Supporting Information for:

Density functional theory characterization of the structures of H_3AsO_3 and H_3AsO_4 adsorption complexes on ferrihydrite

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This supporting information contains surface energy convergence of the Fh(110)-term-A slab with increasing the number of topmost layers allowed to relax unconstrainedly **(Table S1)**, the geometry-optimized structures of the two possible terminations of Fh(110) surface in dry and aqueous conditions (**Figure S1**), the optimized structures of the inner and outer sphere adsorption complexes of $H_2AsO_4^-$ on Fh(110) surface covered with mixed -OH/-H_2O composition (**Figure S2**), and the partial DOS projected on the interacting surface Fe *d*-states and adsorbed H_3AsO_3 O and As *p*-states at -OH/-H_2O covered Fh(110) surface and the iso-surfaces of the electron density difference plot relative to the adsorbed solvated H_3AsO_3 (**Figure S3**) and H_3AsO_4 (**Figure S4**).

Table S1: Surface energy convergence of the Fh(110)-term-A slab with increasing the number of topmost layers allowed to relax unconstrainedly.

No of layers relaxed	Surface energy (γ_r)
1	1.0233
2	0.9054
3	0.8844
4	0.8832
5	0.8830

Figure S1: Geometry-optimized structures of two possible terminations of Fh(110) surface in dry and aqueous conditions. (Atomic colour scheme: Fe = grey, O = red, and H = white).

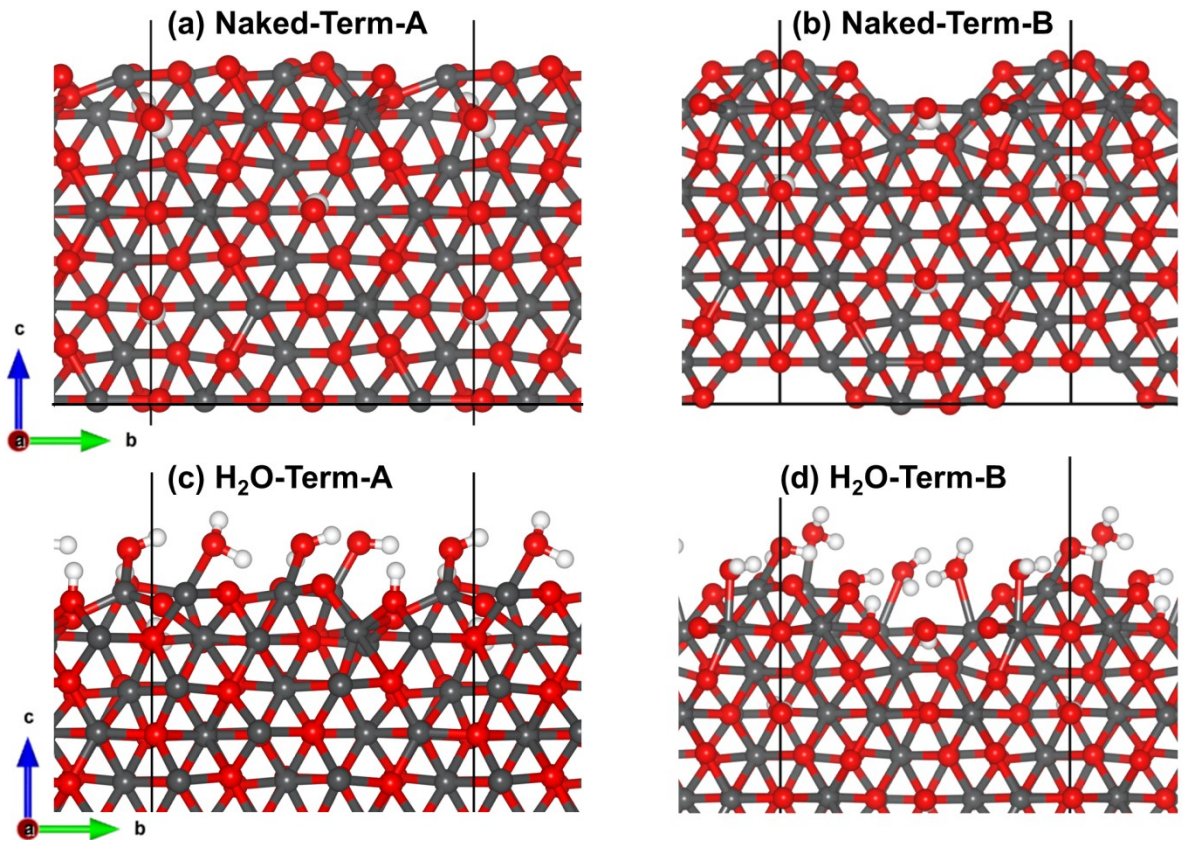

Figure S2: Optimized structures of inner and outer sphere adsorption complexes of $H_2AsO_4^-$ on Fh(110) surface covered with mixed -OH/-H_2O composition. (Atomic colour scheme: Fe = grey, O_{surf} = red, O_{mol} = light slate blue, As = green, and H = white). Bond distances are in Angstrom unit.

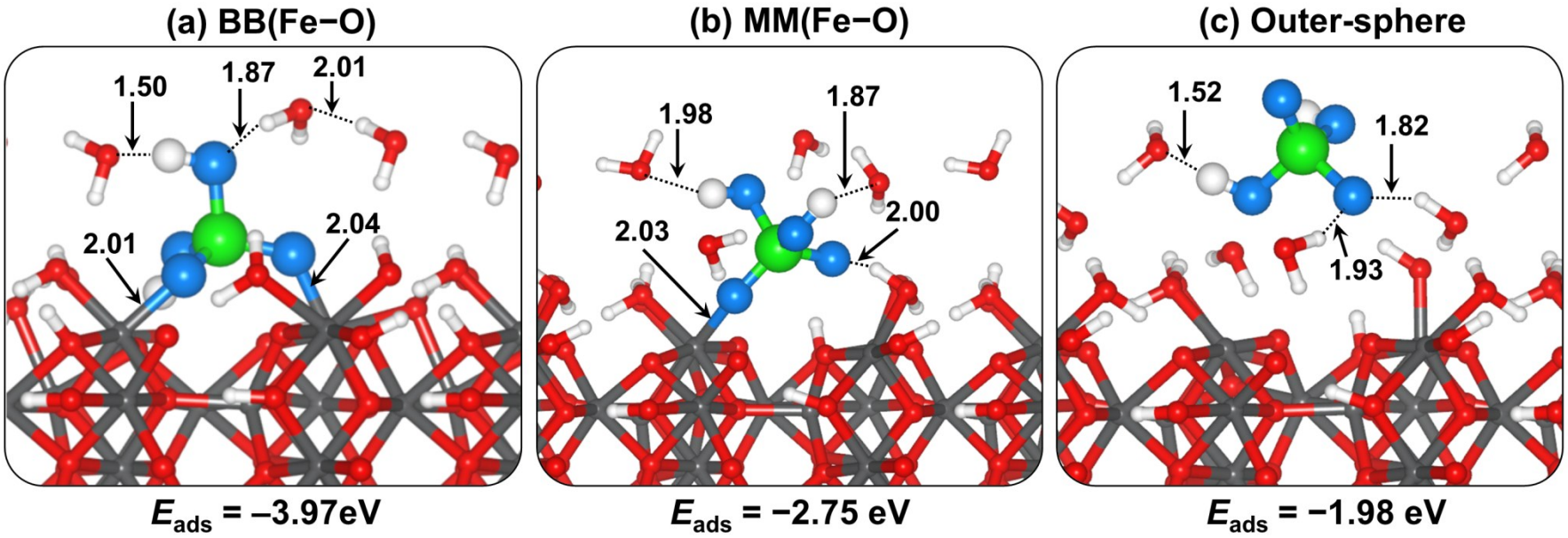

Figure S3: (Left) Partial DOS projected on the interacting surface Fe *d*-states and adsorbed H_3AsO_3 O and As *p*-states at -OH/-H_2O covered Fh(110) surface. (Right) Iso-surfaces of the electron density difference plot relative to the adsorbed solvated H_3AsO_3, showing regions of electron density accumulation (purple) and depletion (orange) by 0.02 e/Å^3, respectively.

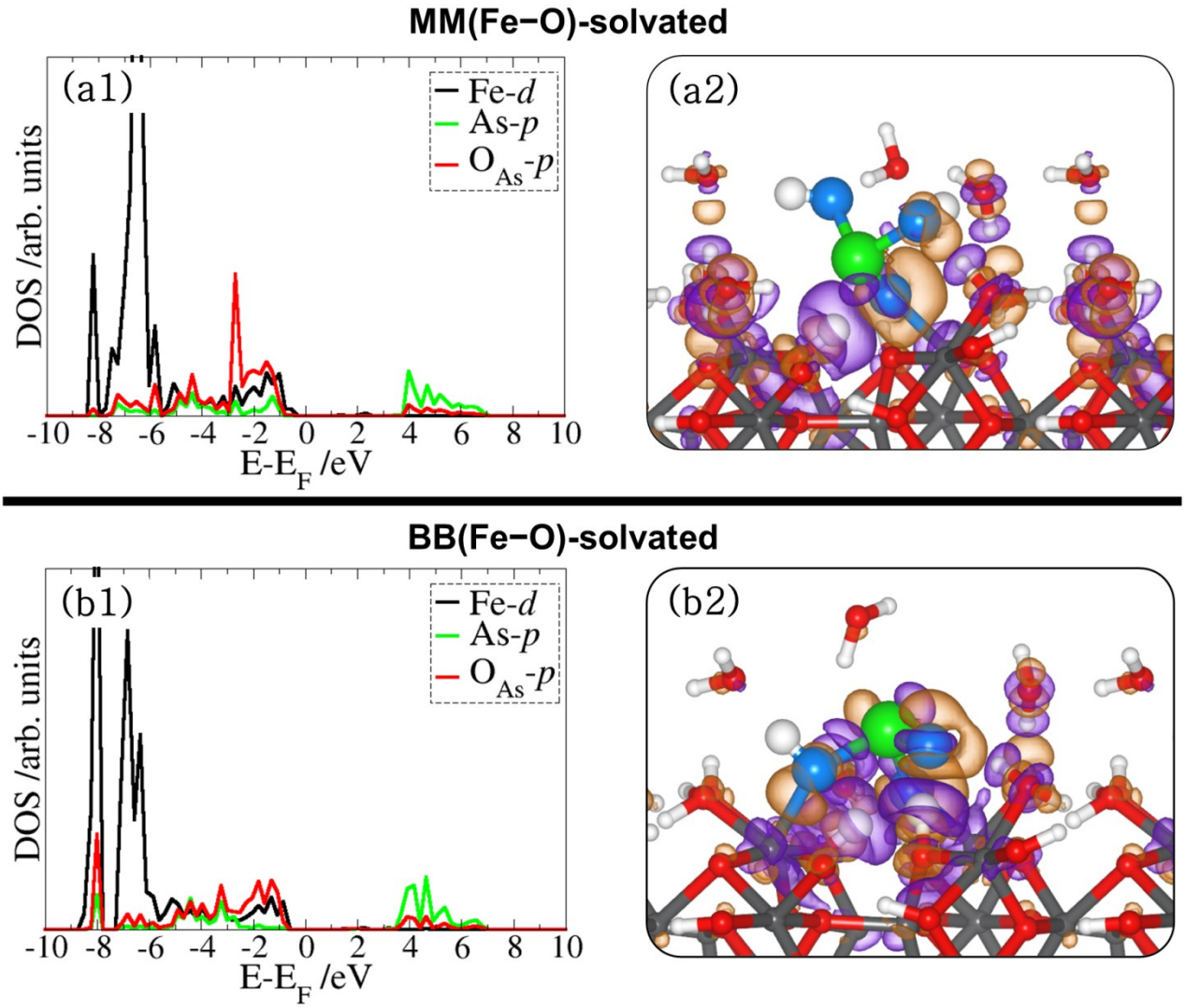

Figure S4: (Left) Partial DOS projected on the interacting surface Fe *d*-states and adsorbed H_3AsO_4 O and As *p*-states at -OH/-H_2O covered Fh(110) surface. (Right) Iso-surfaces of the electron density difference plot relative to the adsorbed solvated H_3AsO_4, showing regions of electron density accumulation (purple) and depletion (orange) by 0.02 e/Å^3, respectively.