Área: INO
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X-ray Photoelectron Fingerprints of High-Valent Ruthenium–oxo Complexes Along the Oxidation Reaction Pathway in Aqueous Environment

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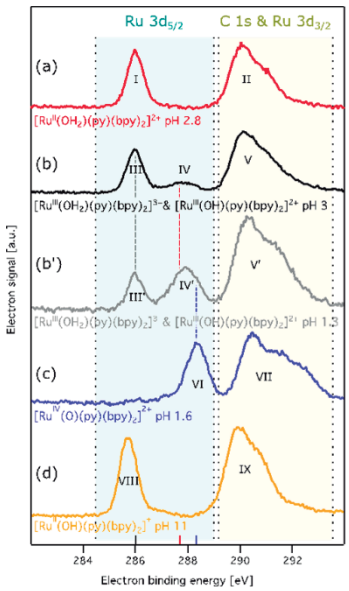
Palavras Chave: Ruthenium Complexes, XPS, *in-operando,* liquid-jet.

Highlights

- In-operando spectroscopy to investigate proton-coupled electron transfer reactions
- Combined theory-experimental approach and synchrotron-based XPS measurements
- The study $[Ru^{IV}=O]^{2+}$ formation

Resumo/Abstract



Recent advances in operando-synchrotron-based X-ray techniques are making it possible to address fundamental questions related to complex proton-coupled electron transfer reactions, such as for instance the electrocatalytic water splitting process. However, it is still a grand challenge to assess the ability of the different techniques to characterize the relevant intermediates, with minimal interference at the reaction mechanism. To this end, we have developed a novel methodology employing X-ray photoelectron spectroscopy (XPS) in connection with the liquid-jet approach to probe the electrochemical properties of a model electrocatalyst, $[RuII(bpy)_2(py)(OH_2)]^{2+}$, in an aqueous environment. There is a unique fingerprint of the extremely important higher valence ruthenium oxo species in the XPS spectra along the oxidation reaction pathway. Furthermore, a sequential method combining quantum mechanics and molecular mechanics (S-QM/MM) is used to unveil the underlying physical chemistry of such systems. This study provides the basis for the future development of *in-operando* XPS techniques for water oxidation reactions.

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