Supporting Information

Electronic Structure Assessment: Combined Density Functional Theory Calculations and Ru $L_{2,3}$-edge X-ray Absorption Near-edge Spectroscopy of Water Oxidation Catalyst

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Contents **Page**

Table 1: Main geometrical parameters of the [3,4]$^{4+}$ structure derived from XRD (1st row) and DFT optimization (all rows but the 1st).

Geometry parameter / Species	distance, Å						Ru-O-Ru	O-RuRu-O dihedral angle
	Ru(1)-O (bridge)	Ru(2)-O (bridge)	Ru-Ru	Ru(1)-OH_2	Ru(2)-OH	H_2O--OH_2		
cis,cis-[Ru^{III}(OH)ORu^{IV}(OH)$(bpy)_4$]$^{4+}$								
XRD data(1)	1.85	1.82	3.66	2.15	1.98	5.56	170.0	117.2
Yang and Baik(2)	1.85	2.08	3.92	2.24	1.95		170.8	133.8
Yang and Baik "eclipsed" enantiomer (2)	1.85	2.17	3.87	2.16	1.99		148.9	12.9
Bartolotti et al(3), gas-phase	1.88	1.82	3.68	2.16	1.91		169.3	72.3
Bartolotti et al(3), COSMO water solvent	1.88	1.82	3.68	2.16	1.91		170.0	118.6
LDA spin-orbit	1.88	1.84	3.70	2.16	1.93		170.2	78.7
LDA scalar*	1.88	1.83	3.69	2.16	1.93		169.8	74.4
LDA spin-orbit N,C 1s FRZ (frozen) core	1.88	1.83	3.69	2.15	1.93	4.76	168.6	69.7
LDA spin-orbit N,C,O 1s and Ru 3d FRZ cores	1.88	1.83	3.70	2.15	1.93	4.73	169.4	68.0
LDA spin-orbit N,C,O 1s and Ru 4p FRZ cores	1.89	1.85	3.73	2.18	1.94	4.78	169.0	69.6
GGA:OPBE	1.91	1.85	3.75	2.27	1.93		172.5	120.8
GGA:OPBE scalar	1.92	1.85	3.76	2.27	1.93	5.41	173.2	109.0
GGA:OPBE scalar without strict convergence	1.91	1.85	3.75	2.29	1.92	4.96	174.2	81.1
GGA:BP scalar	1.93	1.87	3.79	2.24	1.95		173.3	73.7
GGA:BP spin-orbit - N,C 1s FRZ core	1.92	1.87	3.78	2.24	1.95		173.6	119.1
GGA:OLYP scalar	1.92	1.86	3.77	2.31	1.96		172.4	124.4
GGA:OLYP spin orbit	1.93	1.86	3.78	2.31	1.95		172.4	121.2
GGA:PBE-D3 scalar	1.90	1.85	3.74	2.24	1.95		169.1	58.5

Notation: Frozen cores are basis sets of less size comprising frozen cores for carbon and nitrogen (eight basis functions for C and N including polarization one)
* Was used to get XANES

Table 2: Main geometrical parameters of the [3,4]$^{c+}$ deprotonated (charge *c*=3) and protonated (charge *c*=5) species derived from DFT optimization.

Geometry parameter / Species	distance, Å						Ru-O-Ru	O-RuRu-O dihedral angle
	Ru(1)-O (bridge)	Ru(2)-O (bridge)	Ru-Ru	Ru(1)- OH	Ru(2)- OH	H_2O-OH_2		
cis,cis-[Ru^{III}(OH)ORu^{IV}(OH)$(bpy)_4$]$^{5+}$								
Yang and Baik(2)	1.86	2.02	3.87	1.98	1.96	5.11	172.2	107.7
LDA spin orbit	1.85	1.85	3.69	1.95	1.95	5.09	178.7	89.9
LDA scalar*	1.84	1.84	3.68	1.96	1.94	4.97	177.5	77.4
cis,cis-[Ru^{III}(OH)ORu^{IV}(OH)$(bpy)_4$]$^{3+}$								
Yang and Baik(2)-[3,4][5]	2.05	1.87	3.92	2.24	2.24	4.79	179.6	72.7
LDA spin orbit	1.86	1.86	3.72	2.15	2.15	4.29	176.6	45.4
LDA scalar	1.86	1.86	3.71	2.15	2.15	4.49	175.3	57.2
LDA scalar protonated	1.86	1.86	3.72	2.15	2.15	4.35	175.0	45.2
LDA scalar protonated with strict convergence	1.86	1.86	3.71	2.16	2.15	4.59	175.6	67.9

*Was used to get XANES

References

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