

DFT Calculations for Reactive *f*-Element Separations without Solvent

Background. We seek to identify ligand design contributions that promote differential volatility of *f*-metal complexes to facilitate separations that are the impost important chemical challenge in *f*-element chemistry.¹⁻⁵ The undergraduate student in the Vlaisavljevich group will conduct DFT calculations to identify correlations between differences in metal-ligand covalency, intermolecular forces, and molecular structures with the compounds' volatilities. The Vlaisavljevich group has a long-term collaboration with the Daly (U of Iowa) and Girolami (U of Illinois Urbanna-Champaign) groups who are synthesizing new complexes to separate *f*-elements via selective volatilization.⁶⁻⁸

Research Approach. DFT calculations will first be used to evaluate how different ligand substituents in β -ketoiminates, aminodiboranates, and aminoboranates affect metal-ligand bonding and charge distribution in the associated lanthanide and actinide complexes (Figure 1). The goal is to minimize attractive intermolecular forces and maximize electron-electron repulsions in the solid state that help to drive molecules apart. By quantifying these differences, we can deeply understand experimental observations and predict the volatilities of target complexes. Previous dispersion corrected-DFT calculations on similar systems successfully determined the reaction thermodynamics for monomeric, dimeric, and oligomeric *f*-element borohydride complexes.⁶⁻⁸

Previous work involved modelling the solid as gas phase oligomers of increasing length where the coordination and intermolecular bonding patterns were known from experiment.⁸ This was compared to the appropriate monomeric and dimeric species present in the gas phase as the volatile products. Here, we will perform periodic DFT calculations and compute sublimation enthalpies for monomeric volatile complexes with known solid-state structures. We will compare the electrostatic potentials and compute dimerization energies of the molecular monomeric species using standard DFT methods. The goal is to determine if the latter calculations, which are computationally less intensive, can predict trends in volatilities reliably. Calculations will be performed for actinide and lanthanide β -ketoiminates which have not yet been synthesized. Our goal is to predict if these ligands will 1) yield volatile complexes 2) what ligand modifications will improve volatilities, and 3) and how important crystal packing is when assessing the volatilities of compounds *a priori*.

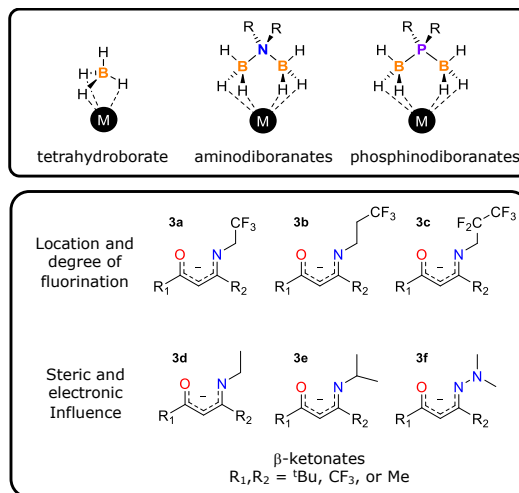


Figure 1. Families of ligands to be tested. Ligands in top box have been synthesized while those in the bottom have not.

References

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