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First-Principles Density Functional Theory Characterisation of the Adsorption Complexes of H_3AsO_3 on Cobalt Ferrite (Fe_2CoO_4) Surfaces

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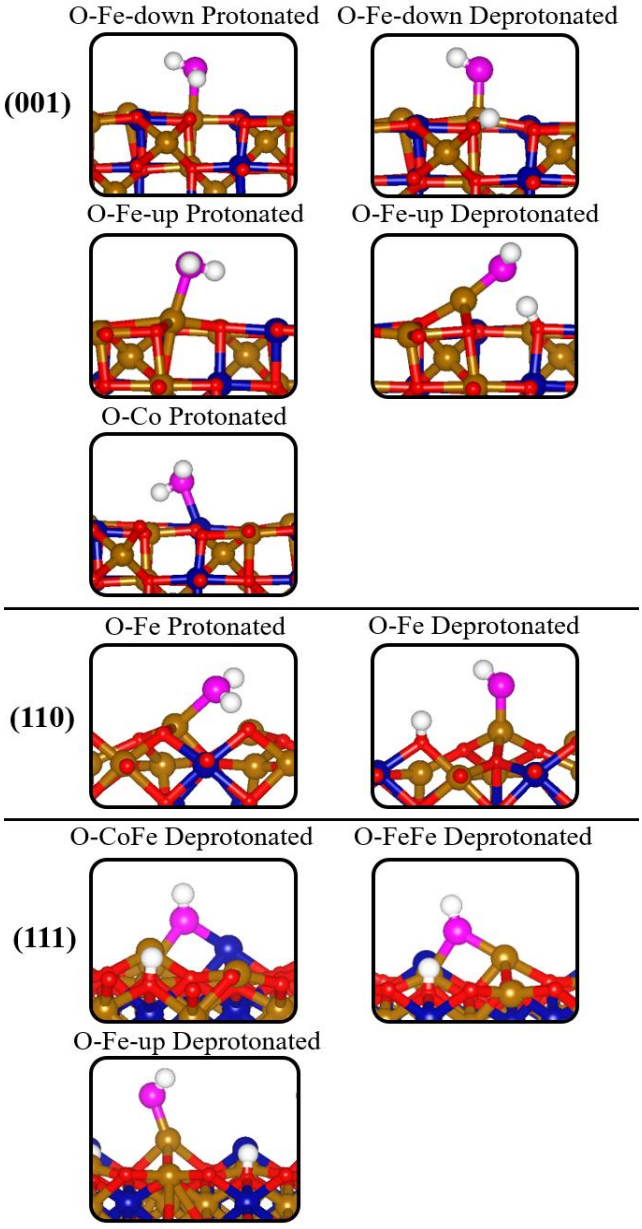


Figure 1. Low-energy adsorption geometries for molecular and dissociative H_2O on the Fe_2CoO_4 (001), (110), and (111) surfaces. (Fe = brown, Co = blue, O_{surf} = red, O_{mol} = purple, H = white).

Table 1. Magnetic moments of Fe_{Td}, Fe_{Oh}, and Co atoms in the bulk and surfaces of Fe_2CoO_4.

System	Fe_{Td}		Fe_{Oh}		Co	
Bulk	4.016		4.154		2.696	
Surface	Dry	Hydrox.	Dry	Hydrox.	Dry	Hydrox.
(001)	3.550	4.047	4.092	4.155	2.701	2.733
(110)	3.851	3.951	3.581	4.077	3.603	3.628
(111)	3.932	4.040	3.526	4.033	2.599	2.662

Table 2. Adsorption energies (eV) and O_{mol}-metal bond lengths (Å) of molecular and dissociated H_2O geometries on the (001), (110) and (111) surfaces of Fe_2CoO_4. (M = nearest surface Fe or Co cation).

Surface	Configuration		E_{ads}	d_{Omol-M}
001	O-Fe-down	Protonated	−0.540	2.268
		Deprotonated	−0.985	1.862
	O-Fe-up	Protonated	−0.637	2.242
		Deprotonated	−0.593	1.874
	O-Co	Protonated	−0.668	2.155
		Deprotonated		
110	O-Fe	Protonated	−1.457	2.126
		Deprotonated	−2.523	1.817
111	O-CoFe	Protonated		
		Deprotonated	−2.164	1.999, 2.074
	O-FeFe	Protonated		
		Deprotonated	−2.150	2.064, 2.051
	O-Fe-up	Protonated		
		Deprotonated	−1.516	1.860

Table 3. Strength of hydrogen bonded interactions with nearest H-O_H_2O or H-OH_surf in all uniquely identified adsorption complexes of H_3AsO_3 on hydroxylated Fe_2CoO_4 (001), (110), and (111) surfaces. (dp = deprotonated).

		Hydrogen Bonded Interactions with Nearest H-O_H_2O or H-OH_surf			
Surface	**Configuration**				
001	MM-O-Co	1.765	1.622 (OH ads)	1.743	2.048 (H_2O ads)
	Outer-Sphere	1.738	1.891	1.735	1.524 (OH ads)
110	MM-O-Fe_{dp}	1.661	1.897	1.581	1.483 (OH ads)
	MM-O-Fe	1.725	1.755	2.083	3.295 (OH ads)
111	BB-Fe-OO-Co	1.565	1.641	2.916	2.861
	BB-Fe-OO-Fe	1.530	1.721	1.734	2.056
	MM-O-Co	2.956 (H_2O ads)	1.558	3.297 (OH ads)	3.527
	Outer-Sphere	1.972	2.224	1.636 (OH ads)	1.528 (OH ads)

Table 4. Bond distances (Å) and corresponding stretching frequencies (cm^{-1}) of O-H bonds in H_3AsO_3 adsorption complexes on dry Fe_2CoO_4 (001), (110), and (111) surfaces. (dp = deprotonated).

		***d*(O1-H)/Å, *v*(O-H) / cm^{-1}**		
Surface	**Configuration**	**(*d*(O1-H)); *v*(O1-H)**	**(*d*(O2-H)); *v*(O2-H)**	**(*d*(O3-H)); *v*(O3-H)**
001	MM-As-Co	(0.995); 3401	(0.978); 3745	(0.989); 3574
	MM-As-Fe	(0.994); 3470	(0.979); 3797	(0.977); 3802
	MM-O-Co	(1.008); 3137(O-H--O_{surf})	(0.994); 3483	(0.978); 3840
	BB-Fe-OO-Co	(0.975); 3765	(0.978); 3746	(0.975); 3740
	BB-Fe-OO-Fe	(0.974); 3762	(0.977); 3775	(0.984); 3693
	BB-Fe-OO-Fe_{dp}	(0.948); 3796	(2.869); 3289_{dp}	(0.978); 3807

	TB-Fe-O_2O-Fe_{dp}	(0.938); 3797	(0.977); 3837	(1.824); 3295_{dp}
110	MM-O-Fe	(0.987); 3663	(0.978); 3826	(0.977); 3794
	BM-OO-Fe	(0.975); 3762	(0.979); 3707	(1.024); 2757(O-H--O_{surf})
	BB-O-AsO-Fe_{dp}	(2.052); 3503_{dp}	(0.980); 3732	(0.978); 3796
111	MM-O-Co	(0.975); 3815	(0.978); 3789	(0.979); 3679
	MM-O-Fe	(1.036); 2638(O-H--O_{surf})	(0.976); 3757	(0.977); 3735
	BB-Co-AsO-Fe_{dp}	(2.033); 3491_{dp}	(0.978); 3739	(0.990); 3480
	BB-Fe-AsO-Fe_{dp}	(1.656); 2968_{dp}	(0.980); 3761	(0.981); 3666
	BB-Fe-OO-Fe_{dp}	(0.980); 3789	(0.975); 3725	(3.396); 3436_{dp}

Table 5. Bond distances (Å) and corresponding stretching frequencies (cm^{-1}) of O-H bonds in H_3AsO_3 adsorption complexes on hydroxylated Fe_2CoO_4 (001), (110), and (111) surfaces. (dp = deprotonated).

		***d*(O1-H)/Å, *v*(O-H) / cm^{-1}**		
Surface	**Configuration**	**(*d*(O1-H)); *v*(O1-H)**	**(*d*(O2-H)); *v*(O2-H)**	**(*d*(O3-H)); *v*(O3-H)**
001	MM-O-Co	(1.680); 3041_{dp}	(1.026); 2768(O-H--O_w)	(0.994); 3422
	Outer-Sphere	(0.975); 3728	(1.005); 3174(O-H--O_w)	(1.039); 2566(O-H--O_w)
110	MM-O-Fe_{dp}	(1.048); 2462(O-H--O_w)	(1.014); 3029(O-H--O_w)	(1.534); 2624_{dp}
	MM-O-Fe	(1.050); 3340	(1.016); 3038	(0.987); 3590
111	BB-Fe-OO-Co	(1.015); 2980(O-H--O_w)	(1.038); 2568(O-H--O_w)	(1.046); 2453(O-H--O_w)
	BB-Fe-OO-Fe	(1.047); 2482	(1.733); 3206_{dp}	(1.000); 3328(O-H--O_w)
	MM-O-Co	(1.054); 2801	(3.101); 3050_{dp}	(0.977); 3767
	Outer-Sphere	2535	(1.019); 2916(O-H--O_w)	(0.975); 3844