Área: FIS

Solvent and Relativistic Effects on Chemical Shifts in Uranyl Carboxylate Complexes: Insights from *Ab Initio* Molecular Dynamics and DFT calculations

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Highlights

^{13}C chemical shift calculations reveal spin-orbit effect. In addition, ^{17}O chemical shift calculations also show sensitivity to solvation.

Resumo/Abstract

A combination of Born-Oppenheimer Molecular Dynamics (BOMD) and DFT calculations[1] was used to evaluate and understand the role of solvation and relativistic effects in ^{13}C and ^{17}O chemical shifts of Uranyl Carboxylate complexes: $(UO_2)C_2H_3O_3$, $(UO_2)(C_2H_4O_3)_2$, $(UO_2)C_3H_5O_3$, $(UO_2)(C_3H_6O_3)_2$ and $(UO_2)(C_2H_3O_2)_2$. This current state of-the-art theoretical method based on AIMD sampling and relativistic DFT with hybrid functionals for NMR calculations was evaluated comparing the theoretical chemical shifts with its experimental values.[2] The ^{13}C chemical shift calculations suggest spin-orbit effect should be considered even thought this nucleus is not directly bonded to the uranyl center, accounting for an average of 27% of the calculated value. The ^{17}O shielding tensor is closely related to the solvation model, where it goes from -831.11 ppm with implicit solvation model (COSMO) to -948.65 ppm when the explicit solvent molecules are considered in the NMR calculation for Uranyl Lactate.

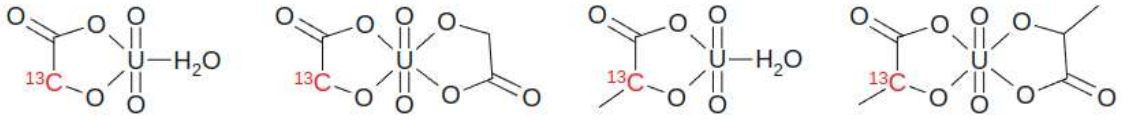

Figure 1. Shielding tensor of highlighted ^{13}C, with and without spin-orbit correction.

[1] A. H. Mazurek, et al.,International Journal of Molecular Sciences. 2021, *22*, 4378.

[2] M. Kakihana, et al., The Journal of Physical Chemistry 1987, *91*, 6128.

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