Evaluation of Density Functional Theory for Modeling the Coordination Chemistry of Uranyl Cation with a Quinoline Quinone-Type Cofactor

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A computational model that can accurately describe the interaction of the bioavailable form of high-valent uranium(VI) (uranyl or $[UO_2]^{2+}$) with biomolecules is a powerful tool for providing atomic-scale quantum chemical description for a diverse set of experimental data . In this work, the performance of density functionals and basis sets, solvation models were evaluated in modeling $[UO_2]^{2+}$ interactions with quinol-type cofactors of bacterial alcohol dehydrogenase.[1]

Recent advances in computational chemistry of actinide compounds have enabled for accurate modeling of the geometric and electronic structures, energetics and reactivity of compounds of f-block elements with the use of hybrid functionals, effective core potentials, relativistic effects, and solvation models.[2,3] Consequently, we combined the most relevant experimental data for $[UO_2]^{2+}$ coordination chemistry and quinol-type biological cofactors in order to develop a computational model that balances both accuracy and cost. We carried out independent systematic methodology evaluations for the organic cofactor (pyrroloquinoline quinone, PQQ) and separately for the solvated form of $[UO_2]^{2+}$ ($[UO_2(H_2O)_5]^{2+}$). We utilized crystallographic structural information and intramolecular distances from X-ray absorption spectroscopic measurements, protonation constants, reduction potentials, and electronic absorption spectra. It was found that the combination of B3LYP/TZVP functional and basis set with the incorporation of both a first explicit shell and outer implicit solvation shells to be a good compromise in computational cost and accuracy for modeling both UO_2^{2+} and its interactions with quinol-type cofactors.

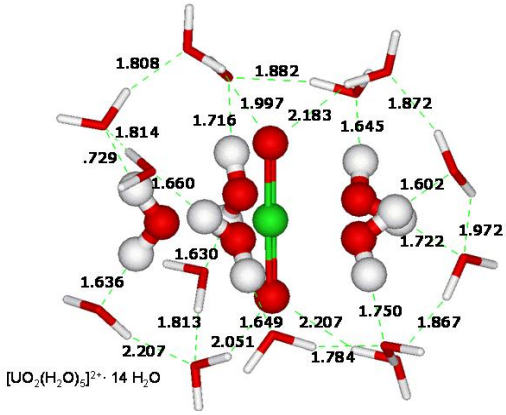

Figure 1: $UO_2(H_2O)_5^{2+}$ complex showing first shell explicit solvation model and hydrogen bond distances

References:

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