

Surface Reactivity and Surface Characterization of Layered β (III)-CoOOH

Material an Experimental and Computational Study

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Experimental section from XPS analysis

The Figure SI-1 shows the SO₂/Co atomic ratio evolution as a function of exposure time for different delay between SO₂ gas probe adsorption and XPS analysis.

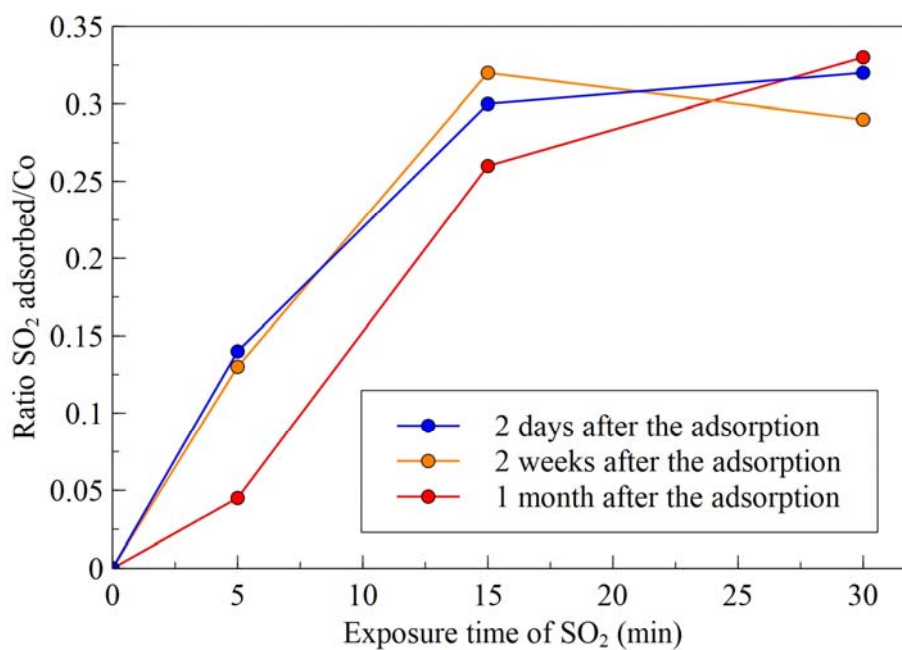


Figure SI-1: Comparison of the SO₂ adsorbed/Co ratio for samples analyzed by XPS 2 days, 2 weeks and 1 month after the experiment

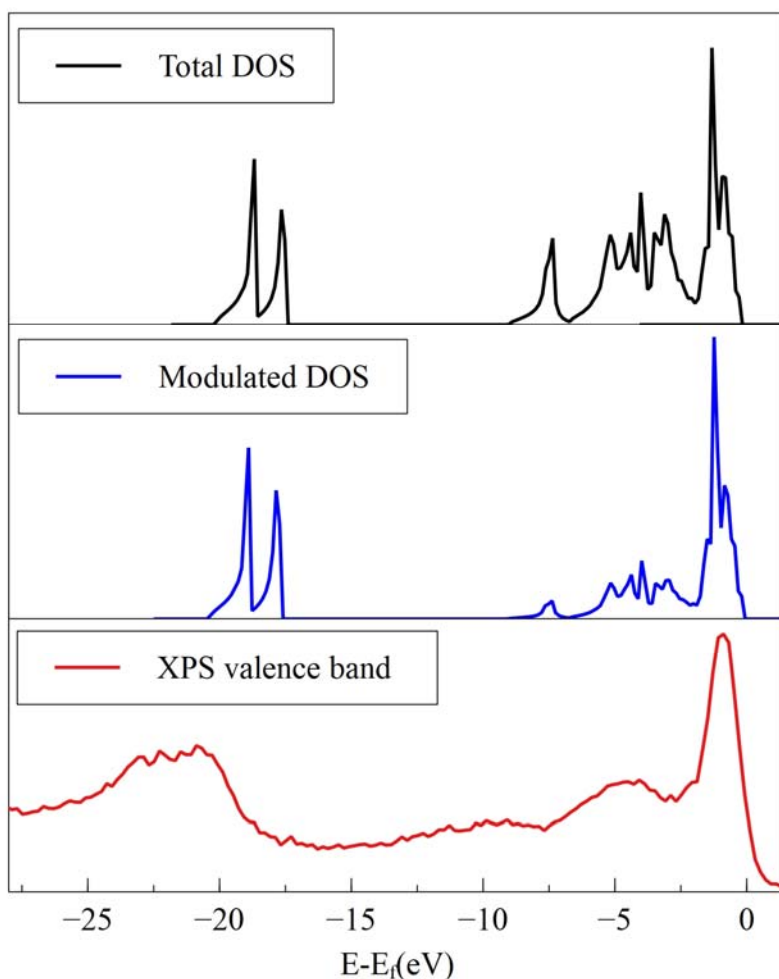


Figure SI-2. Total density of states (black), density of states modulated by photoionization cross-sections (blue) and XPS valence band (red)

In the spectra, there are two main regions: a first one between the Fermi level and -7.5eV which corresponds to the contribution of O 2p and Co 3d, a second zone, between -17.0eV and -25.0eV corresponding to the contribution of O 2s, with two peaks due to the presence of two non-similar environments for the oxygen of the material. As mentioned in the manuscript, for the O 1s core peaks, one of the peaks refers to the oxygen contributing to the oxide part of the material and the second to the hydroxide part.

The difference between the two regions for the theoretical DOS is lower than the difference of the experimental BV because of the functional used in this work. Indeed, the electronic delocalisation is overestimated and in the case of the study of the $\beta(\text{III})\text{-CoOOH}$ material, the

metallic character is intensified. The important criterion in the comparison of DOS with BV is the width of the region between the Fermi level and -7.5eV , which are here similar.

The agreement between the experimental valence band and the theoretical density of states validates the choice of the value of the Hubbard correction used in the calculations.

In addition, the magnetic moment and Bader's charges of the cobalt atom are respectively $0.0\mu_B$ and $1.31e$.

This allows us to deduce from the references established for cobalt that it is Co^{3+} , which is in agreement with the oxidation state determined from Co 2p core peak spectrum.

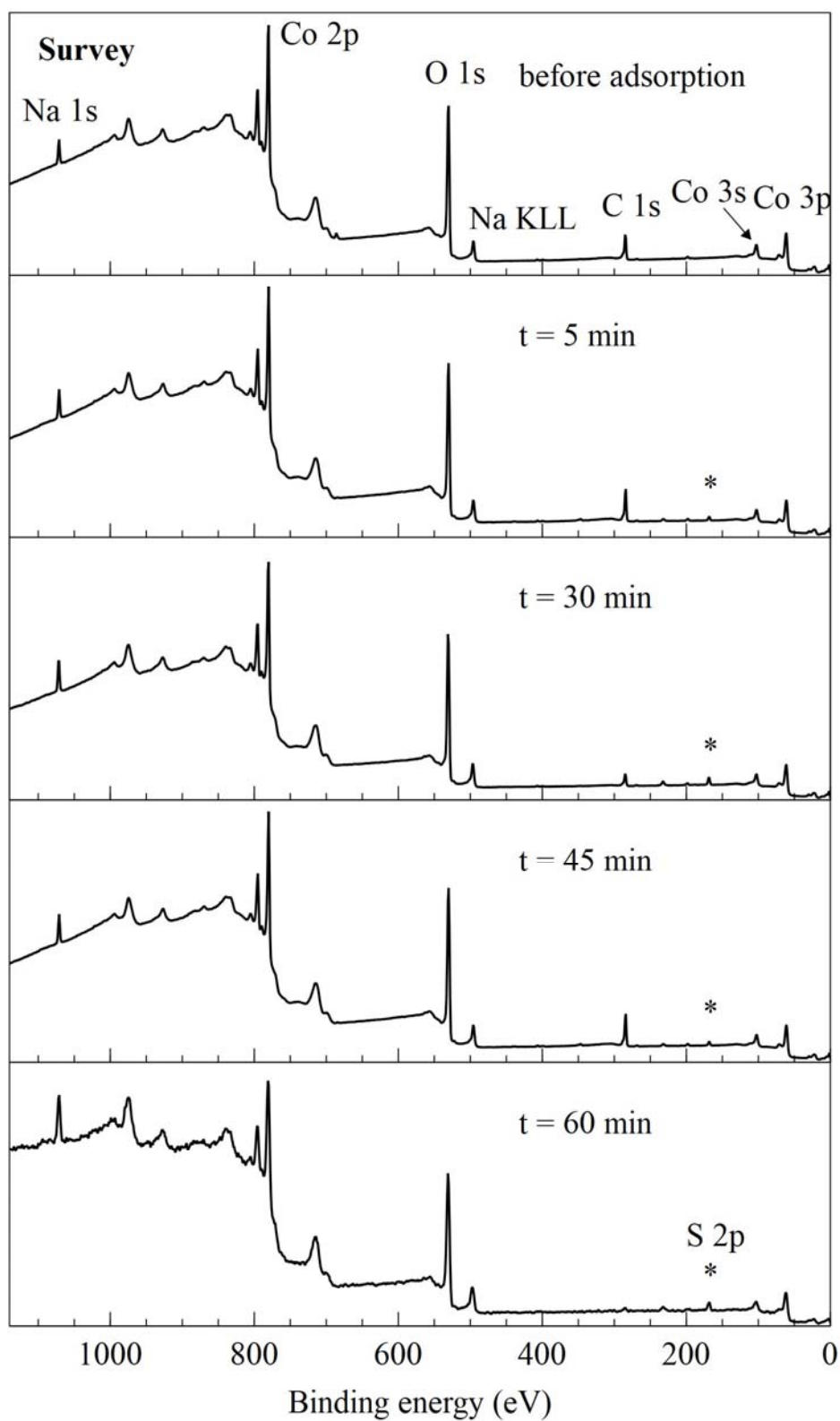


Figure SI-3: Survey XPS spectra before and after an exposure at the SO_2 flow during 5,30, 45 and 60 mins

Figure SI-4 a) and b) depicts respectively the Co 2p and Co 3s core peaks of the β (III)-CoOOH materials before and after several SO₂ adsorption times. Experimental points (dots), envelopes (link between dots) and backgrounds (line) are represented for all spectra.

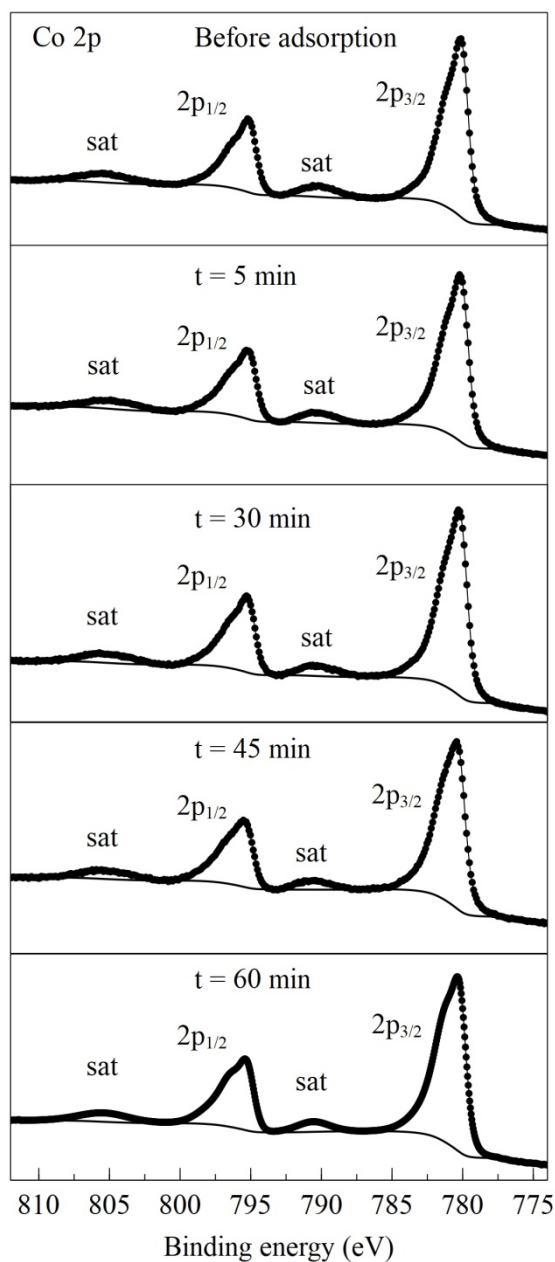


Figure SI-4a: Co 2p core peaks before and after an exposure at the SO₂ flow during 5, 30 and 45 min

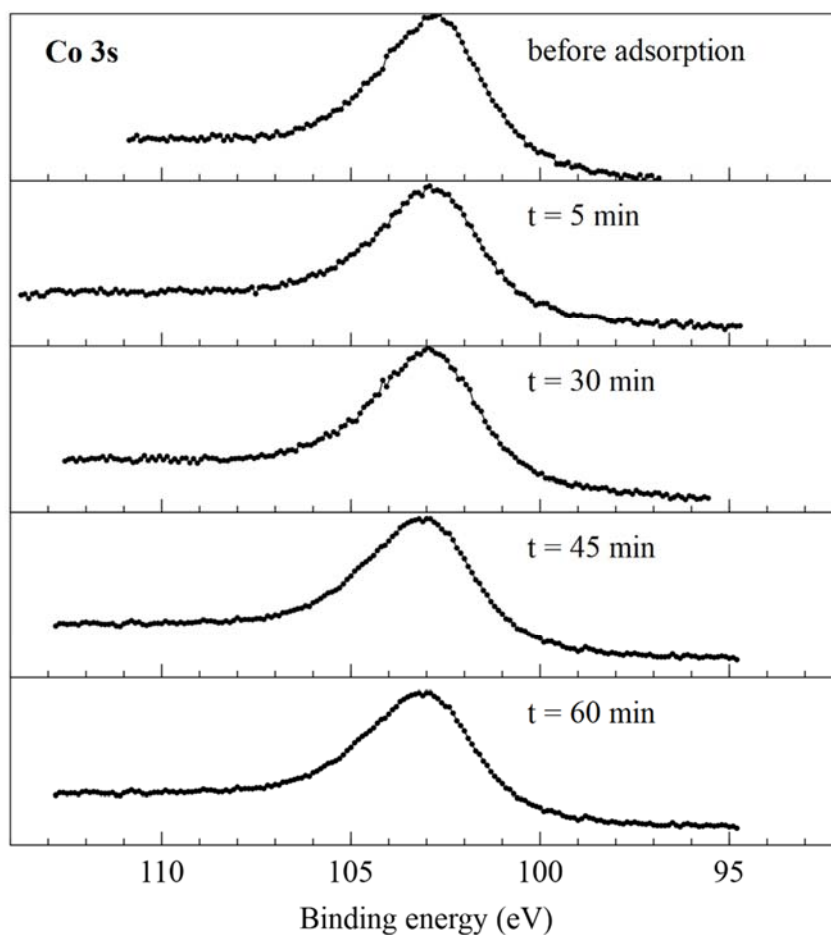


Figure SI-4b: Co 2p core peaks before and after an exposure at the SO₂ flow during 5, 30 and 45 min

The O1s spectra of the β (III)-CoOOH materials after several SO₂ adsorption times are represented in Figure SI-5.

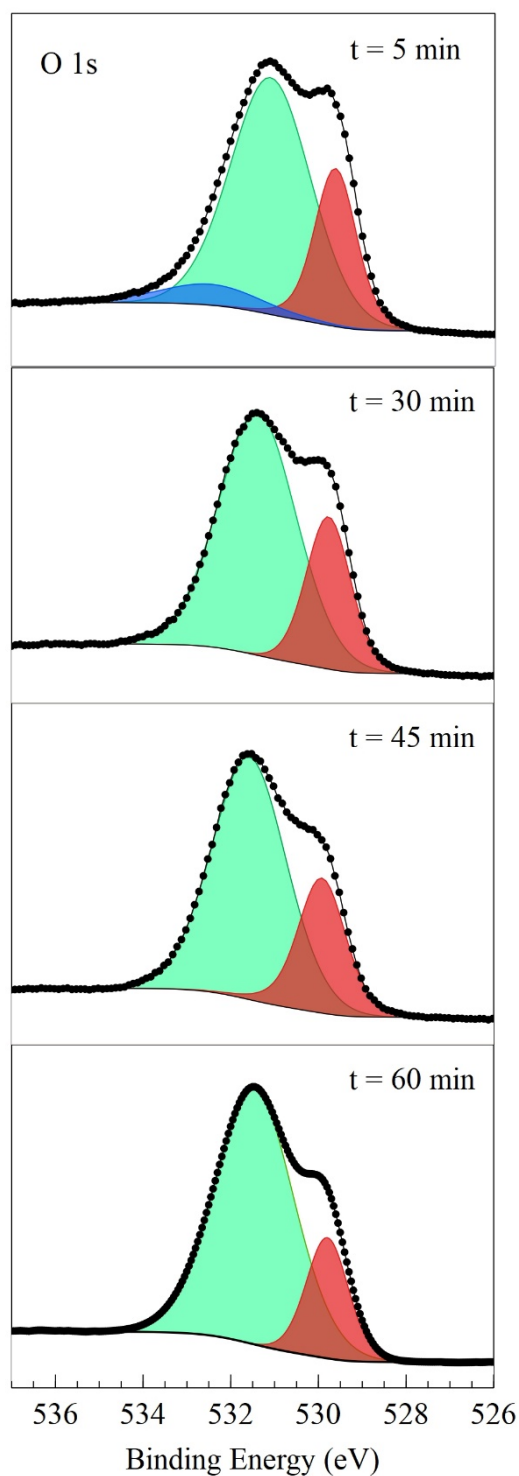


Figure SI-5: O 1s core peaks for an exposure time to the SO_2 flow during 5, 30, 45 and 60 mins (red : oxide anion, green : adsorbed and bulk hydroxide, oxide under coordinated and SO_2 adsorbed)

The atomic percentages of each element of the $\beta(\text{III})\text{-CoOOH}$ materials before and after several adsorption times are reported in Table SI-1. We also report the S/Co atomic percentage ratio

and the detail contribution of the three types of sulphur environments, sulphur in channels, sulfite and sulfate, in the Table SI-1.

Table SI-1: Binding energies and atomic percentages determined from XPS analysis for β (III)-CoOOH before and after an exposure to the SO₂ flow during 5, 15, 30, 45 et 60 mins.

	t = 0 min		t = 5 min		t = 15 min		t = 30 min		t = 45 min		t = 60 min	
	B.E. (eV)	%At Conc	B.E. (eV)	%At Conc	B.E. (eV)	%At Conc	B.E. (eV)	%At Conc	B.E. (eV)	%At Conc	B.E. (eV)	%At Conc
Co 2p		17.6		15.4		16.1		17.3		16.7		15.3
O 1s	529.6	14.6	529.6	13.0	529.8	13.8	529.8	15.1	529.9	15.4	529.8	14.0
	531.0	34.6	531.1	35.6	531.4	41.8	531.4	42.8	531.5	40.9	531.5	48.6
	532.9	4.2	532.5	4.2								
		53.4		52.8		55.6		57.9		59.4		62.6
C 1s	285.0	17.0	285.0	18.8	285.0	11.2	285.0	8.0	285.0	5.2	285.0	3.9
	286.1	3.3	286.4	2.3	286.3	3.5	286.4	3.0	286.5	2.3	286.5	1.4
	288.5	2.4	288.6	2.8	288.9	1.8	289.1	1.3	289.2	1.1	289.0	0.8
		22.8		23.9		16.5		12.3		8.6		6.1
Na 1s	1071.4	4.6	1071.6	5.9	1071.8	7.9	1071.8	8.6	1071.9	9.5	1071.9	7.3
S 2p 3/2 sulfite			166.9	0.1	166.9	0.2	166.9	0.4	167.1	0.5		
S 2p 3/2 sulfate			168.7	1.7	168.7	3.6	168.7	3.8	168.7	4.7	168.5	6.52
S 2p 3/2 channels									169.6	0.7	169.7	1.0
				1.8		3.8		4.2		5.9		7.52
S/Co				0.12		0.23		0.24		0.35		0.49

Bulk calculations on $\beta(\text{III})\text{-CoOOH}$

Hereafter are reported calculation results on bulk $\beta(\text{III})\text{-HCoOOH}$.

Table SI-2: Experimental (Exp.) and computed (Comp.) lattice parameters. Atomic charges and magnetic moments of atoms.

	a (Å)	b (Å)	c (Å)	α	β	γ	Co-O (Å)
Exp.	2.851	2.851	13.15	90°	90°	120°	1.897
Comp.	2.874	2.874	13.027	90°	90°	120°	1.919
	q_{Co}	$\mu_{\text{B}}(\text{Co})$	q_{O}	$\mu_{\text{B}}(\text{O})$	q_{H}	$\mu_{\text{B}}(\text{H})$	
	1.31	0	-0.953	0	0.587	0	

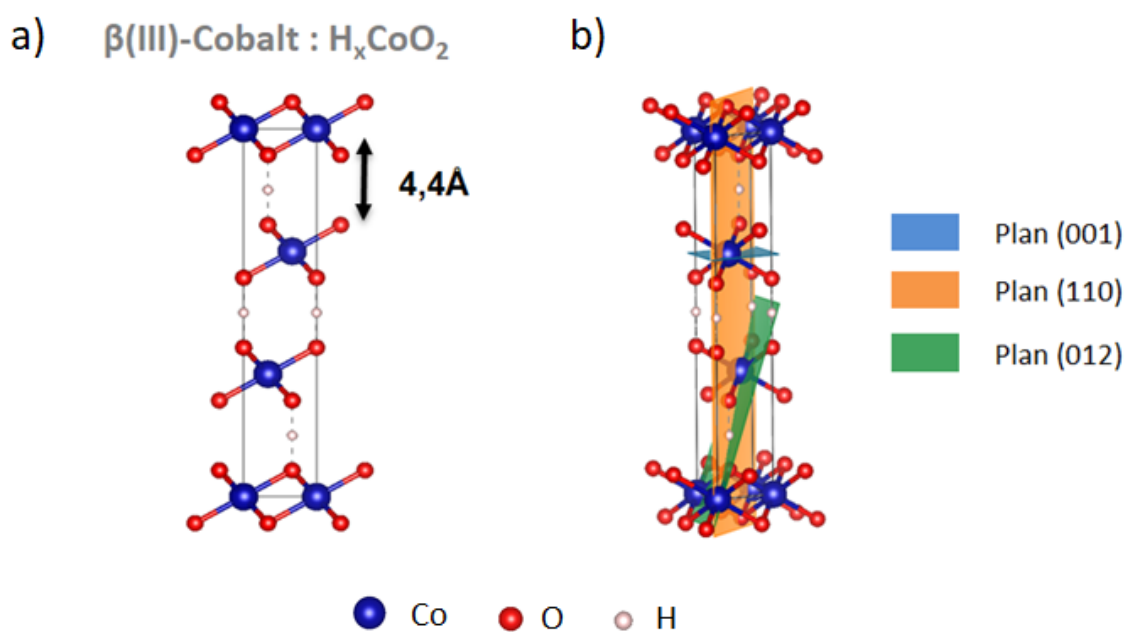


Figure SI-6: a) Bulk of $\beta(\text{III})\text{-CoOOH}$ material, b) planes (001), (110) and (012) in the $\beta(\text{III})\text{-CoOOH}$

Slab calculations

In this work we considered the low index (001), (012), (110), (105) and (101) crystalline surfaces represented using a slab model. Figure SI-6 presents a side view of the slab models used in our calculations and structural characteristics of the unit cells are gathered in Table SI-3.

The (001) slab model consists in the stacking of 5 CoOOH sheets and is of Tasker type⁴ 3. Half of the hydrogen atoms of the top and bottom atomic layers were removed to make a charge compensation. The slab thus obtained is stoichiometric and all cobalt atoms are in the same octahedral ML_6 environment as in the bulk due to not any bond break. The total thickness of the slab is 20Å.

The (012) slab model is closed to a Tasker type 2 and consists of the stacking of 5 three folds layer O-CoH-O. At the top and bottom of the slab, the cobalt atoms are in a ML_5 environment due to the loss of one Co-O bond after the cleavage of the bulk. The thickness of the slab is 10.7Å.

The (110) slab model is a non-polar slab, of Tasker type 1. The slab model was built with the stacking of 5 atomic layers. On the top atomic layer, cobalt atoms are in a ML_4 environment due to the loss of two Co-O bond after the cleavage of the bulk. The thickness of the slab is 5.66Å.

The (101) slab model is a stacking of five CoOOH units with an interplay of cobalt atom layers and OOH layers for a total thickness of 12.1Å. The slab model is of tasker type 3. On the top atomic layer, cobalt atoms are in a ML_5 environment due to the loss of one Co-O bond after the cleavage of the bulk.

The (105) slab model is close to a non-polar surface of Tasker type 1 but the CoOOH atoms are not exactly in the same plane. The slab model consists in the stacking of seven CoOOH atomic

layers with a total thickness of 11.6Å. On the top atomic layer, cobalt atoms are in a ML_5 environment due to the loss of one Co-O bond after the cleavage of the bulk.

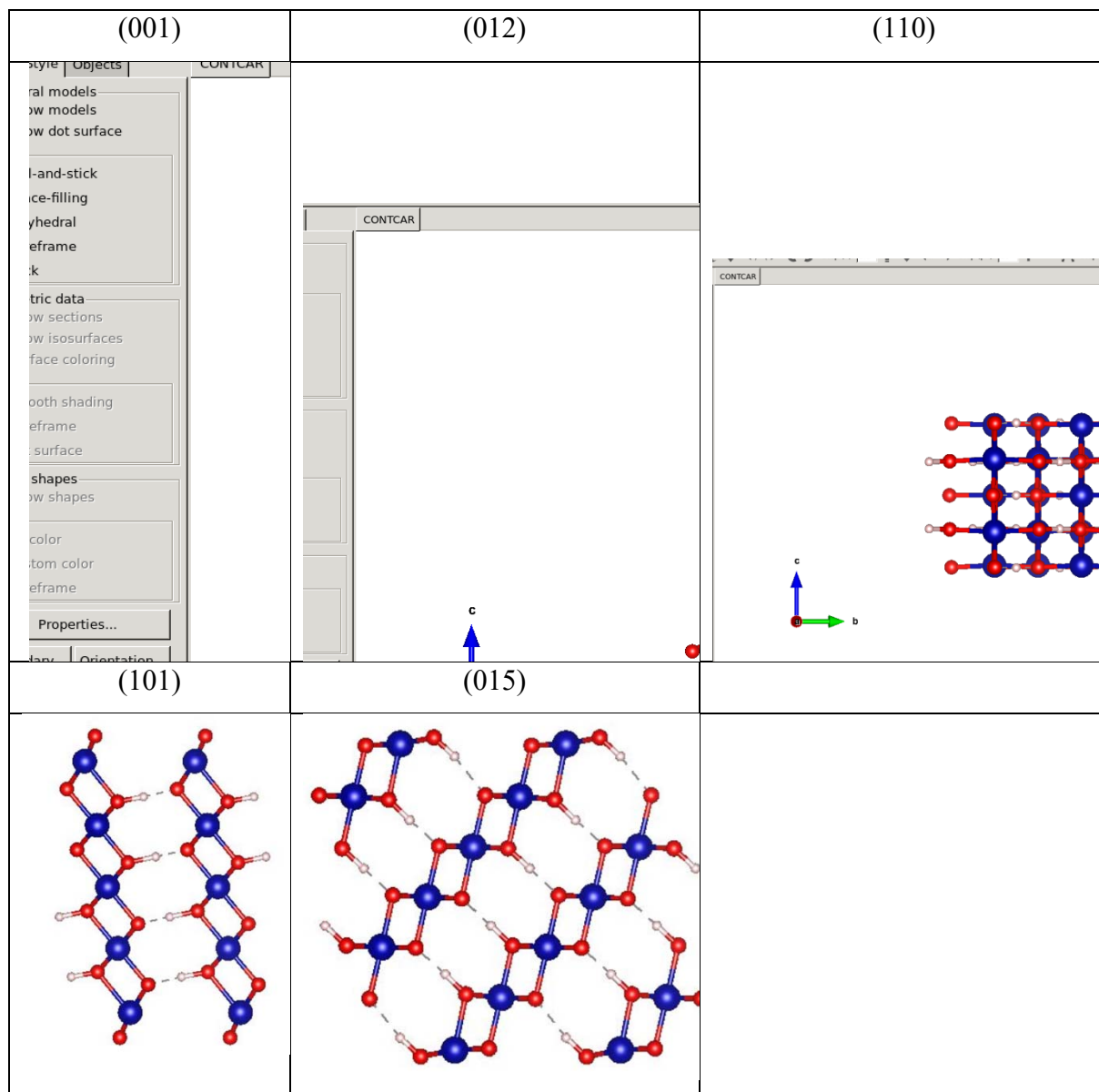


Figure SI-7: Structural parameters of slabs (001), (012), (110), (101) and (015) of $\beta(III)$ - $CoOOH$

Table SI-3: Lattice parameters of slab models

Parameters	Slab (001)	Slab (012)	Slab (110)	Slab (101)	Slab (015)
a (Å)	2.87	2.87	4.65	2.87	2.87
b (Å)	2.87	4.65	5.47	4.65	6.18
c (Å)	34.29	25.16	20.75	27.23	28.93
α (°)	90	90	90	90	90
β (°)	90	90	90	90	90
γ (°)	120	90	121.7	108	103.5

Electronic structure results on slabs (015) and (101)

The following figures present the side view and the electronic structure of cobalt atom on the top and the center atomic layer of slab models (015) and (101)

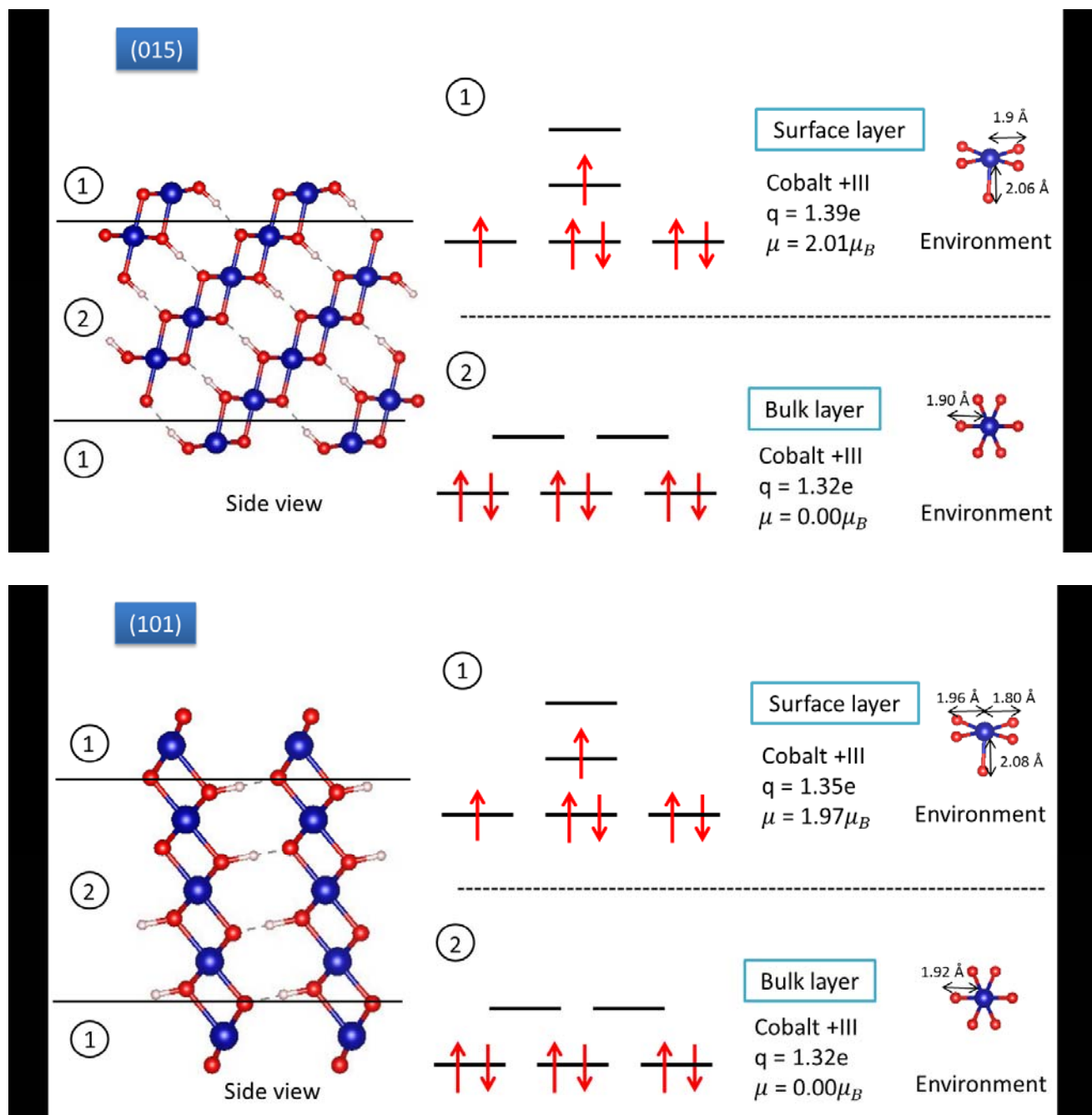


Figure SI-8: Side view and electronic structure of cobalt atom on the top and the center atomic layer of slab models (015) and (101)

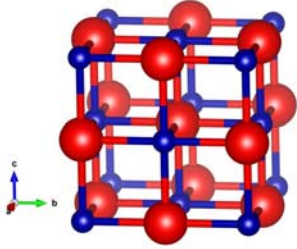
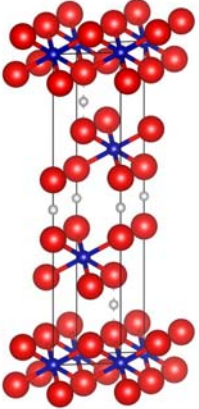
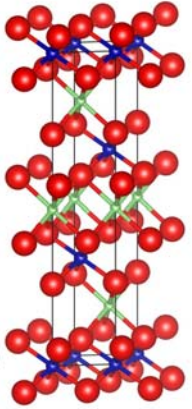
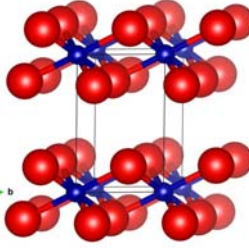
Reference calculations of cobalt oxides

Hereafter we report bulk calculations on CoO, LiCoO₂ and CoO₂ compounds as reference systems for Co^{+II}, Co^{+III} and Co^{+IV} cobalt oxidation degrees, respectively. The calculations were extended by the CoOOH compound, subject of this study for comparison.

The aim of these bulk calculations is to establish a link between local electronic properties such as atomic charges or magnetic moments and the oxidation degrees of the cobalt atoms, as a function of the Co-O bond lengths. The scale of bond lengths is used in order to monitor the ligand field strength. This relationship is helpful in order to suggest a description of the chemical processes taking place in term of oxidation degrees and to compare computational and experimental results. In the following, we assume that the charges and magnetic moments obtained on these bulk structures are transferable to other systems and in particular, slab calculations. Nevertheless, one has to keep in mind that electrons are delocalized objects that cannot be completely described from atomic charges and magnetic moments which are localized representation of the electronic density of the system.

All structures present cobalt atoms surrounded by six oxygen atoms in an octahedral environment, see Table SI-4. CoO is a rocksalt structure with space group $Fm\bar{3}m$ and a lattice parameter $a = 4.2667\text{\AA}$ ¹. LiCoO₂ is a α -NaFeO₂ type structure², space group $R\bar{3}m$. The lattice parameters are $a = 2.815\text{\AA}$, $c = 14.050\text{\AA}$. The fractional coordinate of oxygen atom along the [001] axis is $z = 0.260$. β 3-CoOOH is a hexagonal structure, space group $R\bar{3}m$. The lattice parameters are $a = 2.851\text{\AA}$ and $c = 13.15\text{\AA}$. The fractional coordinate of oxygen atom along the [001] axis is $z = 0.40$. CoO₂ is a hexagonal structure, space group $Pm\bar{3}1$, with lattice parameters $a = 2.8202\text{\AA}$ and $c = 4.2403\text{\AA}$ ³.

Table SI-4: Structures of CoO, β (III)-CoOOH, LiCoO₂ and CoO₂ compounds. Cobalt, oxygen, lithium and hydrogen atoms are in blue, red, green and white respectively.

CoO	β 3-CoOOH	LiCoO ₂	CoO ₂
Co ^{+II}	Co ^{+III}	Co ^{+III}	Co ^{+IV}
			
$Fm\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$Pm\bar{3}1$

For all compounds, a series of calculations was performed using a grid of cell volumes. For each volume, the atomic positions were relaxed keeping the shape and the volume of the cell fixed. The cell volume ranges from 88 to 112 percent of the experimental lattice parameters in an isotropic way. This leads to Co-O bond lengths in a range from 1.88 Å to 2.4 Å. All calculations were done with a plane wave cutoff of 550 eV, a spin polarized wavefunction, a spacing in the reciprocal space of 0.35 Å⁻¹ and a U value of 3.3 eV. The expected electronic configurations for the cobalt atoms are depicted in Table SI-5 considering an octahedral environment and the usual splitting of the 3d atomic orbitals in t_{2g} and e_g groups. Calculations were done for each expected spin multiplicity by constraining the corresponding electronic configurations: low spin (LS) configuration, high spin (HS) configuration and intermediary spin (IS) configuration in the case of Co^{+III} and Co^{+IV} oxidation degrees. If the unit cell contains more than one cobalt atom only ferromagnetic ordering were considered. Then atomic charges and magnetic moments were computed using a Bader decomposition of the electronic density

using a finer grid with a spacing of 0.02Å. The magnetic moments were computed as $n_\alpha - n_\beta$ where n_α and n_β are the number of α and β electrons respectively.

Table SI-5: Spin states of Co in compounds Co^{II}O , $\beta(\text{III})\text{-Co}^{III}\text{OOH}$ and Co^{IV}O_2 in low spin, intermediate spin and high spin configuration

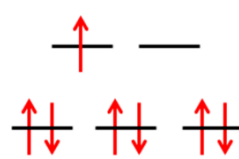
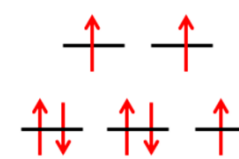
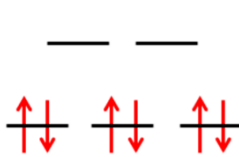
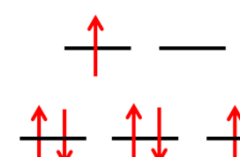
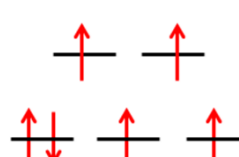

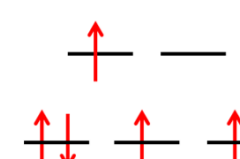
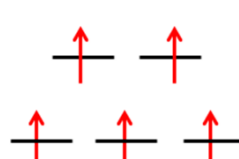
	Low spin (LS)	Intermediate spin (IS)	High spin (HS)
Co^{II}O			
$\text{Co}^{III}\text{OOH}$			
Co^{IV}O_2			

Table SI-6: Reference results CoO

CoO Low spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.83	1.04	0.98	-1.04	0.02	-35.01
1.87	1.06	1.01	-1.06	-0.01	-38.32
1.91	1.07	1.03	-1.07	-0.03	-40.74
1.95	1.08	1.06	-1.08	-0.06	-42.41
1.99	1.08	1.08	-1.08	-0.08	-43.49
2.03	1.09	1.11	-1.09	-0.11	-44.07
2.07	1.09	1.13	-1.09	-0.13	-44.24
2.12	1.09	1.16	-1.09	-0.16	-44.10
2.16	1.08	1.19	-1.08	-0.19	-43.70
2.20	1.08	1.22	-1.08	-0.22	-43.10
2.24	1.07	1.25	-1.07	-0.25	-42.34
2.28	1.06	1.29	-1.06	-0.29	-41.46
2.32	1.05	1.33	-1.05	-0.33	-40.50

CoO High spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.87	1.19	2.6	-1.19	0.4	-35.94
1.91	1.18	2.62	-1.19	0.38	-39.15
1.95	1.18	2.65	-1.18	0.35	-41.49
1.99	1.17	2.66	-1.17	0.34	-43.13
2.04	1.22	2.68	-1.22	0.32	-44.18
2.08	1.21	2.69	-1.21	0.31	-44.75
2.12	1.24	2.7	-1.24	0.3	-44.92
2.16	1.23	2.71	-1.23	0.29	-44.78
2.21	1.25	2.71	-1.25	0.29	-44.38
2.25	1.25	2.72	-1.25	0.28	-43.77
2.29	1.25	2.72	-1.25	0.28	-43
2.33	1.24	2.72	-1.24	0.28	-42.1
2.38	1.22	2.72	-1.22	0.28	-41.1

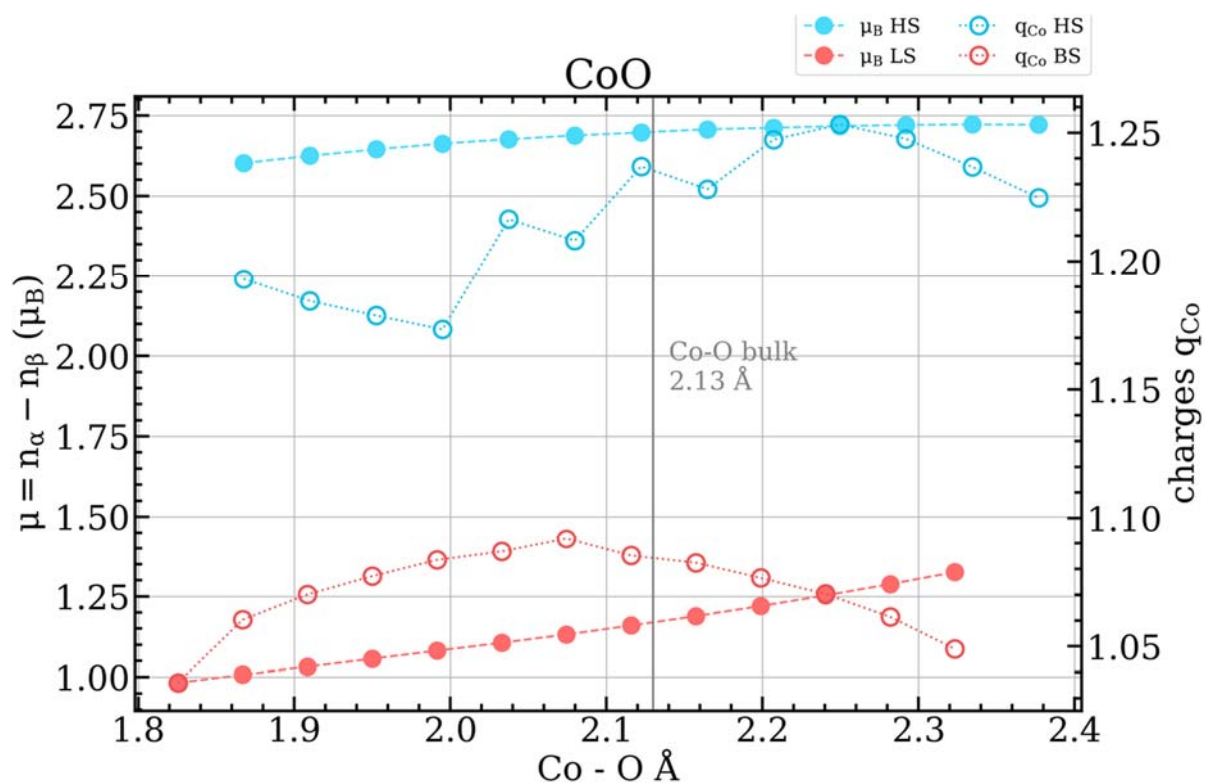


Figure SI-9: Magnetic moments (left axes, filled circles) and atomic charges (right axes, open circles) of cobalt atoms in CoO as a function of the Co-O bond length for low and high spin states.

Table SI-7: Reference results CoO_2

CoO_2 Low spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.66	1.41	0.67	-0.70	0.17	-13.55
1.70	1.41	0.68	-0.70	0.16	-14.76
1.73	1.42	0.75	-0.71	0.13	-15.63
1.77	1.48	1.01	-0.74	0.00	-16.34
1.81	1.47	1.05	-0.74	-0.03	-16.77
1.85	1.47	1.11	-0.73	-0.05	-17.00
1.88	1.46	1.18	-0.73	-0.09	-17.08
1.92	1.45	1.27	-0.73	-0.13	-17.02
1.96	1.44	1.38	-0.72	-0.19	-16.88
2.00	1.43	1.53	-0.72	-0.26	-16.65
2.03	1.42	1.70	-0.71	-0.35	-16.38
2.07	1.41	1.88	-0.71	-0.44	-16.07
2.11	1.40	2.04	-0.70	-0.52	-15.75

CoO_2 Intermediary spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.70	1.55	2.23	-0.77	0.39	-12.71
1.74	1.54	2.25	-0.77	0.37	-13.88
1.78	1.54	2.28	-0.77	0.36	-14.74
1.81	1.53	2.30	-0.77	0.35	-15.34
1.85	1.52	2.32	-0.76	0.34	-15.72
1.89	1.51	2.34	-0.76	0.33	-15.93
1.93	1.50	2.37	-0.75	0.32	-16.00
1.97	1.49	2.39	-0.74	0.31	-15.95
2.01	1.47	2.41	-0.74	0.30	-15.81
2.05	1.46	2.43	-0.73	0.29	-15.60
2.08	1.44	2.44	-0.72	0.28	-15.34
2.12	1.42	2.46	-0.71	0.27	-15.05
2.16	1.41	2.48	-0.70	0.26	-14.73

CoO₂ High spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.74	1.73	3.34	-0.87	0.83	-12.54
1.78	1.72	3.33	-0.86	0.83	-13.65
1.82	1.71	3.32	-0.85	0.84	-14.47
1.86	1.69	3.31	-0.85	0.85	-15.04
1.90	1.65	3.26	-0.83	0.87	-15.41
1.94	1.62	3.22	-0.81	0.89	-15.63
1.98	1.60	3.19	-0.80	0.91	-15.72
2.01	1.57	3.16	-0.79	0.92	-15.70
2.05	1.54	3.12	-0.77	0.94	-15.60
2.09	1.52	3.09	-0.76	0.95	-15.43
2.13	1.49	3.06	-0.75	0.97	-15.20
2.17	1.47	3.03	-0.73	0.99	-14.94
2.21	1.50	3.10	-0.75	0.95	-14.47

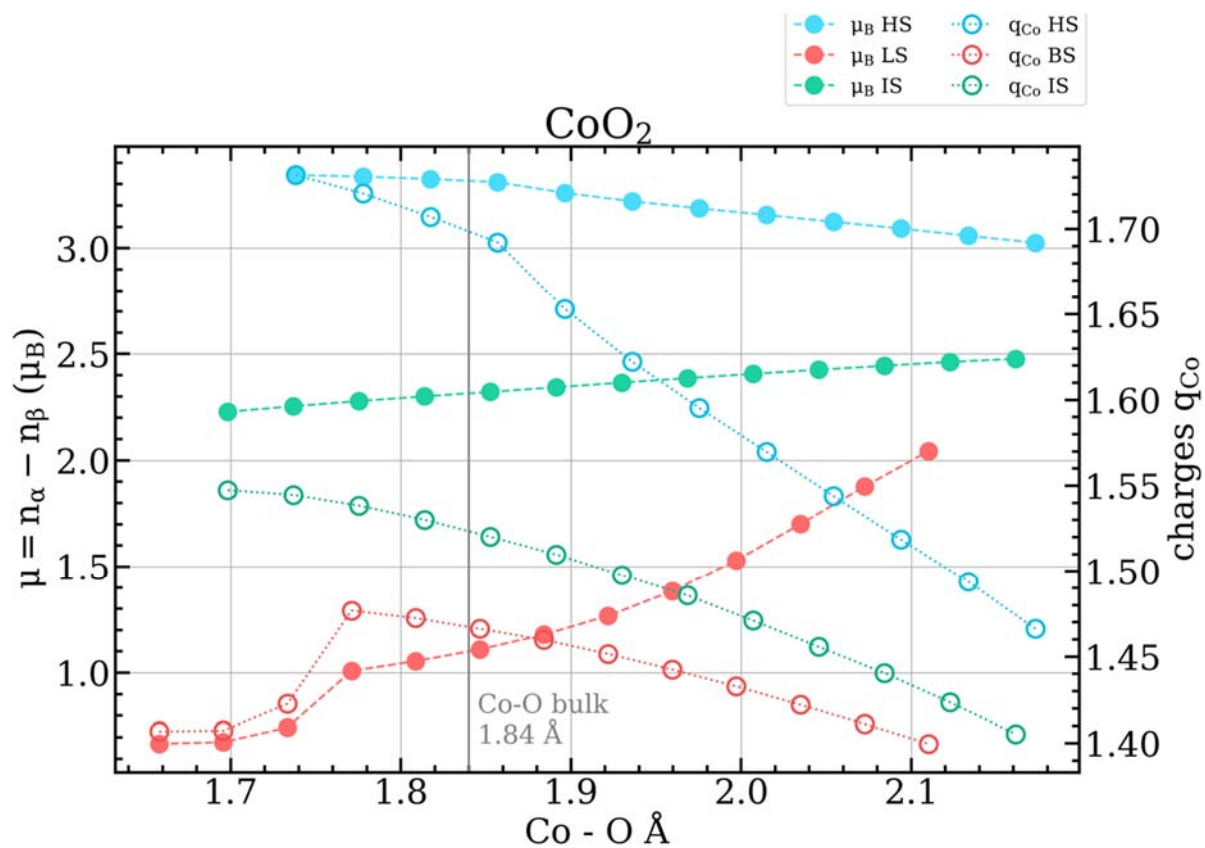


Figure SI-10: Magnetic moments (left axes, filled circles) and atomic charges (right axes, open circles) of cobalt atoms in CoO₂ as a function of the Co-O bond length for low, intermediary and high spin states.

Table SI-8: Reference results LiCoO_2

LiCoO_2 low spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.70	1.21	0.00	-1.01	0.00	-56.39
1.74	1.22	0.00	-1.02	0.00	-60.60
1.78	1.23	0.00	-1.03	0.00	-63.69
1.82	1.24	0.00	-1.04	0.00	-65.86
1.85	1.25	0.00	-1.05	0.00	-67.25
1.89	1.25	0.00	-1.06	0.00	-68.01
1.93	1.26	0.00	-1.07	0.00	-68.25
1.97	1.26	0.00	-1.07	0.00	-68.06
2.01	1.26	0.00	-1.08	0.00	-67.52
2.05	1.26	0.00	-1.07	0.00	-66.71
2.09	1.26	0.00	-1.07	0.00	-65.67
2.13	1.25	0.00	-1.07	0.00	-64.46
2.16	1.25	0.00	-1.07	0.00	-63.12

LiCoO_2 intermediary spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.76	1.33	1.78	-1.07	0.10	-56.68
1.80	1.34	1.83	-1.08	0.08	-60.27
1.84	1.34	1.88	-1.09	0.05	-62.90
1.88	1.35	1.93	-1.09	0.03	-64.73
1.92	1.35	1.99	-1.10	0.00	-65.9
1.96	1.35	2.05	-1.10	-0.03	-66.53
2.00	1.34	2.11	-1.10	-0.06	-66.72
2.04	1.34	2.18	-1.10	-0.09	-66.56
2.08	1.33	2.24	-1.11	-0.12	-66.12
2.12	1.30	2.24	-1.09	-0.12	-63.23
2.16	1.29	2.30	-1.09	-0.15	-62.33
2.20	1.28	2.31	-1.08	-0.16	-61.30
2.24	1.26	2.38	-1.08	-0.19	-60.19

LiCoO ₂ high spin					
Co-O (Å)	q (Co)	μ _B (Co)	q (O)	μ _B (O)	energy (eV)
1.78	1.49	3.02	-1.15	0.48	-55.90
1.82	1.49	3.03	-1.16	0.48	-59.43
1.86	1.53	3.07	-1.18	0.46	-62.79
1.90	1.53	3.08	-1.19	0.45	-64.70
1.94	1.53	3.08	-1.19	0.45	-65.93
1.98	1.52	3.08	-1.19	0.45	-66.60
2.03	1.51	3.08	-1.19	0.45	-66.81
2.07	1.50	3.08	-1.19	0.46	-66.64
2.11	1.49	3.07	-1.19	0.46	-66.16
2.15	1.48	3.06	-1.18	0.47	-65.44
2.19	1.46	3.04	-1.18	0.48	-64.51
2.23	1.43	3.02	-1.16	0.48	-63.44
2.27	1.41	3.00	-1.16	0.50	-62.24

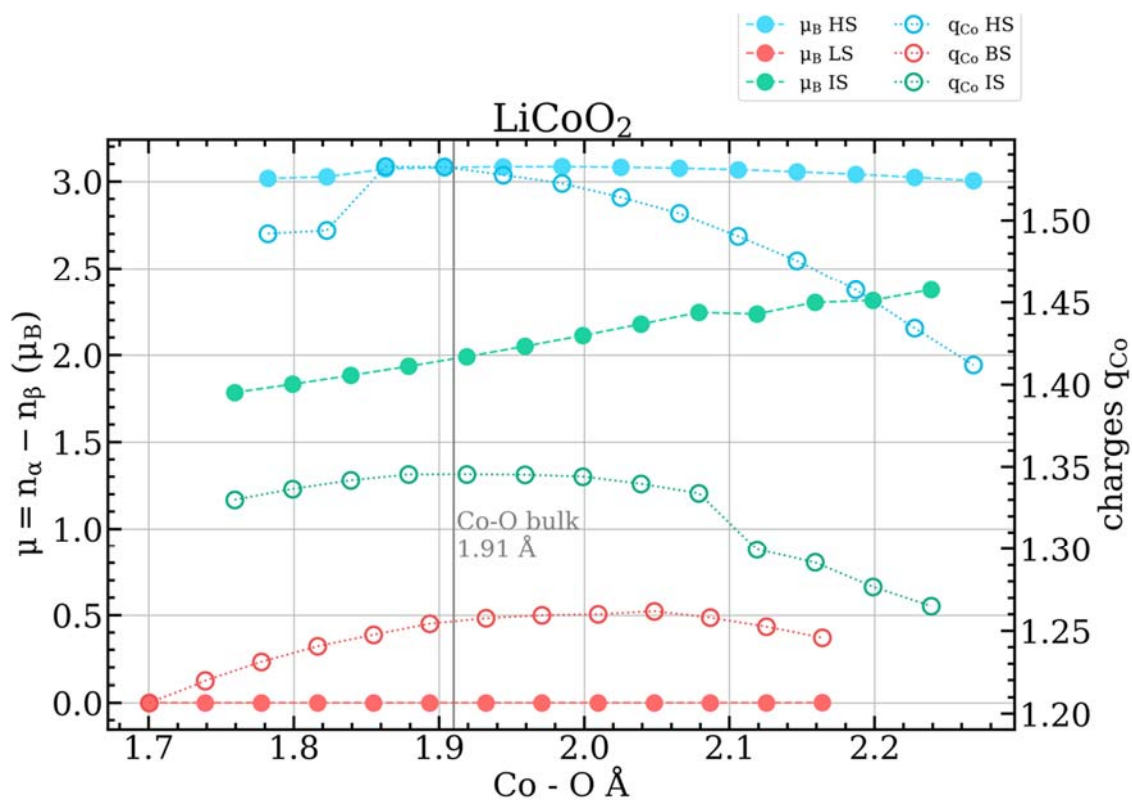


Figure SI-11: Magnetic moments (left axes, filled circles) and atomic charges (right axes, open circles) of cobalt atoms in LiCoO₂ as a function of the Co-O bond length for low, intermediary and high spin states.

Table SI-9: Reference results CoOOH

β3-CoOOH low spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.69	1.24	0.00	-0.94	0.00	-54.92
1.73	1.26	0.00	-0.94	0.00	-59.31
1.77	1.27	0.00	-0.95	0.00	-62.54
1.80	1.28	0.00	-0.95	0.00	-64.81
1.84	1.29	0.00	-0.95	0.00	-66.28
1.88	1.30	0.00	-0.95	0.00	-67.08
1.92	1.31	0.00	-0.95	0.00	-67.33
1.96	1.32	0.00	-0.95	0.00	-67.14
2.00	1.32	0.00	-0.95	0.00	-66.58
2.03	1.32	0.00	-0.95	0.00	-65.72
2.07	1.32	0.00	-0.94	0.00	-64.62
2.11	1.32	0.00	-0.94	0.00	-63.34
2.15	1.31	0.00	-0.93	0.00	-61.91

β3-CoOOH intermediary spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.75	1.38	1.82	-1.01	0.09	-55.40
1.79	1.39	1.87	-1.01	0.06	-59.11
1.83	1.39	1.92	-1.01	0.04	-61.85
1.87	1.40	1.97	-1.00	0.01	-63.75
1.91	1.40	2.03	-1.00	-0.02	-64.98
1.95	1.40	2.09	-0.99	-0.05	-65.65
1.99	1.40	2.15	-1.00	-0.08	-65.86
2.03	1.40	2.21	-0.99	-0.11	-65.69
2.07	1.35	2.12	-0.96	-0.06	-62.75
2.11	1.36	2.21	-0.96	-0.11	-62.42
2.15	1.35	2.28	-0.94	-0.14	-61.48
2.19	1.34	2.34	-0.93	-0.17	-60.41
2.23	1.33	2.40	-0.93	-0.20	-59.22

β3-CoOOH High spin					
Co-O (Å)	q (Co)	μ_B (Co)	q (O)	μ_B (O)	energy (eV)
1.78	1.59	3.09	-1.11	0.45	-54.82
1.82	1.60	3.11	-1.11	0.44	-58.68
1.86	1.60	3.12	-1.11	0.44	-61.54
1.90	1.60	3.13	-1.10	0.43	-63.55
1.94	1.60	3.14	-1.10	0.43	-64.85
1.98	1.60	3.14	-1.09	0.43	-65.57
2.02	1.59	3.13	-1.09	0.43	-65.79
2.06	1.58	3.13	-1.09	0.43	-65.62
2.10	1.52	3.06	-1.05	0.47	-63.91
2.14	1.50	3.04	-1.03	0.48	-63.19
2.18	1.48	3.02	-1.01	0.49	-62.29
2.22	1.45	2.99	-0.99	0.51	-61.24
2.26	1.43	2.96	-0.98	0.52	-60.09

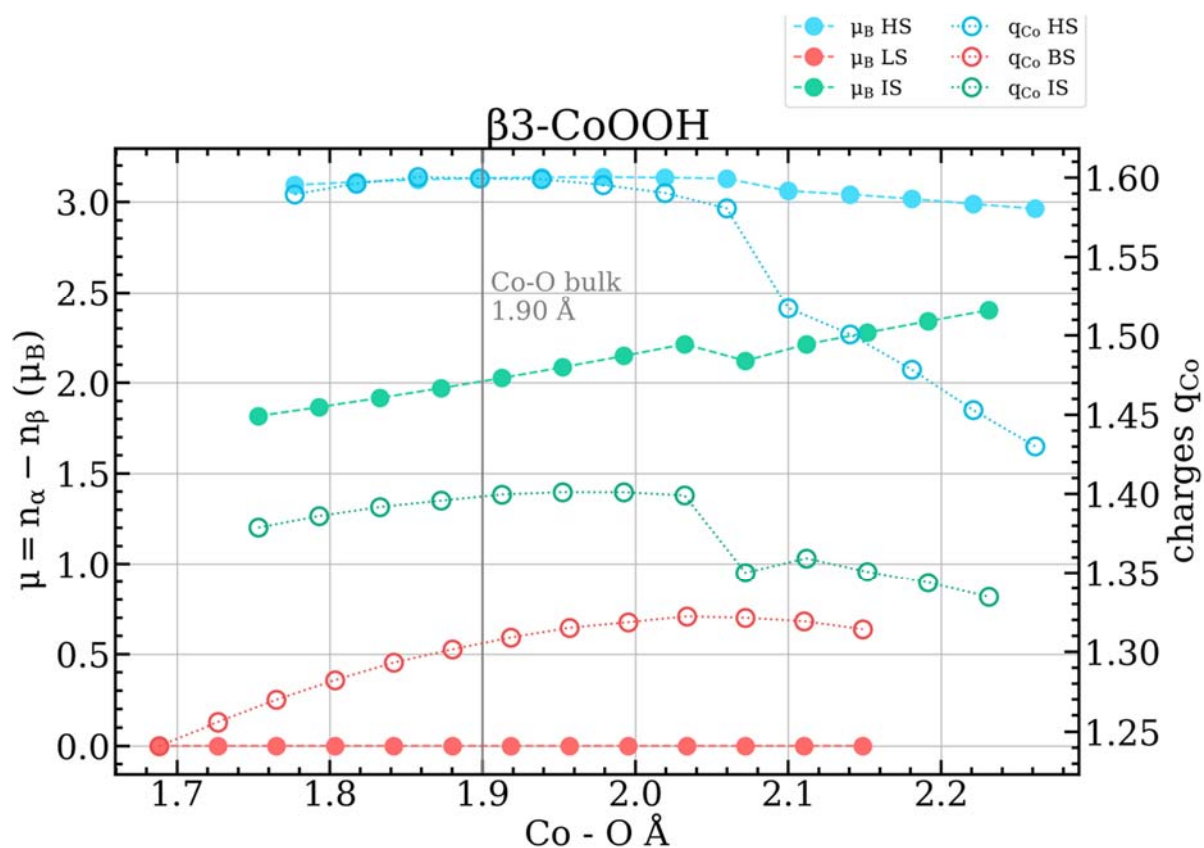


Figure SI-12: Magnetic moments (left axes, filled circles) and atomic charges (right axes, open circles) of cobalt atoms in $\beta(III)$ -CoOOH as a function of the Co-O bond length for low, intermediary and high spin states.

Comparison between LiCoO₂ and CoOOH

LiCoO₂ and $\beta(III)$ -CoOOH compounds are both Co^{+III} compounds. Figure SI-12 provides a superimposition of the magnetic moments and atomic charges of the cobalt atoms in these two compounds as a function of the Co-O bond length and for the three considered spin states. One can see on these plots, that magnetic moments are roughly the same, whatever the spin state. This result reinforces the hypothesis of the transferability of the data obtained on these reference compounds to other systems. Considering the atomic charges, a small shift, from 0.05 to 0.1 electron can be observed between LiCoO₂ and $\beta(III)$ -CoOOH, mainly due to a more ionic character of LiCoO₂. This shift illustrates that magnetic moments are more suitable to probe the oxidation degrees than atomic charges only.

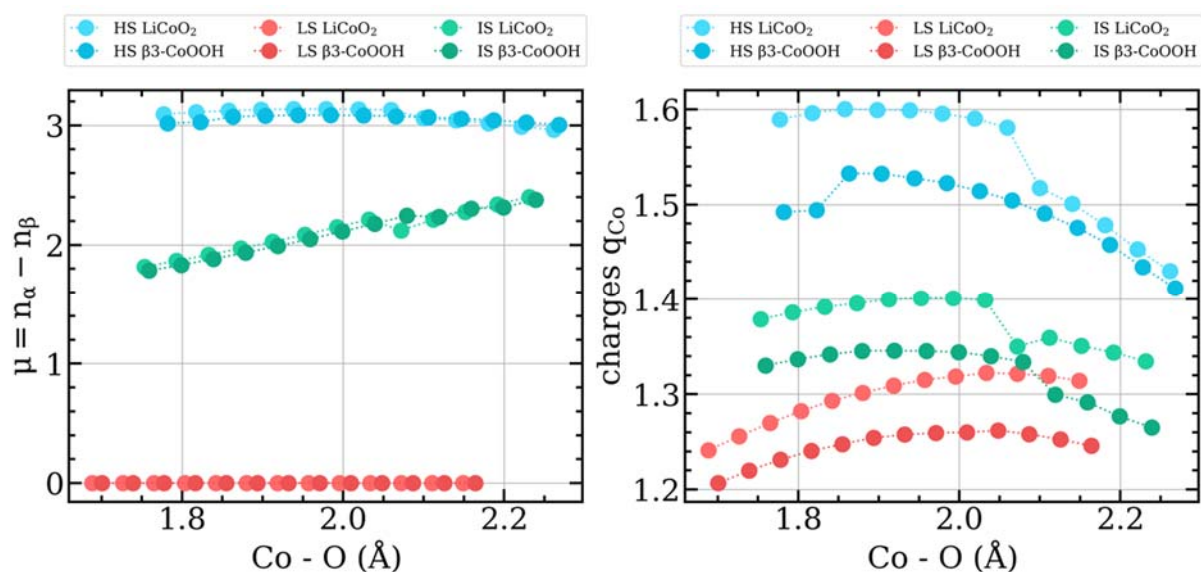


Figure SI-13: Comparison of the magnetic moments (left plot) and atomic charges (right plot) of cobalt atoms of LiCoO₂ and β(III)-CoOOH as a function of the Co-O bond length for low, intermediary and high spin states.

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