

Combining Molecular Dynamics Simulations and First-principles Calculations to Understand the Structural and Spectroscopy Properties of Ru-based CO₂ Reduction Electrocatalyst in Aqueous Environment

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Photoelectrochemical reduction of CO₂ to higher energy products is a promising route to enable a sustainable world growth with reduced impact on the environment. Electrocatalysts such as [Ru(bpy)₂(CO)₂]²⁺ have been successfully employed to convert CO₂ into formic acid in a photoelectrochemical process. However, the underlying mechanisms of these complex reactions are not yet fully resolved. In this work, we have combined ab initio (AIMD) and classical molecular dynamics (MD) simulations with first-principles x-ray spectroscopy calculations to unveil the structure and dynamics of [Ru(bpy)₂(CO)₂]²⁺ in aqueous environment. We have developed a force field where the intramolecular interaction is represented by the Universal Force Field (UFF) while intermolecular parameters (Lennard-Jones and Coulomb potential) are derived from density functional theory (DFT). The ab initio MD simulations have been carried out within the Born-Oppenheimer approach as implemented in VASP code while the classical MD simulations were performed in GROMACS suite package using an *NpT* ensemble. As a first step, we have validated the force field against the AIMD structure. It is possible to see in Figure 1 the RDF and the coordination number and the XPS spectra calculated from different types of level of theory as well.

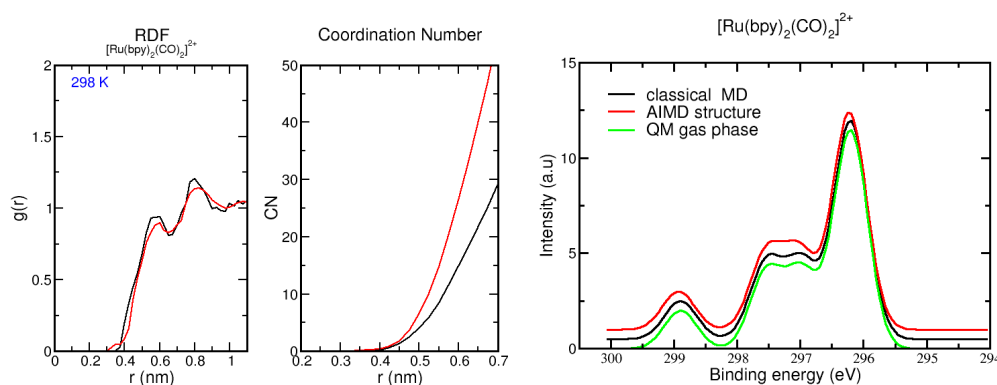


Figure 1. RDF and XPS data from different type of level of theory (Classical MD and AIMD).

Spatial distribution functions (SDF) of water molecules, around the Ru complex, have been used to establish the relationship between the aqueous local environment structure and the XPS properties, within a sequential MD/ab initio theory approach. Once validated this methodology, it opens a great perspective to investigate many other effects related to the solvent environment.