Processing and remediation of nuclear waste requires the development of efficient chemical separation processes, wherein radiologically hazardous products are isolated and removed from voluminous waste streams. The exploration of suitable chelating agents for such separations processes is challenging as actinide chemistry is not well-understood. This is, in part, due to the technical difficulties and expense of working with radiologically hazardous elements. Theoretical modeling of actinide chemistry is highly desirable, but this task poses a severe challenge for computational quantum chemistry models due to the large numbers of metal-centered electrons and the presence of strong relativistic effects. For the development of computational models with truly predictive capabilities it is essential that they can be tested and validated by comparisons with accurate experimental data.

There are clear advantages for using spectroscopic data obtained from gas-phase measurements for the comparisons with theory. The ideal situation is to evaluate predictions for the bare molecule against experimental data that are untainted by interactions with solvent molecules. Gas-phase spectroscopy can provide accurate determinations of rotational constants (and thus geometric structure), electric and magnetic dipole moments, vibrational frequencies, electronic excitation energies, ionization energies and electron affinities. The last two properties reflect the inherent ability of molecules to donate or accept electrons, respectively.

We are using multiple resonance spectroscopy and jet cooling techniques to unravel the complex electronic spectra of Th and U compounds. Recent results for the oxides, sulfides, nitrides and halides will be discussed. Systematic errors in the accepted values for the ionization energies have been discovered, and the patterns of electronic states for these molecules provide information concerning the occupation of the 5f orbitals and their participation in bond formation.