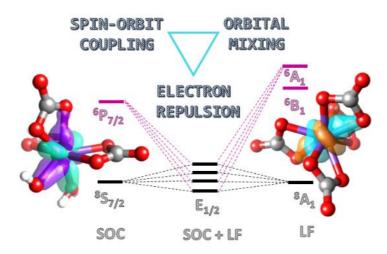
## Theoretical Examination of Covalency in Berkelium(IV) Carbonate Complexes

**Cristian Celis-Barros**,<sup>a</sup> David E. Hobart,<sup>a</sup> Ramiro Arratia-Pérez,<sup>b</sup> Dayán Páez-Hernández,<sup>b</sup> and Thomas E. Albrecht-Schmitt<sup>a</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, Florida State University, Tallahassee, Florida, USA; <sup>b</sup> Center for Applied Nanosciences (CANS), Universidad Andres Bello, Santiago, Chile ccelisbarros@fsu.edu

Elucidating covalency in actinides is gaining attention among the scientific community mainly due to fundamental chemistry aspects but also for separation chemistry purposes. Although covalency is not the main contributor to the chemical bond, it has been demonstrated that small differences in bonding may allow lanthanide/actinide or actinide/actinide separations. The strong complexation of oxygen-donor ligands such as the carbonate ion predominantly stabilizes Bk(IV) over Bk(III). Herein we propose two models of structures present in Bk(IV) aqueous carbonate solutions based on comparisons with experimental data previously reported for Bk(IV) carbonate solutions. Modeling further coordination of Bk(IV) in more basic concentrated carbonate solutions by addition of hydroxyl ligands, modifies the charge transfer spectral band with a second peak appearing toward longer wavelengths, that has also been observed experimentally. The multiconfigurational character of the ground and low-lying excited states is also shown along with strong spin-orbit coupling. Thus, the bonding properties of berkelium(IV) carbonate and carbonate-hydroxyl complexes are dominated by strong Coulombic forces where a non-negligible covalent character is confirmed by NBO analysis and topological studies of the electron density. Bond orders based in natural localized molecular orbitals (NLMOs) show that Bk-OH bonds present enhanced orbital overlap that is reflected in the bond strength.



*Figure 1: Bk(IV) carbonates are a good example of the interplay of spin-orbit coupling, electron repulsion, and covalency through orbital mixing in heavy elements.*