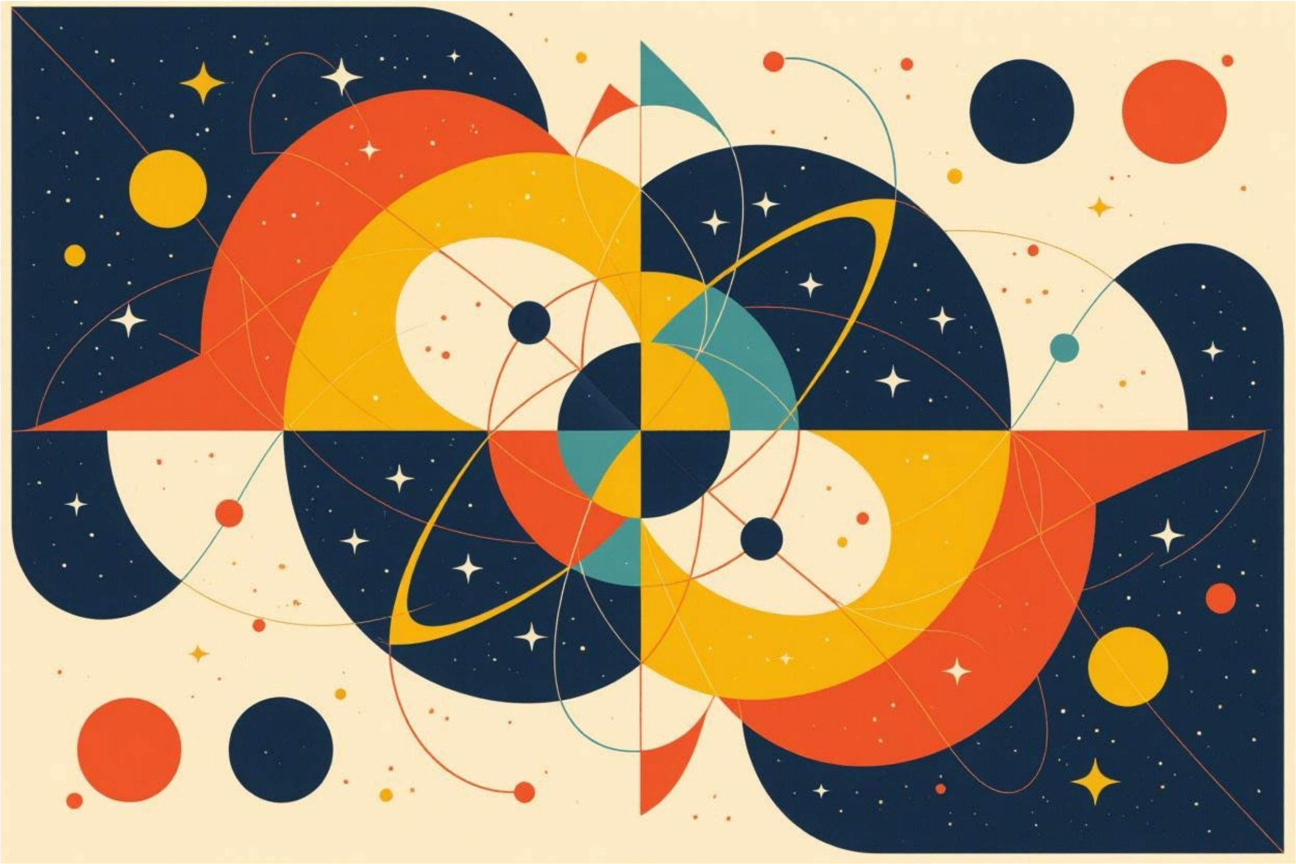
2025 Heavy Element Chemistry Principal Investigators' Meeting



Rockville, MD
April 7-9, 2025

U.S. DEPARTMENT OF ENERGY | Office of Science

Office of Basic Energy Sciences (BES)
Chemical Sciences, Geosciences, and Biosciences Division

Program and Abstracts
for the

2025 Heavy Element Chemistry Principal Investigators' Meeting

Rockville Hilton
1750 Rockville Pike
Rockville, Maryland
April 7-9, 2025

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

Cover art: (Philip Wilk, 2025)

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Foreword

This abstract book provides a record of the thirteenth U.S. Department of Energy Principal Investigators' meeting of the Heavy Element Chemistry program. The Chemical Sciences, Geosciences and Biosciences Division of the Office of Basic Energy Sciences and its predecessors have sponsored research in heavy element chemistry for over seventy years.

The objective of this meeting is to provide a fruitful environment in which researchers with common interests will present and exchange information about their activities, will build collaborations among research groups with mutually reinforcing strengths, will identify needs of the research community, and will focus on opportunities for future research directions. With ample time for discussion and interactions, we emphasize that this is an informal meeting for exchange of information and building of collaborations; it is not a review of researchers' achievements or a forum to choose future directions.

It has been a privilege to serve as the manager of these research programs. In carrying out these tasks, I learn from the achievements and share the excitement of the research of the many sponsored scientists and students whose names appear on the papers in the following pages. I hope that this meeting enhanced research efforts and will nurture future collaborations. I would like to thank all the researchers whose dedication and innovation have advanced our research and made this meeting possible and productive.

Philip Wilk

Agenda

2025 Heavy Element Chemistry Principal Investigators' Meeting

Hilton Washington DC/Rockville Hotel & Executive Meeting Ctr
Monday, April 7 - Wednesday, April 9

Meetings Notes:

The meeting fee includes breakfast and lunch provided at the meeting.

People who did not pay the registration fee will need to pay for their meals.

Sunday, April 6

	Arrival
7 -9 PM	Informal No-Host Meetup at "Olive's"
	Hilton Washington DC/Rockville Hotel & Executive Meeting Ctr

Monday, April 7

8:00 - 9:00	Breakfast
9:00	**Meeting Begins**

April 7, 2025 agenda version

Philip Wilk
Program Manager
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Monday, April 7

8:00 - 9:00 Breakfast

9:00 Meeting Begins — Philip Wilk

Introduction, Agenda, Mini-Workshop Charge

9:15 Session 1 — Cox

9:15	Peter Armentrout Thermochemistry and reactivity of Atomic and molecular actinides
9:40	Kit Bowen Uranium-Containing and Thorium-Containing Anions Studied by Photoelectron Spectroscopy
10:05	Kirk Peterson Accurate ab Initio Thermochemistry and Spectroscopy of Molecules Containing f-block Elements
10:30	break
10:45	Garry Grubbs II and Stephen Cooke Studying f-Electron Contributions in Thorium- and Uranium-Containing Molecules
11:10	David Shuh Electronic Structure and Chemical Bonding in Fundamental Actinide Materials
11:35	Ping Yang Unique chemical Bonding and Electronic Structure Enabled by 5f-Orbitals
12:00	Working Lunch for Collaboration (poster room will be open)

1:00 Session 2 — Persinger

1:00	Thomas Albrecht High-Pressure Effects on Transplutonium Complexes
1:25	Jennifer Wacker Surveying Coordination Modes of Early and Late Actinides in Small Molecules and Macro-molecular Hosts
1:50	Suzanne Bart Investigating the Electronic Structure of Higher Order Actinide Imido Complexes
2:15	break
2:30	Herman Cho Spectroscopic Investigation of Electronic Structure in the Actinide Elements
2:55	John Despotopulos Chemistry at the Extreme Edges of the Periodic Table: Elucidating the Chemical Properties of the Superheavy Elements
3:20	Jennifer Pore Atom-a-time Studies of Late-Actinide Molecule Formation
3:35	break

3:50 Poster Slam — Philip Wilk

(Each poster presenter gets one minute and
one slide, no questions)

Poster Session 1: Even numbered posters (all posters are up)

5:45 Dinner on your own and Collaborate (poster room will be open)

Tuesday, April 8

8:00 - 9:00	Breakfast	
9:00	**Session 3**	**Beaux**
9:00	Richard Wilson	
	Solid State Chemistry of the Transuranium Elements in Alkaline Solution	
9:25	Tori Forbes	
	Impacts of free radicals on the chemistry of neptunium and uranium complexes	
9:50	James Blakemore	
	Actinyl Capture and Bond Activation by Electron Transfer and Acid/Base Chemistry	
10:15	break	
10:30	Gauthier Deblonde	
	Polyoxometalate Chemistry with Heavy Elements	
10:55	William Evans	
	Exploring the Fundamental Chemistry of Actinide Metal Complexes	
11:20	Liane Moreau	
	Exploring actinide nanocrystal growth towards defining 5f surface chemistry	
11:45	TBD	
12:00	Working Lunch for Collaboration (poster room will be open)	
1:15	**Session 4**	**Matson**
1:15	Korey Carter	
	Design of Molecular Spin Qubits Featuring Clock Transitions via Encapsulation of f-Elements in Polyoxometalates	
1:40	Henry La Pierre	
	Molecular Approaches to the Electronic Structure of Actinide Materials	
2:05	Eric Schelter	
	Expressing Tunable Emergent Quantum Phenomena in Molecular Systems with Strong Electron Correlations	
2:30	break	
2:45	Julia Neumann	
	Actinide Speciation in Non-Ideal Solution’	
3:10	Benjamin Stein	
	Americium luminescence for on-line monitoring	
3:35	Lynn Francesconi	
	Hunter / Brookhaven partnership to investigate the speciation of technetium-99 and rhenium in molten salts	
4:00	**Program Update**	**Philip Wilk**
4:20	break	
4:30	**Poster Session 2: Odd numbered posters (all posters are up)**	
5:45	Dinner on your own and Collaborate (poster room will be open)	

Wednesday, April 9

8:00 - 9:00 Breakfast

9:00 Chemical Sciences, Geosciences and Biosciences Division Update — Philip Wilk

Gail McLean, Division Director

9:30 Session 5 — Surbella

9:30	Cory Windorff Pursuing Electronic Structure Studies in Polymetallic Actinide Complexes
9:55	Sky Fortier Synthesis, Reactivity, and Electronic Study of Unsupported and Supported Actinide-Arene Complexes
10:20	Jeffrey Long Towards Actinide-Based Single-Molecule Magnets
10:45	break

11:00 Mini-Workshop

12:00 Lunch on your own / dismissal

Posters

P1	Polly Arnold Actinocenes from Th to Bk
P0A	Rebecca Abergel Circularly Polarized Luminescence: A Tool to Resolve Actinide Electronic Structure
P2	Jochen Autschbach 5f-Shell Bonding in Actinide Complexes
P3	Enrique Batista Surface Reactivity on Actinide Dioxide
P4	Miles Beaux Resolving the f-electron challenge with STM/STS
P5	Richard Cox Development of an Experimental Method to Probe Fundamental Interactions of Transuranics in the Gas Phase
P6	Christopher Dares Modulating Actinide Redox Chemistry with Metal Oxide Electrodes
P7	David Dixon Computational Studies of Structure, Thermodynamic Properties, and Reactivity Across the Actinide Row
P8	Michael Duncan Coordination and Solvation of Actinide Cations
P9	Omar Farha Tunable Uranium Coordination in Metallacarboranes and Metal–Organic Frameworks
P10	Laura Gagliardi Spin-Orbit Coupling with Linearized Pair-Density Functional Theory
P0C	Shane Galley Manipulation of ligand electronic structure to control felement covalency
P11	Andrew Gaunt TransuraniumMolecular Chemistry: Non-aqueous inert atmosphere synthetic chemistry
P12	Trevor Hayton Combining Synthesis and Spectroscopy to Quantify An-L Bond Covalency
P13	Michael Heaven UO2 : Spectroscopic challenges posed by high vibronic state densities
P14	Karah Knope From Complexes to Clusters to Nanoparticles: Controlling Actinide Phase Formation and Reactivity
P15	Xiaosong Li Ab Initio Modeling of f-Element X-ray Absorption Spectroscopy
P16	Ellen Matson Group(IV) Chalcogenides as Redox-active Supports for Early Actinides
P17	Stefan Minasian Actinide Single-Source Precursors (SSPs)
P0B	Michael Morse Electronic Structure, Spectroscopy, and Bond Dissociation Energies of Small Actinide Molecules
P18	Thomas Persinger Maxtrix Isolation Spectroscopy of the Transuranium Elements
P19	Robert Surbella Investigating Am(III) Electronic Structure with Optical Spectroscopy: Challenges and Opportunities
P20	Bess Vlaisavljevich CASPT2 Geometries, Spectra, and Relativistic Electronic Structures of Actinide Species
P21	Justin Walensky Structure, Bonding, and Reactivity of Actinide Complexes
P22	Eric Walter Actinide Tetrafluoride Magnetism and Electronic Structure: Variable Temperature 19F NMR and EPR Relaxation
P23	Ping Yang Autonomous Discovery for Selective Separation of f-Elements

Abstracts

High-Pressure Effects on Transplutonium Complexes

Thomas E. Albrecht, Principal Investigator

Department of Chemistry and Nuclear Science & Engineering Center, Colorado School of Mines, Golden, Colorado 80401

Graduate Students: Zhuanling Bai, Nicholas B. Beck, Jacob P. Brannon

Collaborators: Joseph M. Sperling (Mines), Laura Gagliardi (U. Chicago), Eva Zurek (U. Buffalo)

Overall research goals: To utilize the effects of high pressures on actinide complexes to provide critical insights into their structural adaptability, bond robustness, and *f*-orbital participation in bonding.

Significant achievements during 2023- 2025:

The focus of this presentation is on one of the three themes of our HEC program that utilizes high pressures to systematically alter structure, bonding, and physical properties of coordination complexes that contain the transplutonium elements americium, curium, berkelium, and californium. The unique photophysical properties of Cm(III) create a highly sensitive photoluminescent probe for understanding how the compression and distortion of these complexes alters their electronic structure. One example of this is our studies of an octa-hydrated curium complex $[Cm(H_2O)_8](Hdtp)(dtp)\cdot H_2O$ (**Cm1**, H_2dtp = 2,3-di(tetrazol-5-yl)pyrazine) along with its lanthanide analogues $[Ln(H_2O)_8](Hdtp)(dtp)\cdot H_2O$ (**Ln1**, Ln^{3+} = La^{3+}–Nd^{3+}, Sm^{3+}–Lu^{3+}). These complexes were synthesized and characterized using single crystal X-ray diffraction and a variety of spectroscopic methods. Bond length analysis of $^{VIII}Cm(III)–OH_2$ (where ^{VIII} refers to the coordination number) was compared to $^{VIII}Ln(III)–OH_2$ (Ln^{3+} = Nd^{3+}, and Sm^{3+}) indicating similar $^{VIII}M(III)–OH_2$ bond lengths because of the similar eight-coordinate ionic radii of these $^{VIII}M(III)$ cations. Owing to the reduced coordination number, the $^{VIII}Cm(III)-OH_2$ bond lengths were shorter than previously reported $^{IX}Cm(III)–OH_2$ bonds in $[Cm(H_2O)_9](CF_3SO_3)_3$. The octa-aquo complexes were also characterized by solid-state, UV-vis-NIR spectroscopy in addition to variable-temperature and variable-pressure photoluminescence. Variable-pressure absorption spectra of **Cm1** were compared with **Ln1** and show that the Cm(III) $f \rightarrow f$ transitions have a stronger dependence on pressure than that observed in **Ln1** (Ln^{3+} = Nd^{3+} and Sm^{3+}). The experimental and computational analyses reveal that the monotonic decrease in the computed energy difference between the ground state and the first excited state corresponds with the observed red shift of the photoluminescence peak. This is accompanied by a gradual reduction in the average Cm(III)–OH2 bond length and a delocalization of spin densities, alongside an intensified interaction involving the 5*f* orbitals under increasing pressure. These changes accommodate the new geometry and collectively modify the energy landscape, resulting in peak broadening and quenching.

The second set of complexes that will be discussed are a family of bimetallic actinide complexes, $[(An(pmtz)_2(H_2O)_3)_2(\mu\text{-}pmtz)]_2(pmtz)_2\cdot nH_2O$ (An^{3+} = Cm^{3+}, Bk^{3+}, and Cf^{3+}, $pmtz^-$ = 5-(pyrimidyl)tetrazolate; **Cm1**, **Bk1**, and **Cf1**). They represent the first structurally characterized bimetallic berkelium and californium compounds. The pressure response as determined from UV-vis-NIR transitions vary for **Cm1**, **Bk1**, and **Cf1**. The $5f \rightarrow 5f$ transitions in **Cm1** are notably more sensitive to pressure compared to **Bk1** and **Cf1** and show substantial bathochromic shifting of several $5f \rightarrow 5f$ transitions. In the case of **Bk1**, an ingrowth of a metal-to-ligand charge-transfer transition occurs at elevated pressures because of the accessible Bk^{3+}/Bk^{4+} couple. For **Cf1**, no substantial transition shifting or emergence of MLCT transitions are observed at elevated pressures because of the prohibitive energetics of the Cf^{3+}/Cf^{4+} couple and reduced sensitivity of the $5f \rightarrow 5f$ transitions to the local coordination environment because of the more contracted $5f$ shell versus Cm^{3+} and Bk^{3+}.

Science objectives for 2025- 2027:

For the high-pressure portion of this program, our goal is to continue to push the extremes of periodic table with high pressures because we have demonstrated that this is a powerful tool for gaining systematic control of the physical properties of transplutonium complexes. The largest pressure effects in these complexes observed thus far are with sulfur-donor ligands that are a part of delocalized networks with large dipole moments. These ligands were, in fact, designed to achieve this goal. However, in most cases homoleptic molecules containing such ligands reach a maximum compressibility of the An−S bonds at moderate pressures (ca. 10 GPa) after which point there is a plateau in these distances as a function of pressure. We think that this incompressibility arises from the sulfur ions that surround the metal cations reaching distances where they are in contact with one another and repel one another. More succinctly, the ligands are bumping into each other. This inhibits our ability to continue to alter their electronic structure. Our hypothesis is that redesigning these molecules to be a mix of S- and much smaller N- or O-donors will allow for further compression and enhancement of the hybridization of metal frontier orbitals with ligands orbitals and further alteration of physical properties. As such, we are currently designing and synthesizing molecules that contain combinations of dithiocarbamates (dtc) with either donor-acceptor ligands based on bipyridyl (bipy) derivatives or ligands in the acetylacetonate class similar to 2-thenoyltrifluoroacetone (tta).

Selected Publications supported by this project 2023-2025:

1. Z. Bai, M. Redington, S. Haldar, N. B. Beck, J. M. Sperling, B. Scheibe, J. P. Brannon, E. Zurek, L. Gagliardi, T. E. Albrecht, "High-Pressure Effects on an Octa-Hydrated Curium Complex: An Experimental and Theoretical Investigation," *Journal of the American Chemical Society*, **2025**, *147*, 6137-6148. **DOI:** https://pubs.acs.org/doi/10.1021/jacs.4c17589

2. M. J. Beltran-Leiva, W. N. G. Moore, T. F. Jenkins, W. J Evans, C. Celis-Barros, T. E. Albrecht, "A Comprehensive Approach for Elucidating the Interplay Between $4f^{n+1}$ and $4f^n5d^1$ Configurations in Ln^{2+} Complexes," *Chemical Science*, **2025**, *16*, 2024-2033. **DOI:** https://doi.org/10.1039/D4SC05438E

3. Z. Bai, N. B. Beck, B. Scheibe, J. M. Sperling, J. P. Brannon, B. M. Rotermund, D. Gomez Martinez, T. E. Albrecht, "Investigation of Pressure Effects in the Bimetallic Transplutonium Tetrazolate Complexes $[(An(pmtz)_2(H_2O)_3)_2(\mu\text{-pmtz})]_2(pmtz)_2{\cdot}nH_2O$ (An^{3+} = Cm^{3+}, Bk^{3+}, and Cf^{3+})," *Journal of the American Chemical Society*. **2024**, *146*, 7822-7830. **DOI:** https://doi.org/10.1021/jacs.4c00803

4. J. Warbinek *et al.* "Smooth trends in fermium charge radii and the impact of shell effects," *Nature*, **2024**, *634*, 1075-1079. **DOI:** https://www.nature.com/articles/s41586-024-08062-z

5. B. N. Long, M. J. Beltrán-Leiva, J. M. Sperling, T. N. Poe, C. Celis-Barros, T. E. Albrecht, "Altering the Spectroscopic, Electronic Structure, and Bonding of Curium(III)−Cp′ Upon Coordination of 4,4′−bipyridine," *Nature Communications*, **2023**, *14*, 3774-3783. **DOI:** https://www.nature.com/articles/s41467-023-39481-7

6. H. Zhang, A. Li, K. Li, Z. Wang, X. Xu, Y. Wang, M. V. Sheridan, H.-S. Hu, C. Xu, E. V. Alekseev, Z. Chai, T. E. Albrecht, S. Wang, "Ultrafiltration separation of nanoscale Am(VI)-polyoxometalate clusters from lanthanides," *Nature*, **2023**, *616*, 482-487. **DOI:** https://www.nature.com/articles/s41586-023-05840-z

7. T. N. Poe, H. Ramanantoanina, J. M. Sperling, H. B. Wineinger, B. M. Rotermund, J. Brannon, Z. Bai, B. Scheibe, N. Beck, B. N. Long, S. Justiniano, T. E. Albrecht, C. Celis-Barros, "Isolation of a Californium(II) Crown-Ether Complex," *Nature Chemistry*, **2023**, *15*, 722-728. **DOI:** https://www.nature.com/articles/s41557-023-01170-9

Thermochemistry and reactivity of Atomic and molecular actinides

Peter B. Armentrout, Principal Investigator

Department of Chemistry, University of Utah, Salt Lake City, UT

Undergraduate Students: S. Peter Kraul (B.S., 2023)

Graduate Students: Maria Demireva (Ph.D., 2017), JungSoo Kim (Ph.D., 2021), Sara L. Rockow (M.S., 2022), Amanda R. Bubas (Ph.D., 2023), Brandon C. Stevenson (Ph.D., 2023), Arjun Kafle (Ph.D., 2023), Gonzalo Perez-Maldonado, Thilini Welikumburala

Postdocs: Wenjing Zhang, Satish Kumar

Collaborators: Kirk A. Peterson (Washington State U.), Bert DeJong (LBNL), Richard M. Cox (PNNL)

Overall research goals: The overall project objectives are to examine the thermochemistry and reactivity of actinide compounds of thorium and uranium using guided ion beam tandem mass spectrometry (GIBMS). In particular, we intend to experimentally determine bond dissociation energies (BDEs) that can act as benchmarks for theoretical explorations of the actinides. The experimental work will be accompanied by high-level ab initio calculations to determine mechanisms of reactions, structures of products, and to evaluate what levels of theory are needed to reproduce the experimental thermochemistry. Collaborations with Peterson and de Jong facilitate this latter goal. Collaborations with Cox allow us to extend the work to transUranics.

Significant achievements during 2023-2025:

GIBMS was used to examine the kinetic energy dependent reactions of U^+ with O_2 and CO. In the former reaction, the UO^+ product is formed in a barrierless and exothermic process. Formation of both UO^+ and UC^+ in the reaction of U^+ with CO is endothermic and modelling these data provides 0 K BDEs of $D_0(U^+\text{-}O) = 7.88 \pm 0.09$ eV and $D_0(U^+\text{-}C) = 4.03 \pm 0.13$ eV. These values are within experimental uncertainty of previously reported experimental values. Additionally, the electronic states of UO^+ and UC^+ and the potential energy surfaces for the reactions were explored by quantum chemical calculations, including a full Feller-Peterson-Dixon (FPD) composite approach with correlation contributions up to CCSDT(Q) for UO and UO^+, yielding $D_0(U\text{-}O) = 7.82$ eV and $D_0(U^+\text{-}O) = 7.99$ eV.

Reaction of atomic U^+ with CS_2 forms US^+ in an efficient exothermic reaction and UCS^+ in an inefficient endothermic process. The subsequent reaction of US^+ with CS_2 forms US_2^+ in low-energy endothermic process and UCS_2^+ and UCS^+ at much higher energies. Collision-induced dissociation of US^+ with Xe yields U^+ + S exclusively in an endothermic reaction. Analysis of the kinetic energy dependent cross sections of the endothermic processes yields 0 K BDEs for U^+-S, SU^+-S, U^+-CS, U^+-CS_2, SU^+-CS, and S-UCS^+. Theory is used to explore the structures and electron configurations of these species. The thermochemistry measured in this study was further compared to analogous values previously determined for select group 3 transition metals, lanthanides, and actinides.

Previously, reactions of CO_2 with U^+ were studied using GIBMS and with An^+ ($An^+ = Th^+$, U^+, Pu^+, and Am^+) using triple quadrupole inductively coupled plasma mass spectrometry (QQQ-ICP-MS) in collaboration with Richard Cox at PNNL. Here, we extended this study by employing GIBMS to study the reactions of $U^+ + CO_2$, $UO^+ + O_2$, and the reverse of the former, UO^+ + CO. The reaction of $U^+ + CO_2$ proceeds to form UO^+ + CO with an efficiency of 118 ± 24% as well as generating UO_2^+ + C and UCO^+ + O. The reaction of $UO^+ + O_2$ forms UO_2^+ in an exothermic, barrierless process, and also results in the collision-induced dissociation (CID) of UO^+ to yield U^+. In the UO^+ + CO reaction, formation of UO_2^+ in an endothermic process is the dominant reaction, but minor products of UCO^+ + O and U^+ + (O + CO) are also observed. Analysis of the kinetic energy dependences observed provides the bond energies, $D_0(U^+\text{-}O) = 7.98 \pm 0.22$ and 8.05 ± 0.14 eV, $D_0(U^+\text{-}CO) = 0.73 \pm 0.13$ eV, and $D_0(OU^+\text{-}O) = 7.56 \pm 0.12$ eV. The values obtained for $D_0(U^+\text{-}O)$ and $D_0(OU^+\text{-}O)$ agree well with previously reported literature values. To our knowledge, this is the first experimental measurement of $D_0(U^+\text{-}CO)$. An analysis of the oxide bond energies shows that participation of 5f orbitals leads to a substantial increase in the thermodynamic stability of UO_2^+ relative to ThO_2^+ and especially transition metal dioxide cations.

We also studied reactions of U^+ with N_2 and NO with GIBMS. Reaction cross sections were measured over a wide range of energy for both systems. In each reaction, UN^+ is formed by an endothermic process, thereby enabling the direct measurement of the threshold energy and determination of the UN^+ bond dissociation energy. For the reaction of $U^+ + N_2$, a threshold energy (E_0) of 4.02 ± 0.11 eV was measured, leading to D_0 (UN^+) = 5.73 ± 0.11 eV. The reaction of U^+ + NO yields UO^+ through an exothermic, barrierless process that proceeds with 94 ± 23% efficiency at the lowest energy. Analysis of the endothermic UN^+ cross section in this reaction provides $E_0 = 0.72 \pm 0.11$ eV and therefore D_0 (UN^+) = 5.78 ± 0.11 eV. Averaging the values obtained from both reactions, we report D_0 (UN^+) = 5.76 ± 0.13 eV as our best value (uncertainty of two standard deviations). Combined with precise literature values for the ionization energies of U and UN, we also derive D_0 (UN) = 5.86 ± 0.13 eV. Both BDEs agree well with high-level FPD theoretical treatments in the literature. The formation of UN^+ in reaction of U^+ with NO also exhibits a considerable increase in reaction probability above ~3 eV. Theory suggests that this may be consistent with formation of UN^+ in excited quintet spin states, which we hypothesize are dynamically favored because the number of *5f* electrons in reactants and products is conserved.

Finally, an invited Feature Article in the Journal of Physical Chemistry examined several quantitative aspects of metal ion chemistry and therefore included results for transition metals (NSF), lanthanides (AFOSR), and actinides (HEC/DOE). Our work on the quantitative contributions of f-orbitals to the bonding in AnO_2^+ was highlighted.

Science objectives for 2025-2027:

Data has been collected for the reactions of U^+ with CH_4 (CD_4) and with NH_3 (ND_3). Papers on both reactions are nearing completion. Studies to examine reactions of Th^+ with NH_3 (ND_3) have been initiated. Reactions planned in the near future include studies of U^+ with H_2O (D_2O), reactions designed to measure the US^+ bond energy more precisely, and CID reactions of $U^+(\text{benzene})_{1,2}$ complexes.

Selected publications supported by this project 2023-2025

1. Zhang, W.; Hunt, A. R. E.; Kim, J.; Demireva, M.; Peterson, K. A.; Armentrout, P. B. "Bond Energies of UO^+ and UC^+: Guided Ion Beam and Quantum Chemical Studies of the Reactions of Uranium Cation with O_2 and CO" *Isr. J. Chem.* **2023**, *63*, e202300026. DOI: 10.1002/ijch.202300026
2. Rockow, S.; Bubas, A. R.; Krauel, S. P.; Stevenson, B. C.; Armentrout, P. B. "Thermochemistry of Uranium Sulfide Cations: Guided Ion Beam and Theoretical Studies of Reactions of U^+ and US^+ with CS_2 and Collision-induced Dissociation of US^+" *Molec. Phys.* **2024**, *122*, e2175595. DOI: 10.1080/00268976.2023.2175595
3. Armentrout, P. B. "Quantitative Aspects of Gas-phase Metal Ion Chemistry: Conservation of Spin, Participation of f Orbitals, and C-H Activation and C-C Coupling" *J. Phys. Chem. B (Invited Feature Article)* **2023**, *127*, 9641-9653. DOI: 10.1021/acs.jpca.3c06023
4. Bubas, A. R.; Zhang, W.-J.; Armentrout, P. B. "A Guided Ion Beam Investigation of UO_2^+ Thermodynamics and f Orbital Participation: Reactions of $U^+ + CO_2$, $UO^+ + O_2$, and UO^+ + CO" *J. Chem. Phys.* **2023**, *159*, 244305. DOI: 10.1063/5.0183836
5. Bubas, A. R.; Kafle, A.; Stevenson, B. C.; Armentrout, P. B. "The Bond Energy of UN^+: Guided Ion Beam Studies of the Reactions of U^+ with N_2 and NO" *J. Chem. Phys.* **2024**, *160*, 164305. DOI: 10.1063/5.0204090

Computational studies of magnetism and spectra of actinide complexes

Jochen Autschabch, Principal Investigator

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Graduate students & Postdocs: Laura Motta, Aleksandr Zaichenko, Xiaojuan Yu, Augustine Obeng, Asmita Sen, Kurtis Stanistreet-Welsh, et al.

Collaborators: Stefan Minasian, Rebecca Abergel & Polly Arnold (Berkeley Lab), Herman Cho & Gian Surbells III (PNNL), Trevor Hayton (UC Santa Barbara), James Blakemore (U. Kansas), Lynda Soderholm & Richard Wilson (ANL), R. Gian Surbella III (PNNL), Dumitru-Claudiu Sergentu (U. Rennes, France), Ning Chen (Soochow U., China), et al.

Overall research goals: In this project, we investigate the electronic structures as well as spectroscopic and magnetic properties of chemical compounds with f-elements, i.e. actinides and lanthanides, by quantum theoretical calculations. The main objective is to learn how the observable magnetic, optical, and spectroscopic properties are related to the geometrical structure of the molecules, their chemical bonding, and the nature of the ground and excited electronic states. We develop and apply state-of-the-art relativistic theoretical methods for computations of magnetic resonance parameters (EPR, NMR), magnetic susceptibilities, valence and core excitation spectra (UV-vis and X-ray spectroscopy), magnetic field-induced circular dichroism (MCD) and Mössbauer spectroscopic parameters. A major focus is the involvement of the actinide 5f shell in the chemical bonds. The project goals include developments of new relativistic quantum chemical methods in the open-source NWChem and Molcas quantum chemistry packages, along with new stand-alone open-source software. Density functional theory (DFT) as well as multiconfiguration-wavefunction theory (WFT) with relativistic Hamiltonians are used in this project.

Significant achievements during 2023- 2025:

The main focus of the project during 2023-25 has been on 5f-shell bonding in general, including a study that demonstrated the interconnectedness of 6p ‘pushing from below’ and actinide inverse trans-influence [1]. Collaborations with scientists at National Labs and elsewhere were continued or initiated [2,3,4]. Former postdoc Claudiu Sergentu, now a collaborator, performed the electronic structure calculations for a recent report of a berkelocene [5], a Bk organometallic sandwich complex with the ligand hdcCOT [6] (collaboration with Berkeley Lab), which confirmed the assignment of the ground state as Bk(IV) via multi-configurational wavefunction calculations.

Our collaboration with T. Hayton has continued to be productive, with five new publications since the previous HEC meeting. We conducted joint experimental/theoretical studies of f-element complexes with Th, and U [7], typically with a focus on how metal-ligand covalent bonding impacts the ligand NMR chemical shifts via spin-orbit coupling, a relativistic effect. We recently published an overview of our joint projects and their broader context [8].

Our collaboration with Ning Chen has characterized new interesting new uranium and thorium bonding motifs that present themselves when actinide-containing small-molecule clusters are encapsulated inside fullerene cages. Recent work, for example, reported an unusual Th=C double bond in an encapsulated ThTiC cluster [9]. A 2023 study reported U-C triple-bond character in an encapsulated USc_2C_2 cluster that can be considered an inorganic [1.1.1]propellane analog [10].

Science objectives for 2025- 2027: A major focus of the next two years of research will be the interplay of atomic orbital (AO) energy matching and AO overlap in actinide covalency. During the past year we have developed computational analysis tools to study covalent bond formation in detail as a function of overlap vs. AO energies in a molecule, and we are currently applying them to the $[AnCl_6]^{2-}$ series with An = U, Np, Pu. We will extend the scope of this project during 2026/27 to include also the +III actinide oxidation states with a wider range of actinides (U-Es) and a variety of ligands including CN^-, NCS^-, DPA, HOPO, and Cyanex301. We will also revisit the 6p 'pushing from below' mechanism with these new analysis tools, and search for spectroscopic signatures of 5f covalent bonding. A 237-Np Mossbauer project developed by former postdoc Laura Motta in 2021/22 in a 3-article series will continue with a focus on the quadrupolar splitting. The underlying electric field gradient tensors will be calculated numerically via relativistic CASPT2 methods to explore the accuracy of this method. Previous CASPT2 calculations of Mossbauer isomer shifts indicated that this level of theory should be accurate for predicting 237-Np Mossbauer spectroscopic parameters.

Publications supported by this project 2023-2025 (a selection):

[1] Motta, L. C.; Autschbach, J., 'Actinide inverse trans influence versus cooperative pushing from below and multi-center bonding', Nat. Commun. **2023**, *14*, 4307 (10 pages). https://doi.org/10.1038/s41467-023-39626-8

[2] Skanthakumar, S.; Yu, X.; Autschbach, J.; Soderholm, L., 'Magnetic Properties of Tetravalent Pu in the Perovskites $BaPuO_3$ and $SrPuO_3$', Inorg. Chem. **2023**, *62*, 15891–15901. https://doi.org/10.1021/acs.inorgchem.3c01821

[3] Mikeska, E. R.; Wilson, R. E.; Sen, A.; Autschbach, J.; Blakemore, J. D., 'Preparation of Neptunyl and Plutonyl Acetates to Access Nonaqueous Transuranium Coordination Chemistry', J. Am. Chem. Soc. **2024**, *146*, 21509–21524. https://doi.org/10.1021/jacs.4c04613

[4] Nicholas, A. D.; Arteaga, A.; Ducati, L. C.; Buck, E. C.; Autschbach, J.; Surbella III, R. G., 'Insight into the structural and emissive behavior of a 3-dimensional americium(III) formate coordination polymer', Chem. Eur. J. 2023, 29, e202300077 (10 pages). https://doi.org/10.1002/chem.202300077

[5] Russo, D. R.; Gaiser, A. N.; Price, A. N.; Sergentu, D.-C.; Wacker, J. N.; Katzer, N.; Peterson, A. A.; Branson, J. A.; Yu, X.; Kelly, S. N.; Ouellette, E. T.; Arnold, J.; Long, J. R.; Lukens, W. W.; Teat, S. J.; Abergel, R. J.; Arnold, P. L.; Autschbach, J.; Minasian, S. G., 'Berkelium–Carbon Bonding in a Tetravalent Berkelocene', Science **2025**, *387*, 974–978. https://doi.org/10.1126/science.adr3346

[6] Russo, D. R.; Branson, J. A.; Kelly, S. N.; Sen, A.; Gunther, S. O.; Peterson, A.; Smith, P. W.; Ouellette, E. T.; Arnold, J.; Autschbach, J.; Minasian, S. G., 'Synthesis and characterization of isostructural annulated actinocenes', Chem. Commun. **2025**, *61*, 2504–2507. https://doi.org/10.1039/D4CC06094F

[7] Ordoñez, O.; Yu, X.; Schuerlein, M. A.; Wu, G.; Autschbach, J.; Hayton, T. W., 'An Actinide Complex with a Nucleophilic Allenylidene Ligand', J. Am. Chem. Soc. **2024**, *146*, 28306–28319. https://doi.org/10.1021/jacs.4c09076

[8] Hayton, T. W.; Autschbach, J., 'Using NMR Spectroscopy to Evaluate Metal-Ligand Bond Covalency for the f Elements', Acc. Chem. Res. **2025**, *58*, 488–498. https://doi.org/10.1021/acs.accounts.4c00727

[9] Cao, Z.; Yu, X.; Yao, Y.-R.; Autschbach, J.; Chen, N., 'ThTiC@Cs(6)-C82: Th=C Double Bond in a Mixed Actinide-Transition Metal Cluster', J. Am. Chem. Soc. **2025**, *147*, 3584–3592. URL https://doi.org/10.1021/jacs.4c15253

[10] Jiang, H.; Yu, X.; Guo, M.; Yao, Y.-R.; Meng, Q.; Echegoyen, L.; Autschbach, J.; Chen, N., 'USc2C2 and USc2NC clusters with U–C Triple Bond Character Stabilized inside Fullerene Cages', J. Am. Chem. Soc. **2023**, *145*, 5645–5654. https://doi.org/10.1021/jacs.2c10231

Investigating the Electronic Structure of Higher Order Actinide Imido Complexes

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Dr. Stosh Kozimor, Los Alamos National Laboratory, Los Alamos, NM
Prof. Thomas Albrecht, Colorado School of Mines, Golden, CO

Overall research goals: A high level overview

Our project includes a broad study of lanthanide and actinide elements to explore redox chemistry, heavily loaded pi complexes, and transuranium coordination chemistry. The multidisciplinary studies investigated in our laboratory will substantially contribute to the understanding of the synthesis, bonding, and reactivity of the representatives of the entire f-block and their multiply bonded derivatives. Building on recent results from our laboratory that have demonstrated the synthesis of unprecedented uranium tris(imido) and tetrakis(imido) species, we plan to extend these studies to new systems featuring unprecedented uranium and thorium coordination complexes as well as new neptunium and plutonium chemistry where we will explore understanding and controlling the rich redox chemistry of this element. These studies are complemented by in depth electronic structure studies. These species are fully characterized using ^{1}H NMR, infrared, electronic absorption, electronic paramagnetic resonance and X-ray absorption spectroscopies (Kozimor) as well as X-ray crystallography, electrochemistry, SQUID magnetization (Schelter), and computational methods (Gagliardi). Transuranic analogues, including Np, are studied to understand synthetic, reactivity, and bonding trends across the Periodic Table.

Significant achievements during 2023- 2025:

- Published papers featuring transuranium elements (Np) that shows covalency in the *f*-block, including new solvent adducts.
- Expanded redox-active ligand chemistry with lanthanides, thorium, and transuranic elements.
- Collaborated with Dr. Stosh Kozimor for X-ray Absorption Spectroscopy (XAS) on the entire uranium imido family: $UI_2(NDIPP)$, $UI_2(NDIPP)_2$, $U(NDIPP)_3(THF)_3$, $[U(NDIPP)_4]K_2$, and $[U(NDIPP)_5]K_4(Et_2O)_4$.
- Published two collaborative full articles with Ellen Matson's laboratory on neptunium cluster and pyridinedipyrrolide chemistry.
- Further studies on the characterization and reactivity of $[U(NDIPP)_5]K_4(Et_2O)_4$.
- Collaborated with Prof. Laura Gagliardi's laboratory for the computational study of the electronic structure of $[U(NDIPP)_5]K_4(Et_2O)_4$.
- Collaborated with Prof. Eric Schelter's laboratory for the magnetic study of $[U(NDIPP)_5]K_4(Et_2O)_4$.

- Published tetrabenzylthorium, the long awaited analogue to tetrabenzyluranium.

Science objectives for 2025- 2027:

- Publish uranium pentakis(imido)uranate species, $[U(NDIPP)_5]K_4(Et_2O)_4$, in a high impact journal.
- Make thorium imido derivatives by applying the successful synthetic methods from our corresponding uranium chemistry, which relied on a redox approach.
- Synthesis of neptunium imido derivatives, and expand to plutonium derivatives if possible.
- Simultaneous with the full characterization of $[U(NDIPP)_5]K_4(Et_2O)_4$, we will also begin to explore reactivity of this unusual species.

Publications supported by this project 2023-2025:

7. Valerio, L.R.; Mitchell, A.W.; Lopez, L.M.; Zeller, M.; Bart, S.C.; Matson, E.M. "Neptunium Pyridine Dipyrrolide Complexes" *Organometallics* **2025**, 44, 439-446. https://doi.org/10.1021/acs.organomet.4c00472

6. Rupasinghe, D.M.R.Y.P.; Lopez, L.M.; Poore, A.T.; Baxter, M.R.; Lin, N.J.; Mitchell, A.W.; Zeller, M.; Tian, S.; Bart, S.C.* "Multi-electron Oxidation of Ce(III) Complexes Facilitated by Redox-Active Ligands" *European Journal of Inorganic Chemistry* **2024**, 27, e202300761. https://doi.org/10.1002/ejic.202300761

5. Valerio, L.R.; Shiels, D.; Lopez, L.M.; Mitchell, A.W.; Zeller, M.; Bart, S.C. ; Matson, E.M. "Venturing Past Uranium: Synthesis of a Np(IV) Polyoxomolybdate-Alkoxide Sandwich Complex" *Inorganic Chemistry* **2024**, 63, 22639-22649. 10.1021/acs.inorgchem.4c04428

4. Lopez, L.M.; Uible, M.C.; Zeller, M.; Bart, S.C.* "Lewis base adducts of $NpCl_4$" *Chemical Communications* **2024**, 60, 5956-5959.https://doi.org/10.1039/D4CC01560F

3. Uruburo, C.; Rupasinghe, D. M. R. Y. P.; Gupta, H.; Knieser, R.M.; Lopez, L.M.; Furigay, M.H.; Higgins, F.; Pandey, P.; Baxter, M.R.; Carroll, P.J.; Zeller, M.; Bart, S.C.*; Schelter, E.J.* "Metal-Ligand Redox Cooperativity in Cerium Amine-/Amido-Phenolate-Type Complexes" *Inorganic Chemistry* **2024**, 63, 9418–9426. https://doi.org/10.1021/acs.inorgchem.3c02411

2. Galley, S.S.; Higgins, R.; Kiernicki, J. J.; Lopez, L.M.; Walensky, J.R.; Schelter, E.J.; Zeller, M.; Bart, S.C.* "Synthesis, Characterization, and Reduction of Thorium Pyridinediimine Complexes" *Inorganic Chemistry*, **2023**, 62, 15819-15823. https://doi.org/10.1021/acs.inorgchem.3c01957

1. Rupasinghe, D. M. R.Y. P.; Baxter, M.R.; Zeller, M.; Bart, S.C.* "Isolation and Characterization of Elusive Tetrabenzylthorium Complexes" *Organometallics* **2023**, 42, 2079-2086. https://doi.org/10.1021/acs.organomet.3c00248

Resolving the *f*-electron challenge with scanning probe microscopy/spectroscopy

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Overall research goals: The overarching goals are focused on scanning tunneling microscopy/spectroscopy (STM/STS) measurements and modelling of the electronic structures of single crystal actinide intermetallic samples and isolated actinide containing molecular complexes. Bulk intermetallic samples are fabricated at Los Alamos National Laboratory (LANL) and actinide containing molecular complexes are being supplied by LANL and The University of Kansas (KU) through a collaboration. This work focuses primarily on the neptunium (Np), plutonium (Pu), and americium (Am) series of actinide elements to investigate instabilities existing within the itinerant to localized crossover. The molecular complexes supplied by KU currently contain a single depleted uranium (DU) atom within each molecule, with plans to transition to transuranic containing analogs of the molecules for isolation and probing of individual transuranic atoms. The molecular complexes supplied by LANL contain a single holmium (Ho) atom within each molecule, with plans to transition to Am analogs.

Significant achievements during 2023- 2025: $PuCoGa_5$ crystals were fabricated via a flux method and materials for additional Pu intermetallic crystals have been loaded according to the target compositions and stoichiometries for flux growth. The first-ever atomic resolution STM images of Pu atoms have been obtained from a $PuCoGa_5$ crystal surface. STS data from the $PuCoGa_5$ crystal surface was also collected at cryogenic temperatures revealing the ingrowth of the superconducting gap, a peak at -1.5 eV consistent with photoemission spectroscopy results, and negative differential resistance above the Fermi energy (E_F). Molecular complexes with single uranium atoms were deposited onto HOPG standards by KU and supplied to LANL for measurement. Molecular resolution STM images were obtained for these complexes. Data processing protocols were written in MATLAB for standardization of STS measurement data. As a result of this effort, a data processing error was identified in STS electronic structure data collected from the surface of a metal Pu coupon prior to this current effort. The correction of this error revealed semimetallic behavior of the native surface oxide at room temperature instead of the theoretically predicted semiconductor behavior. An Energy Research Computing Allocations proposal request (ERCAP0027242) titled “Ab-initio investigations of *f*-electron bonding in actinide intermetallics” was submitted and awarded an Allocation Year 2024 DOE Mission Science award from the National Energy Research Scientific Computing Center. Specifically, this award included 100 CPU Node Hours and 51,920 GPU Node Hours from January 17th, 2024 through January 15, 2025. This computing time was used to model Pu chalcogenide compounds and predict stable stoichiometries of selenides and tellurides. While waiting for the first wave of samples to be grown and delivered, the project developed and formalized a generalized representation for multiconfigurational ground state electronic configurations touched on in the original proposal. Specifically, the notation represents quantum mechanical superposition mixing of energy degenerate or near energy degenerate configurations. Combinatorial treatment combined with judicious selection of occupancy configurations based on observations of established ground states and energetic feasibility assumptions resulted in a statistical mechanics approach to describing multiconfigurational ground states. Entropy determination based on this work result in surprisingly reasonable conformity to known bulk molar entropies for solid elemental transition metals in the *d*- and *f*-blocks of the periodic table. These results were expanded upon to estimate the orbital occupancies of elemental Pu with plans to expand the methodology to calculations of orbital occupancies in transuranic compounds with comparison to direct measurements.

Science objectives for 2025- 2027: The atomic resolution imaging and STS spectra of $PuCoGa_5$ will be verified and reproduced under cryogenic conditions and published. Additional transuranic single crystal intermetallics and oxides will receive similar treatment as the $PuCoGa_5$ crystal. Molecular complexes will be imaged at cryogenic temperatures to isolate individual transuranic atoms and probe their electronic structures via STS and published. The computational modelling of Pu chalcogenides will be published. Attempts will be made to grow crystals of the Pu chalcogenide stoichiometries predicted to be stable by the modelling effort. Energetics will be incorporated into the entropic methods and expanded upon to include chemical bonding to better approach the experimentally determined entropy derived from thermodynamic experimental data of the transuranic compounds and published.

Publications supported by this project 2023-2025:

1. Benjamin Ray Heiner and Miles Frank Beaux II "Scanning Tunneling Spectroscopy of Surface-oxidized Gallium-stabilized δ-phase Plutonium", *Surfaces and Interfaces*, 2024, *55*, 105424, https://doi.org/10.1016/j.surfin.2024.105424.
2. Miles Frank Beaux II, "An under-approximation of entropy for elemental multiconfigurational ground state electronic structures" *AVS Quantum Science*, **2024**, *6*, 020801, https://doi.org/10.1116/5.0207956.
3. Miles Frank Beaux II, "An over-approximation of entropy for elemental multiconfigurational ground state electronic structures" *AVS Quantum Science*, **2023**, *5*, 020801, https://doi.org/10.1116/5.0146430.

LA-UR-25-22121

Actinyl Capture and Bond Activation by Electron Transfer and Acid/Base Chemistry

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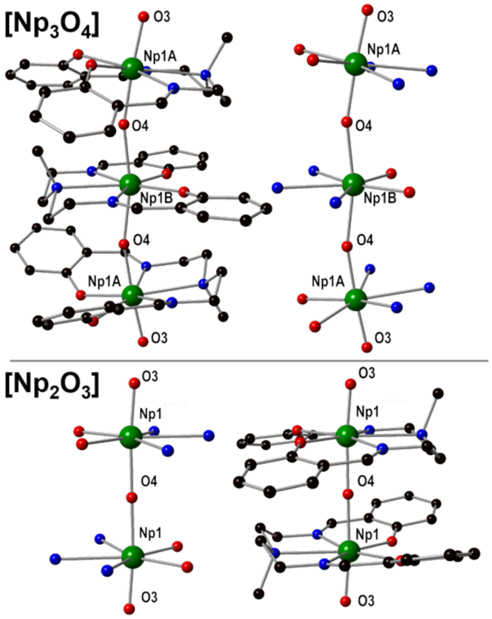
Collaborators: Jochen Autschbach (SUNY Buffalo), Miles Beaux (LANL), Robert Gericke (HZDR, Germany), David Grills (BNL), Ron Grimm (Worcester Polytechnic University), Timothy Jackson (University of Kansas), Henry La Pierre (Georgia Tech), Dmitry Polyansky (BNL), Tonya Vitova (Karlsruhe Institute of Technology, Germany), and Richard Wilson (ANL).

Overall research goals: The overall goal of this work is to develop a molecular-level understanding of An–O bond activation induced by redox processes, with an emphasis on defining the influence of ligand structure and actinide reduction potential on the outcomes of chemical reactivity. Consequently, the electron transfer (ET), acid/base chemistry, and proton-coupled electron transfer (PCET) properties of U, Np, and Pu complexes are being explored, with transuranium chemistry being conducted at Argonne National Laboratory (ANL). Products of ET and PCET reactivity are being characterized, including new examples of oxo-bridged multimetallic species. Time-resolved kinetic methodologies are targeted for development to interrogate the mechanisms underpinning An–O bond activation, as are measurements of electrode-surface-immobilized actinide species that represent an opportunity to address the f-electron challenge in an interfacial environment.

Significant achievements during 2023- 2025:

Generally speaking, recent work has involved development of chemical and electrochemical approaches to preparing redox-active molecular actinide complexes for study of electronic properties and reactivity. A signature focus of this work has been on macrocyclic and non-macrocyclic complexes containing actinyl (AnO_2^{n+}) motifs. At Kansas, several classes of heterobimetallic complexes have been developed in order to quantify the influence of secondary mono-, di-, and tri-valent cations on uranyl reduction potentials. Additionally, macrocyclic scaffolds have been developed that enable solution studies of uranyl species ligated by crown-ether-like moieties; these crown ether uranyl complexes display quite positively shifted reduction potentials and unique classes of reactivity that remain under active investigation. In particular, a platinum-templated crown ether complex of the uranyl ion has been prepared and characterized, and this complex features the most positive U^{VI}/U^{V} reduction potential yet measured for a non-oxo-functionalized uranyl system. Collaborative X-ray spectroscopy, magnetic studies, and quantum chemical calculations are underway to investigate the origins of the tunable actinide redox chemistry.

In 2023, collaborative work with Dr. Richard Wilson on transuranium chemistry conduced at ANL was initiated. This effort focused initially on developing neptunyl and plutonyl acetates as starting materials for further synthetic applications. Using these materials, monometallic Np(VI) and Pu(VI) complexes were prepared and their redox reactivity studied. A rich chemistry leading to more reduced, multimetallic species is being developed now, and influences of acid/base chemistry, proton-coupled electron transfer (PCET), and disproportionation reactivity are being mapped. Unusual examples of di-, tri-, and tetra-nuclear complexes of Np and/or Pu have been uncovered, affording new opportunities to study the reactivity of transuranium species in a controlled fashion. Distinctive features of the collaborative work include a focus on water-tolerant metal-organic coordination chemistry, parallelized application of electroanalytical and chemical redox methods to understand reactions involving electron transfer, and application of advanced spectroscopic measurements (Raman, infrared, and UV-vis-NIR) to interpret the chemical properties of prepared and/or observed species. A strategy being pursued in the transuranium chemistry is leveraging established and/or useful features of aqueous actinide chemistry to afford access to new organic-soluble complexes.



Molecular structures from single-crystal X-ray diffraction analysis of two examples of the multimetallic, oxo-bridged complexes being studied in this work are shown above. These complexes are denoted **[Np$_3$O$_4$]** and **[Np$_2$O$_3$]**. Outer-sphere solvent molecules, all hydrogen atoms, and the minor orientations of organic ligand backbone disorder are omitted for clarity.

Science objectives for 2025- 2027:

Three objectives are being pursued. (1) Macrocyclic ligand systems are under development for use in uncovering the factors driving the relationship between actinyl reduction potential and bond activation. (2) Understanding is being sought regarding the role of redox chemistry and proton-coupled electron transfer (PCET) in influencing and/or controlling the solution reactivity of molecular uranyl, neptunyl, and plutonyl complexes. Work with transuranium elements will be executed in collaboration with Dr. Richard Wilson at ANL. And, (3) work is underway to resolve the influence of *f*-electrons in the bonding and electronic properties of surface-confined and/or solvated molecular actinyl complexes through experiment and theory.

Selected publications supported by this project 2023-2025:

1. Riddhi R. Golwankar, T. Davis Curry II, Cecilia J. Paranjothi, and James D. Blakemore, *Inorg. Chem.* **2023**, *62*, 9765–9780*,* doi: 10.1021/acs.inorgchem.3c00084
2. Riddhi R. Golwankar, Alexander C. Ervin, Malgorzata Z. Makos, Emily R. Mikeska, Vassiliki-Alexandra Glezakou, and James D. Blakemore, *J. Am. Chem. Soc.* **2024**, *146*, 9597–9604, doi: 10.1021/jacs.3c12075.
3. Emily R. Mikeska, Richard E. Wilson, Asmita Sen, Jochen Autschbach, and James D. Blakemore, *J. Am. Chem. Soc.* **2024**, *146*, 21509-21524, doi: 10.1021/jacs.4c04613.
4. Emily R. Mikeska, T. Davis Curry, Richard E. Wilson, and James D. Blakemore, *Dalton Trans.* **2024**, *53*, 19126-19142, doi: 10.1039/D4DT02557A.
5. Riddhi R. Golwankar, Malgorzata Z. Makos, Nathalia Cajiao, Michael L. Neidig, Allen G. Oliver, Cynthia S. Day, Victor W. Day, Vassiliki-Alexandra Glezakou, and James D. Blakemore, *Inorg. Chem.* **2024**, *63,* 24542–24553, doi: 10.1021/acs.inorgchem.4c03349.
6. Emily R. Mikeska, Richard E. Wilson, and James D. Blakemore, *Chem. Eur. J.* **2025**, *31*, e202402963, doi: 10.1002/chem.202402963.

Uranium-Containing and Thorium-Containing Anions Studied by Photoelectron Spectroscopy

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Collaborators: Lan Cheng (Johns Hopkins U), David Dixon (U Alabama), Kirk Peterson (Washington State U), Bess Vlaisavljevich (U Iowa), Isuru Ariyarathna (LANL), Laura Gagliardi (U Chicago), Peng Yang (LANL), Puru Jena (Virginia Com U), Enrique Batista (LANL), Evangelos Miliordos (Auburn U)

Overall research goals: Our DOE grant (DE-SC002297) focuses on uranium-containing and thorium-containing anions studied in the gas phase (*in vacuo*) by negative ion photoelectron spectroscopy with the objective of obtaining electronic structure information primarily about the anions' corresponding neutral species. When conducted in partnership with theorists doing synergetic calculations, this work leads to a deeper understanding of the chemical bonding involved in the systems under study. Computational collaborations are integral to our work. We provide theorists with bench-mark experimental data that allows them to check and improve their methodologies, and they assist us in interpreting our data beyond that which can be gleaned from the spectra alone. The names of our ten theory collaborators are listed above. The uranium and thorium anionic systems that we study fall into three categories: 1. uranium-containing and thorium-containing molecular anions, 2. metal-metal bonding in actinide-transition metal, hetero-dimeric anions, 3. ligated anionic molecular, metal-metal, and uranyl complexes.

Significant achievements during 2023- 2025: Over the past two years, we have measured the negative ion photoelectron spectra of many anion systems. Beyond the 12 anionic systems listed in the titles of the five published papers shown below, we have also completed taking the anion photoelectron spectra of $U_3O_{8-10}^-$, $UO_2F_2^-$, UCl_{1-4}^-, UCN^-, $ThO_2(CO)_n^-$, $UO_2(CO)_n^-$, $ThO_2(CO)(H_2O)^-$, $U(CO)_{1-8}^-$, $Th(CO)_{1-8}^-$, UC_2^-, $US_{1,2}^-$ (submitted), USO^-, Th_n^-, U_n^-, $(UO_2)_n^-$, $UO_2(CH_3CO_2)_2^-$, $NdF_{1,2}^-$, $UOCl_2^-$, $UAu_{1,2}O^-$, $U_2Au_n^-$, $UPtO^-$, $UO_2(CO_2H)^-$, $U(NH_3)_n^-$, $Th(NH_3)_n^-$, $ThAuO_{1,2}^-$, and $UO_2(CH_3CO)_3^-$. We are especially excited to have been able to measure the spectra of $U_3O_8^-$, the famous 'yellow cake' of nuclear technology, and of ligated species that are relevant to separations science used in nuclear waste clean-up operations. For almost every system listed here, one of our computational collaborators (listed above) has shown strong interest in conducting calculations on them and collaborating with us in pursuit of a joint paper. This experiment/theory synergistic coordination is at the heart of our "business plan" for unveiling the electronic and geometric structural mysteries of these anions and therefore their neutral counterparts. The main constraint on progress is the relative speed at which our experiments and their calculations can be done. Given the complexities inherent in actinide systems, i.e., relativistic effects, large spin-orbital interactions, and the sheer number of electrons, calculations on them take a very high degree of skill and considerable time. Nevertheless, our theory collaborators are actively working the above systems and have already provided preliminary results of several of them.

Science objectives for 2025- 2027: While working with our computational collaborators to bring the above-described experimental/theoretical studies to publication, *we* will also continue our work in the three categories of uranium-containing and thorium-containing anions listed above. Target systems of particular interest include UB^- and ThB^-, where we have strong computational support in-waiting, and the ligated systems: $UO_2(OH)_2^-$, $U(C_5H_5)_n^-$, $UO_2(C_2O_4)_n^-$, and $U(C_8H_8)^-$, which we expect to make with our electrospray anion source. New objectives include fundamental studies of UF_6, the singly most important molecule in nuclear technology. Electron attachment to UF_6 is poorly understood, but our Rydberg electron transfer set-up is uniquely suited to explore this incredibly strange system. We will also make and explore the salts of UF_6. These form spontaneously by charge transfer, due to the unknown but likely very high electron affinity of UF_6. We will study them through their anions, e.g., $(Na^+UF_6^-)^-$. We hope to bracket the (unknown) electron affinity of UF_6 by using metals of different ionization energies to form (or not to form) their corresponding salts by charge transfer. We imagine that these incredibly stable salt systems may find roles in future nuclear reactors that utilize molten salts as both fissile reactants and coolants. Another very important objective going forward involves our participation in the use of a multi-purpose spectroscopic apparatus being built at PNNL. We hope to measure the electron affinity of species, such as PuO_2^- there.

Publications supported by this project 2023-2025:

1. M. Yuan, B.A.Tufekci, J. Xu, K. Foreman, M. Heaven, E. Batista, K. Bowen, P. Yang, "Structural and Electronic Properties of Anionic $(ThO_2)_n^-$ (n=2-4) Clusters" *Inorg. Chem.*, **2025**, https://doi.org/10.1021/acs.inorgchem.4c04954.
2. B.A Tufekci, T. Chiba, J. Xu, L. Cheng, K. Bowen, "Activation of H_2O by ThO_2^- : Experimental and Computational Studies" *J. Phys. Chem. A*, **2025**, https://doi.org/10.1021/acs.jpca.4c06238.
3. B.A. Tufekci, K. Foreman, J. Romeu, D. Dixon, K. Peterson, L. Cheng, K.H. Bowen, “Anion photoelectron spectroscopy and ab-initio studies of the UF^- anion", *J. Phys. Chem. Lett.*, **2024**, https://doi.org/10.1021/acs.jpclett.4c02845.
4. M. Marshall; Z. Zhu, T.-S. Nguyen, B.A. Tufekci, K. Foreman, K.A. Peterson, K. H. Bowen, "Anion photoelectron spectroscopy and chemical bonding of ThS_2^- and $ThSO^-$", *J. Chem. Phys.* , **2024**, https://doi.org/10.1063/5.0229157.
5. R. Harris, Z. Zhu, B.A. Tufekci, Deepika, P. Jena, K. A. Peterson, K. Bowen, "Electronic Structure and Anion Photoelectron Spectroscopy of Uranium-Gold Clusters UAu_n^-, n = 3 – 7", *J. Phys. Chem. A.*, **2023**, https://doi.org/10.1021/acs.jpca.3c03452.

Design of Molecular Spin Qubits Featuring Clock Transitions via Encapsulation of f-Elements in Polyoxometalates

Korey Carter, Principal Investigator

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Graduate Students: Primadi Subintoro, Ecem Çelik

Collaborators: Samuel Greer, Ben Stein, Stosh Kozimor (LANL), Stephen Hill (NHMFL), Jennifer Wacker (LBNL), Ellen Matson (Rochester), Pere Miro, Bess Vlaisavljevich (Iowa), Erik Henriksen (Wash U St. Louis)

Overall research goals: This project will establish an understanding of how to tune metal-ion crystal fields within f-element polyoxometalate (POM) complexes so that atomic clock transitions can be systematically harnessed for the design of electron spin qubits. This will involve the development of detailed magneto-structural correlations for families of lanthanide and actinide POM complexes so that mechanisms for spin-lattice and spin-spin relaxation can be ascertained as a function of changes in lattice packing, metal-ion symmetry, and spin-phonon coupling. POM complexes are structurally characterized via X-ray diffraction to extract detailed atomistic information that is the evaluated in the context of vibrational spectroscopy, magnetic susceptibility, electron paramagnetic resonance, and far-IR magnetospectroscopy results to improved experimental understandings of magnetism and spin dynamics in f-element systems.

Significant achievements during 2023- 2025:

Metal-ion crystal fields within POM complexes can be tuned by altering the composition and packing of the lattice species. We started work funded by this award in 2023 by asking the question of why a clock transition was observed in the holmium Lindqvist polyoxometalate (HoW_{10}) complex and not in other similar lanthanide species. The aim of this question was to develop and then apply this knowledge to the project objectives focused on developing POM chemistry for transuranic systems and engineering f-element POMs to systematically take advantage of clock transitions. Initial research involved synthesis and characterization of the entire series of lanthanide Lindqvist (LnW_{10}) POMs, which we hypothesized would tell us more about how POM properties change as a function of the identity of the metal center – knowledge that would be directly beneficial for translating U(IV) chemistry to Pu(IV). Interestingly, we found that more subtle structural changes had a bigger impact on vibrational properties of the POMs as packing of lattice cations and water molecules affected the extent to which metal-ion point group symmetry was distorted away from ideal D_{4d} geometry. Notably, the HoW_{10} complex was the only non-Kramers ion to adopt the structural polymorph featuring the smallest deviations from ideal symmetry, which provided insight into why clock transitions could not be accessed by switching out the lanthanide metal center within W_{10} POM complexes and led us to investigate to what extent we could control the composition and packing of the lattice around POM complexes.

Lattice counterions impact the structure and properties of U(IV) POM complexes. Based on the results from our initial study focused on LnW_{10} complexes, we aimed to include a wider range of charge balancing species in synthetic efforts moving forward. We first developed this chemistry for uranium(IV) Lindqvist (LnW_{10}) POMs where we have been able to synthesize POM complexes featuring varying combinations of alkali metals (from Li^+-Cs^+) in the lattice depending on the counterion source and reaction conditions. U(IV) is a non-Kramers actinide with a ground state that matches Ho(III) in $HoW_{10,}$ and we found that we could increase the extent of ion-pairing interactions with POM complexes when K^+, Rb^+, and Cs^+ were used as charge balancing counterions. These interactions perturb the U(IV) crystal field and initial manifestations of these changes were noted in vibrational spectroscopy results. Notably, multi-frequency high field continuous wave electron paramagnetic resonance (EPR) experiments, conducted in collaboration with Sam Greer and Ben

Stein (LANL), did not show any signals, which indicates that U(IV) cations in W_{10} complexes may feature singlet ground states, and magnetometry experiments to confirm these findings are in-progress.

Tuning the packing and composition of the lattice around POM complexes provides pathway to engineer metal-ion crystal fields. The synthetic procedures developed for UW_{10} complexes that allowed for tuning the composition of the lattice counterions have been applied to the HoW_{10} model system, resulting in eight new analogues of this species. In collaboration with Steve Hill (NHMFL) and Ben Stein and Samuel Greer (LANL) we have begun studying these POMs using X-band, Q-band, and multi-frequency high field EPR spectroscopy. Results thus far have revealed that *g*-tensor values for HoW_{10} complexes at 63 GHz move substantively as a function of charge balancing cation, while higher frequency measurements did not feature any signals indicating that transitions become purer (and therefore more forbidden) at higher fields. These results suggest the ground states of HoW_{10} complexes are connected by a degenerate perturbation that allows for activation of parallel mode $\Delta M_J = 0$ transitions. Indeed, parallel mode X-band peaks in the HoW_{10} complex with Rb^+ are observed and feature many similarities with the HoW_{10} complex from the literature that features an atomic clock transition. Initial pulsed EPR data has been collected and optimization processes to determine the ideal extent of diamagnetic dilution for this complex are underway, which will facilitate a comparison of how spin-lattice and spin-spin relaxation times for this complex change as a function of lattice composition and packing. Moreover, magnetometry data on HoW_{10} complexes has recently been collected, which confirmed that different combinations of lattice counterions (and their respective interactions with POM complexes) subtly impact ground state energy multiplets for each species via perturbations of the metal-ion crystal field.

Standing up plutonium chemistry capabilities at the University of Iowa. Beyond POM synthesis and characterization, our other major focus has been standing up laboratory space to conduct transuranic experiments, specifically with ^{237}Np and ^{242}Pu. This has involved engagement with the Radiation Safety Office at the University of Iowa as well as training graduate students in best practices for safely handling radioactive materials. Ahead of starting transuranic work, POM synthetic processes have been optimized, scaled down, and further refined to work from metal stock solutions rather than solid starting materials. Isotope recovery procedures to ensure that ^{237}Np and ^{242}Pu can be recycled after each round of experiments have been developed, and POM synthesis with plutonium commenced in January 2025.

Science objectives for 2025- 2027:

- Structurally and spectroscopically characterize POM complexes with ^{242}Pu and ^{237}Np featuring Lindqvist, Keggin, and Wells-Dawson anions
- Obtain pulsed EPR data on selected f-element POM complexes with accessible clock transitions to evaluate spin-spin relaxation times
- Use model Ho(III) systems to elucidate how changes in lattice packing impact spin-lattice relaxation times
- Develop understanding of how zero field splitting in POM complexes can be affected by metal-ion oxidation states using model $4f^7$ and $5f^7$ systems

Publications supported by this project 2023-2025:

1. Primadi J. Subintoro and Korey P. Carter, “Delineating the effects of counterions on the structural and vibrational properties of U(IV) Lindqvist polyoxometalate complexes” **In Revision** *Inorganic Chemistry,* **2025**, DOI: 10.26434/chemrxiv-2025-mg1dr.
2. Primadi J. Subintoro and Korey P. Carter, “Structural and vibrational properties of lanthanide Lindqvist polyoxometalate complexes” *Dalton Transactions,* **2024**, *53*(22), 9526-9539, DOI: 10.1039/D4DT00786G.

Spectroscopic Investigation of Electronic Structure in the Actinide Elements

Herman Cho, Principal Investigator

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Project Team: Eric Walter, Robert G. Surbella III
Postdoctoral Fellows: Khyati Anand, David Schnable, Ana Arteaga, Khusboo Rana, Trent Graham, Sejun Park (now at LANL)

Collaborators: Jochen Autschbach (University at Buffalo, State University of New York), Christopher Cahill (George Washington University), Lucas Ducati (University of São Paulo, Brazil), Tori Forbes (University of Iowa), Artem Gelis (University of Nevada Las Vegas), Amy Hixon (University of Notre Dame), Henry La Pierre (Georgia Institute of Technology), May Nyman (Oregon State University)

Overall research goals: The objective of this project is to map the evolution of electronic structure and chemical bonding in complexes containing elements spanning the pivotal sequence **Th-Pa-U-Np-Pu-Am-Cm**. where the members undergo a transformation that allows for significant covalency at lower Z. A key strategy in this project is to focus on structure types where multiple elements can be substituted into similar coordination environments to allow a systematic study of electronic structure as a function of atomic number. Through measurements of electric field gradients, hyperfine couplings, magnetic shieldings, nuclear spin couplings, and electronic energy levels we endeavor to quantify electron sharing between actinide centers and ligands and elucidate bond hybridization.

Significant achievements during 2023- 2025:

Actinide tetrafluorides. Fluorine-19 NMR spectra of An(IV)F_4 powders have been acquired in magnetic fields of 7.05 and 11.74 T over a range of temperatures. These reveal significant deviations from classic f-element behavior, providing direct evidence of strong electron correlations.

Uranyl NMR and NQR. Experimental ^{35}Cl and ^{37}Cl NMR spectra of $Cs_2UO_2Cl_4$, together with NQR measurements of the Cl EFG tensor have been used to evaluate electronic structure models calculated by density functional theory methods applied to different cluster sizes and with differential functionals. Similar methods have also been used to obtain EFG data for ^{85}Rb and ^{87}Rb in $RbUO_2(NO_3)_3$.

Synthesis and Optical Spectroscopy. In collaboration with J. Autschbach and L. Ducati, we used computational techniques to study the electron density distribution within Pu–Cl and Pu–NO_3 bonds to infer ionic vs. covalent character, while a natural localized molecular orbital (NLMO) analysis was used to investigate 5f, 6d, 6p, and 7s orbital participation.

Science objectives for 2025- 2027:

Actinide tetrafluorides. We seek evidence for electronic correlations and/or fluctuating valence states through variable temperature spectroscopic probes of the An-F interaction in AnF_4 (An = Th, U, Np, Pu, Am). Electron sharing and correlation effects are expected to increase as Z decreases, leading to deviations in measured internal fields from predictions based the assumption of localized, uncorrelated electrons on the metal center and the assumption of localized, uncorrelated metal electrons.

Actinide dioxides. The tetrafluorides and dioxides both have metals in the +4 oxidation state, but differ in one important respect: the dioxides have a cubic structure, which implies that atom–atom interactions in the dioxides will be exclusively of the scalar variety, unlike couplings in the tetrafluorides, which have an anisotropic component. Shifts or splittings may therefore be definitively attributed to interactions mediated by electron sharing such as Fermi contact.

High valent (An(VI), An(VII)) complexes. We are interested in measurements of EFG tensors, magnetic shieldings, and hyperfine shifts of ligand nuclei in high-valent actinide complexes to track the progression from covalency to electron localization as An traverses U to Am.

Optical spectroscopy of An(III) complexes, An = Am, Cm. We hypothesize that optical spectra will display shifts driven by the nephelauxetic effect, where red shifts correlate with more mixing of metal–

ligand orbitals and greater 5f-orbital participation and blue shifts exhibit the opposite trend. We are preparing a series of crystalline compounds, including salts, chelators, and MOFs, and will acquire electronic spectral energies and lifetimes, which will be interpreted in terms of electronic structure.

Selected publications supported by this project 2023-2025:

1. Graham, Trent R.; Castillo, Joel; Sinkov, Sergey; Gelis, Artem V.; Lumetta, Gregg J.; Cho, Herman, “Multiplicity of Th(IV) and U(VI) HEH[EHP] Chelates at Low Temperatures from Concentrated Nitric Acid Extractions.” *Inorg. Chem.* **2023**, *62*, 792-801. https://doi.org/10.1021/acs.inorgchem.2c03307
2. Arteaga, Ana; Nicholas, Aaron D.; Ducati, Lucas C.; Autschbach, Jochen; Surbella, III, R. Gian, “Americium Oxalate: An Experimental and Computational Investigation of Metal-Ligand Bonding.” *Inorg. Chem.* **2023**, *62*, 4814-4822. http://dx.doi.org/10.1021/acs.inorgchem.2c03976
3. Arteaga, Ana; Nicholas, Aaron D.; Sinnwell, Michael A.; McNamara, Bruce K.; Buck, Edgar C.; Surbella, R. Gian, III, “Expanding the Transuranic Metal-Organic Framework Portfolio: The Optical Properties of Americium (III) MOF-76.” *Inorg Chem* **2023**, *62*, 21036-21043. http://dx.doi.org/10.1021/acs.inorgchem.3c02742
4. Hall, Gabriel B.; Campbell, Emily L.; Bessen, Nathan P.; Graham, Trent R.; Cho, Herman; RisenHuber, Matthew; Heller, Forrest D.; Lumetta, Gregg J., “Extraction of Nitric Acid and Uranium with DEHiBA under High Loading Conditions.” *Inorg. Chem.* **2023**, *62*, 6711-6721. http://dx.doi.org/10.1021/acs.inorgchem.3c00288
5. Kohlgruber, Tsuyoshi A.; Surbella III, R. Gian, $(NH_4)_2[UO_2cl_4].2H_2O$, “A New Uranyl Tetrachloride with Ammonium Charge-Balancing Cations.” *Acta Crystallographica Section E* **2023**, *79*, 702-706. http://dx.doi.org/10.1107/S2056989023005753
6. Nicholas, Aaron D.; Arteaga, Ana; Ducati, Lucas C.; Buck, Edgar C.; Autschbach, Jochen; Surbella, R. Gian, “Insight into the Structural and Emissive Behavior of a Three-Dimensional Americium(III) Formate Coordination Polymer.” *Chem-Eur J* **2023**, *29*, 11. http://dx.doi.org/10.1002/chem.202300077
7. Park, Sejun; Walter, Eric D.; Soderquist, Chuck Z.; Sinkov, Sergey I.; Cho, Herman, “Temperature Dependence of Nuclear Quadrupole Resonance and the Observation of Metal-Ligand Covalency in Actinide Complexes: ^{35}Cl in $Cs_2UO_2Cl_4$.” *J. Phys. Chem. A* **2023**, *127*, 7. http://dx.doi.org/10.1021/acs.jpca.3c04657
8. Ramanathan, Arun; Walter, Eric D.; Mourigal, Martin; La Pierre, Henry S., “Increased Crystal Field Drives Intermediate Coupling and Minimizes Decoherence in Tetravalent Praseodymium Qubits.” *J. Am. Chem. Soc.* **2023**, *145*, 17603-17612. http://dx.doi.org/10.1021/jacs.3c02820
9. Herder, Jordan A.; Kruse, Samantha J.; Nicholas, Aaron D.; Forbes, Tori Z.; Walter, Eric D.; Cho, Herman; Cahill, Christopher L., “Systematic Study of Solid-State U(VI) Photoreactivity: Long-Lived Radicalization and Electron Transfer in Uranyl Tetrachloride.” *Inorg Chem* **2024**, *63*, 4957-4971. http://dx.doi.org/10.1021/acs.inorgchem.3c04144
10. Park, Sejun; Surbella, R. Gian; Sinkov, Sergey I.; Philips, Adam B.; Autschbach, Jochen; Cho, Herman, “Electric Field Gradients at Rubidium Sites in Rubidium Uranyl Nitrate and Quadrupole Moments of ^{85}Rb and ^{87}Rb.” *Chem. Phys.* **2024**, *576*, 6. http://dx.doi.org/10.1016/j.chemphys.2023.112094
11. Arteaga, Ana; Arino, Trevor; Moore, Guy C.; Bustos, Jenna L.; Horton, Matthew K.; Persson, Kristin A.; Li, Jun; Stickle, William F.; Kohlgruber, Tsuyoshi A.; Surbella III, R. Gian; Nyman, May, “The Role of Alkalis in Orchestrating Uranyl-Peroxide Reactivity Leading to Direct Air Capture of Carbon Dioxide,” *Chem. Eur. J.* **2024**, *30*, e202301687. https://doi.org/10.1002/chem.202301687
12. Hastings, Ashley M.; Williams, Ashley; Surbella III, Robert G.; Hixon, Amy E.; Arteaga, Ana; “Structural characterization of a new samarium–sodium heterometallic coordination polymer,” *Acta Cryst. E* **2024**, *80*, 267-270. https://doi.org/10.1107/S2056989024001051
13. McCusker, Thomas L.; Vanagas, Nicole A.; Szymanowski, Jennifer E. S.; Surbella III, Robert G.; Bertke, Jeffery A.; Arteaga, Ana; Knope, Karah E., “Elucidating trends in synthesis and structural periodicity in a series of tetravalent actinide–oxo hexamers,” *Cryst. Eng. Comm.* **2025**, *27*, 507-515. **https://doi.org/10.1039/D4CE01042F**
14. Asmussen, R. Matthew; Westesen, Amy M.; Alvarez, Christian; Peterson, Reid A.; Cordova, Elsa; Cho, Herman; Branch, Shirmir D.; Walter, Eric D.; Hall, Gabriel B.; Orgnic, Andrew L.; Carney, Andrew M.; “The simultaneous removal of technetium and iodine from Hanford tank waste,” *Chem. Eng. J.* **2024**, *490*, 151449. https://doi.org/10.1016/j.cej.2024.151449

Modulating Actinide Redox Chemistry with Metal Oxide Electrodes

Christopher Dares, Principal Investigator

Department of Chemistry and Biochemistry, Florida International University, Miami, FL

Graduate Students: Jeffrey McLachlan, Gabriela Ortega, Mariel Morales Duque, Barbara Garcia, Rodrigo Lacau

Collaborators: Stosh Kozimor (LANL); Thomas Albrecht (CSM)

Overall research goals: To develop new ways to prepare *f*-elements in unusual oxidation states and to subsequently study these compounds.

Significant achievements during 2023- 2025:

In follow up work to our achievement to quantitatively oxidize Am(III) to Am(VI), we have demonstrated the quantitative photoelectrochemical oxidation of Np(V) to Np(VI). This is simpler oxidation, but it shows that our electrodes are extensible to other actinides.

We performed further surrogate studies involving the photoelectrochemical oxidation of Ce(III) to Ce(IV) with our photoanodes and have a paper submitted for publication to ACS Applied Materials and Interfaces that showcases a method to extract Ce based on a selective photoelectrochemical deposition step followed by an electrochemical stripping step. The electrode in this case can be regenerated for successive deposition and stripping cycles.

Our efforts to fabricate visible light absorbing electrodes that facilitate redox reactions was a large challenge this year. We expended a large effort on iron oxide-based electrodes, which after trying different conditions, did not work. Thankfully, our bismuth vanadate layered TiO_2 electrodes absorb visible light and photochemically facilitating the oxidation of Ce(III) to Ce(IV) using visible light (455 nm). These electrodes photocatalytically oxidize UO_2 to UO_2^{2+} with visible light, which suggests they are good candidates for TRU photo-electrochemical oxidations.

Gabriela Ortega successfully defended her PhD in Fall 2024. Prior to her defense, she completed a 6-month internship at LANL working with Stosh Kozimor. This work focused on characterizing a uranium and neptunium complex with a Schiff-base ligand. When coordinated to UO_2^{2+} the complex, in the absence of water or oxygen, there is a reversible U(VI/V) couple which is cathodically shifted 0.63 V relative to the solvent-complex. These complexes effectively shut down the disproportionation of U(V) by disrupting the formation of cation-cation interaction species. If water or oxygen are present, an aquo or dioxygen complex is formed and results in irreversible reductions to a new U(V) species which are likely the result of proton-coupled electron transfers. When the Schiff-base ligand is coordinated to Np(VI), the result is an anodic shift of 0.11 V. This difference in direct of redox potential shift upon complexation is highly unusual. Currently there are two hypotheses to explain this. One is that Np complexes may not be mono-metallic (crystal structure of the U complex has a single uranium center, while no crystal data of the Np complex were acquired). This hypothesis is based on similar features observed in other neptunium complexes. An alternative hypothesis is that upon complexation of Np(VI) to the Schiff base ligand, there is an intermolecular redox change, where Np(VI) is reduced to Np(V) and the ligand is oxidized by one electron to a stable radical. The oxidized ligand therefore anodically shifts the Np(VI/V) couple. This hypothesis is consistent with XANES data which suggest the Np-Schiff base complex is more consistent with Np(V) than Np(VI). EPR studies are proposed to establish additional evidence. The results of this work are currently written as a paper for *Inorganic Chemistry* but is pending additional work related to the structure of the Np complex.

We have developed a new hydroxypyridinone (HOPO) ligand that includes a phosphonic acid group. In solution, the HOPO and phosphonic acid groups bind to *f*-elements. The phosphonic acid can also be used to anchor the ligand to a metal oxide surface. While our work with this ligand is progressing, it appears to operate differently than tripolyphosphate (P_3), favoring the formation of U^{4+} over UO_2 even in mildly acidic (pH 4.8) conditions. The binding affinity for uranium with HOPO is more oxidation state specific than P_3, which will improve catalytic turnover since the binding site won't be occupied by the oxidized product.

Science objectives for 2025- 2027:

We would like to continue our work with the phosphonic acid functionalized HOPO ligand. We will perform solution titrations (NMR & UV-vis) to evaluate the mode(s) of binding and use electrochemistry to evaluate changes in oxidation state stability with uranium (as UO_2^{2+} and as U^{4+}).

We would also like to continue the work we are doing related to the photoelectrochemical oxidation of actinides using ligand modified electrodes. This will be our first foray into ligand modified electrodes for **photo**electrochemical work as all previous photoanodes have used bare metal oxide surfaces. We will start with tripolyphosphate and other previously established ligands including POMs, dipyrazinylpyrazines, and methyl diphosphonate.

We would also like to continue the work we have been doing with Stosh Kozimor at LANL related to molecular actinide species, though would like to move towards establishing a platform to study X-ray absorption spectra of actinide species coordinated to ligands at the surface of an electrode. We would also like to commence studies on the use of photoelectrochemical oxidation state adjustment of f-elements using ligand modified electrodes. All previous studies have been done with metal oxides without ligands. The inclusion of ligands at the surface is expected to shift redox potentials cathodically making the combined photo-electrochemically driven oxidations easier since weaker oxidants are required. A major goal here is to eventually use visible light to perform difficult oxidations.

We are still struggling to find a suitable lab to perform electrochemical and photoelectrochemical work with TRU elements as work-controls in place at INL make it effectively impossible to carry out.

Publications supported by this project 2023-2025:

Jian Li, Zhengqiu Yang, Xiao Guo, Xinghua Guo, Yuzhuo Sun, Dan Liang, Guiyan Zhang, Yusuke Tamaki, Xun Chen, Christopher Dares, Thomas J. Meyer, Degao Wang "Visible Light Driven Water Oxidation Initialized by Surface Bound Ru^{IV}=O Catalyst with Chloride as Mediator" *J. Amer. Chem. Soc.* **2025** (In review).

Alain R. Puente Santiago, Tianwei He, Md Ariful Ahsan, Shery Welsh, Mohamed Noufal, Edison Huixiang Ang, Jamie Warner, Christopher Dares, "An Atomistic View of the Dynamic Behaviour of Single Atom/Nanocluster Electrocatalytic Active Sites" *Energy and Environ. Sci.* **2025** (in review).

Joy Spears, Mina Shawky Adly, Edison Castro, Alain R. Puente Santiago, Luis Echegoyen, Tianwei He, Christopher Dares, and Mohamed Noufal "Understanding the Effects of Adduct Functionalization on C60 Nanocages for the Hydrogen Evolution Reaction" *Nanoscale Horiz.* **2025**, 10, 719-723. https://doi.org/10.1039/D4NH00586D

Christopher Dares "Polyoxometalate derivatized metal oxide electrodes" US Patent 11725293B2 **2023**.

Polyoxometalate Chemistry with Heavy Elements

Gauthier Deblonde, Principal Investigator

Nuclear and Chemical Sciences division, Glenn T. Seaborg Institute, Lawrence Livermore National Laboratory, Livermore, CA.

Postdoctoral Researchers: Ian Colliard (LLNL), Ashley Hastings (LLNL).

Collaborators: May Nyman (OSU), Christopher Colla (LLNL), Derrick C. Kaseman (LLNL).

Overall research goals:

This DOE Early Career project's overarching approach is to leverage a class of molecules called polyoxometalates (POMs) to advance the heavy element chemistry field. The main goals of the project are: 1) overcome the limitations inherent to classic radiochemical techniques (e.g., high research isotope consumption; low throughput); 2) unlock novel coordination chemistry and spectroscopic tools for heavy elements by leveraging POMs' peculiar chemistry relative to traditional molecules, 3) leverage these novel compounds to decipher the electronic, spectroscopic, and magnetic properties of actinide and lanthanide elements, and 4) develop efficient POM-driven radiochemical separations for heavy elements.

Significant achievements during 2023- 2025:

✓ Efficiency of heavy element compound syntheses and characterization improved by a 10,000%

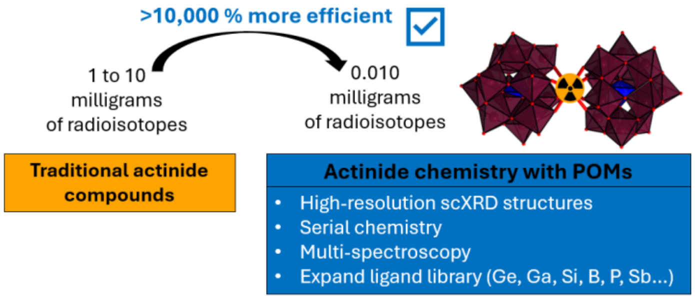

Fig. 1. POMs ligands for heavy elements allows for the efficient use of research isotopes and unlock the possibility of doing serial chemistry with actinides. More info in refs 1, 2, 3, 4, 7 and 8.

Using POMs as ligands for heavy elements allows for the efficient use of research isotopes and unlocks the possibility of doing serial chemistry. During these first ~18 months of the project, our team was able to obtain six new single crystal XRD structures with curium and six with americium, plus more with other actinides to be submitted for publication. The POM-based microscale technique developed at LLNL has so far yielded 9 new curium compounds, 6 new americium compounds (all characterized via scXRD, Raman, UV-vis absorbance, and luminescence when applicable) — while only requiring ~0.15 milligrams of the two actinides combined (^{243}Am and $^{246/248}$Cm) — demonstrating the efficiency of our method. The behavior of the actinide POM compounds departs from the traditional ones (e.g., organometallics) by their site symmetry, lattice organization, and also spectroscopic properties. The POM approach is now being implement to look at systematic trends across the f-block. We now routinely synthesize transuranic POM compounds, affording a unique platform to study heavy elements but also to train the next generation of transuranic chemists.

Highlights for this period include:

- Successful synthesis & characterization of the first Peacock–Weakley POM compound. containing a transplutonium element (curium; $NaCs_8[Cm(W_5O_{18})_2]\cdot 14H_2O$).
- Successful synthesis & characterization of the first americium(III) POM compounds.
- Expansion of the ligand library for heavy elements: successful synthesis & characterization of transplutonium compounds with ligands containing B^{3+}, Ga^{3+}, Sb^{3+}, Si^{4+}, Ge^{4+}, P^{5+}.

✓ Unlock study of the electronic properties of actinides beyond the first-coordination sphere.

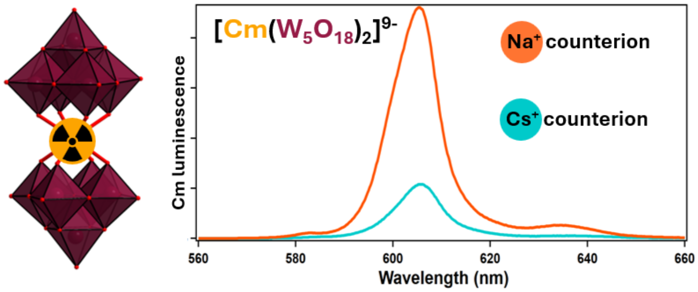

Fig. 2. A curium complex with a Weakley-Peacock polyoxometalate was isolated. Relative to the analogous europium complex, curium luminescence is impacted differently by the alkali counter ions (here, Na^+ vs. Cs^+). See refs 1, 2, 3, and 8.

Traditional approaches for metal-ligand systems often focus on the first coordination sphere of the studied metal, such as determining metal-oxygen bond distances via single crystal XRD structures or via EXAFS. While these approaches have been used at length, they often ignore the rest of compounds and may miss some long-range effects coming from the central metal ions (here, an heavy element cation). We here leverage the POM platform to unravel subtle but compounding effects that the actinides have on the overall compounds' structures and their spectroscopic properties. Our serial approach unraveled distinct trends for americium and curium versus their lanthanide counterparts, both in the solution-state and solid-state. For example (Fig. 2), cesium ions alter the luminescence properties of $[Cm(W_5O_{18})_2]^{9-}$ more than sodium ions but, $[Eu(W_5O_{18})_2]^{9-}$ exhibits the opposite behavior. More examples will be given during this presentation.

Science objectives for 2025- 2027:

- Expand POM microscale approach to other radioisotopes.
- Continue leveraging POMs to harvest structural and spectroscopic information on actinides.
- Develop separation strategies based on POMs.

Publications supported by this project 2023-2025:

1. I. Colliard & G.J.-P. Deblonde. "Characterization of the first Peacock–Weakley polyoxometalate containing a transplutonium element: curium bis-pentatungstate $[Cm(W_5O_{18})_2]^{9-}$." *Chemical Communication*, **2024**, 60, 5999-6002. DOI: 10.1039/D4CC01381F. Front cover article.

2. I. Colliard & G.J.-P. Deblonde. "Polyoxometalate Ligands Reveal Different Coordination Chemistries Among Lanthanides and Heavy Actinides." *JACS Au*, **2024**, 4, 7, 2503-2513. DOI: 10.1021/jacsau.4c00245. Supplementary cover article.

3. I. Colliard & G.J.-P. Deblonde. "From+ I to+ IV, alkalis to actinides: Capturing cations across the periodic table with polyoxometalate ligands." *Inorganic Chemistry*, **2024**, 63, 16293-16303, DOI: 10.1021/acs.inorgchem.4c02254

4. I. Colliard & G.J.-P. Deblonde. "Isolation and characterization of a new polyoxometalate ligand, $H_3SbW_{14}O_{50}{}^{10-}$, and its interactions with f-elements." *Chemical Communication*, **2025**, 61, 941-944, DOI: 10.1039/D4CC05558F.

5. G.J.-P. Deblonde & I. Colliard. "Synthesis and structural characterization of a hydrated sodium–caesium tetracosatungstate(VI), $Na_5Cs_{19}[W_{24}O_{84}]\cdot 21H_2O$." *Acta. Cryst. E*, **2024**, 80, 6, 667-670. DOI: 10.1107/S2056989024004778.

6. G.J.-P. Deblonde & I. Colliard. "Crystal structure of hexachlorothallate within a caesium chloride–phosphotungstate lattice $Cs_9(TlCl_6)(PW_{12}O_{40})_2\cdot 9CsCl$." *Acta. Cryst. E*, **2024**, 80, 7, 721-724. DOI: 10.1107/S2056989024005565.

7. A. M. Hastings M., I. Colliard, D. C. Kaseman, C. A. Colla, G.J.-P. Deblonde. "Unlocking Neptunium(IV) Aqueous Chemistry via Polyoxometalate-Mediated Reduction and Stabilization." *Under review.*

8. I. Colliard & G.J.-P. Deblonde. "Similar but different: structural and spectroscopic characterization of series of neodymium, europium, americium, and curium coordination complexes." *Under review; revision stage.*

Chemistry at the Extreme Edges of the Periodic Table: Elucidating the Chemical Properties of the Superheavy Elements

John Despotopulos, Principal Investigator

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Collaborators: Ken Gregorich, Tony Huynh, Kelly Kmak, Roger Henderson, Carlos Valdez, William Kerlin, Tashi Parsons-Davis, Jackie Gates (LBNL), Laura Gagliardi (U. Chicago)

Overall research goals:

The periodic table is a working document that arranges elements into groups (columns) and periods (rows) based on their fundamental chemical properties. The position of elements on the periodic table corresponds to trends in chemical behaviour, atomic size, and electronic configurations. In particular, elements within the same group, homologs, have similar chemical properties. The correct placement of newly discovered elements is vital to preserving the periodic table in its current form as a graphical description of chemical properties. However, when a new transactinide element (atomic number > 103) is discovered, it has traditionally been placed in the periodic table solely based off its atomic number, Z, the number of protons in the nucleus. Due to relativistic effects, which increase with Z^2, this placement may not be correct as these superheavy elements may not behave similarly to the direct homologs in the same group. Only through studying the chemical properties of these elements can their correct position on the periodic table be confirmed.

The goal of this proposed research is to perform the first aqueous-phase chemical studies of Cn. This will incorporate both experiments to elucidate the chemical properties and theoretical descriptions, through collaborations with the University of Chicago, to fully understand and interpret the experimental results. Using the results from these ground-breaking experiments, further experiments can be fielded through a first-of-its-kind US-based program to explore the properties of the heaviest elements on the periodic table in novel ways integrating both theory and experiments.

Significant achievements during 2023- 2025:

This is a project which regained funding late FY24. Thus far a position and energy sensitive flow-through liquid scintillation detector has been built and is undergoing testing for integration with a microfluidic chemistry system for on-line studies of the transactinides. Synthesis of thiacrown ethers, molecules of interest for Cn and Fl chemistry, has been accomplished with gram quantities available for on-line experiments.

Science objectives for 2025- 2027:

In the coming year we plan to test the liquid chemistry system and detector off-line with homologs of Cn. A recoil transfer chamber for collecting transactinides and delivering them to the chemistry apparatus will be designed and built with collaboration at LBNL. In future years, we will integrate the chemistry and detection system with the BGS at the 88-inch cyclotron at LBNL and test the system with homologs of Cn produced on-line before proceeding with experiments on transactinides.

Computational Studies of Structure, Thermodynamic Properties, and Reactivity Across the Actinide Row

David A. Dixon, Principal Investigator

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Postdoctoral Fellows: João G. F. Romeu, Kayleigh Barlow, Visiting graduate student: Felipe Dutra
Collaborators: Kirk Peterson (WSU), Richard Wilson (ANL), Jennifer Pore (LBNL), Kit Bowen (Johns Hopkins), Karah Knope (Georgetown)

Overall research goals: The overall goal is to use the most reliable computational chemistry tools available to make predictions to help explain and then to guide experimental results leading to an improved understanding of the actinides and their chemistry. A careful treatment of all important effects including multi-reference character, scalar relativistic effects, additional electron correlation, and spin-orbit coupling is incorporated to predict bond energies (BDEs), heats of formation, ionization energies (IEs), electron affinities, redox properties, and Brønsted and Lewis acidities and basicities as these quantities help to control actinide molecular structures and reactivity. The methods are chosen to fit the size of the system ranging from small molecules to large, solvated clusters.

Significant achievements during 2023-2025: Calculations of the bonding of second row atoms (Li to F) to U for $UX^{0/+/-}$ have been completed at the MRCI and Feller-Peterson-Dixon (FPD) levels. The same calculations were made for neutral WX to enable a detailed comparisons of the properties for UX with WX. For WX, the BDE is greater than for UX for X = Li to N and lower than BDE(UX) for X = O and F, mostly due to the higher IE of W than U as ionic character becomes more important going from Li to F. This work is in collaboration with the Peterson and Bowen groups.

The properties of M_2O_5 for M = V, Nb, Ta, and Pa were predicted and showed that Pa clearly has actinide behavior. The Pa=O bond is predicted to be the strongest in this series. The heats of formation of the MF_5 species were calculated to provide additional benchmarks.

Bond dissociation energies (BDEs) and spectroscopic parameters for the ground states of YbO and NoO were calculated at the Brueckner doubles (BD(T)) level based on the closed-shell configurations $Yb^{2+}(4f^{14})O^{2-}(2p^6)$ and $No^{2+}(5f^{14})O^{2-}(2p^6)$. For YbO, the BD(T) BDE (3.93 eV) and vibrational frequency (686.3 cm^{-1}) are consistent with the experiment. For NoO, the calculated BDEs are 3.07 eV (BD(T)) and 3.08 eV (CCSD(T)) and are expected to be good to ±3 kcal/mol (±0.13 eV). Potential energy curves (PECs) for the spin-orbit (Ω) states associated with the $f^{13}s^1$ configurations of YbO and NoO were calculated at the SA-CASSCF/SO-CASPT2/aQ-DK level. PECs considering both the $f^{13}s^1$ and f^{14} configurations were calculated at this level as the ground states are expected to be contain both configurations.

An extensive set of calculations using DFT and CCSD(T) have been performed on $An^{2+}(N_2)_x$ and $An^{2+}(H_2O)_x$ for up to x = 6 and An = Ac and No in support of the experimental efforts at LBNL. The binding energies for the H_2O complexes are larger than for the N_2 complexes. The binding energies for No^{2+} are in general larger than for Ac^{2+} consistent with No^{2+} being a harder dication.

We have completed an extensive study of redox potentials of the actinides U - Am in H_2O in a broad range of oxidation states under both acid and base conditions. In most cases, the calculated redox potentials are within 0.2 V of experiment. Estimated values in the literature are not reliable for unknown oxidation states. This work has been extended to Ac, Th, and Pa in acid with similar results. The calculations were done for oxidation states from 0 up to VII (as appropriate) using the B3LYP functional in most cases, Stuttgart small core pseudopotential basis sets for the actinides, and explicit (30 H_2O molecules)/implicit treatment of the aqueous solvent using the self-consistent reaction field COSMO and SMD approaches for the implicit solvation. This work provides the first complete set of the redox potentials of actinides up to Am in acidic aqueous media starting from the bulk up to the +VII oxidation state

Science objectives for 2023-2025: We will complete a study of the hydrolysis of $(ThO_2)_n$ nanoclusters for up to n =6 with complete hydrolysis for up to n = 4 and half hydrolysis for n = 5 and 6. We will complete a study of AnF_x with one F atom beyond the normal maximum valence building on the novel structure found for ThF_5. This will be extended to the cations of AnF_x in the maximum oxidation state to determine if this novel structure controls the IE. We will examine other compounds of No with F and O in different oxidation states in collaboration with the LBNL group and compare the results to the corresponding Yb compounds. We will calculate the properties of $M^{2+}(N_2)_x$ and $M^{2+}(H_2O)_x$ for up to x = 6 and M = Ra and Lw in support of the experimental effort at LBNL as well as small molecule versions of these metal ions with O and F as ligands. We will calculate the properties of Pa with first row atoms to better understand the periodicity of the actinides in collaboration with the ANL group. Other projects with the ANL group include interactions of DMSO with different actinides and properties of Pu complexes. We will calculate the properties of neutral and anionic ThO_2 interacting with CO molecules with the Bowen group as well as the properties of other anionic and neutral Th and U species to aid in interpreting the experimental spectra. We will complete the prediction of redox potentials in acidic aqueous media for Cm to Lr in various oxidation states. We will complete a study of the interaction of two and three F^- ligands with AnO_2^{2+} building on our AnO_2^{2+} work. A goal is to compare the oxide vs. fluoride 'walls' in terms of actinide complex stability as well as on structures.

Publications supported by this project 2023-2025

1. Lontchi, E.; Mason, M. M.; Vasiliu, M. Dixon, D. A. Prediction of the Structures and Heats of Formation of MO_2, MO_3, and M_2O_5 for M = V, Nb, Ta, Pa. *PhysChemChemPhys*, **2023**, *25*, 8223-8970. DOI: 10.1039/D3CP00380A
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3. Lontchi, E.; Vaslilu, M.; Dixon, D. A. Hydrolysis Reactions of the High Oxidation State Dimers Th_2O_4, Pa_2O_5 U_2O_6 and Np_2O_6. A Computational Study. *J. Phys. Chem. A*, **2023**, *127*, 6732–6748, DOI: 10.1021/acs.jpca.3c03455
4. Shore, M. C.; Nicholas, A. D.; Edwards, K. C.; de Melo, G. F.; Bertke, J. A.; Dixon, D. A.; Knope, K. E. Structural Chemistry of Penta- and Hexanitrato Thorium(IV) Complexes Isolated Using N-H Donors. *CrystEngComm*, **2024**, *26*, 1380–1398, DOI: 10.1039/D3CE01319G
5. Dutra, F. R.; Vasiliu, M.; Gomez, A. N.; Xia, D.; Dixon D. A. Prediction of Redox Potentials for U, Np, Pu, and Am in Aqueous Solution. *J. Phys. Chem. A*, **2024**, *128*, 5612-5626. DOI: 10.1021/acs.jpca.4c02902
6. Romeu, J. G. F.; Hunt, A. R. E.; de Melo, G. F.; Peterson, K. A.; Dixon, D. A. Energetic and Electronic Properties of $UO^{0/+/-}$ and $UF^{0/+/-}$. *J. Phys. Chem. A*, **2024**, *128*, 5586-5604. DOI: 10.1021/acs.jpca.4c02845
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8. Tufekci, B. A.; Foreman, K.; Romeu, J. G. F.; Dixon, D. A.; Peterson, K. A.; Cheng, L.; Bowen, K. H. Anion Photoelectron Spectroscopy and Ab-Initio Studies of the UF^- Anion. *J. Phys. Chem. Lett.* **2024**, *15*, 48, 11932–11938. DOI: 10.1021/acs.jpclett.4c02845
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10. Romeu, J. G. F.; Dixon, D. A. Energetic and Electronic Properties of AcX and LaX (X = O and F). *J. Phys. Chem. A* **2025**, *129*, 1396-1410. DOI: 10.1021/acs.jpca.4c08358
11. Dutra, F. R.; Dixon, D. A. Prediction of Redox Potentials for Different Oxidation States of U, Np, Pu, and Am in Alkaline Aqueous Solution. *J. Phys. Chem. A* **2025**, *129*, WEB ASAP, DOI: 10.1021/acs.jpca.4c08794

Exploring the Fundamental Chemistry of Actinide Metal Complexes

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Overall research goals: The goal of this project is to expand fundamental knowledge of actinide chemistry by exploring the synthesis, physical properties, and reactivity of complexes of uranium and thorium in the +2 and +3 oxidation states with collaborative extensions to transuranium chemistry.

Significant achievements during 2023-2025: Only two areas are described. A. The Importance of the Triisopropylsilyl-Substituted Cyclopentadienyl Ligand, $[C_5H_4(Si^{i}Pr_3)]^{1-}$, $(Cp^{TIPS})^{1-}$. The first crystallographically characterized molecular Th(II) complex was reported in 2015 as part of this project and was isolated employing a *di-silyl*-cyclopentadienyl ligand, $[C_5H_3(SiMe_3)_2]^{1-}$, $(Cp'')^{1-}$, in the complex, $(Cp''_3Th^{II})^{1-}$ [*Chemical Science* **2015**, *6*, 517]. No other examples of Th(II) complexes were isolated *in the next eight years*, until our recent discovery of $[K(crypt)][Cp^{TIPS}{}_3Th^{II}]$ (crypt = 2.2.2-cryptand) using the *mono-silyl*-cyclopentadienyl $[C_5H_4(Si^{i}Pr_3)]^{1-}$ ligand, $(Cp^{TIPS})^{1-}$. This new Th(II) complex was synthesized by reducing $Cp^{TIPS}{}_3Th^{IV}Br$ with excess potassium graphite (KC_8) [2].

Furthermore, the $(Cp^{TIPS})^{1-}$ ligand has provided the first *mono-silyl*-cyclopentadienyl *Th(III)* complex of any kind: $Cp^{TIPS}{}_3Th^{III}$ [3]. Although the *di-silyl*-substituted Th(III) complex Cp''_3Th^{III} was known since 1986, the *mono-silyl*-substituted Th(III) analog, $[C_5H_4(SiMe_3)]_3Th^{III}$, is too unstable to be isolated, even though the *mono-silyl*-substituted U(III) analog, $[C_5H_4(SiMe_3)]_3U^{III}$, was crystallographically characterized in 1986.

The large effect of changing the SiR_3 substituent from R = CH_3 to $CH(CH_3)_2$ was unexpected since the SiR_3 groups are distant and point away from the Th(III) and Th(II) ions. The demonstration that such a small change in a distant part of the ligand has such a large effect on the thermal stability of Th(III) and Th(II) complexes suggests that careful choice of ligands may open up new actinide chemistry and allow more control in separations technology.

B. Unexpected Formation of a Th(III) $(Arene)^{2-}$ Complex. We previously found that the addition of simple alkali metal salts, MX (M = Li, Na, K; X = H, Cl, Me) to the Th(III) complex, Cp''_3Th^{III}, generated the Th(II) complex, $(Cp''_3Th^{II})^{1-}$, and a Th(IV) byproduct, $Cp''_3Th^{IV}X$ [*Chem. Comm.* **2022**, *58*, 5289]. This was surprising since the MX reagents are not strong reducing agents like the KC_8 originally used to synthesize $(Cp''_3Th^{II})^{1-}$. This result suggested the existence of a highly reactive intermediate like $(Cp''_3Th^{III}X)^{1-}$.

While trying to isolate $(Cp''_3Th^{III}Me)^{1-}$, we have identified a new Th(III) reduced arene complex, namely $Cp''_2Th^{III}(C_6H_6)Th^{III}Cp''_2$ [7]. This can be synthesized not only from $Cp''_3Th^{IV}Me$ and potassium graphite (KC_8), but also from Cp''_3Th^{III} and MeLi. The reduction of benzene in these reactions is surprising since Th(III) complexes are typically not strong enough reductants to reduce arenes. Moreover, the more reducing Th(II) complex, $(Cp''_3Th^{II})^{1-}$, does not reduce arenes! Clearly, there is a reactive intermediate present in this thorium system that has no precedent.

Science objectives for 2025-2027: Only two research thrusts are described. I. $(Cp^{TIPS})^{1-}$ Chemistry. The surprising chemistry delivered by the $[C_5H_4(Si^iPr_3)]^{1-}$ ligand will be explored further. The reactivity of $[K(crypt)][Cp^{TIPS}{}_3Th^{II}]$ will be compared with that of $[Cp''_3Th^{II}]^{1-}$, the only other complex of a $6d^2$ ion in the periodic table. The synthesis of the U(II) analog, $[K(crypt)][Cp^{TIPS}{}_3U^{II}]$, as well as rare-earth metal complexes $[K(crypt)][Cp^{TIPS}{}_3Ln^{II}]$ will be pursued for comparisons of reactivity as a function of electron configuration and metal size. Extension of this chemistry to the transuranium elements will be pursued since small scale synthesis conditions have been developed for the $Cp^{TIPS}{}_3M^{III}$ complexes of M = Th, U, and La with protocols to obtain crystalline products quickly to avoid radiation decay.

II. Sulfur Donor Atom Ligands. The synthesis of An(III) and An(II) complexes of second row main group donor atoms will be pursued. Low oxidation state actinide chemistry is dominated by ligands with either C, N, or O donor atoms. New uranium and thorium complexes of the sterically bulky terphenylthiolate ligand $[SC_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}^iPr_3)_2]^{1-}$ $[(SAr^{iPr6})^{1-}]$ will be synthesized and their reactivity explored to evaluate second row donor atom effects.

Some of the *Publications supported by this project in 2023-2025:*

1. Justin C. Wedal, Jesse Murillo, Joseph W. Ziller, Brian L. Scott, Andrew J. Gaunt, and William J. Evans, "Synthesis of Trimethyltriazacyclohexane (Me_3tach) Sandwich Complexes of Uranium, Neptunium, and Plutonium Triiodides: $(Me_3tach)_2AnI_3$" *Inorg. Chem.* **2023**, *62*, 5897-5905. DOI: 10.1021/acs.inorgchem.2c03306
2. Joseph Q. Nguyen, Lauren M. Anderson-Sanchez, Willian N. G. Moore, Joseph W. Ziller, Filipp Furche, and William J. Evans, "Replacing Trimethylsilyl with Triisopropylsilyl Provides Crystalline $(C_5H_4SiR_3)_3Th$ Complexes of Th(III) and Th(II)" *Organometallics* **2023**, *42*, 2927-2937. DOI: 10.1021/acs.organomet.3c00343
3. Cory J. Windorff, Conrad A. P. Goodwin, Joseph M. Sperling, Thomas E. Albrecht-Schönzart, Zhunling Bai, William J. Evans, Zachary K. Huffman, Renaud Jeannin, Brian N. Long, David P. Mills, Todd N. Poe, and Joseph W. Ziller, "Stabilization of Pu(IV) in $PuBr_4(OPCy_3)_2$ and Comparisons with Structurally Similar $ThX_4(OPR_3)_2$ (R = Cy, Ph) Molecules" *Inorg. Chem.* **2023**, *62*, 18136-18149. DOI: 10.1021/acs.inorgchem.3c02575
4. Joseph Q. Nguyen, Olaf Nachtigall, Brynn N. Turpin, Joseph W. Ziller, and William J. Evans, "Phenylsilyl-Substituted Tetramethylcyclopentadienide Uranium Chemistry: Magnesocenes vs Grignard Reagents" *Organometallics* **2023**, *42*, 3473-3482. DOI: 10.1021/acs.organomet.3c00420
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6. Joseph Q. Nguyen, Justin C. Wedal, Joseph W. Ziller, Filipp Furche, and William J. Evans, "Investigating Steric and Electronic Effects in the Synthesis of Square Planar $6d^1$ Th(III) Complexes" *Inorg. Chem.* **2024**, *63*, 6217-6230. DOI: 10.1021/acs.inorgchem.3c04462
7. Lauren M. Anderson-Sanchez, Ahmad Rajabi, Justin C. Wedal, Filipp Furche, and William J. Evans "Surprising Syntheses of Reduced-Arene Inverse Sandwich Complexes of Thorium: $[Cp''_2Th]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_5R)$ [R = H, Me; Cp'' = $C_5H_3(SiMe_3)_2$]" *Organometallics* **2024**, *43*, 2027-2035. DOI: 10.1021/acs.organomet.4c00240
8. Joseph Q. Nguyen, Olaf Nachtigall, Austin J. Ryan, Brynn N. Turpin, Joseph W. Ziller, and William J. Evans, "Synthesis and Structure of Heteroleptic $[C_5Me_4(SiMe_2{}^tBu)]^{1-}$ Uranium(III) Compounds" *Organometallics* **2024**, *43*, 2767-2776. DOI: 10.1021/acs.organomet.4c00325

Impacts of free radicals on the chemistry of neptunium and uranium complexes

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Overall research goals: My long-term research goal is to identify the critical chemical components that influence the bonding of actinyl cations and provide a greater understanding of the observed chemical and physical properties of these species. The objective of this proposal is to develop a fundamental understanding of how free radicals interact with high valent neptunium and uranium using radical initiators to systematically evaluate the impacts on redox stability and molecular speciation. Of particular interest is neptunium (Np-237) because of the significant challenges in stabilizing redox states due to both the inherent electronic structure and higher activity. The overall hypothesis is that free radicals will interact with actinyl cations to vary the oxidation state, create meta-stable actinide free radical complexes, and/or create cascading reactions with co-solutes that impact the stability of ligands in the system. These hypotheses will be tested through evaluation of the following research objectives: (1) Evaluate interactions of neptunyl and uranyl cations in the presence of specific free radicals in acidic solutions; (2) Determine the influence of free radicals on the stability of actinyl complexes containing organic chelators; (3) Identify the impacts of free radicals on the oxidation state of neptunium under basic conditions.

Significant achievements during 2023- 2025:

Expanding our understanding of Np(VII) chemistry (Objective 3): The stability of Np(VII) has been a longstanding question, with most studies indicating that the heptavalent state is only stable under high alkalinity and is most readily achievable through oxidation with hydroxyl radicals formed during chemical ozonlysis. High base concentrations has limited the coordination chemistry of Np(VI) to the $[NpO_4(OH)_2]^{4-}$ species, which has been characterized in both solid-state and solution species. Our computational efforts indicate that protonation of the axial hydroxide anion to form water would result in a more labile species that could result in ligand substitution. Using a computationally guided approach, we explored the stability of Np(VII) under a range of pH conditions and demonstrated that the Np(VII) oxidation state could be stabilized at lower pH values than previously expected, which expands the chemical space and possibility of ligand exchange in this system.

Identifying how to use EPR spectroscopy of the ligand to understand actinyl behavior (Objective 2): Understanding the behavior of free radicals in the presence of the actinyl cation requires that we have the tools to evaluate both the metal cation and the ligand. One tool that is routinely utilized in free radical chemistry is the use of spin traps, such as 5,5-dimethyl-1-pyrroline N-oxide (DMPO). The challenge is that these molecules are designed for biological systems and their use under different pH regimes and the presence of actinides has not been fully explored. We have evaluated their use in both U(VI) and Np(VI) under high alkaline conditions, developing an understanding of how spin traps behave under these conditions. In addition, we have utilized DMPO as a tool to evaluate superoxide reactivity with hexavalent uranyl and neptunyl species, highlighting the differences in these actinide metal cations.

Evaluating differences in U(VI) and Np(VI) superoxide chemistry (Objective 1): We have utilized chemical radical initiators to create U(VI) peroxo/superoxo complexes and previously demonstrated that the superoxide radical can be stabilized in the presence of U(VI) in ways that have not been observed elsewhere on the periodic table. We have extended this work to Np(VI) and have characterized novel Np(VI) triperoxo/superoxo complexes using new synthetic methodologies to isolate solid state coordination complexes in high yields. In addition, we have characterized these complexes using Raman and EPR spectroscopy to further understand the interactions between the actinyl cation and reactive oxygen species within this system.

Science objectives for 2025- 2027:

Further characterization of actinyl peroxo/superoxo complexes: Having isolated Np(VI) peroxo/superoxo complexes, we plan to further evaluate these species with a specific focus on coupling of the unpaired spins and impacts on reactivity. In addition, we plan to explore Np(V) peroxo/superoxo complexes that have been postulated to exist and identify the impact of carbonate on the stability and reactivity of these complexes under basic conditions.

Reactivity of inorganic substrates in the presence of actinyl free radical complexes: We have previously demonstrated that presence of reactive oxygen species can lead to oxidation of phosphonates to form phosphate species and we are currently expanding the number of phosphate substrates to identify the mechanism of the oxidation reaction.

Enhance our understanding of Np(VII) chemistry through ligand exchange reactions on the axial position: Based upon our titration study, we know that the chemical space for Np(VII) is larger than we initially expected and the axial hydroxide anion should be able to be more easily replaced after protonation. Therefore, we plan to try ligand substitution reactions with halides and other monodentate complexes and explore changes in the Np(VII) bonding, spectroscopy, and electronic structure within these complexes.

Evaluate actinyl reactivity with carbonate radicals: In addition to peroxo/superoxo complexes, the actinyl cation is expected to form stable complexes with the carbonate radical. We are further exploring the stabilization of this radical within U(VI), Np(V), and Np(VI) systems and the potential molecular complexes that may be formed under these conditions. In addition, we plan to identify any additional cascade reactions that may occur in the presence of carbonate radicals that my further change the behavior of the actinyl cation within these systems.

Select Publications supported by this project 2023-2025:

Samarasiri, Vidumini S., Rajapaksha, Harindu, McGee, Sarah, Mason, Sara E., Forbes, Tori Z.* "Formation of U(VI) peroxide nanoclusters from radical cascade reactions." In preparation*, Dalton Transaction*

Benthin, Grant C., Rajapaksha, Harindu, Markun, Emma L., Mason, Sara E. and Forbes**,** Tori Z.* "Probing the Protonation and Stability of Heptavalent Neptunium with Computational Guidance." (2024) *Dalton Transactions,* 3, 16170-16185 DOI:10.1039/D4DT01706D

Rajapaksha, Harindu, Benthin, Grant C. Markun, Emma L., Mason, Sara E. and Forbes, Tori Z.*****, "Synthesis, characterization, and Density Functional Theory investigation of $(CH_6N_3)_2[(NpO_2)Cl_3]$ and $Rb[(NpO_2)Cl_2(H_2O)]$ chain structures", (2024) *Dalton Transactions* 53, 3397-3406. DOI: 10.1039/D3DT03630H

Kravchuk, Dmytro V., Augustine, Logan J., Pyrch, Mikaela, M. F., Benthin, Grant C., Rajapaksha, Harindu, Mason, Sara E., Batista, Enrique R., Yang, Ping, and Forbes, T. Z.* "Insights into the mechanism of neptunium oxidation to the heptavalent state", (2024) *Chemistry – A European Journal* 30, e202304049. DOI: 10.1002/chem.202304049

Rajapaksha, H., L. J. Augustine, S. E. Mason, and T. Z. Forbes***** "An experimental and computational effort to determine the formation enthalpy and vibrational properties of solid-state uranyl halides and its influence by hydrogen bonds." (2023) *Angewandte Chemie International Edition*, 33, e202305073

Synthesis, Reactivity, and Electronic Study of Unsupported and Supported Actinide-Arene Complexes

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Collaborators: Bess Vlaisavljevich (University of Iowa), Andrew Gaunt (LANL), Cory Windorff (New Mexico State University), Liane Moreau (Washington State University)

Overall research goals:

This work aims to investigate the synthesis, reactivity, and electronic properties of actinide complexes, with a particular emphasis on uranium and its interactions with arene ligands. Our research explores two distinct yet interrelated systems: (a) an unprecedented class of unsupported uranium-arene sandwich complexes that we have pioneered, and (b) actinide-arene complexes featuring supported, or "tethered," interactions. By examining these complementary systems, each exhibiting unique bonding motifs, we seek to assess the role of metal valence orbitals in bonding. These complexes will serve as fundamental platforms for studying the chemical and physical behavior of early actinides and transuranic elements, providing insights into their bonding and reactivity.

Significant achievements during 2023- 2025:

Our funding under the BES HEC program began in September 2024. Since then, we have focused on two main research directions: (1) the improved synthesis and electronic structure characterization of homoleptic uranium arene-metalates of the form $[U(arene)_3]^{2-}$ (**1**) and (2) the reduction and reactivity studies of the N,N-tethered arene complex $L^{Ar}UI(DME)$ (**2**) (L^{Ar2-} = 2,2″-bis(Dippanilide)-p-terphenyl; Dipp = 2,6-diisopropylphenyl). These systems illustrate two distinct modes of uranium-arene interactions, unsupported and supported. The solid-state molecular structures of representative compounds for each bonding type are shown in **Figure 1**.

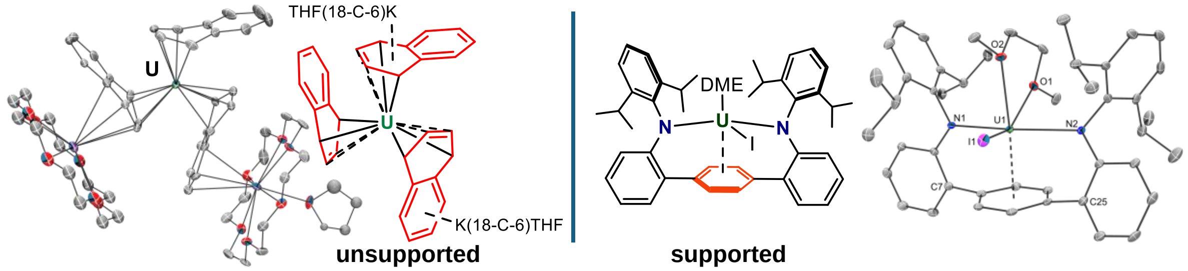

Figure 1. Unsupported and supported uranium arene systems of interest.

(1) Building upon our success in the synthesis of unsupported uranium-arene metalate complexes, we have synthesized a series of homoleptic and heteroleptic uranium-arene compounds, namely $\{[K(18\text{-}c\text{-}6)][K(18\text{-}c\text{-}6)](\mu\text{-}\eta^4{:}\eta^4\text{-}C_{10}H_8)_2U(\eta^4\text{-}C_{10}H_8)\}$ (**1-napth**), $\{[K(THF)_2(\mu\text{-}THF)_2K(THF)_2](\mu\text{-}\eta^6{:}\eta^4\text{-}C_{20}H_{12})(\mu\text{-}\eta^4{:}\eta^4\text{-}C_{20}H_{12})U(\eta^4\text{-}C_{20}H_{12})\}_n$ (**1-pery**), and heteroleptic $\{[K(18\text{-}c\text{-}6)][K(18\text{-}c\text{-}6)](\mu\text{-}\eta^4{:}\eta^4\text{-}C_{14}H_{10})_2U(I)(\eta^4\text{-}C_{14}H_{10})\}$ (**1-anth**). While the structures of these molecules have been known to our group for some time, under the support of this award, we have optimized the synthesis of these complexes, achieving yields of nearly 60% for all three compounds.

Initial reactivity study of these complexes is ongoing with a current focus on arene-exchange reactions to generate mixed uranium-arenides of the form $[U(\eta^4\text{-}C_{10}H_8)_{3\text{-}n}(arene)_n]^{2-}$, allowing us to study the structural and electronic property changes that occur upon ligand exchange. The redox chemistry of these systems is also of high interest.

Additionally, we are conducting a comprehensive electronic structure study of these molecules using XANES, XPS, and SQUID magnetometry. **Figure 2** presents the XANES data for our tris(arenides) in comparison to other organometallic uranium complexes, such as Cp_3U and $U(COT)_2$. The absorption edge energy of the arene-metalates approaches that of $UI_3(dioxane)_{1.5}$, a U(III) reference standard, while also falling within the lower range of U(IV) complexes. Based on this, along with a close analysis of the metrical parameters from the solid-state molecular structures of **1**, we assign the tris(arenides) as containing tetravalent uranium.

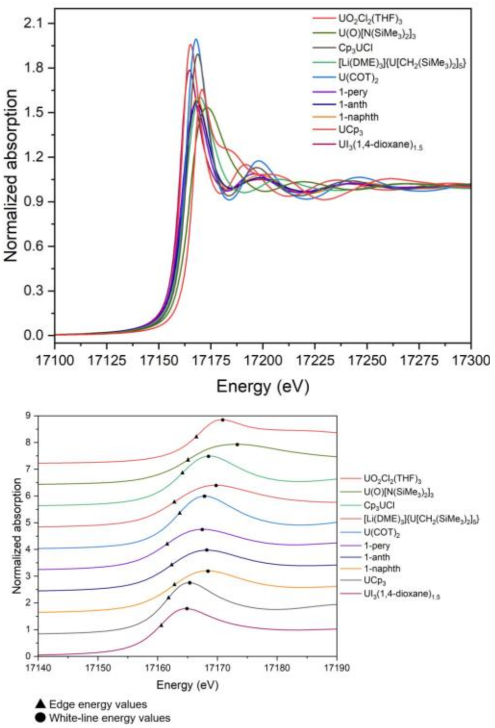

Figure 2. XANES spectra of **1** and reference compounds.

(2) We are exploring the reduction chemistry of **2**. Preliminary reactivity studies show that treatment of **2** with 1 equiv. of KC_8 in THF in the presence of 2.2.2-cryptand leads to the formation of the reduced product [K(cryptand)][$L^{Ar}UI$] (**3**). Curiously, in stark contrast to other tethered uranium-arene complexes, the reduction of our system does not result in formation of U(II) but rather two-electron reduction of the coordinated ring accompanied by oxidation of the metal center from U(III) to U(IV). The reduction of the central arene ring is made obvious by severe structural distortions consistent with the formation of reduced cyclohexadiene dianion (**Figure 3**).

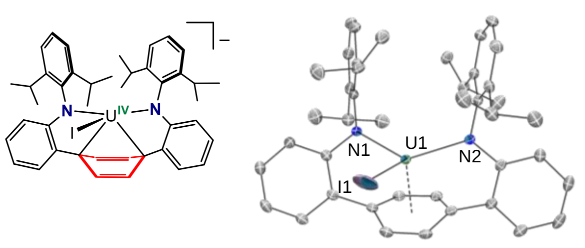

Figure 3. Structure of **3**.

The redox properties of **3**, principally its propensity to under multi-electron transfer chemistry, are currently under investigation. For instance, addition of diazobenzene to solutions of **3** appear to produce a bis(imido) species; however, characterization of this product is ongoing.

Science objectives for 2025- 2027:

With these highly reduced systems in hand, we intend to explore their redox chemistry with various reagents, including π-acids such as isocyanides (R–N≡C) and CO. While we anticipate that this will lead to reductive cleavage or coupling of the substrates, it is also possible that new low-valent uranium species may be accessible through π-acid stabilization. If the reactivity of **1** parallels that of related d-block systems, we expect these uranium arene-metalates to serve as a highly reactive source of "naked" uranium. Additionally, the electronic structure analyses of our molecules is ongoing and will be investigated using a range of advanced methods.

Leveraging our collaborations with the Gaunt Group at LANL and the Windorff Group at NMSU, we are preparing to extend this chemistry to transuranic elements. Scale-down efforts are currently underway in anticipation of graduate student Frank MacGregor's summer internship with Gaunt at LANL through the Seaborg Institute GRA program. As part of this internship, Frank will continue work on an ongoing collaborative project investigating actinide-carbon (An–C) interactions.

Hunter / Brookhaven partnership to investigate the speciation of technetium-99 and rhenium in molten salts

Lynn C. Francesconi, Principal Investigator

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Faculty: Donna McGregor, Benjamin P. Burton Pye, Gustavo Lopez, Lehman College of CUNY
Postdoctoral Fellow: Kazuhiro Iwamatsu, Hunter College of CUNY
Graduate Students: Ramsey Salcedo, Hunter College of CUNY, Hossam Elshendidi, Rachel Greenberg, Lehman College of CUNY
Undergraduate Student: Erika Relyea, Hunter College of CUNY
Collaborators: James Wishart, Anatoly Frenkel, Brookhaven National Laboratory

Overall research goals: This project investigates the chemistry of technetium-99 (Tc) in molten salts (MS). Molten salt reactors (MSRs) are one of the most promising emerging nuclear reactor technologies. Removing the fission products is challenging, therefore understanding what chemical forms the fission products take in MS is key to designing effective separation systems. Studies on the speciation of very important fission product, technetium-99, in MS are lacking, and that is the gap that this project intends to fill. *Objective 1.* Understand Tc-Cl complex speciation in low-melting chloride salts (ionic liquids, ILs) that are good proxies for examining the speciation (coordination and electron transfer properties) of various Tc and Re valence states because they offer only chloride ions for coordination to the metal ions. *Objective 2.* Elucidate the effects of molten salts' strong cation-anion interactions on Tc and Re speciation using pure molten $ZnCl_2$. The goal is to understand how the cation-anion interactions intrinsic to $ZnCl_2$ control the Tc–solvent (salt) interactions. *Objective 3.* Interpret the speciation and redox chemistry of Tc and Re in $ZnCl_2$-KCl, a complex, tunable salt system. Building on the characterization in molten $ZnCl_2$, $ZnCl_2$-KCl mixtures are used to explore how Tc and Re speciation can be controlled by tuning mixture composition over temperatures up to 550 °C.

Significant achievements during 2023- 2025:

Objective 1: We prepared Tc and Re chlorides of oxidation states III, IV, V, VI, and VII to benchmark structures and oxidation states in the non-coordinating ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (emim NTf_2). X-ray absorption spectroscopy, XAS, of the Re chlorides demonstrated a clear L_3-edge shift as a function of oxidation state in emim NTf_2 as well as in acetonitrile. We are analyzing the EXAFS data presently.

Objectives 2 and 3: We started the project using rhenium as a surrogate for technetium-99. While molten salt capabilities were being developed in our lab at Hunter, we began our investigations of Re redox reactions by using pulse radiolysis to measure the reaction kinetics of hexachlororhenate (Re^{IV}, K_2ReCl_6) with radiation-induced solvated electrons (e_s^-) in molten LiCl-KCl eutectic. We selected LiCl-KCl eutectic because prior data exists comparing the rate constants and activation energies, enthalpies and entropies for solvated electron reactions with transition metals in eutectic LiCl-KCl from the work of the Molten Salts in Extreme Environments (MSEE) EFRC directed by co-PI, Dr. James Wishart.

We measured the decay of e_s^- absorbance at 660 nm in neat LiCl-KCl and five K_2ReCl_6 concentrations from 400 to 500 °C. The rate constant for the reaction of e_s^- with $ReCl_6^{2-}$ at 400 °C was $(6.2 \pm 0.2) \times 10^{10}\ M^{-1}s^{-1}$. This is in the range for a recent study of first row transition metal additives in LiCl-KCl eutectic (Iwamatsu, Wishart, manuscript in preparation). The average pseudo-first order rate constants as a function of Re(IV) concentration and temperature are shown in Fig. 1A. The Arrhenius and Eyring plots for the reaction of e_s^- with K_2ReCl_6 are shown in Fig. 1B and compared with those of Cr^{III} from a recent MSEE publication (DOI 10.1039/d4cp04190a). The relevant activation parameters for $ReCl_6^{2-}$ and Cr^{III}, as representative for the first-row transition metals, are shown in Table 1. Detailed interpretation of the activation parameters requires additional information, but it is notable that E_a and $\Delta H^{\ddagger}$ for Re(IV) are slightly larger than those for Cr(III) and the activation entropy, $\Delta S^{\ddagger}$, is positive for Re(IV) while it is negative for Cr (III).

Table 1. Rate constants and activation parameters for Re(IV) and Cr(III) reactions with e_S^- in LiCl-KCl.

Metal Ion	d electron occupancy	k x 10^{10} M^{-1} s^{-1} @400 °C	A x 10^{13} M^{-1} s^{-1}	E_a kJ mol^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J mol^{-1} deg-1
Re (IV)	$5d^3$	6.2 ± 0.2	8.3-13.7	40-44	34-38	5-10
Cr (III)	$3d^3$	6.1 ± 0.3	3.9 ± 0.4	35.4 ± 0.7	28.6 ± 0.4	-1.6 ± 0.5

We measured L_1- and L_3- edge XAS, data at NSLS II (beamline 6-BMM) for Re chlorides mixed with LiCl-KCl eutectic, heated to 450°C and cooled. Analysis of these data, compared to controls, to determine oxidation state and Re coordination is in progress.

Significant achievements also include the procurement and ongoing installation of a glovebox for handling molten salts in the Tc lab at Hunter and a Cary 5000 spectrometer with a custom-built furnace for optical measurements of Tc and Re in MS at elevated temperature. The lab at Hunter is being set up to replicate capabilities of MSEE for technetium MS research. We are also installing a glovebox for ionic liquid work at Lehman College. These are important steps in setting up the necessary infrastructure to support the work.

Science objectives for 2025- 2027:

Objective 1: We plan to dissolve Tc and Re chlorides, i.e. $(Bu_4N)_2[Re^{III}_2Cl_8]$ in non-coordinating ionic liquids, ILs, where the chloride content is increased by adding increasing amounts of the chloride-based IL, likely emim Cl, to the solution of the corresponding NTf_2 IL. The optical absorption spectra and XAS will be monitored to determine if a structural change occurs. As we add more chloride to the IL, we may observe oxidation of the Re^{III} to Re^{IV} and formation of $Re^{IV}Cl_6^{2-}$.

Objectives 2-3: We plan to conduct X-ray Absorption Spectroscopy, XAS, on K_2ReCl_6 in LiCl-KCl eutectic at elevated temperatures in cells housed in a bespoke mini-furnace that will allow *in situ* transmission and fluorescence XAS at NSLS II beamline 8-ID. The XAS data will be collected from RT to 450°C in 50-degree increments. During this grant period, the laboratory at Hunter College is presently being set up for Tc MS work and then we will investigate the pulse radiolysis of the LiCl-KCl eutectic with K_2TcCl_6 as we have with the Re analog, above. We plan to conduct XAS on K_2TcCl_6 in LiCl-KCl at elevated temperatures using the bespoke furnace at NSLS II. We will also begin optical and XAS studies of Re/Tc chlorides in $ZnCl_2$ eutectics. We plan to examine the speciation and redox chemistry of Tc and Re in $ZnCl_2$-KCl, a complex, tunable salt system.

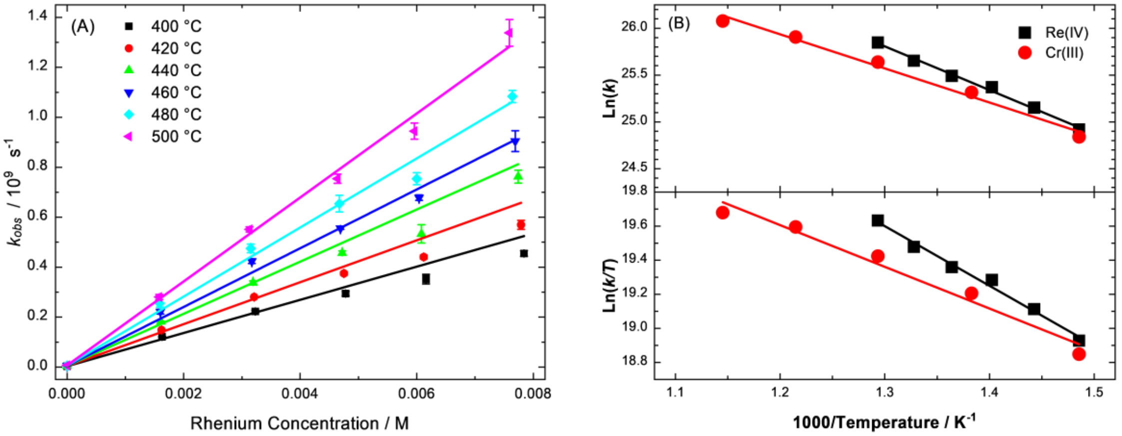

Figure 1 (A) Average observed pseudo-first-order rate coefficients as a function of rhenium(IV) concentration and temperature and (B) Arrhenius: top and Eyring: bottom plots for reaction of e_S^- with rhenium(IV) (black) or Cr(III) (red) using measured rate coefficient at temperature from 400 to 600 °C.

Publications supported by this project 2023-2025: None at this time.

Quantum Chemical Treatment of Strongly Correlated Systems Containing Heavy Elements

Laura Gagliardi, Principal Investigator

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Postdoctoral Scholars: Andrea Darù, Soumi Haldar
Collaborators: Thomas E. Albrecht (Colorado School of Mines), Suzanne C. Bart (Purdue University), Eric J. Schelter (University of Pennsylvania), John D. Despotopulos (Lawrence Livermore National Laboratory) Omar Farha (Northwestern University), Eva Zurek (University at Buffalo)

Overall research goals: The proposed work aims to develop and use electronic structure theories and software to model spectroscopic properties of small actinide molecules, actinide based single molecule magnets and systems containing super-heavy elements The methodologies that we employ and develop further involve multireference wave functions, based on the active space concept. We explore the LASSCF (localized active space self-consistent field) method, which factorizes a wave function within the active space into separate localized parts, significantly reducing the number of configurations required for the wave function representation, compared to the corresponding complete active space counterpart. We then employ active space wave functions as starting points for subsequent pair-density functional theory (MC-PDFT) calculations of the total energy of different electronic states, with the inclusion of spin-orbit coupling.

Significant achievements during 2023- 2025:

During the grant period in collaboration with the group of Omar Farha we have studied electronically tunable low-valent uranium metallacarborane compounds.[1] While conventional metallocenes rely on steric modifications of cyclopentadienyl (Cp) ligands, metallacarboranes use three-dimensional dicarbollide (dc) ligands, which allow for electronic tuning without significantly altering coordination geometry. The Farha's group synthesized uranium metallacarboranes with B-functionalized dc ligands containing increasingly electron-withdrawing aryl groups. We performed density functional theory (DFT) calculations on these species to understand how tuning the electronic properties of the dc ligands affects the electronics of the U(III) center and the relative contribution of 5f orbitals to metal-ligand bonding interactions. The highest occupied molecular orbitals (Mos) are primarily uranium-centered, confirming that the first oxidation event corresponds to U(III) oxidation. Lower MOs are mainly derived from the dc or Cp ligands. Functionalization of the dc ligand does not significantly impact the 5f character of these orbitals or metal–ligand bonding interactions. Binding free energy calculations show that ligand binding strength increases with more electron-withdrawing functional groups. Additionally, the HOMO energy decreases as the Hammett constant increases, indicating greater stabilization of the uranium center. These computational trends align with cyclic voltammetry results, which show increasing oxidation potential with more electron-withdrawing substituents.

We have collaborated with the groups of Thomas Albrecht and Eva Zurek on the study of an octa-hydrated curium compound. The Albrecht's group synthesized and characterized $Cm(H_2O)_8$ (dtp)·H_2O (Cm1), along with its lanthanide analogues $Ln(H_2O)_8$ (dtp)·H_2O (Ln1, $Ln^{3+} = La^{3+}$–Nd^{3+}, Sm^{3+}–Lu^{3+}). The single-crystal X-ray diffraction and spectroscopic analyses reveal that Cm(III)–OH_2 bond lengths are comparable to those of eight-coordinate lanthanide analogues but shorter than previously reported nine-coordinate Cm(III) complexes. The study also examines the optical properties of these complexes using solid-state UV-vis-NIR spectroscopy and variable-temperature/pressure photoluminescence. Under increasing pressure, Cm1 exhibits a stronger dependence of f → f transitions compared to its lanthanide counterparts. Our computational study based on multireference calculations, in agreement with experiments, suggests that pressure induces a red shift in photoluminescence due to a decrease in Cm(III)–OH_2 bond lengths, spin density delocalization, and enhanced 5f orbital interactions. These structural and electronic modifications lead to peak broadening and quenching, providing insights into the pressure-dependent behavior of curium coordination complexes.

Science objectives for 2025- 2027:

We will develop a a cost-effective approach to accurately account for both electron correlation and spin-orbit coupling (SOC) effects within the framework of MC-PDFT. Specifically, we combine a multi-state formulation of MC-PDFT which allows to compute close lying electronic states, a typical scenario in actinide chemistry, called linearized PDFT, LPDFT, with the treatment of SOC using quasi-degenerate perturbation theory. This methodology is under implementation in the open source PySCF-Forge package. We will employ this method, in combination also with LASSCF wave functions, to study actinides and lanthanide compounds that can be potential magnetic systems. We will also collaborate with experimentalists in the program to complement their measurements. Specifically, we plan to work with John D. Despotopulos who has synthesized some super-heavy element compounds and would like us to characterize their electronic structure. Moreover, we are collaborating with Suzanne C. Bart and Eric J. Schelter towards the characterization of a penta(imido)uranate tetraanion which features five terminal uranium-nitrogen multiple bonds.

Publications supported by this project 2023-2025:

1. K. O. Kirlikovali, A. Gómez-Torres, A. Sauza-de la Vega, A. Darù, M. D. Krzyaniak, P. Garg, C. D. Malliakas, M. R. Wasielewski, L. Gagliardi, and O. K. Farha, “Electronically Tunable Low-Valent Uranium Metallacarboranes”, *Inorg. Chem*, **2025**. DOI: 10.1021/acs.inorgchem.4c04431
2. Z. Bai, M. Redington, S. Haldar, N. B. Beck, J. M. Sperling, B. Scheibe, J. P. Brannon, E. Zurek, L. Gagliardi, and T. E. Albrecht, “High-Pressure Effects on an Octa-Hydrated Curium Complex: An Experimental and Theoretical Investigation”, *J. Am. Chem. Soc*., **2025**. *147*, 6137–6148 DOI: 10.1021/jacs.4c17589
3. S. Haldar, L. A. Mariano, A. Lunghi, and L. Gagliardi, “Role of Electron Correlation Beyond the Active Space in Achieving Quantitative Predictions of Spin-Phonon Relaxation”, *J. Chem. Theory Comput*., **2025**. DOI: 10.1021/acs.jctc.4c01696

Manipulation of ligand electronic structure to control f-element covalency

Shane Galley, Principal Investigator

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Collaborators: Stosh Kozimor (LANL), David Shuh (LBNL), Ping Yang (LANL), Enrique Baptista (LANL)

Overall research goals:

The primary objective of this proposal is to integrate thermodynamic complexation and electrochemical data of transuranic elements with computational and spectroscopic analyses of covalency. This approach aims to elucidate how variations in ligand electronic structure influence ligand-actinide interactions and their overall binding strength. A key focus is placed on the chemistry of trans-plutonium actinides, with the goal of developing a more predictive framework for actinide coordination behavior.

Research efforts have primarily centered on nitrogen-based ligand systems, particularly polyaminopolycarboxylates and dipicolinic acid (DPA) derivatives. Previous studies have demonstrated that ligand polarizability and electron donation play crucial roles in stabilizing nitrogen-actinide interactions. This research builds on those findings by advancing DPA investigations while expanding to a promising new ligand, diaminephenanthroline diamide (DAPhen). Preliminary results suggest that DAPhen possesses several desirable properties, including ease of synthesis, the ability to form well-defined f-element crystals, and tunability through the introduction of electron-donating or withdrawing groups at various positions.

Despite the availability of extensive extraction data for long-chain alkylated DAPhen derivatives, fundamental coordination studies—including spectroscopic, electrochemical, and computational investigations—remain limited, particularly for trans-americium elements. This research addressed this gap by providing a deeper understanding of ligand-actinide interactions through a multidisciplinary approach.

Significant achievements during 2023- 2025:

Experimental efforts have examined nitrogen-based ligand systems, assessing their electronic effects on actinide complexation. Initial solvent extraction studies with Am(III) using modified DPA ligands (e.g., morpholine-DPA, methoxy-DPA, and nitro-DPA) revealed the impact of electron donation and withdrawal on stability constants. The protonation of the morpholine group significantly altered ligand electronic properties, demonstrating the importance of protonation equilibria in metal binding.

To complement experimental work, synchrotron-based spectroscopic studies (XANES, EXAFS) were conducted at Berkeley Lab's Advanced Light Source to probe metal-ligand bonding in Nd(III), Sm(III), and Eu(III) complexes. The results provide direct insight into covalency trends, aiding computational modeling efforts. Density Functional Theory (DFT) calculations at Los Alamos National Laboratory further support these findings, revealing shorter metal-nitrogen bond lengths in electron-donating systems and longer bonds in electron-withdrawing systems.

Electrochemical studies of Ce(IV)/Ce(III) redox couples using DPA derivatives demonstrated a ±200 mV shift in reduction potential depending on ligand functionalization. These findings suggest that ligand modifications directly influence redox stability, which is critical for selective actinide-lanthanide separations. Planned Pu(IV)/Pu(III) studies will extend this work to f-block redox chemistry.

Studies on the DAPhen ligand system explored its potential in solvent extraction applications, particularly for separating Am(III) from Cm(III) and lanthanides. Crystallographic data revealed a consistent 10-coordinate binding mode across trivalent metals, with solvent extraction experiments confirming Am(III) selectivity over Cm(III) and lanthanides. Similar trends were observed for Bk(III) and Cf(III), suggesting electronic factors play a key role in selectivity.

Science objectives for 2025- 2027:

Over the next few years, this project will focus on refining our understanding of actinide-ligand interactions by systematically varying ligand electronic structures and assessing their impact on metal binding and stability. Particular attention will be given to trans-plutonium actinides, including Bk(III) and Cf(III), where data remain limited. Experimental efforts will integrate thermodynamic, spectroscopic, and electrochemical techniques to quantify covalency and determine how ligand modifications influence complex stability. Parallel computational studies, including DFT modeling, will provide electronic structure insights that complement experimental findings. Beamline spectroscopy will further validate theoretical predictions by examining ligand-field effects on actinide oxidation states and bonding environments.

Publications supported by this project 2023-2025:

1. Pereiro, Felipe A. Galley, Shane S., Jackson, Jessica J. Shafer, Jenifer C., “Contemporary Assessment of Energy Degeneracy in Orbital Mixing with Tetravalent f-Block Compounds” *Inorg. Chem,* **2024**, *Vol*, Pages, DOI: https://doi.org/10.1021/acs.inorgchem.3c03828
2. Arko, Brian T., Dan, David, Adelman, Sara L., Kimball, D. B., Kozimor, Stosh A., Shafer, Jenifer C., “Electron Transfer Between Neptunium and Sodium Chlorite in Acidic Chloride Media” *New J. Chem.,* **2024**, *48*, 1907-1918, DOI: https://doi.org/10.1039/D3NJ03730D
3. Pu, Ning, Archer, Emma M., He, Xihong, Chen, Jing, Rao, Linfeng, Shafer, Jenifer C., Yang, Ping, Xu, Chao. “Tuning Selectivity to f-Element through Bonding and Solvation Effects of a Sulfur Donor Ligand” *Inorg. Chem.*, **2024**, *63*, 6845-6853, DOI: https://doi.org/10.1021/acs.inorgchem.4c00297
4. Archer, Emma M., Galley, Shane, S., Jackson, Jessica A. Shafer, Jenifer C., “Investigation of f-Element interactions with Functionalized Diamides of Phenanthroline-Based Ligands” *Solv. Extr. Ion Exch.,* **2023**, *41*, 697-740, DOI: https://doi.org/10.1080/07366299.2023.2239866

Studying *f*-Electron Contributions in Thorium- and Uranium-Containing Molecules

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Stephen Cooke, Co-principal Investigator

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Natural and Social Sciences, SUNY-Purchase College, Purchase, NY
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Post-doctoral Fellow: Alexander R. Davies
Collaborators: Kirk Peterson (WSU)

Overall research goals: This primarily experimental project involves the implementation of laser ablation-equipped chirped pulse, Fourier transform microwave (CP-FTMW) and cavity Fourier transform microwave (FTMW) spectroscopy to probe the rotational spectra of small (i.e. less than five atoms) uranium- and thorium-containing molecules produced in supersonic expansions of argon gas. Initially, one of our research goals involved specific target compounds in which we hoped to determine geometric structures, electronic ground states, rotational, fine, and hyperfine spectroscopic constants of UF, UCl, UBr, UI, US, UN, UC, ThCl, UP, and USi as well as polyatomic targets ThO_2, ThS_2, and UO_2Cl_2. Our second goal was less specific and aimed at identifying products of the laser ablation event of U and Th with a host of binding gas partners such as, but not limited to, Cl_2, CO, CO_2, acetylene, methane, O_2, and N_2. Thirdly we aimed to develop strategies and building partnerships for handling transuranium-containing compounds in the same types of experiment.

Significant achievements during 2023- 2025:

We have successfully collected multiple spectra in which thorium and uranium have been ablated in the presence of O_2, OCS, SO_2, and SF_6. Initially, we were seeking out spectra of targeted compounds in line with research goal number 1. However, these have proven difficult to locate to date. Instead, and in keeping with goal number 2 we have been able to successfully identify some of the products formed in the aforementioned laser ablation experiments. The OCS precursor gas been the most productive to date and we have identified SUO_2 and OThS in the ablation products of U/Th with OCS. It is worth noting that this is the first time that pure rotational spectroscopy has been successfully used to study polyatomic actinide-containing compounds. The spectra were strong enough to observe S-34 spectra which allows an accurate evaluation of the molecular geometries. The strength of the observed spectra suggests that the laser ablation synthetic method is effective at producing interesting molecules. The difficulties encountered, which we are now starting to overcome, involve the density of spectral features in the recorded spectra. Many transitions are observed for which we have developed a protocol and software to characterize. Transitions are observed that do not need the laser turned on, or do need the laser turned on but are independent of the metal being ablated, or there are the desirable transitions that need the laser turned on and require a specific metal to be ablated. Furthermore, to gain further insight to the observed species we have also pursued analogous Ce- and Hf-containing compounds. The spectra from these latter molecules provides useful contrast to the U- and Th-containing compounds.

Science objectives for 2025- 2027:

Our greatest successes have been ablating metals in the presence of precursor gases and identifying reaction products according to our second goal above. We currently have spectra that are currently unassigned and work will continue on the analyses. Work will continue on software development for the handling of recorded spectra, largely toward automated routines that can, using multiple background spectra, subtract unwanted features and leave only desirable features. This will greatly increase our throughput of spectral analysis which is currently a bottleneck. The experimental work will also continue with spectrometer upgrades and the use of different precursor gases. These will include SF_6, CO, Cl_2, short chain alkanes/alkenes, and others. We are particularly keen to pursue chlorine, nitrogen, bromine or iodine bearing compounds as these nuclei possess nuclear electric quadrupoles which will cause observable hyperfine splittings on the pure rotational transitions. Once analyzed, these splittings provide a direct insight into the electric field gradient at the nuclei and, as such, reveal a great deal about the nature of the chemical bond and be informative as to the role of *f*-electrons.

Publications supported by this project 2023-2025:

1. Joshua E. Isert, Josie R. Glenn, Stephen A. Cooke, Garry S. Grubbs II, "Pure rotational spectroscopic measurements on the electronic ground states of Hafnium monosulfide and Thorium monosulfide in highly excited vibrational states" *Journal of Molecular Spectroscopy*, **2024**, *406*, 111952, https://doi.org/10.1016/j.jms.2024.111952
2. Joshua E. Isert, Alexander R. Davies, Garry S. Grubbs II, Stephen A. Cooke, "Laser ablation syntheses of OThS and OCeS and their characterization by rotational spectroscopy" *Physical Chemistry Chemical Physics*, **2025**, *27*, 1804-1808, https://doi.org/10.1039/D4CP04382K
3. Joshua E. Isert, Garry S. Grubbs II, Stephen A. Cooke, "Pure rotational spectroscopic measurements on a uranium-containing polyatomic compound: SUO_2" *Chemical Physics Letters*, **2025**, *858*, 141726, https://doi.org/10.1016/j.cplett.2024.141726

Actinide bonding insights from high-resolution spectroscopy.

Michael C. Heaven, Principal Investigator

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Postdoctoral Researcher: Dr. Jiande Han
Collaborators: Richard Wilson (ANL), Thomas Persinger (ANL), Ping Yang (LANL), Timothy Steimle (ASU), Anh Li (Georgia Institute of Technology), Lan Cheng (Johns Hopkins University), Kit Bowen (Johns Hopkins University.)

Overall research goals:

The role of the 5f electrons in actinide bond formation is one of the central issues of actinide chemistry. This is a subtle question that can be investigated using a combination of strategic experimental measurements and state-of-the-art theoretical calculations. The primary objective of this program is to obtain high-resolution spectroscopic data for prototypical actinide molecules in the gas phase. There is a critical need for such data as the results obtained from condensed phase measurements are complicated by solvent-solute or lattice interactions. For the current stage of theoretical method development, the presence of these perturbations in the test data set can often obscure the relationship between measured and calculated properties. The ongoing studies are focused on the characterization of the ground and low-lying electronic states of prototypical actinide compounds. These are the states that determine both the physical and chemical properties of the molecules, and they are also the most amenable for detailed theoretical investigations. Experiments carried out to date show that photoionization and laser induced fluorescence techniques are well suited for studies of the low-lying electronic state structures of actinide cations. We are exploring the limitations imposed on optical spectroscopy by the electronic complexity (density of vibronic states) of open-shell polyatomic actinide species.

Significant achievements during 2023- 2025:

Electronic spectra of OThF have been recorded within the 21740 – 29410 cm^{-1} range using fluorescence excitation, dispersed fluorescence, and two-color photoionization techniques. Jet expansion cooling was used to reduce the rotational temperature of the OThF to approximately 30 K. The spectrum exhibited well-defined vibronic bands. Rotational resolution was not achieved, but partially resolved rotational contours were examined for the more intense features. Electronic structure calculations for OThF were carried out using relativistic equation-of-motion coupled cluster methods. The predicted molecular constants for the ground state were in good agreement with the spectroscopic data, while the energies of electronically excited states were found to be sufficiently accurate to permit the assignment of the more intense vibronic states. Density functional theory calculations yielded an IE that was close to the measured value. Dispersed fluorescence spectra induced by excitation of the lower energy bands were dominated by the emission back to the ground state zero-point level. Weaker transitions to the singly excited vibrational levels were observed, and these were used to determine the ground state fundamental frequencies. Dispersed fluorescence spectra obtained using higher energy excitation were qualitatively different, exhibiting spectrally broad emission features at longer wavelengths. This structure was attributed to extensive state mixing with the vibronic manifolds built on lower energy electronically excited states. Viewed in a wider context, the results for OThF and previous results for UO_2 indicate that, with increasing excitation energy, actinide-containing polyatomic molecules experience extensive state mixing that produces severe spectral congestion. This greatly complicates the task of extracting molecular constants from the electronic spectra. It is a problem that can be mitigated by focusing future experiments on the lowest energy, spectroscopically accessible excited states.

The rotational structure of electronic spectra provides unambiguous information concerning molecular structure and bonding. However, we have often encountered conditions where the rotational structure for polyatomic actinide molecules was intrinsically unresolvable. This problem was discussed in the study of OThF reported above (Rodriguez et al., *J. Chem. Phys.* 162, 024305 (2025)), and it arises from the extremely high state densities associated with open-shell actinides. UO_2 is a prototypical oxide of interest from the perspectives of both basic science and technological applications. To locate bands with of UO_2 with resolvable rotational structure we examined the far-red / near IR spectral range using a Raman-shifted dye laser and time-gated fluorescence detection. Several bands in this range exhibited rotational fine structure. Analysis of the structure established that the electronic angular momentum was quantized along the molecular axis. This condition would only be present for a linear geometry. The electronic angular momentum of the ground state was found to be Ω=2u, and the U-O bond length was 1.79 Å. Dispersed fluorescence spectra provided the first measurement of the ground state symmetric stretch vibrational interval. High-level computational predictions for UO_2 have been validated by these results.

Science objectives for 2025- 2027:

The next step for our work on UO_2 will be to push to higher resolution using a ring dye laser system (<100 MHz linewidth). This effort will include measurement of the magnetic g-factor for the ground state using the Zeeman effect. Knowledge of the *g*-factor will facilitate a detailed analysis of the ground state electronic configuration. Our work on UN has shown that the *g*-factor provides a particularly sensitive probe of the electron distribution among the 5f orbitals. Further characterization of the monoxide will focus on the field-free nuclear spin splittings present in the ground state of ^{235}UO. Initial surveys of the electronic spectra of thorium and uranium carbides (MC and MC_2) will be carried out with the aim of testing recently published computational predictions.

Publications supported by this project 2023-2025:

Arianna Rodriguez, Jiande Han, Jiarui Yan, Michael C. Heaven, Lan Cheng, "Electronic spectroscopy and excited state mixing of OThF" *J. Chem. Phys.* **2025** *162*, 024305, DOI https://doi.org/10.1063/5.0245862

Mingbin Yuan, Burak A. Tufekci, Jinheng Xu, Jinheng, Kathryn Foreman, Michael C. Heaven, Enrique R. Batista, Kit H. Bowen, Ping Yang, "Structural and Electronic Properties of Anionic $(ThO_2)_n^-$ (n=2-4) Clusters" *Inorg. Chem.* **2025**, DOI https://pubs.acs.org/doi/abs/10.1021/acs.inorgchem.4c04954

Thomas D. Persinger, Michael C. Heaven, Richard E. Wilson, "Uranyl Fluorescence in Acidic Solution: Quenching Effects by Tetramethylammonium (TMA^+)" *ChemRxiv*, **2024** DOI 10.26434/chemrxiv-2024-9wc7v

Anh T. Le, Xi-lin Bai, Michael C. Heaven, Timothy C. Steimle, "High resolution electronic spectroscopy of uranium mononitride, UN" *J. Chem. Phys.* **2023** *158,* 244301, DOI 10.1063/5.0157884

From An complexes to metal-oxo clusters and nanoparticles: trends in An(IV) periodicity, structure, and behavior

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Overall research goals: Structure underpins chemical behavior. For the actinides, speciation depends largely on oxidation state, and our knowledge of the structural and energetic properties of tetravalent actinide (thorium, uranium, neptunium, and plutonium) complexes is quite limited. To fill this knowledge gap, our research efforts have focused on the synthesis, structural characterization, and properties of Ce, Th, U, and Pu solid-state phases. Specifically, our group has sought to elucidate the effects of ligand- and counterion- identity on tetravalent actinide species formation and stabilization. Towards this end, we have examined the solution and solid-state chemistry of cerium and tetravalent actinide complexes and clusters in aqueous halide (i.e. chloride and bromide), nitrate, and carboxylate donor ligand systems. Moreover, we have interrogated the role that counterion identity and corresponding outer coordination sphere interactions such as hydrogen bonding, ion pairing, and π-π stacking interactions, have on actinide structural chemistry. Through this work, we have identified trends in structure for the early actinides, Th-Pu, and demonstrated that noncovalent interactions are an important synthetic tool for stabilizing and controlling the solubility and reactivity of otherwise elusive An^{IV} complexes and $Ce^{III/IV}$ or An^{IV} clusters. We also initiated investigations into nonaqueous systems with tunable ligand scaffolds to expand $Ce^{III/IV}$ and An^{IV} cluster chemistry.

Significant achievements during 2023- 2025: Previously we showed that non-covalent interactions could be used to isolate an anionic trimeric species, $[Th_3(H_2O)_2Cl_{10}(OH)_5]^{3-}$, for Th. Further, using small angle X-ray scattering, we showed that the trimeric species was solution stable and despite its absence, should be included in descriptions of thorium aqueous chemistry. Building on these observations, we examined the alkali counterion controlled solubility of U(IV)-chloride complexes, and found that alkali-counterion identity governed the phases that precipitated. Li^+ precipitated a $[U_4O_2Cl_{18}]^{6-}$ unit, Na^+ and K^+ yielded $UCl_4(H_2O)_4$ complexes, and Rb^+ and Cs^+ resulted in UCl_6^{2-}. The spectroscopic properties of the compounds were analyzed using Raman and UV-Vis-NIR absorption spectroscopy. As expected, the UV-vis-NIR spectra of the compounds exhibited transitions consistent with uranium in the +4-oxidation state, yet clear differences in absorption band splitting were observed. Overall, this work demonstrated the utility of noncovalent interactions in tuning the crystallization behavior of various metal complexes from otherwise identical reaction solutions and provided further evidence that counterions impact the composition and structure of actinide complexes isolated in the solid state. In addition to these chloride systems, we also examined aqueous bromide systems. Pyridium yielded three novel solid-state U(IV) bromide compounds, including a linear oxo bridged U(IV) dimer, $U(H_2O)_4Br_4$, and UBr_6^{2-}. We expanded this series to include other nitrogen heterocycles and isolated a series of UBr_6^{2-} complexes that are charge balanced by cationic N-H heterocycles. Interestingly, the compounds exhibit rich optical behavior, ranging from red to yellow, which we attribute to differences in charge transfer transitions.

In addition to halide ligand systems, we also examined the synthesis and structural chemistry of U(IV) complexes isolated from other monoanionic ligand systems using N-H donors. We found that the structural chemistry is dominated by $[U(NO_3)_6]^{2-}$. Importantly, we showed that the outer sphere cations could be used to control the rate of oxidation of U^{IV} to U^{VI}. In fact, for one of the compounds, we demonstrate a single-crystal-to-single-crystal phase change that involves oxidation of uranium, and reduction of nitrate. The phase change could be monitored by single crystal X-ray diffraction and UV-vis-NIR absorption spectroscopy.

We also examined the ligand and counter-cation stabilization of Ce- and An-oxo clusters. We prepared a series of An(IV) hexanuclear clusters decorated by benzoate (An = Th, U, Np, Pu) and elucidated differences in the synthesis parameters, and trends in structural periodicity. We have also used alkali and HPy^+ counterions to isolate a number of Ce-oxo clusters, ranging from Ce_{22} to Ce_{52}.

Science objectives for 2025- 2027:

Going forward, our group aims to further elucidate the effects of noncovalent interactions on the structure and reactivity of An complexes and clusters. Our group has recently brought online a laboratory equipped to handle Np and our future efforts will focus on applying what we have learned in Ce, Th and U systems to Np.

We are also interested in understanding the phase space between molecules, clusters, and nanoparticles. To achieve this, we look to examine both aqueous and nonaqueous cluster chemistry, and the relationship between metal-oxo clusters and the size, shape, morphology, and assembly of AnO_2 nanoparticles.

Selected Publications supported by this project 2023-2025:

1. McCusker, T. L.; Vanagas, N. A.; Szymanowski, J. E. S.; Surbella, R. G.; Bertke, J. A.; Arteaga, A.; Knope, K. E. Elucidating trends in synthesis and structural periodicity in a series of tetravalent actinide-oxo hexamers. *CrystEngComm,* **2025**, 27, 507-515. DOI: 10.1039/D4CE01042F
2. Blanes-Díaz, A.; Wacker, J. N.; Szymanowski, J. E. S.; Bertke, J. A.; Knope, K. E*****. Isolation of a chloride capped cerium polyoxo nanocluster built from 52 metal ions. *Chem. Commun.,* **2024,** *60*, 12185-12188. DOI: 10.1039/D4CC03144J
3. Shore, M. C.; Nicholas, A. D.; Vasiliu, M.; Edwards, K. C.; de Melo, G. F.; Bertke, J. A.; Dixon, D. A.; Knope, K. E.* Structural Chemistry of Penta- and Hexanitrato Thorium(IV) Complexes Isolated Using N–H Donors. *CrystEngComm* **2024**, 26, 1380-1398. DOI: 10.1039/D3CE01319G.
4. Blanes-Díaz, A.; Shohel, M.; Rice, N. T.; Piedmonte, I.; McDonald, M. A.; Jorabchi, K.; Kozimor, S. A.; Bertke, J. A.; Nyman, M.; and Knope, K. E.* Synthesis and Characterization of Cerium-Oxo Clusters Capped by Acetylacetonate. *Inorganic Chemistry* **2023** *63* (21), 9406-9417. DOI: 10.1021/acs.inorgchem.3c02141

Molecular Approaches to the Electronic Structure of Actinide Materials

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Collaborators: Ivan A. Popov (Washington State U.), Bess Vlaisavljevich (U. Iowa), Xiaosong Li (U. Washington), Samuel Greer (LANL), Benjamin Stein (LANL), Dimosthenis Sokaras (SSRL), Florian Kleemiss (Aachen), Alexander Steiner (University of Liverpool), John Bacsa (Emory)

Overall research goals: The understanding and control of the electronic structure in actinide materials is essential to the US-DOE mission. Key materials for national security and energy production such as plutonium metal and plutonium nitride remain challenging from an electronic structure perspective. This program develops a systematic molecular and spectroscopic approach to understanding the electronic structure and properties of plutonium and other mid-actinide materials. This approach is particularly germane to the determination of single-ion properties emerging from the competition of crystal field and spin-orbit coupling. This research program pairs synthetic actinide (^{232}Th, ^{238}U, ^{237}Np, ^{242}Pu, and ^{243}Am) studies with synchrotron spectroscopies and physical property studies to break down the challenge of understanding the electronic structure of *f*-element systems Our efforts to-date have focused on the analysis of several phenomena including intermediate coupling, multiconfigurational electronic structures (ground state degeneracy including hybridization with ligand/band states), and mixed-valence in metal ions (*i.e.* mixed *f/d* occupancy and mixed- oxidation states). Understanding and controlling the manifestation of these phenomena is crucial for understanding the physics underpinning topological insulators such as PuB_6, superconductors such as $PuCoGa_5$, and multiconfigurational insulators such as CmO_2.

The principal goal of the proposed synthetic, physical, and spectroscopic studies is to disentangle the complex electronic structure of actinide materials building from the single-ion properties of the actinides. The synthetic studies are supported by ligand design strategies to access rare or unprecedented actinide oxidation states in low coordination number and high-symmetry complexes to facilitate quantitative spectroscopic and magnetic characterization. These complexes are designed to be evaluated spectroscopically by multi-edge XAS (including high energy resolution fluorescence detected, HERFD), resonant inelastic X-ray scattering (RIXS), and electronic absorption, electron paramagnetic resonance, and nuclear magnetic resonance (EPR and NMR) spectroscopies, as well as by magnetometry, in order to establish clear correspondence between spectroscopic signature, electronic structure, and physical properties.

Significant achievements during 2023- 2025:

- Ligand development to lead to low-disorder, high-resolution structures on small scale reactions of actinide isotopes.
- Synthetic, crystallographic, electrochemical, and spectroscopic studies with Np imidophosphorane complexes lead to identification of unique cathodically shifted potentials and accessibility of unusual high-valent complexes.
- Isolation of four-coordinate, non-MLMB supported pentavalent Np complex and quantification of the kinetics and thermodynamics of proton-coupled electron transfer chemistry.
- Extended electrochemical analysis of pentavalent, non-MLMB complexes to Pu and quantified kinetics and thermodynamics of proton-coupled electron transfer chemistry at Pu

and found divergence in rate and driving force – stemming from changing role of energy-degeneracy driven covalent bonding.

- Reported the synthesis, characterization, and computational analysis for a series of ytterbium complexes, including a mixed-valence Yb_2^{5+} complex featuring a remarkably short Yb···Yb distance of 2.9507(8) Å. These tools offer a clear path forward in the development of both metal-metal bonding and mixed-valence IVCT transitions in complexes of *f*-block elements.
- Extended new class of ligand to actinide systems as path to new low-coordinate, high-valent mid-actinide complexes.

Science objectives for 2025- 2027:

- Complete studies with new imidophosphorane ligand on Np and Pu to seek isolation of Np^{6+} and Pu^{5+} complexes.
- Develop low-steric profile ligands for the synthesis of mixed-valent actinide clusters.
- Extend heteroleptic imidophosphorane complexes to Np and Pu.

Publications supported by this project 2023-2025:

1. Andrew C. Boggiano, Julie E. Niklas, Maximillian G. Bernbeck, and Henry S. La Pierre,* "$U^{4+/5+/6+}$ in a Conserved Pseudo-Tetrahedral Imidophosphorane Coordination Sphere," *Inorganic Chemistry*, **2025**, 64, *5*, 2489–2495.

2. Kaitlyn S. Otte, Julie E. Niklas, Chad M. Studvick, Charlotte L. Montgomery, Alexandria R. C. Bredar, Ivan A. Popov,* and Henry S. La Pierre,* "Proton-Coupled Electron Transfer at the $Pu^{5+/4+}$ Couple," *Journal of the American Chemical Society*, **2024**, *146*, 31, 21859-21867. DOI: 10.1021/jacs.4c06319.

3. Julie E. Niklas, Kaitlyn S. Otte, Chad M. Studvick, Sabyasachi Chowdhury-Roy, Bess Vlaisavljevich, John Bacsa, Florian Kleemiss, Ivan A. Popov,* and Henry S. La Pierre,* "A Tetrahedral Neptunium(V) Complex," *Nature Chemistry*, **2024**, 1490-1495. DOI: 10.1038/s41557-024-01529-6.

4. Michael Roy, Thaige P. Gompa, Samuel M. Greer, Ningxin Jiang, Lila S. Nassar, John Bacsa, Benjamin W. Stein, and Henry S. La Pierre,* "Intervalence Charge Transfer in Non-bonding, Mixed-Valence, Homobimetallic Ytterbium Complexes," *Journal of the American Chemical Society*, **2024**, 146, *8*, 5560-5568. DOI: 10.1021/jacs.3c13906.

5. Julie E. Niklas, Kaitlyn S. Otte, Chad E. Studvick, John Bacsa, Ivan A. Popov,* and Henry S. La Pierre,* "Divergent Stabilities of Tetravalent Cerium, Uranium, and Neptunium Imidophosphorane Complexes," *Angewandte Chemie, International Edition*, **2023**, 62(34), e202306580. DOI: 10.1002/anie.202306580.

6. Julie E. Niklas, Chad M. Studvick, John Bacsa, Ivan A. Popov,* and Henry S. La Pierre* "Ligand Control of Oxidation and Crystallographic Disorder in the Isolation of Hexavalent, Uranium Mono-oxo Complexes," *Inorganic Chemistry*, **2023**, *62*, 5, 2304–2316. DOI: 10.1039/D2SC06263A.

Multi-spin-physics Multi-reference Methods for Heavy-Element Chemistry

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Post-Docs: Ryan Beck
Collaborators: Ping Yang (LANL), Enrique R. Batista (LANL), Prof. Henry La Pierre (GeorgiaTech), Prof. Bess Vlaisavljevich (University of Iowa)

Overall research goals:

The goal of this project is to introduce a new multi-spin-physics multi-reference many-body framework in which the fundamental spin interactions (spin-(own)-orbit, spin-(other)-orbit, and spin-spin) are domain-separated based on their importance in different regimes of heavy-element chemistry, integrated in a distributed active space framework. The proposed work is designed to accurately predict heavy-element properties from molecular orbitals to many-body excited states, from atomic electronic structures to molecular complexes with multiple heavy-element centers, and from core to valence electrons. We will steer away from perturbative approximations in favor of a truly variational multi-reference method that allows for domain- and spin-separation.

The research lays the foundation for the potential research paradigm shift from using a single relativistic operator toward choosing the right spin-physics for the right heavy-element chemistry problem. The final product includes new computational capabilities that offer unprecedented accuracy and physical insights for predicting chemical properties and spectroscopies of heavy-element complexes.

The diverse activities in this project provides a supportive environment for the professional development of the students and postdoctoral researchers in the heavy-element community. New educational pathways in collaboration with national laboratory researchers are developed to train the next generation of heavy-element chemistry theorists.

Significant achievements during 2023-2025:

During this funding period, we published seven peer-reviewed articles and released a new version of our open-source software package, incorporating novel algorithms and methodologies developed with the support of this grant. Several key methodological breakthroughs were achieved, enabling low-cost, high-accuracy calculations of relativistic electronic structure methods for heavy-element systems. Highlights include:

- We achieved a major methodological breakthrough in relativistic multiconfigurational methods by developing a small-tensor-product distributed active space (STP-DAS) algorithm. This innovation effectively eliminates the memory bottlenecks that have long limited the applicability of multireference methods in heavy-element chemistry. With this approach, we can now perform configuration interaction calculations involving billions of determinants on a standard laptop. With access to high-performance computing (HPC) resources, this method can be scaled to handle problems involving trillions, or even quadrillions of determinants.

- In collaboration with Ping Yang and Enrique Batista, we successfully elucidated the spectroscopic characteristics of the M-edge spectrum of actinyl complexes. Application of variational relativistic many-body methods revealed hidden shake-up many-electron excitations, which make the M-edge absorption spectrum feature-rich but complicate straightforward covalency analysis.

- We developed, for the first time, fully correlated Dirac–Coulomb–Breit (DCB) many-body methods within the complete active space (CAS) framework for molecular systems. Benchmark studies demonstrate that these correlated DCB methods can achieve sub-meV accuracy in fine-structure energy predictions.

- We introduced a spin-separation technique for the Dirac–Coulomb–Breit Hamiltonian, laying the groundwork for adopting different zeroth-order references in the highly accurate perturbative treatment of spin–orbit and spin–spin interactions.

Science objectives for 2025-2027:

We have three specific plans for the next phase of this work:

- Application to Actinide and Heavy-Element Complexes: We will apply the relativistic multi-spin-physics Dirac–Coulomb–Breit multireference framework to investigate chemical bonding in triatomic uranium species such as NUN and CUO, as well as other heavy-element complexes. This work will be carried out in collaboration with Prof. Vlaisavljevich (University of Iowa) and Prof. La Pierre (Georgia Tech).
- Method Development: We will continue advancing the development of four-component Dirac–Coulomb–Breit multireference configuration interaction (MRCI) methods, incorporating the new multi-spin-physics formalism.
- Large-Scale Calculations with STP-DAS: Leveraging the small-tensor-product distributed active space (STP-DAS) algorithm, which enables configuration interaction calculations involving trillions of determinants, we will address the long-standing challenge of accurately modeling the U_2 molecule using the full Dirac–Coulomb–Breit MRCI method without compromise.

Selected Publications supported by this project 2023-2025

- D. Tang, S. Sun and X. Li, "Exact-Two-Component Complete Active Space Method with Variational Treatment of Magnetic Field and Spin–Orbit Coupling: Application to X-ray Magnetic Circular Dichroism Spectroscopy", Journal of Chemical Theory and Computation, 2024, 20, 9917–9927.
- H. Hu, S. Upadhyay, L. Lu, A. J. Jenkins, T. Zhang, A. Shayit, S. Knecht and X. Li, "Small Tensor Product Distributed Active Space (STP-DAS) Framework for Relativistic and Non-relativistic Multiconfiguration Calculations: Scaling from 10^9 on a Laptop to 10^{12} Determinants on a Supercomputer", Chemical Physics Reviews, 2024, 5, 041404.
- C. Liao, C. E. Hoyer, R. Banerjee Ghosh, A. J. Jenkins, S. Knecht, M. J. Frisch and X. Li, "Comparison of Variational and Perturbative Spin–Orbit Coupling within Two-Component CASSCF", Journal of Physical Chemistry A, 2024, 128, 2498–2506.
- J. N. Ehrman, K. Shumilov, A. J. Jenkins, J. M. Kasper, T. Vitova, E. R. Batista, P. Yang and X. Li, "Unveiling Hidden Shake-Up Features in the Uranyl M4-Edge Spectrum", JACS Au, 2024, 4, 1134–1141.
- S. Sun, J. Ehrman, T. Zhang, Q. Sun, K. G. Dyall and X. Li, "Scalar Breit Interaction for Molecular Calculations", Journal of Chemical Physics, 2023, 158, 171101.
- C. E. Hoyer, L. Lu, H. Hu, K. D. Shumilov, S. Sun, S. Knecht and X. Li, "Correlated Dirac–Coulomb–Breit Multiconfigurational Self-Consistent-Field Methods", Journal of Chemical Physics, **2023**, 158, 044101.

Exploring actinide nanocrystal growth towards defining 5f surface chemistry

Liane Moreau, Principal Investigator

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Graduate Students: William Vance

Collaborators: n/a

Overall research goals:

The overall research goal of this project is to determine the mechanisms behind actinide nanocrystal growth pathways in order to elucidate periodic trends in surface chemistry attributes and bonding characteristics across the 5f row. By comparing differences in the nanoparticle growth pathways of different actinides, we will be able to determine differences in the surface chemistry and ligand binding characteristics between the actinide elements. This data will then be used in conjunction with advanced X-ray methods to draw connections to the role of 5f electrons in bonding behaviour. Deliverables include 1) methods to synthesize actinide oxide nanoparticles (including trans-uranium elements) with precise size and shape control, 2) insight into the periodic trends in actinide surface bonding behaviour and reactivity, and 3) determination of actinide nanoparticle electronic structure as a function of increasing 5f occupancy.

Significant achievements during 2023- 2025:

Since funds for my project were only released in November 2024, current achievements on this project have been limited. However, my group has made significant initial progress on developing a high throughput setup for nanoparticle synthesis in microscale quantities which we will continue to work on in the 2025-2027 block.

Science objectives for 2025- 2027:

- Continue to develop a high throughput setup for nanoparticle synthesis in microscale quantities
- Synthesize actinide oxide nanoparticles using homogeneous nucleation in organic media
- Use small, faceted single crystal nanoseeds to induce heterogeneous growth of actinide oxide nanoparticles with preferred orientation
- Use wide-angle x-ray scattering (WAXS) and high-resolution transmission electron microscope (HRTEM) nano-diffraction to determine long-range crystallography and polycrystallinity in actinide oxide nanoparticles
- Perform extended x-ray absorption fine structure (EXAFS) measurements and ab-initio modeling analysis to determine local ordering and defect chemistry
- Use heterogeneous models of surface versus bulk trends to elucidate nanoparticle surface structure

Publications supported by this project 2023-2025:

1. Vance, William; Moreau, Liane, “Mechanisms behind ThO_2 nanorod growth.” (in progress)

Electronic Structure, Spectroscopy, and Bond Dissociation Energies of Small Actinide Molecules

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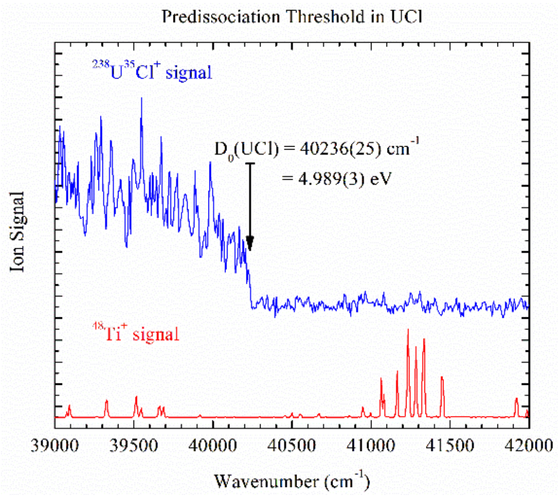
Graduate Students: Dakota M. Merriles, Joshua Ewigleben, Thomas T. Kawagoe, Yexalen Barrera-Casas

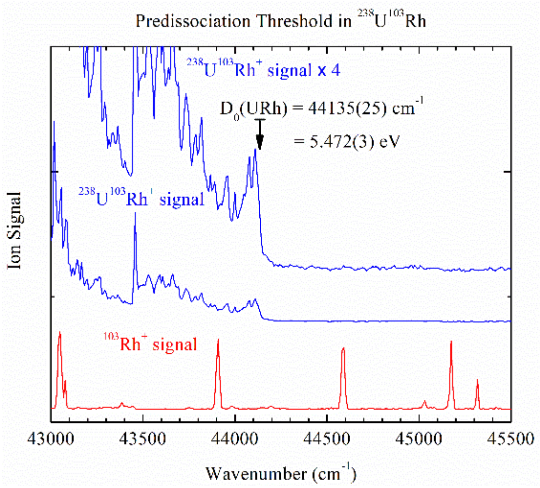
Overall research goals: In this experimental program, we seek to obtain detailed, precise information concerning the electronic structure, spectroscopy, and bond dissociation energies (BDEs) of small thorium and uranium molecules and ions that can be used to assess computational approaches for these systems. The work is focused on advancing our understanding of the role of the 6*d* and 5*f* electrons in the electronic structure of these species. Computational chemistry finds these molecules to be quite challenging, due to the high electronic state density and the highly correlated electronic motions in the partially filled 6*d* and 5*f* subshells. In addition, relativistic effects, including spin-orbit interactions, are of great importance in the actinides. Accurate benchmark data is critically needed to assess method developments in this field.

Significant achievements during 2023- 2025: In a recently published study,[1] we have measured the bond dissociation energies of SU-S, OU-S, and U-Se as 4.910(3) eV, 5.035(4) eV, and 4.609(9) eV, respectively. For the triatomics, a delayed two-color R2PI method was required to allow sufficient time for the molecules to dissociate prior to the ionization laser pulse. By introducing this delay, highly precise bond dissociation energies were obtained. This work has prompted Kirk Peterson's group to perform high-level calculations on these species, with results that are in excellent agreement with our measured BDE values.

After pursuing laser ablation studies of uranium compounds for a few months, my group turned to NSF-supported work to measure the ionization energy of RhC. It was found that uranium that had been deposited within the laser ablation fixture was being vaporized and it reacted with the ablated rhodium to form diatomic URh. We scanned over the bond dissociation threshold and measured D_0(URh) = 5.472(3) eV, in good agreement with the Knudsen effusion measurement of 5.34(18) eV. David Dixon has now calculated URh to have a $d\sigma^2\ d\pi^4\ d\delta^4\ s\sigma^2\ 5f\varphi^1\ 5f\delta^1\ 5f\pi^1$, $^4I_{4.5}$ ground state. The $d\sigma$, $d\pi$, and $s\sigma$ orbitals have contributions on both atoms and are bonding orbitals; the $d\delta$ orbitals are localized on Rh and are nonbonding. The nonbonding 5f orbitals remain localized on U. Thus, URh may be considered to have a quadruple bond. The computed BDE of 5.37 eV (large core CCSD(T) method) is in excellent agreement with our measurement. A joint publication is in preparation.

My graduate students, Thomas Kawagoe and Dakota Merriles have measured the BDEs of the diatomic thorium halides, ThCl, ThBr, and ThI, obtaining values of 5.077(6) eV, 4.391(4) eV, and 3.537(8) eV, respectively. The value for ThCl is very close to a computational result by the Peterson and Heaven groups, who obtained 5.131 eV. Similarly, it is in good agreement with a Knudsen effusion value of 5.03(6) eV. The result for ThBr, however, differs substantially from Knudsen effusion values of Hildenbrand and Lau, who obtained 3.73(6) eV, revised to 3.87(6) eV in a subsequent review. The BDE of ThI has not previously been measured. Thomas Kawagoe has likewise measured the BDEs of UCl, UBr, and UI, obtaining values of 4.989(3) eV, 4.299(13) eV, and 3.449(8) eV, respectively. These compare to Knudsen effusion values of 4.64(9) eV, subsequently revised to 4.51(6) eV for UCl; and 3.87(8) eV, revised to 3.87(6) eV for UBr. No previous measurement exists for UI. From this work, we see that the Knudsen effusion BDE values for ThBr, UCl, and UBr significantly underestimate the strength of the AnX bond. A manuscript on these BDE measurements of ThCl, ThBr, ThI, UCl, UBr, and UI is in preparation and will be published in a collaborative effort with computational results from Kirk Peterson's group.





Ionization energies (IEs) of the AnX halide molecules, were measured using a resonant two-photon ionization scheme. In the first step, the first laser was scanned in the visible or near infrared while the second laser was set to a wavelength that could ionize any states that were excited. This allowed excited vibronic states to be located. In a second step, the first laser was fixed on a wavelength to populate an excited state, and the second laser was scanned to locate the ionization threshold for this excited state. The sum of the two photon energies, at threshold, provided the IE of the molecule. For verification, the process was repeated using two other intermediate states. The process was tested on ThCl, giving IE(ThCl) = 6.364(10) eV, in excellent agreement with Heaven's value, 6.3658(6) eV. We then applied it to ThBr, obtaining a value of IE(ThBr) = 6.336(11) eV. In combination with the neutral molecule BDEs, these results allow the BDEs of the cationic species to be obtained to high precision. We plan to extend these measurements to ThI, UCl, UBr, and UI.

My student, Joshua Ewigleben, is making good progress bringing our ion photodissociation spectrometer online. Our initial design, which employed laser ablation in a high-pressure chamber (30 mTorr), transmission through an ion funnel, pre-trapping in a hexapole trap, and travel through an octopole ion guide to a quadrupole mass filter simply didn't work. Josh has completely redesigned the source, moving the laser ablation source into higher vacuum (~10^{-5} Torr) and injecting the ions directly into the octopole ion guide. The new design works very well, yielding mass-selected atomic ion currents of roughly 3×10^8 ions/pulse. He has successfully trapped 10,000 mass-selected ions, transmitted them through a second quadrupole mass filter, and has gotten the ion counting detection system working. We are now concentrating on the photodissociation process and are currently working to reduce background signal induced by photoelectrons generated by stray laser light.

Science objectives for 2025- 2027: We are currently working to rotationally resolve vibronic features in the spectrum of UC, to allow the bond length and ground state Ω value to be experimentally determined. We will also measure the UC ionization energy and combine these results in a manuscript with our previously measured BDE, 4.304(3) eV. We will generate and measure the bond dissociation energies of ThSi and USi and complete the measurements of the ionization energies of ThI, UCl, UBr, and UI. We are in the process of solving the photoelectron problem in the ion photodissociation spectrometer and will measure the BDEs of ThO^+, UO^+, and the ThX^+ and UX^+ halide cations. We expect these measurements to be straightforward once the photoelectron problem is solved using a telescope to narrow the probe laser beam diameter. Following these measurements we will move on to other actinide cations.

Publications supported by this project 2023-2025:

1. Kimberly H. Tomchak, Jason J. Sorensen, Erick Tieu, and Michael D. Morse, "Predissociation-based measurements of bond dissociation energies: US_2, OUS, and USe," *J. Chem. Phys.*, **2024**, *161*, 044306, https://doi.org/10.1063/5.0220813.

Actinide Speciation in Non-Ideal Solutions

Julia Neumann, Principal Investigator

Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL.

Collaborators: Richard E. Wilson (ANL).

Overall research goals: The aim of this program is to improve our understanding of actinide speciation in non-ideal solutions, in particular highly alkaline and concentrated electrolytes. These environments promote interionic interactions between dissolved species, resulting in non-classical chemical reactivity that goes beyond the scope of current thermodynamic descriptions. Specifically, we are interested in species formed through long-range interactions, for example ion association complexes, and seek to understand their molecular structures, formation mechanisms, and thermodynamics. By combining chemical synthesis with spectroscopy and scattering techniques, we can link measurable thermodynamic quantities with observable structural properties. Gaining insight into the chemical, energetic, and structural interactions that control the formation of these species in non-ideal solutions is crucial to the nuclear energy sector, impacting areas such as nuclear waste treatment and storage as well as modern coolants in advanced reactor technologies, and are more broadly relevant for water-in-salt electrolytes in energy storage and deep eutectics for chemical separations.

Significant achievements during 2023- 2025: This is a new effort initiated at ANL in the spring of 2025. Previously, our group focused on actinide speciation in concentrated nitrate electrolytes in the acidic pH range. While the speciation in alkali nitrate solutions could be thermodynamically described by the uranyl aquo ion and uranyl mononitrate complex, exceptionally high interaction parameters were determined in the case of the tetramethyl ammonium nitrate (TMA-NO_3). These parameters were correlated to unusual changes in the luminescence properties of U(VI). Notably, strong luminescence quenching was observed, likely due to the formation of a ternary TMA-U(VI)-NO_3 complex (Nayak et al. 2024, Persinger et al. 2024).

Science objectives for 2025- 2027: The objectives of this program are to experimentally study the solution speciation of the early actinides Np, Pu, Am, and Cm in near-neutral and alkaline non-ideal conditions, with the goal of correlating thermodynamics with observable chemistry and structure. The work will focus on obtaining both thermodynamic parameters and structural information of dissolved species as well as a mechanistic understanding of the chemistry leading to their formation. Of particular interest to this project are ion association complexes, specifically ternary complexes formed from hydrolyzed actinide species through interionic interactions with electrolyte cations. For example, in the presence of high concentrations of alkaline earth metal ions such as Ca^{2+}, $Ca_x[An(OH)_n]^y$ complexes are formed [1]. While the existence of these species has been proposed to be responsible for anomalous increases in actinide solubility at high alkalinity for a variety oxidation states and ligands, the exact molecular structures, stoichiometries, and formation mechanisms of these ion association complexes are often speculative and spectroscopically unvalidated.

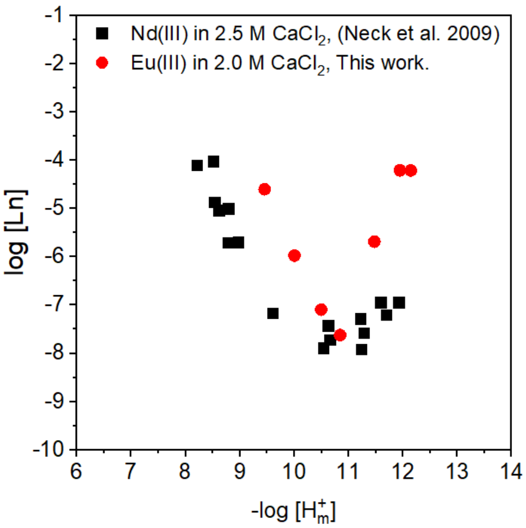


Figure 1. Initial benchmarking solubility tests for Eu(OH)$_3$ compared to published data for Nd(OH)$_3$ [2] in concentrated $CaCl_2$ solutions.

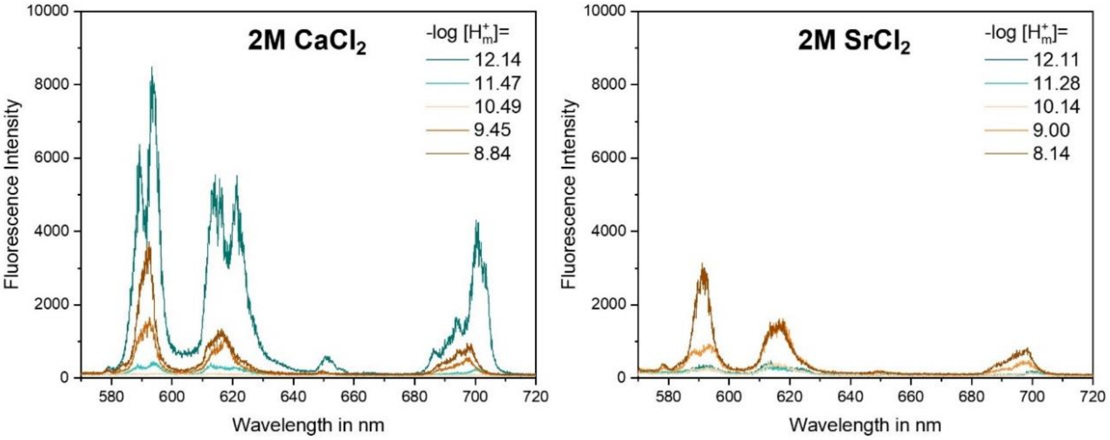


Figure 2. Fluorescence spectra of Eu(III) in concentrated $CaCl_2$ and $SrCl_2$ solution in the alkaline pH range.

In anticipation of the work using Am and Cm, preliminary benchmarking experiments were conducted using the surrogate Eu(III). Our initial studies of $M_x[Eu(OH)_n]^y$ chemistry focuses on different counter-ions with a systematic modulation in hydrolysis constants. Solubility tests in concentrated $CaCl_2$ solutions show the expected solubility increase by four orders of magnitudes for $pH_m > 11$ in $CaCl_2$ (Figure 1), caused by ternary $Ca_x[Eu(OH)_n]^y$ complexes [1]. Eu luminescence spectra confirm the existence of these species in concentrated $CaCl_2$ but show major differences in the Eu speciation in $SrCl_2$ (Figure 2). Specifically, ternary complexes are not formed in $SrCl_2$ up to pH_m~12.11, as the Eu luminescence intensity remains barely above the detection limit. These preliminary results corroborate our hypothesis that the stability ranges of ion association complexes shift depending on the hydrolysis properties of the counter-ion. Future work will give further insights into mechanistic origins as well as the molecular structures and stoichiometries of the formed complexes.

Additionally, we are interested in the reactivity of ion association complexes involving the early actinides in higher oxidation states, which exhibit unpredictable redox behavior at high alkalinity. These systems offer significantly higher solubility compared to trivalent actinides, allowing us to study solution speciation using traditional absorption and vibrational spectroscopy, as well as synchrotron-based X-ray spectroscopy and scattering techniques. This approach enables us to determine complex formation constants for spectroscopically validated and characterized species.

Overall, the project aims to provide a systematic understanding of the chemistry of ion association complexes across the actinide series. By uncovering trends in molecular structures and energetics controlling their reactivity, our work improves our ability to predict how these species affect actinide solubility and speciation at high alkalinity and in non-ideal solutions.

Publications supported by this project 2023-2025:

1. Nayak, Srikanth, and Richard E. Wilson. "Spectroscopic investigation of cation effects in U(VI)-NO_3-complexation in aqueous solutions." *Chemrxiv,* **2024**.

2. Persinger, Thomas, Michael Heaven, and Richard Wilson. "Uranyl Fluorescence in Acidic Solution: Quenching Effects by Tetramethylammonium (TMA^+)." *Chemrxiv,* **2024**.

Bibliography:

1. Rabung, Thomas et al. "A TRLFS study of Cm(III) hydroxide complexes in alkaline $CaCl_2$ solutions" *Radiochimica Acta* **2008**, 96, 551-559.

2. Neck, Volker et al. "Thermodynamics of trivalent actinides and neodymium in NaCl, $MgCl_2$, and $CaCl_2$ solutions: Solubility, hydrolysis, and ternary Ca-M(III)-OH complexes." *Pure and Applied Chemistry* **2009**, 81, 1555–1568.

Matrix Isolation Spectroscopy of the Transuranium Elements

Thomas Persinger, Principal Investigator

Heavy Element and Separation Science Group, Argonne National Laboratory, Lemont, IL
Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL

Collaborators: Richard Wilson (ANL), Michael Heaven (Emory University), Lan Cheng (Johns Hopkins University) and David Dixon (University of Alabama)

Overall research goals: The goal of this research program is to investigate the structure and electronic properties of actinide molecules using optical spectroscopy, principally matrix isolation FT-IR spectroscopy, to explore the role and influence that the 5*f* electrons have in shaping the chemical properties of the early actinides. The influences of the 5*f* electrons on the chemistry of the actinide elements can be probed spectroscopically using a variety of rotational, vibrational and electronic spectroscopy techniques, with a focus on isolating small actinide molecules. The aim of this research is to perform vibrational spectroscopy on small actinide molecules isolated in a cryogenic, inert matrix and to provide vibrational structures as well as experimental information regarding metal-ligand interactions. Investigations involving periodic series of actinide elements with the same ligand can elucidate trends in the chemistry of these elements and inform how the 5*f* electrons impact metal-ligand bonding and molecular geometry. Measuring the vibrational motions of actinide molecules provides important molecular constants that are critical benchmarks for accurate quantum chemical calculations used to predict actinide structure, bonding and chemical reactivity.

Significant achievements during 2023- 2025: Uranyl Fluorescence Spectroscopy: The quenching effect of tetramethylammonium (TMA^+) on uranyl (UO_2^{2+}) fluorescence was investigated using steady-state and time-resolved fluorescence spectroscopy. **Figure 1** shows that TMA^+ quenched the fluorescence and greatly reduced the lifetime of the UO_2^{2+} excited state far more efficiently than other alkali metal or quaternary ammonium cations. Emission spectra showed that TMA^+ pushed the equilibrium of the solution toward greater UO_2^{2+} nitrate complexation relative to other cations tested. Experiments involving the deuteration of solvent and TMA^+ ruled out quenching mechanisms such as hydrogen abstraction and vibrational energy transfer, and additional experiments involving ultrafast laser spectroscopy were recommended to effectively study the quenching dynamics. The results of this work indicated a probable link between this quenching behavior and the selective inhibition of UO_2^{2+} precipitation in the presence of TMA^+.

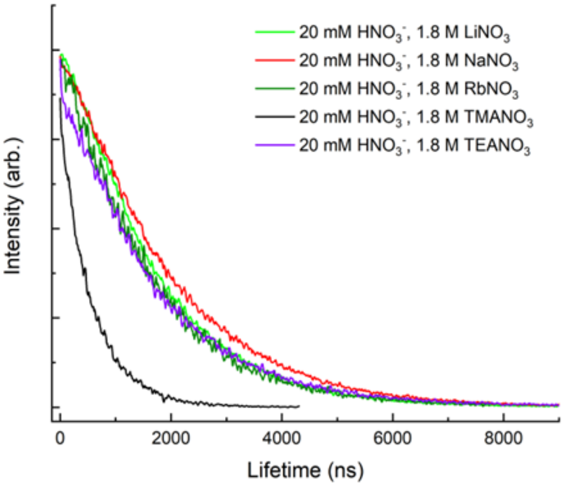
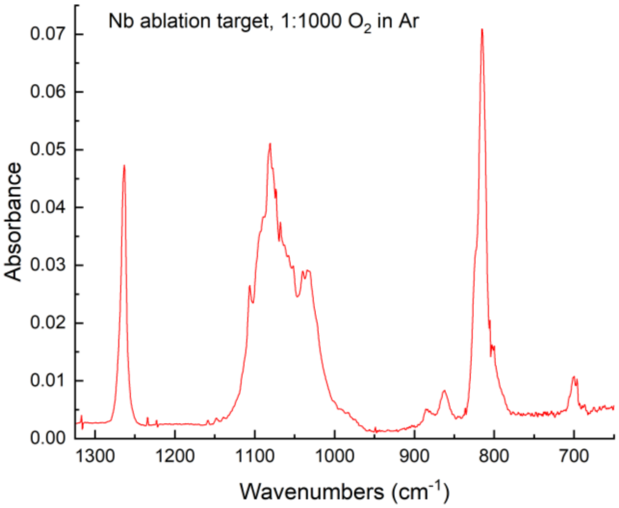


Fig. 1 Fluorescence decay of uranyl at 510 nm, excitation wavelength of 394nm. TMA^+ shown to be more effective at quenching uranyl.

Matrix-Isolation FT-IR Spectroscopy: A matrix isolation FT-IR spectrometer for carrying out transuranium small molecule spectroscopy was constructed in the radiological laboratory facility at Argonne. Preliminary tests to become familiar with the new instrument and to find optimal experimental conditions are underway with transition metal homologues of the actinides (e.g., Nb and Ta for Pa; W and Mo for U). Deposition of metal species on an inert matrix is achieved using laser ablation of a metal source and gas-phase collisions under ultra-high vacuum, allowing for measurement of vibrational spectra using small sample quantities (µg). This matrix isolation instrument is one of a kind in its ability to safely perform spectroscopic experiments on transuranic molecules. The vibrational modes of several metal oxide molecules have been observed, and additional experiments are underway, optimizing the experimental conditions to improve the spectral resolution of the spectra. **Figure 2** shows the FTIR spectra of matrix isolated niobium oxide species trapped in an Ar matrix.



Science objectives for 2025- 2027: The facilities and supply of transuranium material at Argonne National Laboratory allow for matrix isolation experiments involving all early actinides (Th-Cm). The first objective is to identify periodic trends in vibrational frequencies, molecular structures and chemical reactivity of An_xO_y small molecules, as actinide oxides are ubiquitous in actinide chemistry.

Protactinium resides at a crucial turning point between transition metal and actinide character due to the proximity in energies between its 6*d* and 5*f* orbitals, resulting in mixed participation in chemical bond formation. Matrix isolation experiments can confirm current predictions of PaO_2 having linear geometry, an indication of 5*f* orbitals being involved in bond formation. Gas-phase experiments involving matrix isolation FTIR spectroscopy on $PaO^{0/+}$ and $PaO_2^{0/+}$ would provide new and valuable spectroscopic information that would give insight into the bonding character of Pa in the simplest molecular systems. Isotopic substitution experiments ($^{16/18}O_2$) can be used to investigate the geometry of PaO_2 based on shifts in the frequencies of its vibrational motions. To assist in the analysis and interpretation of the vibrational spectra, collaborations with computational chemists Lan Cheng and David Dixon, are established providing theory to compare with experimental data.

The formation and entrapment of transuranium oxide molecules in a Ne matrix is another objective of the project, which provides spectroscopic constants under conditions that are analogous to the gas-phase. Actinide molecules in matrix isolation experiments have been found to form complexes with heavier noble gas matrices, while neon remained too inert for complexation. Open-shell actinide molecules are notorious for having a high density of electronic states at low energies and that complexation with the matrix can result in a reordering of electronic state energies. Experiments involving NpO_2 and PuO_2 in a Ne matrix will provide vibrational spectra that are more accurate to gas-phase conditions, and which should be closer in value to current gas-phase models. Changes in molecular geometry across the early actinide (Th – Cm) oxides, as a result of the stabilization of the 5*f* shell, will also be explored by measuring the IR-active vibrational modes of polyatomic actinide oxide systems. Accessible oxidation states vary across these elements and changes in vibrational frequencies across the early actinides due to change in valency and geometry are expected and will reveal trends in reactivity with oxygen in gas-phase conditions.

Publications supported by this project 2023-2025:

1. Thomas D. Persinger, Michael C. Heaven and Richard E Wilson, "Uranyl Fluorescence in Acidic Solution: Quenching Effects by Tetramethylammonium (TMA^+)", [Submitted to PCCP January 2025], **2024**, DOI: https://doi.org/10.26434/chemrxiv-2024-9wc7v.

Exploring the Nature of f-Element Soft Donor Interactions Using Electronically Tunable Azolate Ionic Liquids

Robin D. Rogers, Principal Investigator

Department of Chemistry, University of Wyoming, Laramie, WY

Postdocs: Ethan Hiti, Geetha Bolla

Collaborators: Hannah Wineinger and Thomas Albrecht (Colorado School of Mines)

Overall research goals: To advance the understanding of how f-elements interact with moderately soft donors, a heavily investigated yet open question which is of prime importance in spent nuclear fuel processing and fundamental inorganic chemistry. We intend to transfer this chemistry from 4*f* elements to transuranic elements, particularly in the study of hydrolysis of Pu(III).

Significant achievements during 2023- 2025:

The PI moved this research program to the University of Wyoming in August 2023 in order to help develop a new Actinide Center at the University and as part of a new UW focus on nuclear chemistry. While new N-donor complexes have been prepared and structurally characterized, the most progress has arisen from our study of Ce(III) hydrolysis products as a stand-in for Pu(III). Our initial paper in this area reported the formation and isolation of $[\mathrm{Ce_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_2(\mu_3\text{-}Cl)_2(Cl)_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_{12}}]\cdot\mathrm{7H_2O}$[3] and since then we have isolated a variety of similar, but structurally complex, isostructural compounds where the 4-amino-1,2,4-triazole ($\mathrm{4\text{-}NH_2\text{-}1,2,4\text{-}Triaz}$) ligand seems to play an organizing role. These results suggest promiscuity in secondary ligands as these compounds crystallize and that the symmetric nature of the core results in crystallization of many disordered fragments which appear crystallographically indistinct (**Fig. 1**). Our most recent results (the subject of this poster) have allowed us to further isolate and structurally characterize intermediate hydrolysis products from no hydrolysis to dimers and tetramers (**Fig. 2**), and ultimately hexamers, as exemplified by $[\mathrm{Ce(\mu_2\text{-}Cl)Cl_2(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_2}]_n$, $[\mathrm{M_2Cl_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_4(4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_2}]$ (M = Ce, Nd), $[\mathrm{Ce_2(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_2}]_n$, $[\mathrm{M_4(\mu_3\text{-}OH)_4(\mu_2\text{-}Cl)_4Cl_4(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_4}]_n\cdot 4n\mathrm{H_2O}$ (M = Ce, Nd), and $[\mathrm{Ce_6(\mu_6\text{-}Cl_{0.25})(\mu_3\text{-}OH)_4(\mu_3\text{-}Cl_{0.75})_4Cl_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_{12}}][\mathrm{CeCl_6}][\mathrm{Cl}]_2\cdot\mathrm{3H_2O}$ (the last one another example of the very complex nature of hexamers which can be isolated).

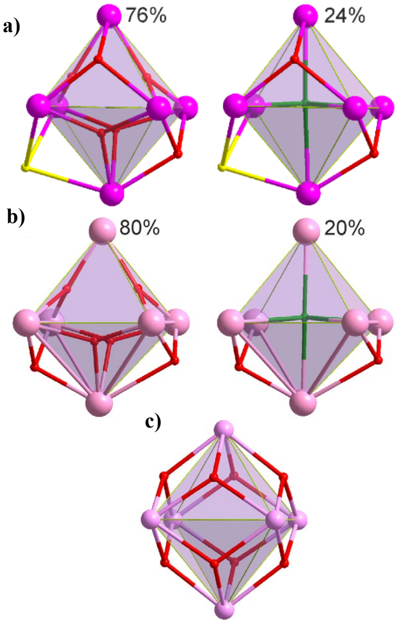
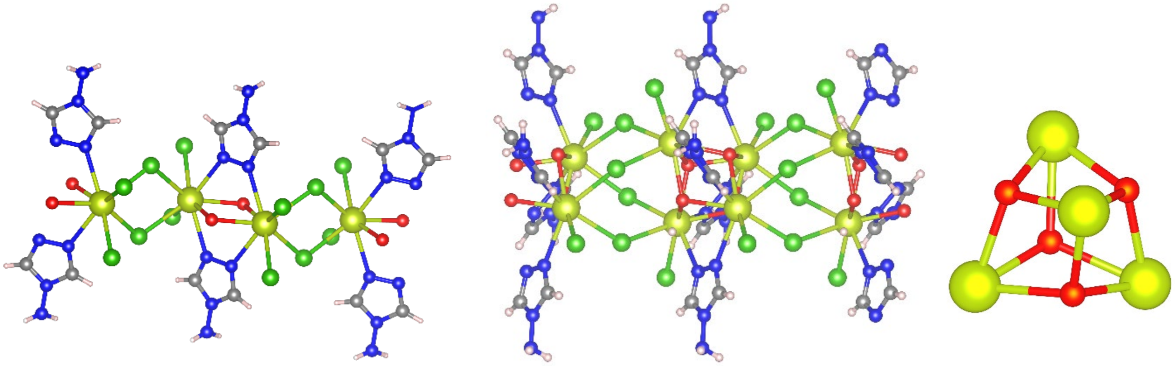


Fig. 1. Contributions to the disordered core model in the crystal structure refinement of (**a**) $[\mathrm{Eu_6(\mu_6\text{-}Cl)_{0.23}(\mu_3\text{-}O_{0.77})_4(\mu_3\text{-}O)_{2.6}(\mu_3\text{-}Cl)_{0.4}Cl_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}triazole)_{12}}]$, (**b**) $[\mathrm{Ho_6(\mu_6\text{-}Cl)_{0.21}(\mu_3\text{-}O_{0.79})_4(\mu_3\text{-}OH)_2Cl_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}triazole)_{12}}][\mathrm{Cl}]_{3.4}$, and (**c**) the fully ordered core in $[\mathrm{Nd_6(\mu_3\text{-}OH)_8Cl_6(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}triazole)_{12}}][\mathrm{Cl_4}]\cdot\mathrm{2H_2O}$.[4]



a) b)

Fig. 2. The recently observed polymeric dimer $[Ce_2(\mu_2\text{-}O)_2(\mu_2\text{-}Cl)_2(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_2]_n$ (**a**) and polymeric tetramer $[Ce_4(\mu_3\text{-}OH)_4(\mu_2\text{-}Cl)_4Cl_4(\mu_2\text{-}4\text{-}NH_2\text{-}1,2,4\text{-}Triaz)_4]_n\text{•}4nH_2O$ (**b**) hydrolysis products.

Science objectives for 2025- 2027:

We have initiated a collaboration with Ms. Hannah Wininger and Prof. Thomas Albrecht at the Colorado School of Mines to take our hydrolysis chemistry to Np and Pu. Currently experiments are in progress to study ^{237}Np(IV) and later in the year Pu(III) and Pu(IV) when stocks become available. This work will be complemented by our continued work with lanthanide stand-ins at the University of Wyoming.

Publications supported by this project 2023-2025:

1. Ethan A. Hiti; Manish K. Mishra; Volodymyr Smetana; Anja-Verena Mudring; Robin D. Rogers, “Isolation of anhydrous tetrabutylphosphonium lanthanide hexa- and penta-nitrates from ionic liquids,” *Polyhedron* **2023**, *232*, 116277, 7 pp, https://doi.org/10.1016/j.poly.2022.116277.
2. Olivier Renier; Guillaume Bousrez; Volodymyr Smetana; Anja-Verena Mudring; Robin D. Rogers, “Investigation of the Role of Hydrogen Bonding in Ionic Liquid-Like Salts with both N- and S-Soft Donors,” *CrystEngComm* **2023**, *25*, 530-540, https://doi.org/10.1039/d2ce00961g
3. Hannah Wineinger; Volodymyr Smetana; Ethan A. Hiti; Glib Baryshnikov; Fengrui Qu; Hans Ågren; Anja-Verena Mudring; Robin D. Rogers, “Trapping An Unexpected/Unprecedented Hexanuclear Ce(III) Hydrolysis Product with Neutral 4-Amino-1,2,4-triazole,” *Eur. J. Inorg. Chem.* **2023,** *26*, e202300450, 10 pp., https://doi.org/10.1002/ejic.202300450.
4. Ethan A. Hiti; Wineinger, H.; Volodymyr Smetana; Anja-Verena Mudring; Robin D. Rogers, “Exploring the Role of Neutral 4-Amino-1,2,4-triazole in the Formation of Hexanuclear f-Element Hydrolysis Products,” *Cryst. Growth Des.* **2024**, *24*, 834-842, https://doi.org/10.1021/acs.cgd.3c01318.
5. Ethan A. Hiti; Geetha Bolla; Robin D. Rogers, “Crystallographic Evidence for Formation of M_6O_8/M_6O_9 f-Element Clusters in Hydrolysis Reactions,” *Cryst. Growth Des.* **2025**, *25*, xxx-xxx, https://doi.org/10.1021/acs.cgd.5c00141.

Solid State Chemistry of the Transuranium Elements in Alkaline Solution

Richard E. Wilson, Principal Investigator

Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL
Collaborators: David K. Shuh (LBNL), Linda Young (ANL), Steve Soutworth (ANL), Lan Cheng (JHU), David A. Dixon (UAlabama), Valerie Vallet (CNRS-Lille), Tori Forbes (UIowa).

Overall research goals: We aim to synthesize high-valent actinide oxides, typically synthesized as crystalline powders, using high-temperature solid state reactions or high temperature flux growth methods as single crystals from concentrated aqueous hydroxide electrolytes under mild thermal conditions facilitating knowledge of actinide reactivity in alkaline solution and the structure property relationships of the resulting solid phases. This work provides new opportunities to understand actinide speciation in the solid state. The ability to actinide synthesize molecules as single crystals and the ability to determine their detailed structural properties facilitates the study of their spectroscopic and magnetic properties in the solid state advancing our knowledge of 5f-electron behavior.

Significant achievements during 2023- 2025: Recent efforts in our laboratory with U(VI), Np(VI), and Pu(VI) have demonstrated that concentrated alkali metal hydroxide solutions are effective in promoting crystal growth of oxide compounds, Figure 1, opening a new opportunity to study the structures, synthesis, reactivity, and electronic properties of these ions and their compounds.

<ins>Synthesis of Li_2NpO_4 and Li_4NpO_5:</ins> Reacting aliquots of NpO_2^{2+} solution with LiOH suspensions under 5M at 155 °C leads to quantitative isolation of $Li_2Np(VI)O_4$, while concentrations of LiOH slurries at 10M or above allow us to precipitate $Li_4Np(VI)O_5$. For the $Li_2Np(VI)O_4$ crystals isolated at low LiOH concentrations, we observe two slightly elongated $Np{=}O_{ax}$ distances of about 1.89 Å with four equatorial $Np\text{-}O_{eq}$ oxo ligands measuring at 2.16 Å, an expected coordination for Np(VI) in solid state compounds. However, the $Li_4Np(VI)O_5$ phase that precipitates at higher LiOH loading, shows a complete reversal of this coordination environment with four shorter $Np{=}O_{eq}$ oxo ligands at 1.99 Å and two longer $Np\text{-}O_{ax}$ at 2.21 Å. While both compounds formally contain Np(VI), the unusual distances in the first coordination sphere of neptunium in $Li_4Np(VI)O_5$ resembles Np(VII) coordination in the $[Np(VII)O_4(OH)_2]^{3-}$ anion. Thus, utilizing such synthetic methodologies gives us a unique insight into the solid-state speciation and structures of high valent actinides that deviates from generally reported or expected values.

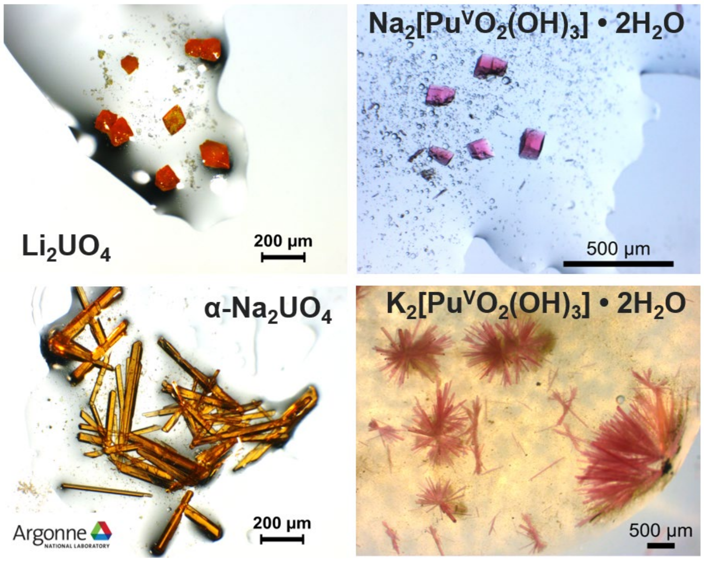


Figure 1: Representative crystals of actinide oxides and hydroxides isolated from alkali metal hydroxide solutions

<ins>Redox Control in Pu Hydroxides:</ins> Exploratory synthesis using the methods demonstrated to be successful for the isolation of U and Np phases was extended to plutonium. Significantly, the

inclusion of redox reagents into the synthesis demonstrated the ability to deliberately reduce the initial Pu(VI) starting material resulting in the isolation of the first Pu(V) hydroxide phases. This work sets the foundation for studying the electronic properties of these rare Pu(V) phases and underscores the ability to provide rational and deliberate synthetic control to these systems. The non-ideal and extreme environments of these chemical systems requires that studies of the fundamental redox transformations in these systems be studied.

Science objectives for 2025- 2027:

- Further study the synthesis of actinide and transuranium oxides and hydroxides from aqueous alkaline solutions focusing on correlation of the solid state speciation with that observed in solution prior to precipitation.
- Investigate the electrochemical properties of the actinides in concentrated hydroxide solutions in order to quantify the redox properties that are occurring in solution as a function of alkali metal concentrations and the chemistry of the alkali metal cation.
- Probe the spectroscopic and magnetic properties of these well-characterized materials with the goal of advancing our predictive understanding of 5f-electron behavior and properties. These studies will include optical and X-ray spectroscopy (XANES, RIXS), and magnetometry. The resulting spectroscopic and magnetic data will be interpreted in concert with computational and theoretical chemists to develop and refine our predictive capabilities for 5f-electron chemistry.

Publications supported by this project 2023-2025 (selection):

1. Xu Wang, Gilles Doumy, Anne Marie March, C.J. Otolski, Richard E. Wilson, Donald Walko, Lan Cheng, Steven H. Southworth, "*Resonant X-ray Emission Across the L_3 Edge of Uranium Compounds*" Journal of Physics B: Atomic, Molecular and Optical Physics. **2025** https://doi/org/10.1088/1361-6455/adac96

2. Emily R. Mikeska, Richard E. Wilson, Asmita. Sen, Jochen Autschbach, James Blakemore. *"Preparation of Neptunyl and Plutonyl Acetates to Access Nonaqueous Transuranium Coordination Chemistry" Journal of the American Chemical Society*, **2024** https://doi.org/10.1021/jacs.4c04613

3. Michael L. Tarlton, Thomas D. Persinger, Nicole M. Byrne, Tyra C. Douglas, Andrey Yakovenko, Richard E. Wilson. *"Rare Earth Nitrate Hybrid Double Perovskites $[Me_4N]_2[MLn(NO_3)_6]$ (M = Na-Cs, Ln = La-Lu ex. Pm)." Inorganic Chemistry*. **2023** https://doi.org/10.1021/acs.inorgchem.3c02081

4. D.C. Hutchison, Dmytro V. Kravchuk, Harindu Rajapaksha, Samantha Stegman, Tori Z. Forbes, Richard E. Wilson. *Synthesis of Single Crystal Li_2NpO_4 and Li_4NpO_5 from Aqueous Lithium Hydroxide Solutions under Mild Hydrothermal Conditions." Inorganic Chemistry*. **2023** https://doi.org/10.1021/acs.inorgchem.3c02460

5. Hanna Oher, Andre S.P. Gomes, Richard E. Wilson, David D. Schnaars, Valerie Vallet, "*How Does Bending the Uranyl Unit Influence its Spectroscopy and Luminescence?" Inorganic Chemistry*. **2023** https://doi.org/10.1021/acs.inorgchem.3c00847

Pursuing Electronic Structure Studies in Polymetallic Actinide Complexes

Cory J. Windorff, Principal Investigator

Chemistry and Biochemistry Department, New Mexico State University, Las Cruces, NM

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Overall research goals:

We seek to understand the electronic structure and reactivity of homo- and heterometallic non-aqueous actinide clusters. Homometallic clusters are prepared *via* ammonolysis of actinide alky complexes supported by substituted cyclopentadienides, or other strongly coordinating ligands. There is literature precedent for the ammonolysis of trivalent rare-earth complexes to give well defined trimetallic clusters. Taken together, this work can be used to further expand to the trans-uranium elements, in particular, neptunium, plutonium, and americium. The reduction chemistry of these clusters is of interest, in particular for the opportunity to study the movement of electrons within and between actinide clusters.

Studies on heterometallic compounds focus on the electronic communication of an actinide with a transition metal. For initial studies titanium is chosen, as reduced forms present clear electronic structure, allowing focus to be paid to the actinide. There is a suitable titanium based metalloligands in the literature known to coordinate a variety of metals, including rare earth elements. The close proximity of the metals means there are opportunities for direct or indirect Ti-M communication. We seek to prepare analogous and related actinide complexes to study Ti-An communication.

These studies provide important information on intra/inter-electron transfer process and mixed valence information on the actinides. These studies may also uncover new opportunities in multi-electron reduction processes mediated with the actinides. Further, the presence of nitrogen bases mean that protons/hydrogen atoms may also be delivered to/from the substrate as part of reactivity. This work will also support the training of students that will serve as the next generation of nuclear workers, in particular in the handling of radioactive materials.

Significant achievements during 2023- 2025:

In an effort to quantify the number of 5*f*-electrons in a given compound, a large collaborative effort was led by researchers at the Karlsruhe Institute of Technology.[1] The study examined a shoulder peak present in actinide M_4 edge Resonant Inelastic X-ray Scattering (RIXS) spectra. The work showed that the intensity of the peak correlated with the number of 5*f*-electrons of a compound. An important contribution was to study the number of *f*-electrons present in the formal U^{II} complex $\{[C_5H_3(SiMe_3)_2]_3U^{II}\}^{1-}$, which has been assigned as a $5f^3 6d^1$ configuration. The RIXS spectrum was consistent with an $5f^3$ electron count but displayed a small shift in energy from $[C_5H_3(SiMe_3)_2]_3U^{III}$. The U^{II} compound was confirmed to be intact and showed little evidence of oxidation by ^1H NMR spectroscopy. This provides evidence that $5f^3 6d^1$ is likely the configuration of this U^{II} compound. The U^{IV} complex $[C_5H_3(SiMe_3)_2]_3U^{IV}Cl$ was also measured and was consistent with the expected $5f^2$ configuration. This work will provide value in future studies for compounds with unusual or ambiguous formal oxidation states.

Initial efforts focused on the preparation of heterometallic titanium-*f*-element clusters based on the Ti-metalloligand $Cp^*_3Ti_3(\mu_3\text{-}N)(\mu\text{-}NH)_3$ **1**, ($Cp^* = C_5Me_5$). Although several $Cp^*_3Ti_3(\mu_3\text{-}N)(\mu_3\text{-}NH)_3REX_3$, **2-Ti/RE** (X = Cl, Otf) are known, **2-Ti/Ce** (X = Cl, I) and **2-Ti/Nd** (X = Cl) have not been reported and were prepared. Ce and Nd are sought as size analogs of Pu and am, respectively.

Furthermore, **2-Ti/Ce** (X = I) and **2-Ti/Nd** (X = Cl) have been reduced and characterized as $\mathrm{Cp^*_3Ti_3(\mu_3\text{-}N)(\mu_3\text{-}NH)_3REX_2(\mu\text{-}X)K(18\text{-}crown\text{-}6)}$, **3-Ti/RE**. **3-Ti/RE** are similar to literature reports on **3-Ti/Y** with a single electron delocalized among the Ti centers. Efforts to prepare uranium analogs using $\mathrm{UCl_4}$, $\mathrm{UI_4(DIOX)_2}$, and $\mathrm{UI_3(DIOX)_{1.5}}$ (DIOX = 1,4-dioxane) were inconclusive. A protonolysis scheme using $\mathrm{Cp^*UBn_3}$ (Bn = $\mathrm{CH_2C_6H_5}$) gave an isolable product characterized as $\mathrm{Cp^*_3Ti_3(\mu_3\text{-}N)_4UCp^*}$, **4-Ti/U**, as characterized by X-ray crystallography, **Fig. 1**.

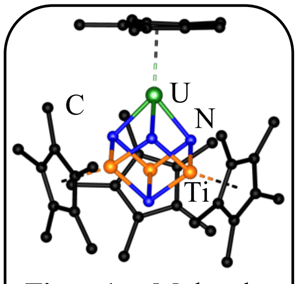

Fig. 1. Molecular plot of $\mathrm{Cp^*_3Ti_3(\mu_3\text{-}N)_4UCp^*}$, **4-Ti/U**

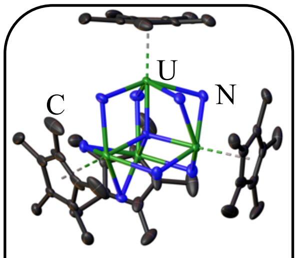

Fig. 2. Molecular plot of $\mathrm{Cp^*_4U_4(\mu_4\text{-}N)(\mu\text{-}N)_8(H)_{15}}$, **5**

The ammonolysis of $\mathrm{Cp^*TiMe_3}$ to give **1**, led to the question of what complex would form for an analogous uranium reaction. When $\mathrm{Cp^*UBn_3}$ is reacted with an excess of $\mathrm{NH_3(g)}$, tetra- and hexanuclear species as $\mathrm{Cp^*_4U_4(\mu_4\text{-}N)(\mu_3\text{-}N)_8(H)_{15}}$, **5**, $\mathrm{Cp^*_6U_6(\mu_6\text{-}N)(\mu\text{-}N)_8(H)_{16}}$, **6**, and $\mathrm{Cp^*_6U_6(\mu_3\text{-}N)_2(\mu\text{-}NH)_{12}}$, **7**, **Fig. 2**. Efforts to use stoichiometric amounts of $\mathrm{NH_3}$ (g) or $\mathrm{NH_3}$ (DIOX), gave similar results. Efforts to prepare chalcogen analogs using $\mathrm{HECPh_3}$ (E = O, S) or $\mathrm{SePPh_3}$ gave the related hexanuclear clusters $\mathrm{Cp^*_6U_6(\mu_3\text{-}O)_2(\mu\text{-}O)_{12}(H)_{10}}$, **8**, $\mathrm{Cp^*_6U_6(\mu_6\text{-}E)(\mu_3\text{-}E)_8}$ (E = S, **9**; Se, **10**), respectively.

Science objectives for 2025- 2027:

Future efforts will focus on further understanding the reduction and reactivity of the cluster complexes. These efforts will focus on chemical reduction using alkali metals or $\mathrm{H_2}$, measurement by cyclic voltammetry, and spectroscopic measurements by UV-vis-NIR, multi-nuclear/variable temperature NMR, and EPR spectroscopies as appropriate. The spectroscopic studies will include compounds labeled with ^{15}N and/or ^{2}H as appropriate. When possible structural studies using X-ray crystallography will be performed. Collaborative efforts will aim to study the spectroscopic signatures and bonding in the cluster complexes using magnetic, X-ray absorption (XAS), and theoretical techniques. With some complexes showing limited solubility, efforts to prepare analogous compounds using more solubilizing cyclopentadienes will be made, namely $\mathrm{(C_5R_4SiMe_3)^{1-}}$ (R = H, Me), and $\mathrm{[C_5H_3(SiMe_3)_2]^{1-}}$, among others. Other ligands including cyclooctatetrenide ligands, $\mathrm{(C_8R_8)^{2-}}$, may also be prepared to further tune the solubility and nuclearity profiles of the clusters. Some limited reactivity will also be examined using unsaturated substrates to determine reduction capacity and if protons play a role in reactivity.

Attention will also turn to the preparation of transuranium (Np, Pu, Am) complexes. Prepparation will begin with appropriate reactions scaled down to those typical of transuranium chemistry, 20-80 μmol. Initial work will be accomplished through collaborative efforts while facilities are prepared for the handling of Np and Pu at NMSU. This will also serve to appropriately train students on how to work in such a specialized laboratory.

Publications supported by this project 2023-2025:

1. Bianca Schacherl, Michelangelo Tagliavini, Hanna Kaufmann-Heimeshoff, Jörg Göttlicher, Marinella Mazzanti, Karin Popa, Olaf Walter, Tim Pruessmann, Christian Vollmer, Aaron Beck, Ruwini S. K. Ekanayake, Jacob A. Branson, Thomas Neill, David Fellhauer, Cedric Reitz, Dieter Schild, Dominique Brager, Christopher Cahill, **Cory J. Windorff**, Thomas Sittel, Harry Ramanantoanina, Maurits W. Haverkort, and Tonya Vitova, "Resonant inelastic X-ray scattering tools to count 5*f* electrons of actinides and probe bond covalency" *Nature Communications*, **2025**, *16*, 1221 DOI: 10.1038/s41467-024-54574-7.