Theoretical Study of Solvent Effects on the Electronic Properties of Mononuclear Ru/Aqua Catalysts for Water Splitting



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X-ray Photoelectron Fingerprints of High-Valence Ruthenium–Oxo Complexes along the Oxidation Reaction Pathway in an Aqueous Environment

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Physical Chemistry

Catalyst for Water Splitting

Schematic representation of the two mechanistic pathways for O–O bond formation: (i) solvent water nucleophilic attack (WNA) and (ii) interaction of two M–O units (I2M)

Oxidação da água por complexos de Ru





Reactions for water splitting:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
$$4H^+ + 4e^- \rightarrow 2H_2$$

 $2H_2O \rightarrow 2H_2 + O_2$

WNA – Water Nucleophilic attack I2M - Two Metal-Oxo Entities

How to follow this reaction in solution ?

Recent advances *in operando*-synchrotron-based X-ray Photoelectron Spectroscopy (XPS) are making it possible to address fundamental questions related to complex proton-coupled electron transfer reactions, for instance, the electrocatalytic water splitting process, because it is atom specific and could follow the oxidation and deprotonation of the metallic atom.



Then, the oxidation and the deprotonation of a Ru-aqua complexes were studied by XPS: $[Ru^{II}(OH_2)]^{+2}$, $[Ru^{III}(OH_2)]^{+1}$, $[Ru^{III}(OH_2)]^{+3}$, $[Ru^{III}(OH)]^{+2}$ and $[Ru^{IV}(O)]^{+2}$, where the ligand is one pyridine (py) and two bipyridine (bpy)₂.

Studied system: 5 Ru-aqua complexes with different oxidation



Experiment: X-ray photoelectron spectra were recorded with a liquid-jet injection system at the SOL3PES endstation at beamline U49-2-PGM1 at the synchrotron facility BESSY II (Germany). Peak signaling: (VII) [Ru^{II}(OH)]⁺¹ in 285.7eV < (II) [Ru^{II}(OH₂)]⁺² and (II) [Ru^{III}(OH)]⁺² in 286.0eV < (IV) [Ru^{III}(OH₂)]⁺³ in 287.7 < (VI) [Ru^{IIV}(O)]⁺² in 288.2eV with shift of ~2.5eV.

Theoretical: Calculations of the binding energy (BE) of Ru(3d) in vacuum were performed with the Slater-Janak method that obtain the Kohn–Sham eigenvalue energy of the core-level state with half-occupation using DFT PBE/PAW.

The BE of the complexes follow the tendency of the total charge of the complexes: $[Ru^{II}(OH)]^{+1} < [Ru^{II}(OH_2)]^{+2} < [Ru^{III}(OH)]^{+2} < [Ru^{III}(OH_2)]^{+3}$ with shift of ~5eV. THIS RESULT IS NOT CONSISTENT WITH EXPERIMENTAL XPS SPECTRUM.

The solvent effect should be important to explain the XPS spectrum.

Experimental XPS spectrum



Our approach for modeling the solvent

• <u>Sequential Hybrid Methods (S-QM/MM)</u> Two step procedure: First, system configurations are generated using MM simulations, then statistically relevant configurations are used in the QM calculations.

Statistical analysis 5 correlation Function of Energy, $C(i)=0.47e^{(-i/25)}+0.48e^{(-i/634)}$ 0.8 0.6 0.4 200 250 300 50 100 150 350 Interval of configurations, i Solvation shell analysis 2.0 $\mathop{\rm CM}_{\rm CMCM}^{1.5}(z)$ 0.5 Ab initio calculations (QM) 0.0 L 0.0 2.0 4.0 6.0 8.0 10.0 12.0 14.0 16.0 18.0 Classical force field (MM) r [Angstrom] 7/15

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Solute polarization and geometry relaxation with Iterative S-QM/MM

Georg, Coutinho, Canuto, J. Chem. Phys. 126, 34507 (2007) Franco, Brandão, Fonseca, Georg, J. Chem. Phys. 145, 194301 (2016)





Structural properties:

The geometries are mostly rigid with some flexibility in the water and pyridine orientation (results of MD simulations). The solvent effect is negligibly in the structure of the complexes. However, the oxidation and deprotonation changes the Ru-O distance and causing also a transeffect.







Charges obtained with the QM electrostatic fit in vacuum and <u>in solution</u> of the groups: aqua/hydro/oxo, Ru and (bpy)₂py. The green arrows show the electron flux with the solvent effect.

Order of the Ru effective charge in gas: $[Ru^{II}(OH)]^{+1} < [Ru^{III}(OH_2)]^{+3} < [Ru^{III}(OH)]^{+2}$ and $[Ru^{II}(OH_2)]^{+2}$ and $[Ru^{II}(OH_2)]^{+2}$ and $[Ru^{II}(OH_2)]^{+2}$ and $[Ru^{II}(OH_2)]^{+2} < [Ru^{III}(OH_2)]^{+2}$ Order of the XPS binding energy: $[Ru^{II}(OH)]^{+1} < [Ru^{II}(OH_2)]^{+2}$ and $[Ru^{III}(OH_2)]^{+2} < [Ru^{III}(OH_2)]^{+3} < [Ru^{III}(OH_2)]^{+2}$



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 $[Ru^{II}(OH)]^{+1} < [Ru^{II}(OH_2)]^{+2}$ and $[Ru^{III}(OH)]^{+2} < [Ru^{III}(OH_2)]^{+3} < [Ru^{IV}(O)]^{+2}$



Summary and Conclusions:

- We used the sequential-QM/MM procedure combining DFT QM calculations with Monte Carlo and Molecular Dynamics simulations to calculate core-binding enegy of Ru(3d) and C(1s) of Ru-Aqua complexes.
- The calculated XPS spectra of the Ru-aqua complexes with the first solvation shell show excellent agreement with the experimental trends.
- The [Ru^{IV}O]²⁺ complex stands out with a precise fingerprint in the experimental XPS spectra.
- The observed chemical shift turned out to be strongly influenced by the explicit solvation effect, which induces a specific charge polarization on the complex.

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Parametrization of the (a) $Ru^{II}(H_2O)^{2+}(a)$ and (b) $Ru^{II}(OH)^+$ complexes: QM calculations with DFT B3LYP/aug-cc-pVDZ/PP(Ru)



Senesta et al. J. Chem. Theor. Comp., 12, 3681 (2016): $RuCl_6 + NH_3$, CH_4 and H_2O . Adlhart et al. Angew. Chemie, 41, 4484 (2002): Ru carbene.

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Solvation:

We performed MD simulations of the Ru-Aqua complexes in aqueous solution and in the water-vacuum interface.

3.0

2.5

2.0

1.0

0.5

0.0 🖵

2

HOOM 1.5



UV-visible absorption spectrum of other complexes:



Comparison between experimental and theoretical results

Table 1. Experimental and Theoretical Values of the Core-Level Binding Energies (BEs) in Electronvolts and Their Shifts in Relation to the $[Ru^{II}(OH_2)(py)(bpy)_2]^{2+}$ Complex (ΔBE) in Electronvolts^a

			theoretical				
	experimental		vacuum		solvated		
Ru 3d _{5/2}	BE	ΔBE	BE	ΔBE	BE	ΔBE	
$[Ru^{II}(OH)(py)(bpy)_2]^+$	285.7 (VIII)	-0.3	289.6	-1.7	285.6	-0.4	
[RuII(OH2)(py)(bpy)2]2+	286.0 (I)	0.0	291.3 [290.9]	0.0 [0.0]	286.0	0.0	
$[Ru^{III}(OH)(py)(bpy)_2]^{2+}$	286.0 (III)	0.0	292.6	1.3	286.0	0.0	
$[\mathrm{Ru}^{\mathrm{III}}(\mathrm{OH}_2)(\mathrm{py})(\mathrm{bpy})_2]^{3+}$	287.7 (IV')	1.7	294.2 [294.0]	2.9 [3.0]	286.3	0.3	
$[Ru^{IV}(O)(py)(bpy)_2]^{2+}$	288.2 (VI)	2.2	293.2 [293.2]	1.9 [2.3]	287.5	1.5	

^{*a*}The theoretical values were shifted by -2.51 eV for better comparison with the experimental data. In parentheses are the labels of the peaks of Figure 2a–d. In brackets are the values calculated including the complex and the explicit water molecules hydrogen bonded to the coordinated OH₂, OH⁻, and O²⁻ ligands.



