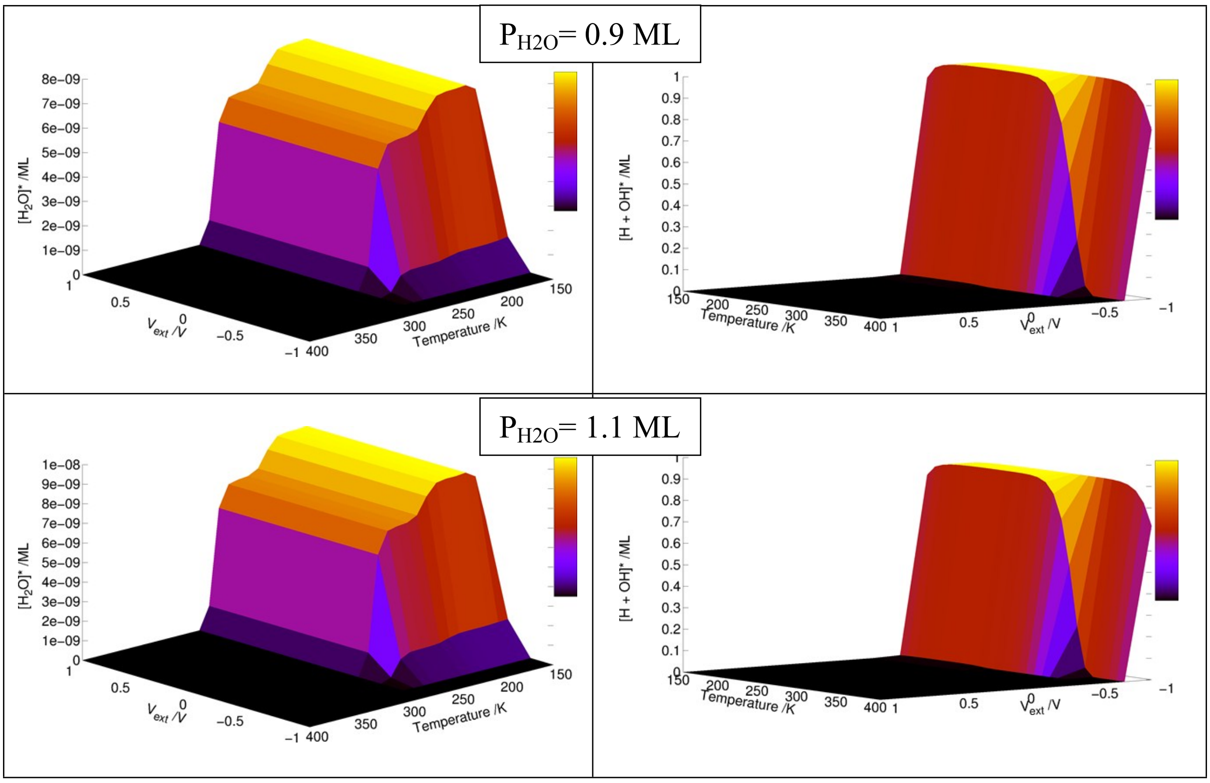


P_{H2O}= 0.5 ML



P_{H2O}= 0.7 ML





P_{H2O}= 0.9 ML

P_{H2O}= 1.1 ML

References

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