Supporting Information for:

Structures and properties of $As(OH)_3$ adsorption complexes on hydrated mackinawite (FeS) surfaces: A DFT-D2 study

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This supporting information contains the detailed information on all other conformations of $As(OH)_3$ adsorption complexes, structural parameters and vibrational frequency assignments at the water-FeS{001}, water-FeS{011}, and water-FeS{111} interfaces. It contains three Figures and four Tables.

Figure S1: Optimized outer- and inner-sphere adsorption complexes of $As(OH)_3$ on FeS(001) surface, in side (top) and top (bottom) views. (Colour scheme: (Colour scheme: Fe = grey, S = yellow, As = green, O_{water} = red, $O_{As(III)}$ = pink, and H = white).

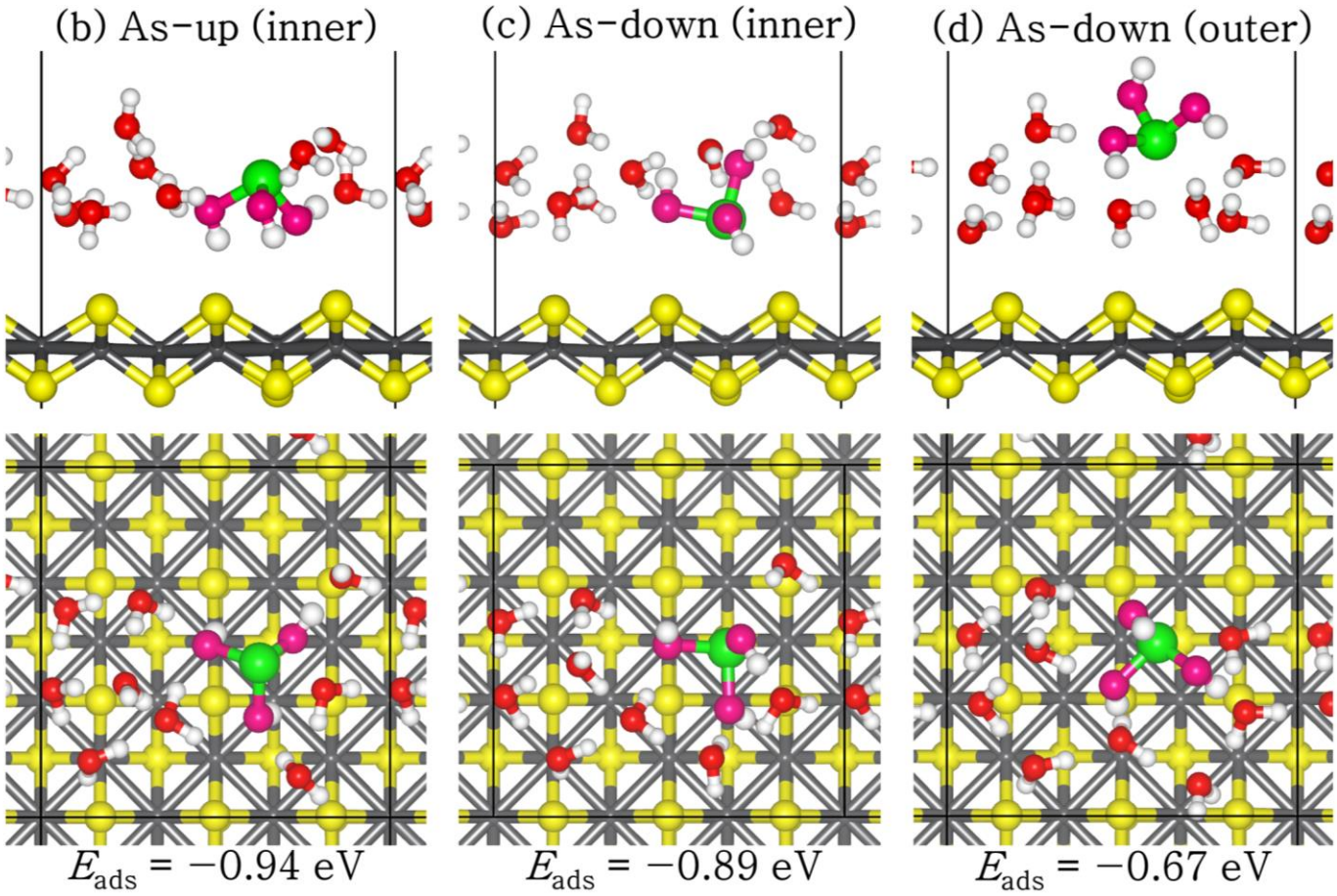

Figure S2: Optimized adsorption complexes of $As(OH)_3$ on FeS(011) surface, in side (top) and top (bottom) views. (Colour scheme: Fe = grey, S = yellow, As = green, O_{water} = red, $O_{As(III)}$ = pink, and H = white).

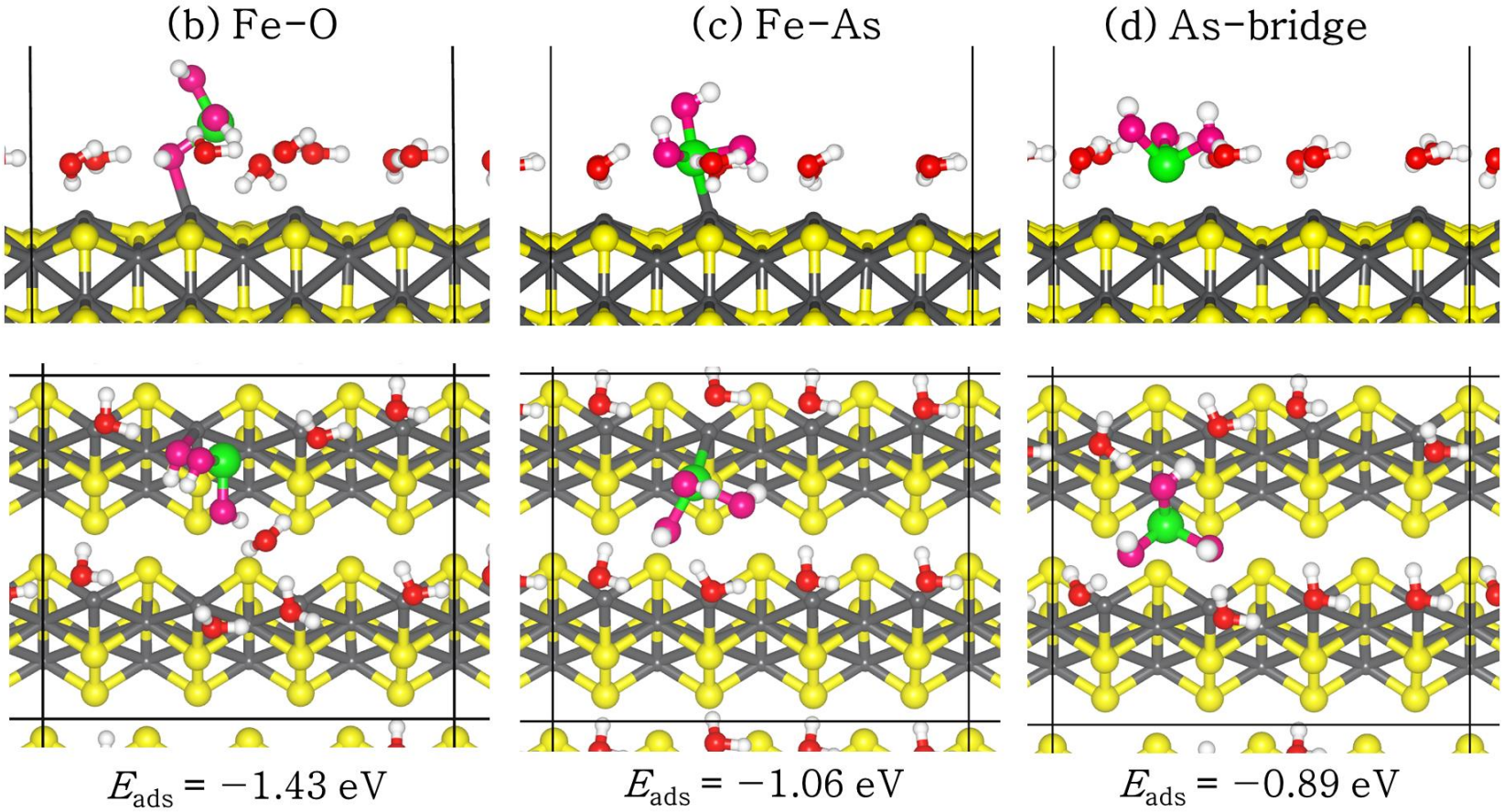

Figure S3: Optimized adsorption complexes of $As(OH)_3$ on FeS(011) surface, in side (top) and top (bottom) views. (Colour scheme: Fe = grey, S = yellow, As = green, O_{water} = red, $O_{As(III)}$ = pink, and H = white).

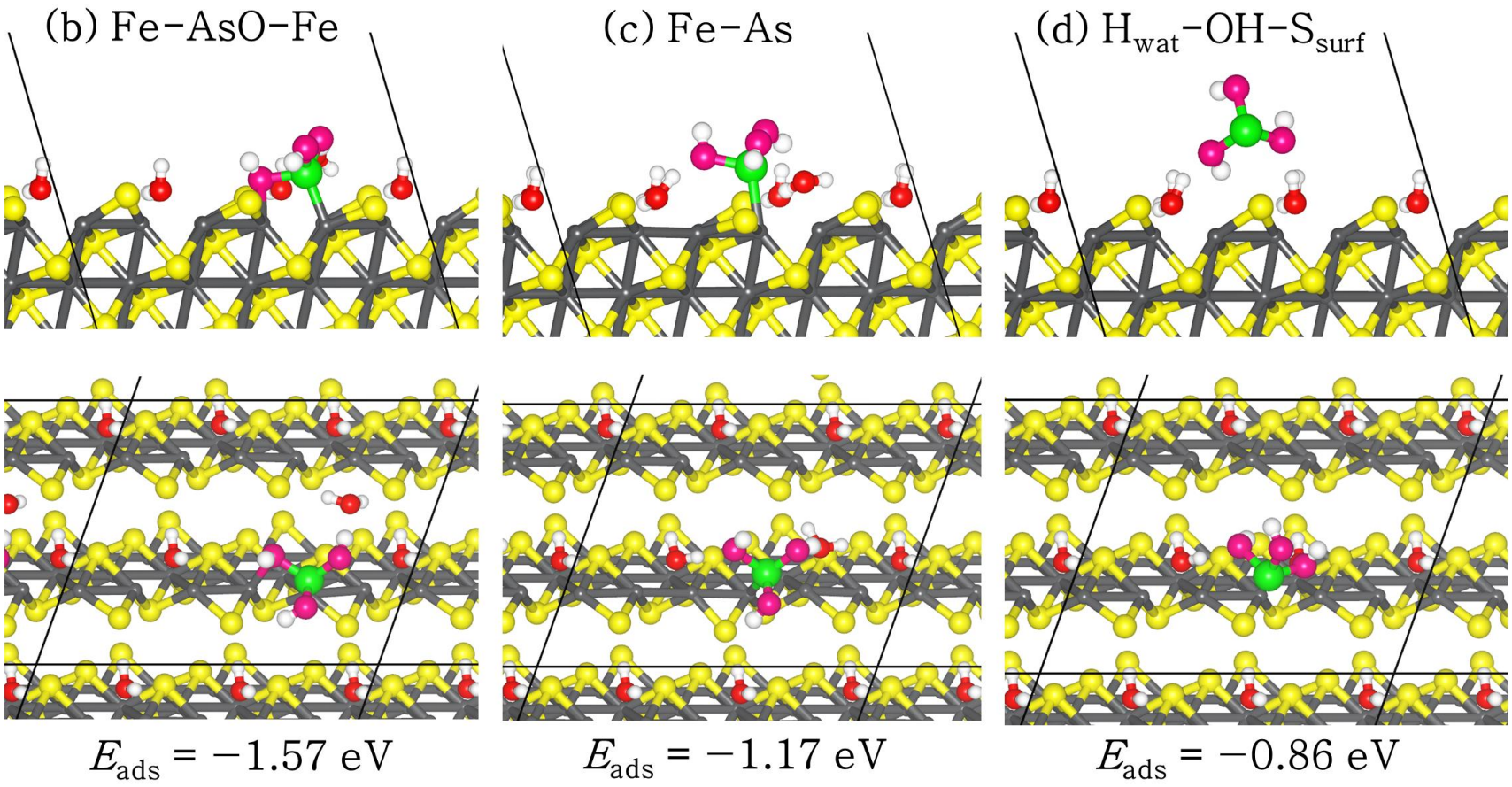

TABLE S1: Adsorption energies, variation of the total Bader charge, representative geometrical parameters, and interatomic distances of $As(OH)_3$ adsorption complexes at water−FeS{001} surface.

Configuration	As−up (inner)	As−down (outer)	As−down (inner)
E_{ads} /eV	–0.94	–0.89	–0.67
$\sum q$ /e^-	0.02	0.01	0.02
d(As–O) /Å	1.867	1.864	1.875
	1.941	1.809	1.772
	1.772	1.789	1.866
d(O–H) /Å	0.979	0.995	0.980
	0.980	0.978	1.046
	1.031	1.002	0.975
d(H_{mol}–O_{wat}) /Å	1.578	1.709, 1.773	1.512
d(H_{wat}–O_{mol}) /Å	1.714, 1.800	1.613	1.811, 2.158
d(H_{wat}–S) /Å	2.502	2.318	2.819
d(H_{mol}–S) /Å	2.635	4.425	2.438
d(As–S) /Å	4.377	5.656	3.688

TABLE S2: Adsorption energies, variation of the total Bader charge, representative geometrical parameters, and interatomic distances of $As(OH)_3$ adsorption complexes at water−FeS{011} surface.

Configuration	Fe−O	Fe−As	As−bridge
E_{ads} /eV	–1.43	–1.06	–0.89
$\sum q$ /e^-	0.21	0.18	0.08
d(As–O) /Å	1.907	1.907	1.869
	1.793	1.840	1.883
	1.787	1.838	1.866
d(O–H) /Å	1.011	0.981	0.976
	0.983	0.978	0.993
	0.978	0.985	0.978
$d(H_{mol}–O_{wat})$ /Å	1.652	3.157	1.854
$d(H_{wat}–O_{mol})$ /Å	1.829	1.734, 2.489	1.640, 1.683, 1.708
d(O–Fe) /Å	2.216	3.968	3.545
d(As–S) /Å	4.147	2.960	3.404
d(As–Fe) /Å	3.348	2.464	3.787

TABLE S3: Adsorption energies, variation of the total Bader charge, representative geometrical parameters, and interatomic distances of $As(OH)_3$ adsorption complexes at water−FeS{111} surface.

Configuration	Fe−AsO−Fe	Fe−As	H_{wat}−OH−S_{surf}
E_{ads} /eV	–1.57	–1.17	–0.86
$\sum q$ /e^-	0.22	0.16	0.01
d(As–O) /Å	1.835	1.853	1.860
	1.788	1.794	1.848
	1.758	1.783	1.816
d(O–H) /Å	1.014	0.991	0.980
	0.988	0.986	0.978
	0.980	0.978	0.978
d(H_{mol}–O_{wat}) /Å	1.659	1.784	2.800
d(H_{wat}–O_{mol}) /Å	3.838	1.619	1.600, 1.740
d(H_{wat}–S) /Å	2.033	2.023	2.033
d(H_{mol}–S) /Å	2.426	2.352	3.549
d(O–Fe) /Å	2.091	3.332	3.557
d(As–S) /Å	3.078	3.195	3.271
d(As–Fe) /Å	2.217	2.530	4.235

Table S4: Molecular vibrational frequencies (in cm^{-1}) of adsorbed $As(OH)_3$ at water−FeS interfaces.

		ν(As−O)			ν(O−H)		
Surface	Configuration	As−O1	As−O2	As−O3	O1−H	O2−H	O2−H
	Free $As(OH)_3$	700.8 (710)[a]	639.1 (655)[a]	638.3 (655)[a]	3738.1	3711.5	3674.7
FeS(001)	As−up−inner	715.2	553.7	460.5	3648.4	3637.0	2666.1
	As−down−outer	684.61	636.4	563.9	3679.3	3317.0	3177.2
	As−down−inner	718.0	564.3	546.3	3644.6	3607.7	2446.9
FeS(011)	As−bridge	562.4	529.7	523.1	3708.8	3695.0	3381.9
	Fe−As	584.9	570.1	462.9	3700.4	3659.5	3530.9
	Fe−O	696.1	654.4	599.5	3680.6	3621.9	3011.3
FeS(111)	Fe−AsO−Fe	686.6	639.7	573.0	3644.7	3451.0	2977.6
	Fe−As	670.4	629.6	549.2	3708.1	3485.8	3403.5
	Fe−O	634.0	586.5	557.6	3701.5	3674.6	3633.1

[a]Loehr, T.M.; Plane, R.A. Raman spectra and structures of arsenious acid and arsenites in aqueous solution. *Inorg. Chem*. **1968**, ***7***, 1708−1714.