INL/CON-22-69052-Revision-0

Recent Advances in Radiation-Induced Actinide Redox Chemistry

September 2022

Changing the World's Energy Future

Gregory P Horne

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Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Gregory P. Horne
Center for Radiation Chemistry Research

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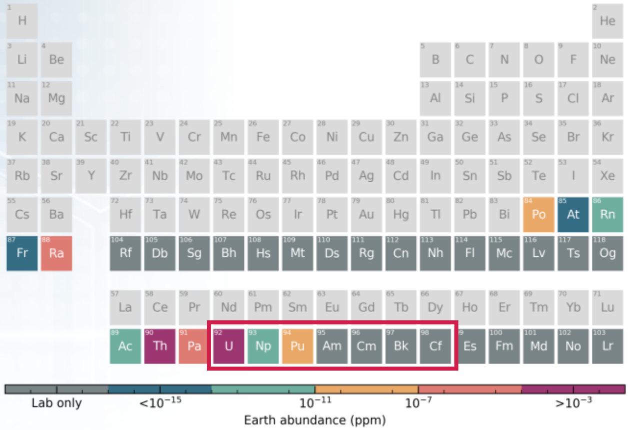

PLUTONIUM FUTURES THE SCIENCE 2022

September 26-29, 2022 | Avignon, France

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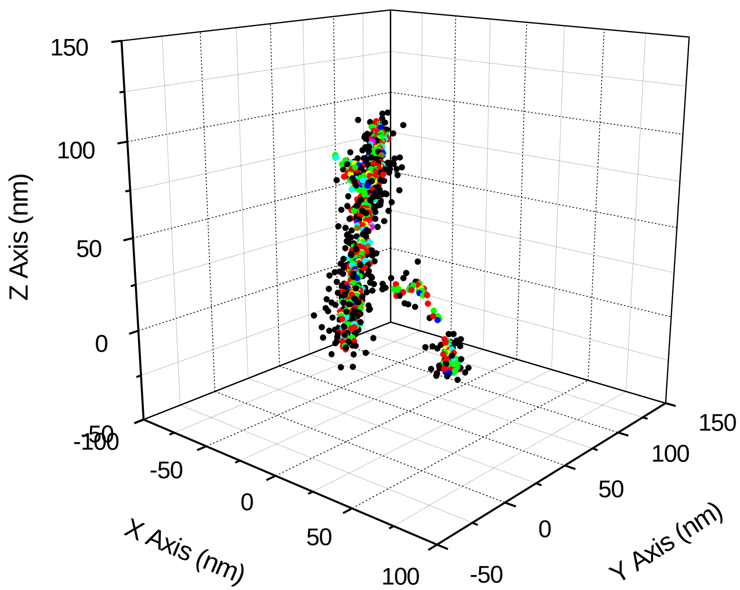
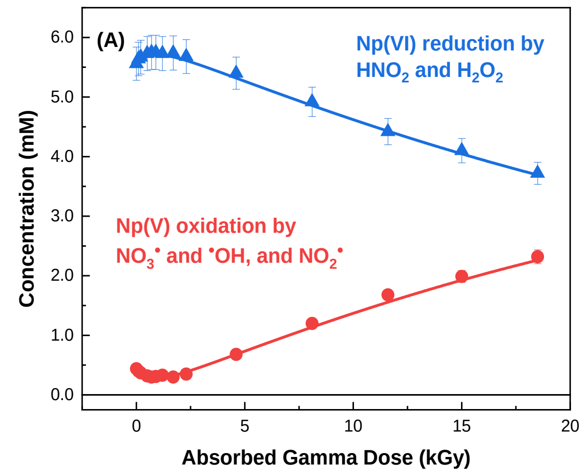
Actinide Radiation Chemistry

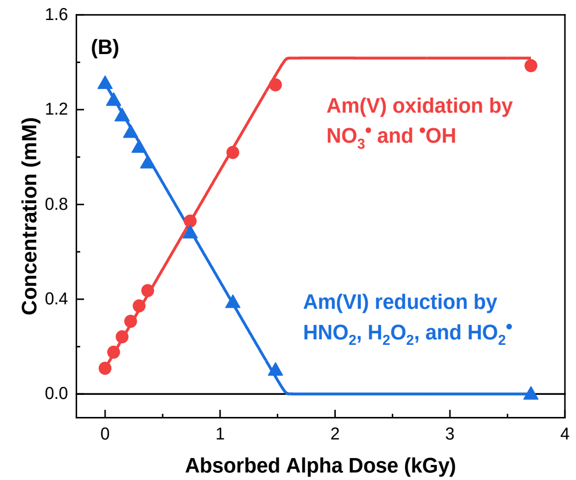
$$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$$

$$NO_3^- + e^-/H^\bullet \rightarrow \rightarrow \rightarrow HNO_2$$

$$HNO_3 + {}^\bullet OH \rightarrow NO_3^\bullet + H_2O$$







- Gordon, Sullivan, and Ross, *J. Phys. Chem. Ref. Data* **1986**, *15*, 1357.
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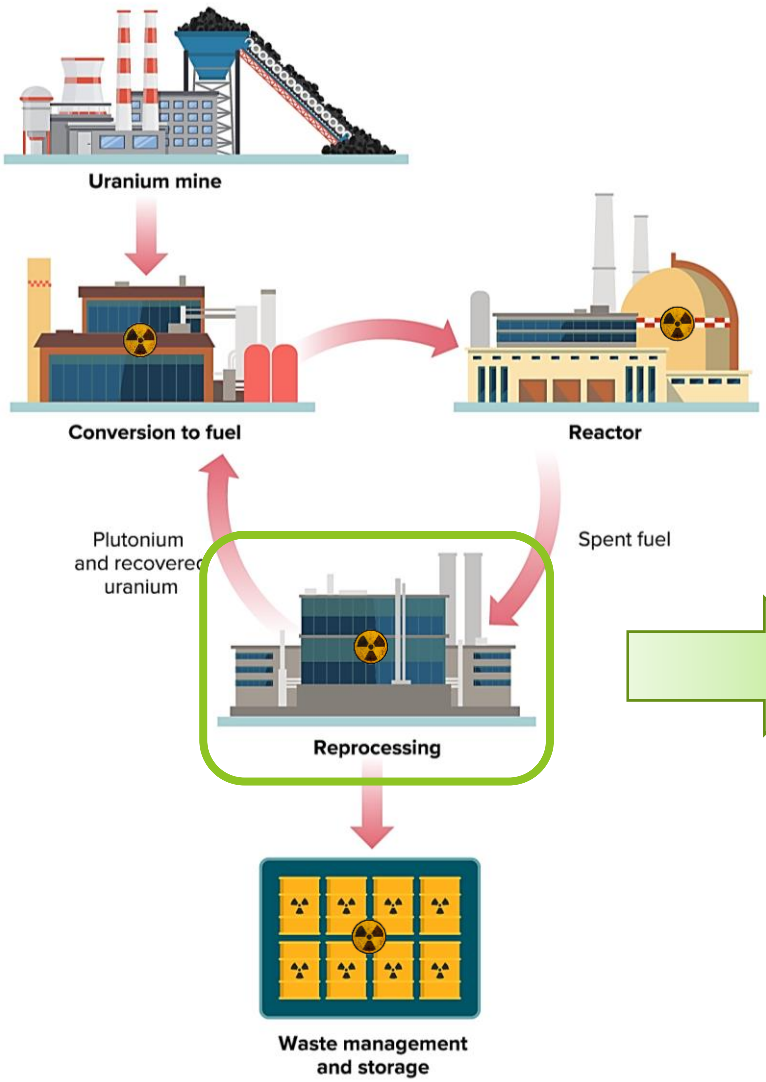
- Mincher and Mezyk, *Radiochim. Acta* **2009**, *97*, 519.
- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.
- Horne, Grimes, Mincher, and Mezyk, *J. Phys. Chem. B* **2016**, *120 (49)*, 12643.
- Horne, Grimes, Bauer, Dares, Pimblott, Mezyk, and Mincher, *Inorg. Chem.* **2019**, *58*, 8551.

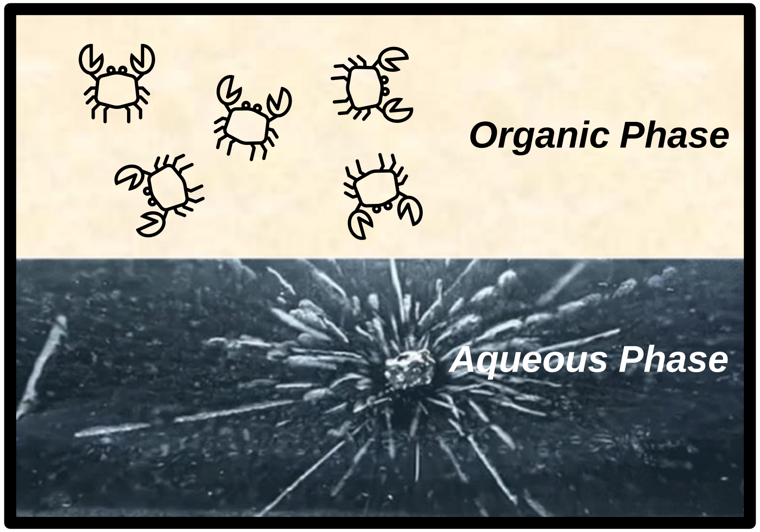
Reprocessing Used Nuclear Fuel



Solvent Extraction Reprocessing

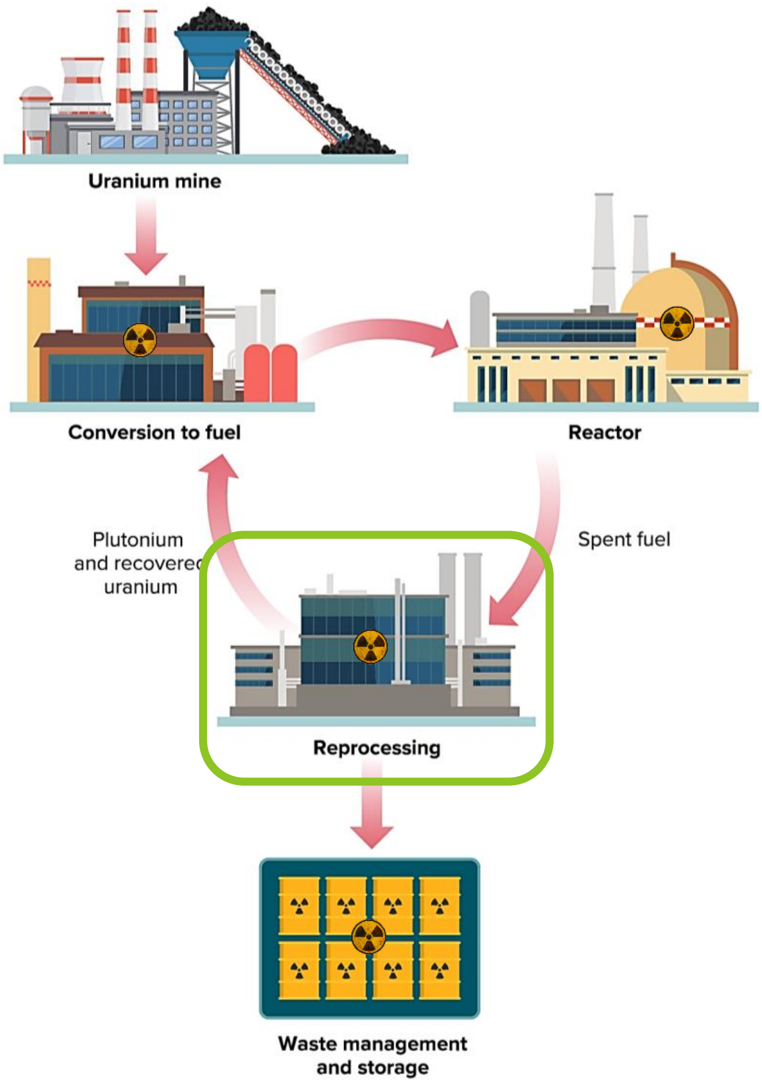
Ligands/organic diluent:HNO_3/H_2O

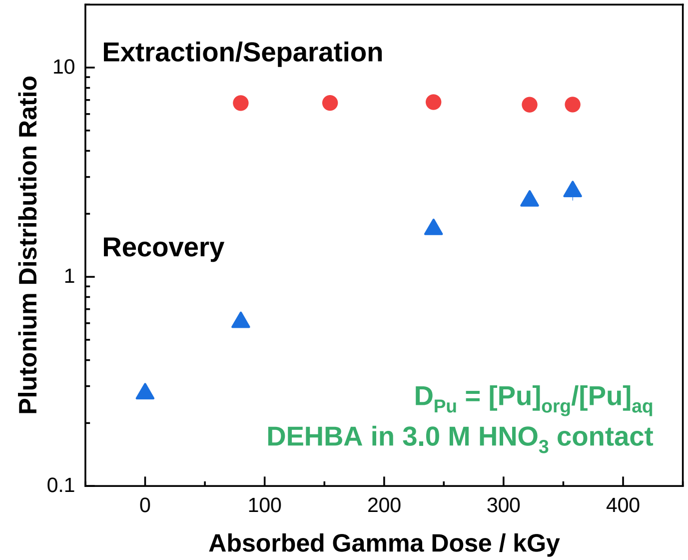
(± additives)

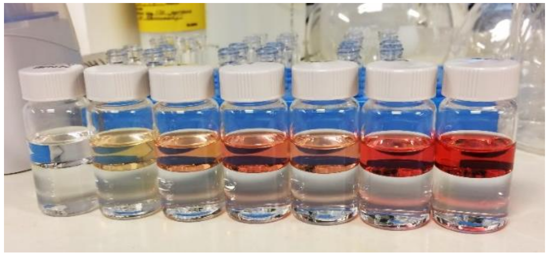


- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- Bruffey *et al.*, Innovative Separations R&D Needs for Advanced Fuel Cycles Workshop, August 30-September 1, 2021. Report for the US Department of Energy, Office of Nuclear Energy Workshop on Innovative Separations R&D Needs for Advanced Fuel Cycles, **2022**.

Reprocessing Used Nuclear Fuel







Increasing Gamma Dose

- Horne, Zarzana, Grimes, Rae, Ceder *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, Mezyk, Mincher, Zarzana, Rae, Tillotson, Schmitt, Ball, Ceder, Charbonnel, Guilbaud, Saint-Louis, and Berthon, *Rad. Phys. Chem.*, **2020**, *170*, 108608.

Complexation Effects

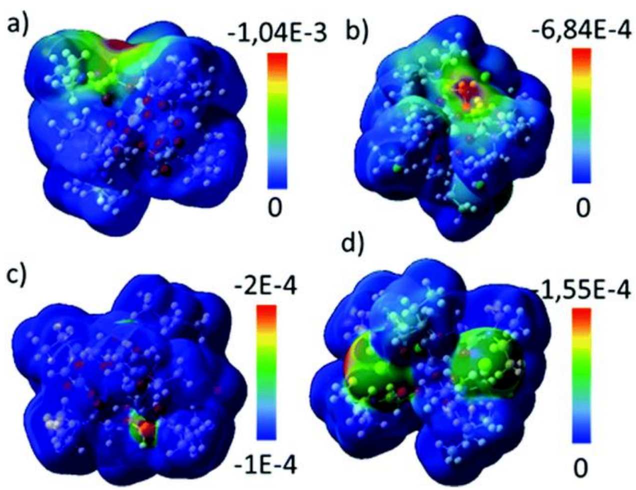
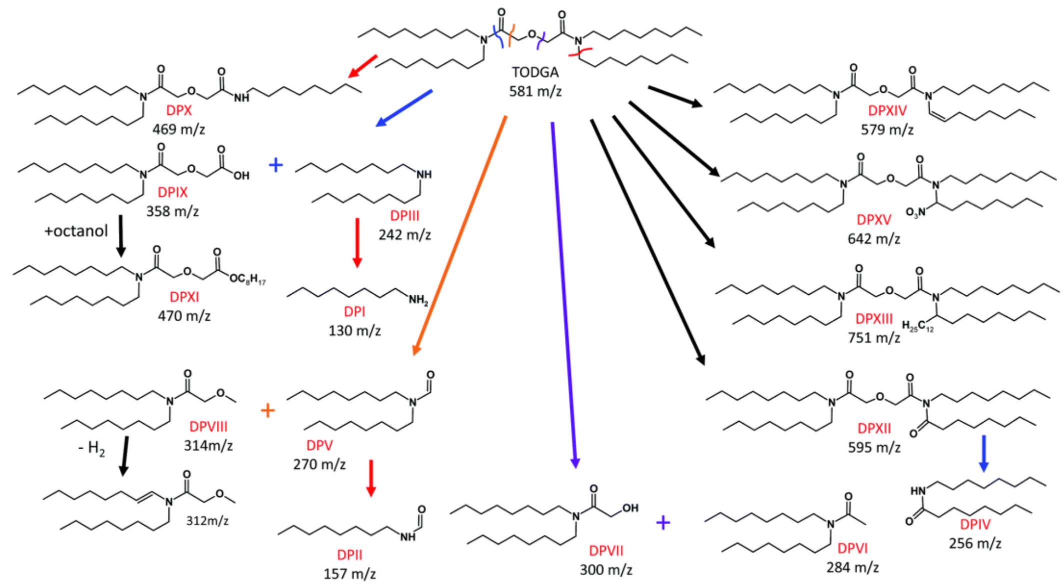
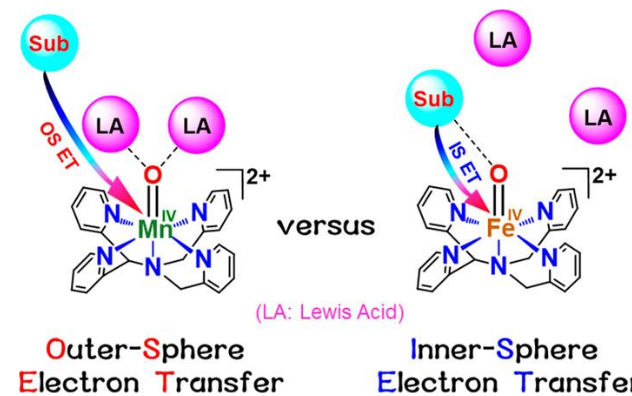


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.





"…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products." Kimberlin *et al.*, *PCCP,* **2022**, *24*, 9213.

Sharma, Lee, Li, Nam, and Fukuzumi, *Inorg. Chem.*, **2019**, *58 (20)*, 13761.

- Bhattacharyya and Kundu, Int. *J. Radiat. Phys. Chem.*, **1971**, *3*, 1.
- Kundu and Matuura, *Int. J. Radiat. Phys. Chem.*, **1975**, *7*, 565.
- Ilan and Czapski, *Biochimica et Biophysica Acta*, **1977**, *498*, 386.
- Buettner, Doherty, and Patterson, *Fed. Euro. Biochem. Soc.*, **1983**, *158 (1)*, 143.
- Kimberlin, Saint-Louis, Guillaumont, Cames, Guilbaud, and Berthon, *PCCP*, **2022**, *24*, 9213.

Research Goals

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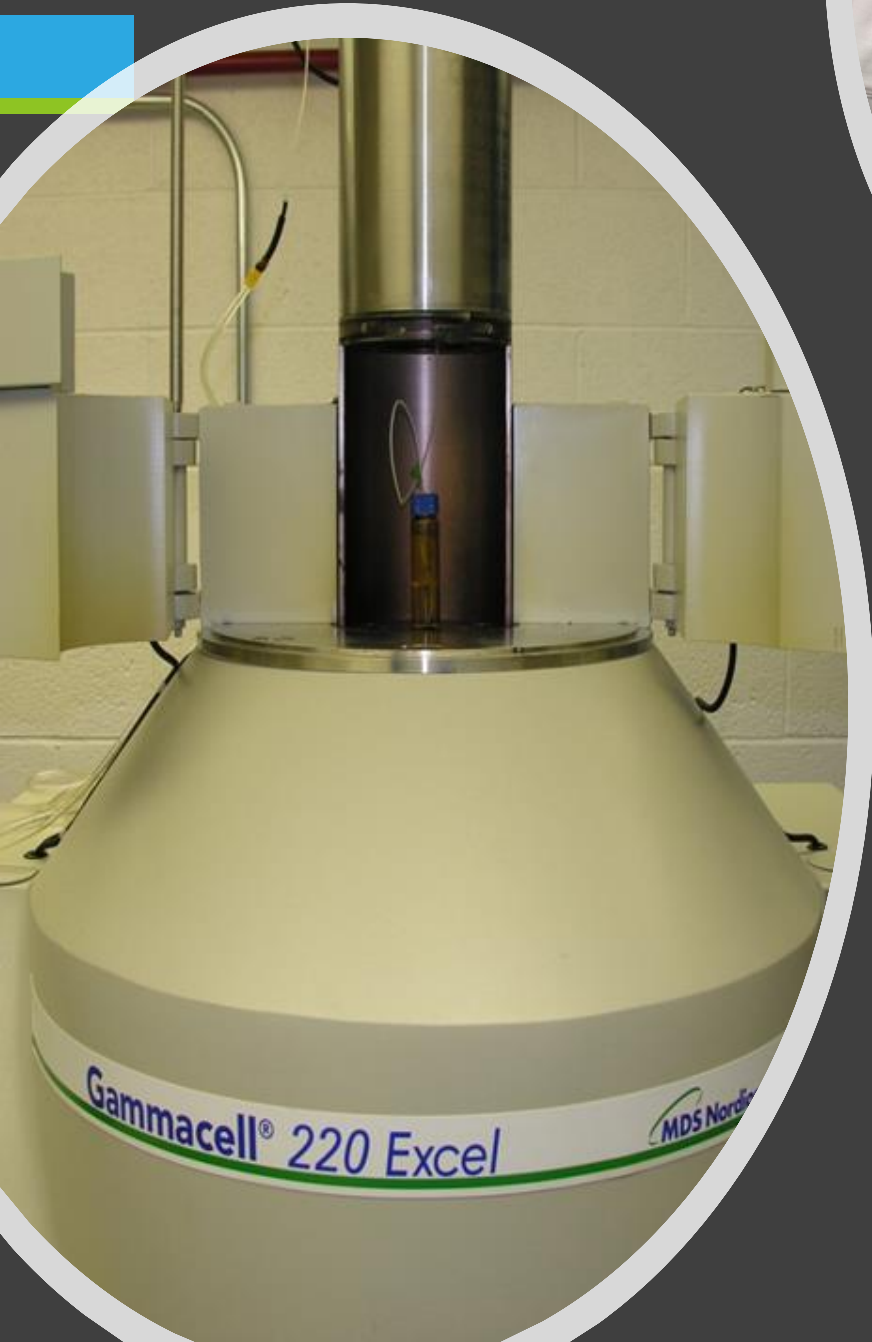
1. Understand the basic radiation chemistry of the actinides in formally non-complexing media.

2. Elucidate the mechanisms underpinning the impact of actinide complexation on ligand radiolysis.

3. Develop multiscale modeling codes for the prediction of radiation-induced chemistry, speciation, and transport of the actinide series in any media.

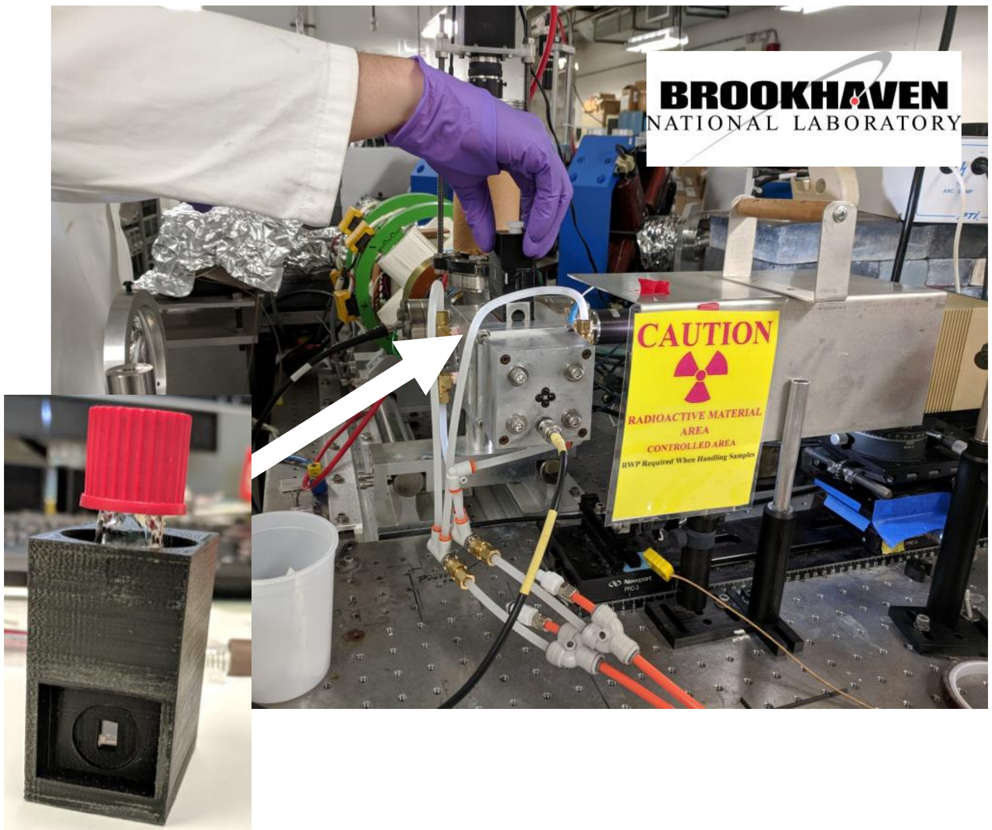
Center for Radiation Chemistry Research

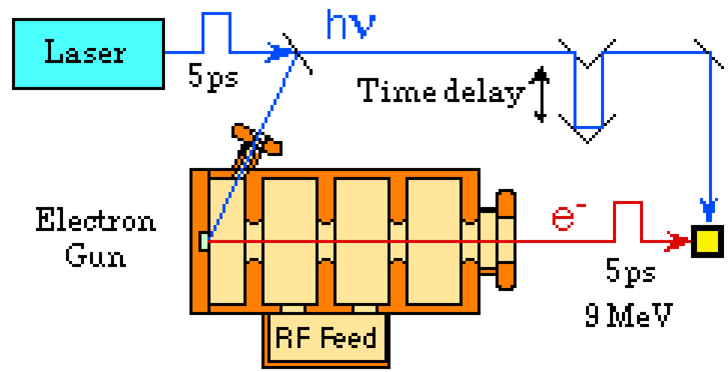
- https://cr2.inl.gov/SitePages/Home.aspx
- https://inl.gov/article/center-for-radiation-chemistry-research-takes-a-forgotten-science-into-the-future/



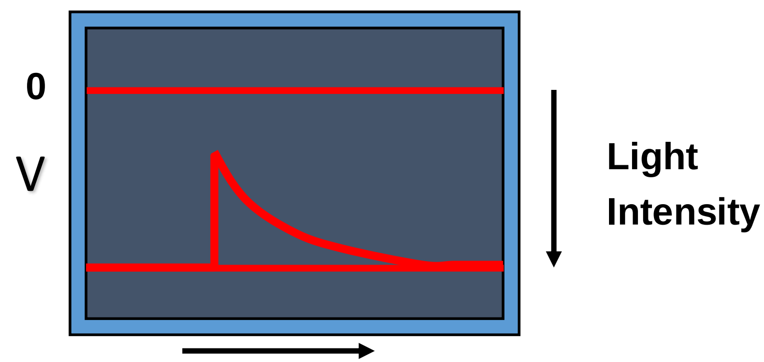
Radiation Chemistry Techniques

Electron Pulse Radiolysis





Transients are detected by optical absorption changes.



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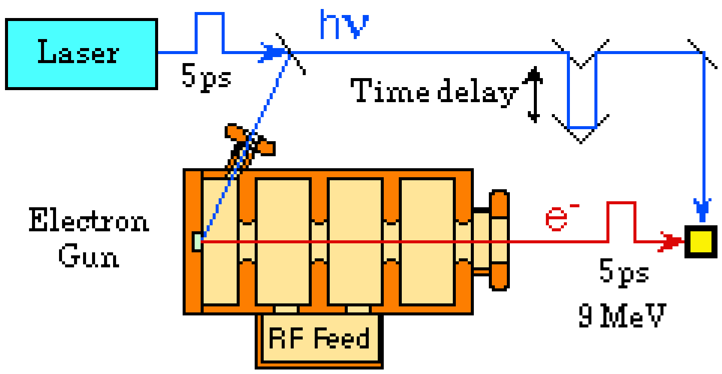
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

Radical Isolation

- **Hydrated Electron** (e_{aq}^-): $HClO_4$/0.5 M tBuOH/N_2-saturated.
- **Hydrogen Atom** ($H^{\bullet}$): ~ 100 µM PCB/$HClO_4$/50 mM tBuOH/N_2-saturated.
- **Hydroxyl Radical** ($^{\bullet}OH$): ~ 100 µM KSCN/10 mM $HClO_4$/N_2O-saturated.
- **Nitrate Radical** ($^{\bullet}NO_3$): ~ 6.0 M HNO_3/N_2O-saturated.
- **Dodecane Radical Cation** ($RH^{\bullet+}$): 0.5 M DCM/*n*-dodecane.



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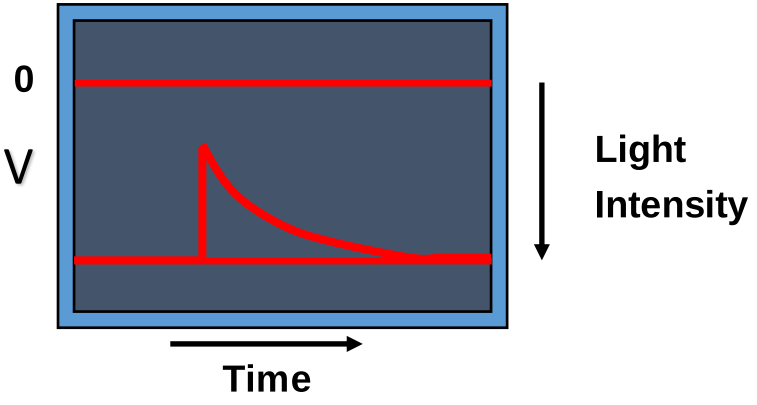
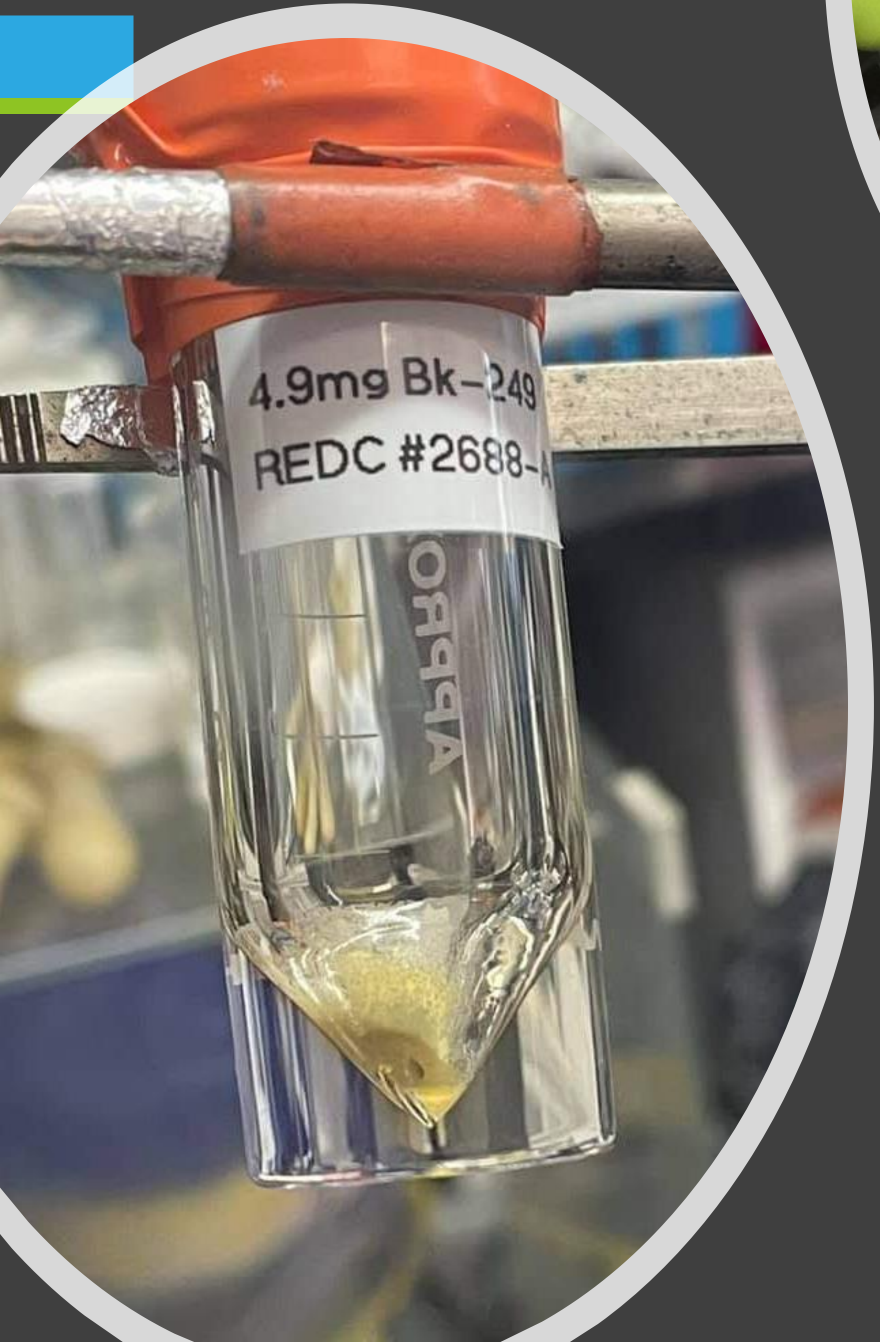
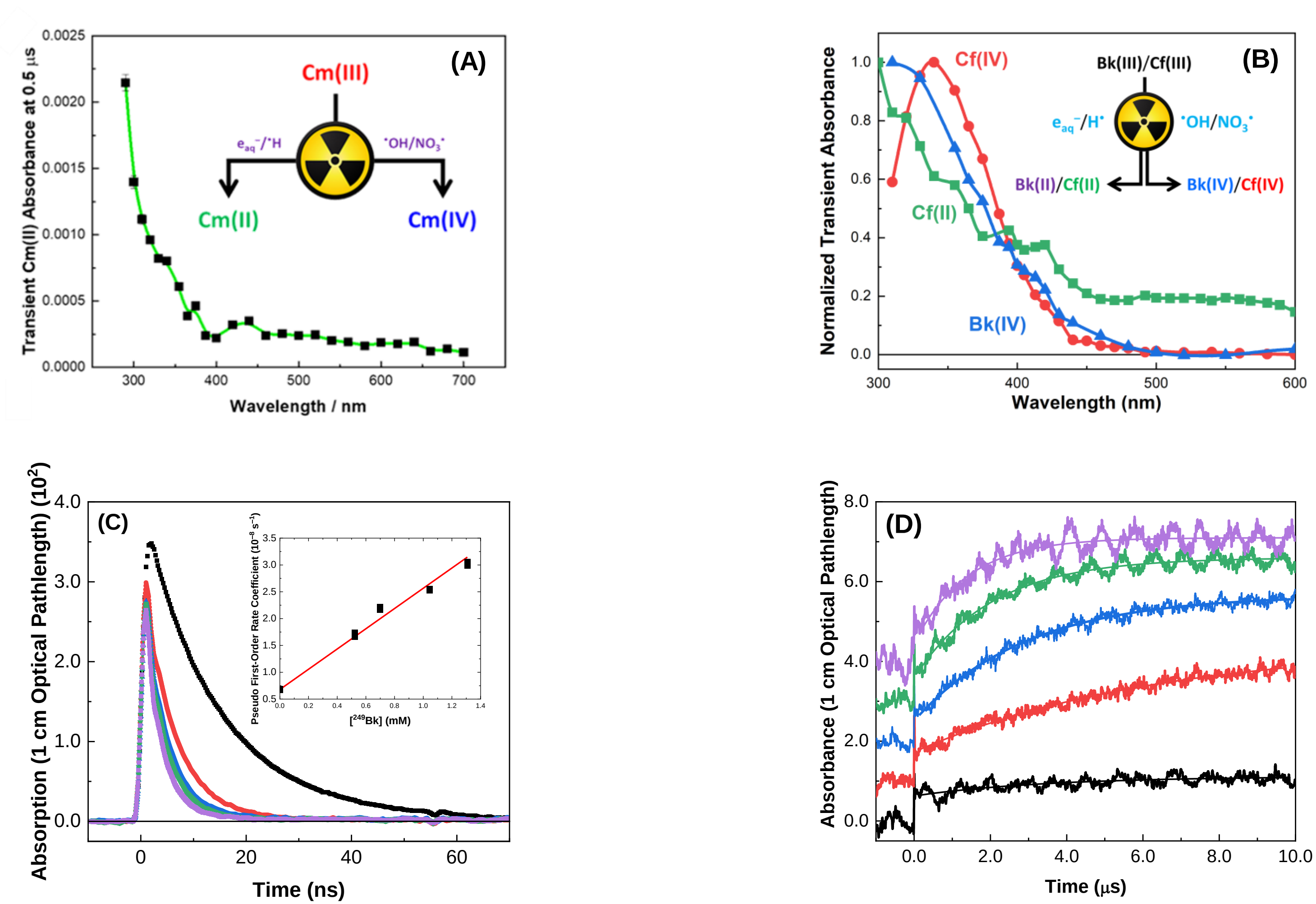


• Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data*, **1988**, *17*, 513.

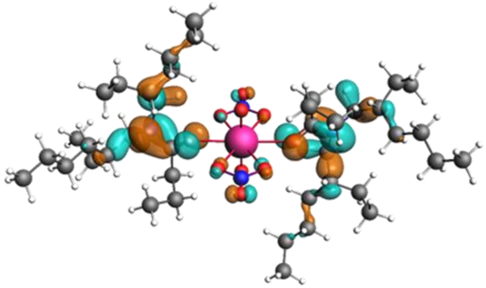


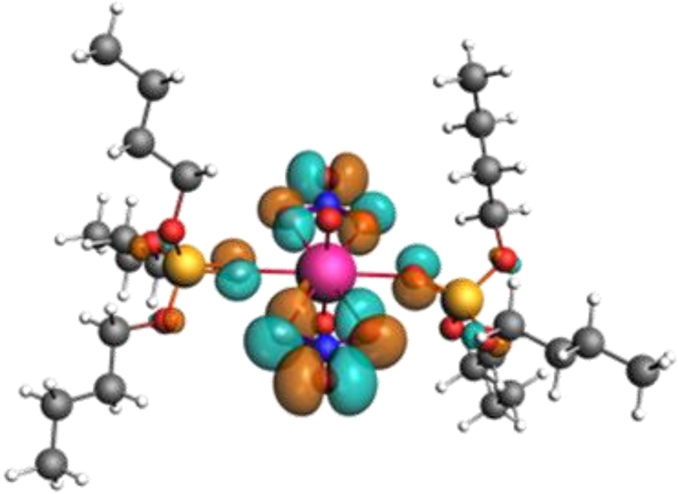
Radiation-Induced Actinide Redox Chemistry

Non-Traditional Oxidation States…



- Horne, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Trans.* **2021**, *50*, 10853.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Beck, Gomez Martinez, Beshay, Peterman, Layne, Johnson, Cook, Albrecht-Schönzart, and Mezyk, *Inorg. Chem.*, **2022**, *61 (28)*, 10822.





Impact of *f*-element Complexation on Radiolytic Behavior

f-element Complexes of HEH[EHP]

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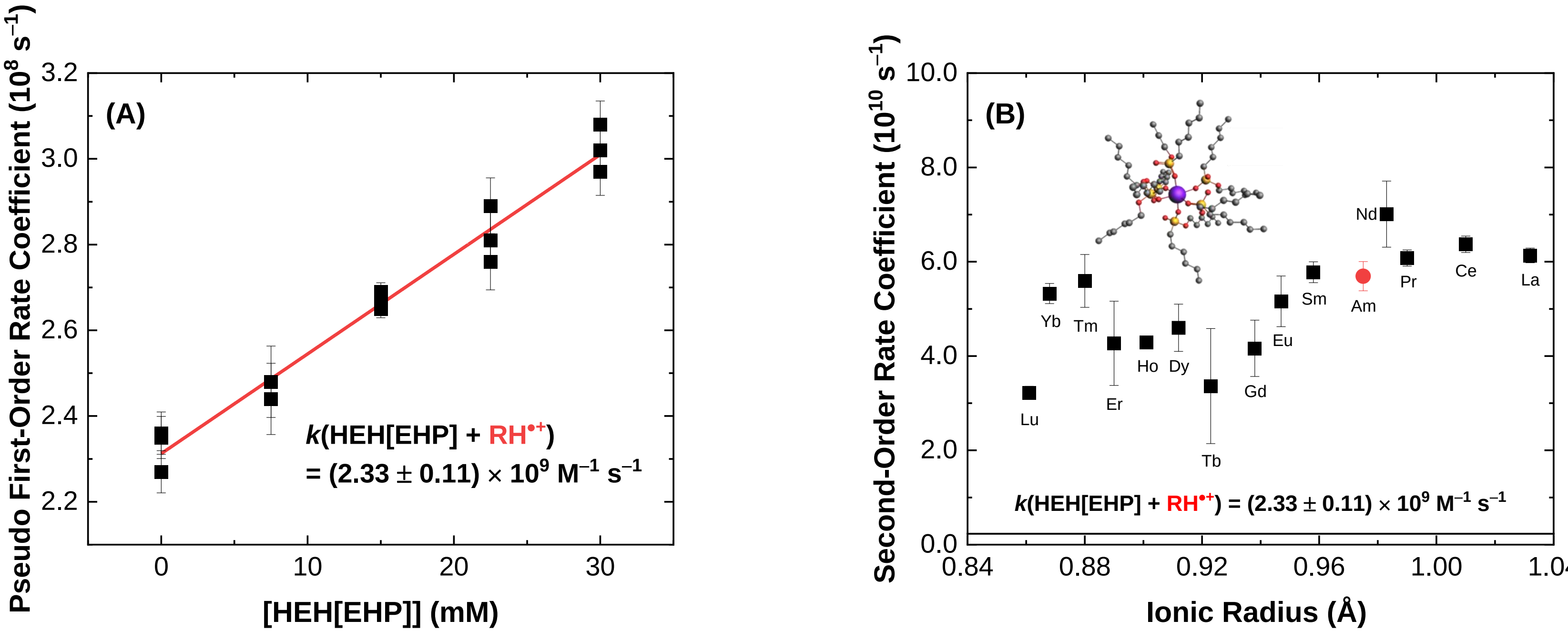
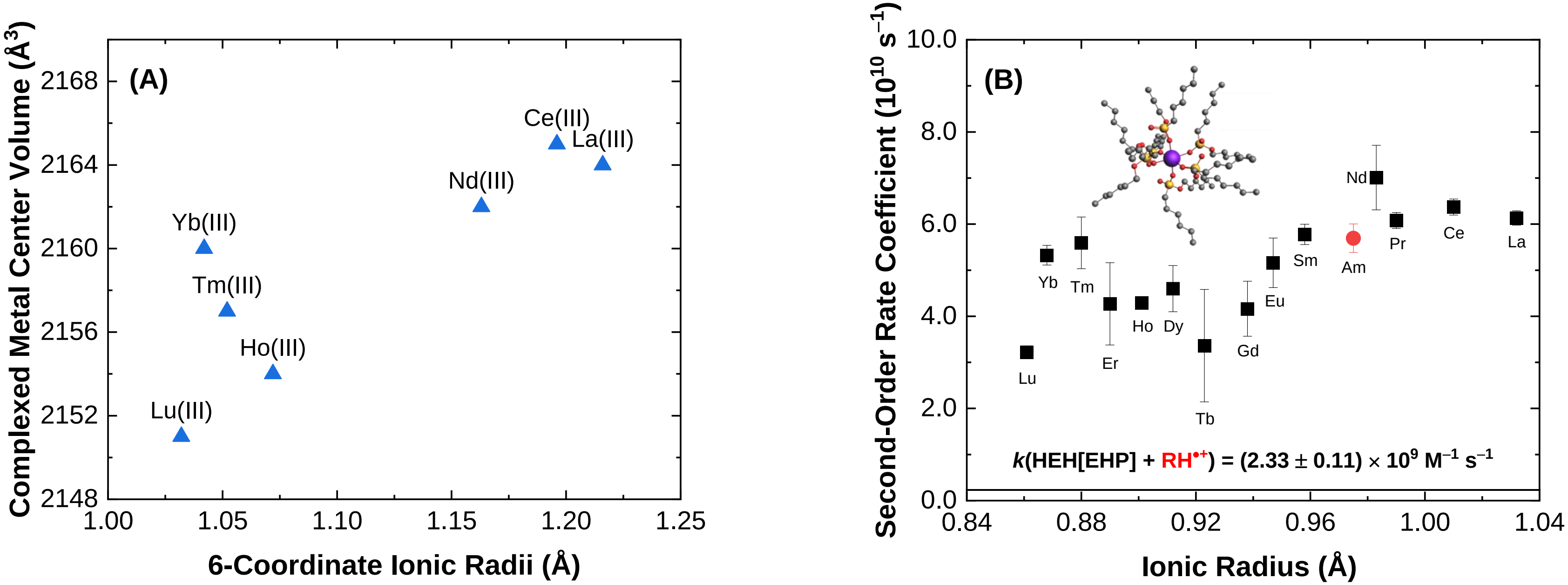


- **Methodology:** Δ[HEH[EHP]]/[M{(HEH[EHP])$_2$}$_3$] in 0.5 M DCM/*n*-dodecane; **RH$^{\bullet+}$** decay measured at 800 nm over 200 ns using the BNL *Laser Electron Accelerator Facility* (LEAF).

- Baxter, Cellis-Barros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *in preparation*.

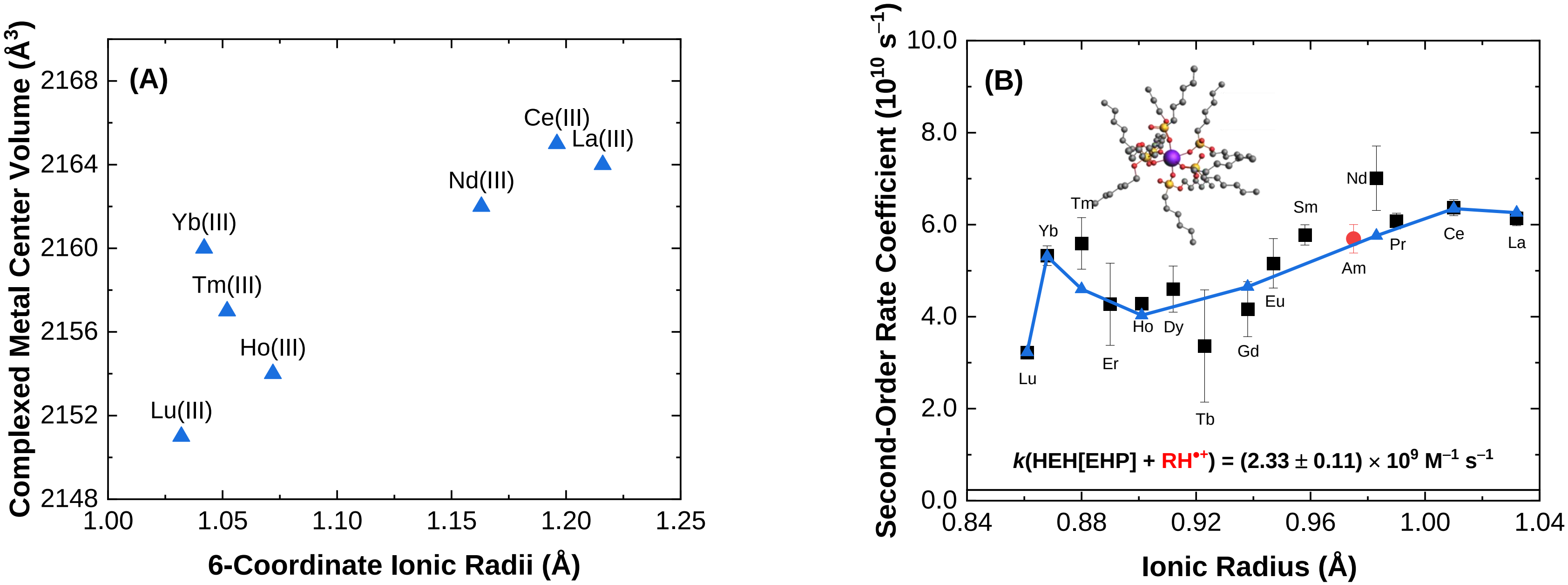
Size Matters…



- **Computations:** Geometry optimization using ADF2020 (*GGA OPBE functional* + *ZORA/STO-TZP basis set for all atoms*); Wave functions using ORCA (*Hybrid PBE0 functional* + *DKH-def2-SVP/DKH-def2-TZVP/SARC-DKH-TZVP*); and QTAIM metrics obtained from DFT wave functions using the AIMALL software.

- Baxter, Cellis-Barros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *in preparation*.

Size Matters…



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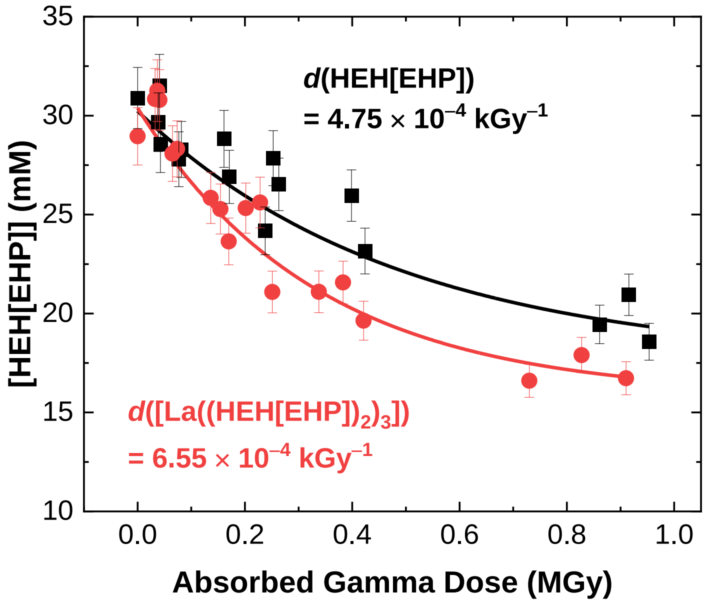
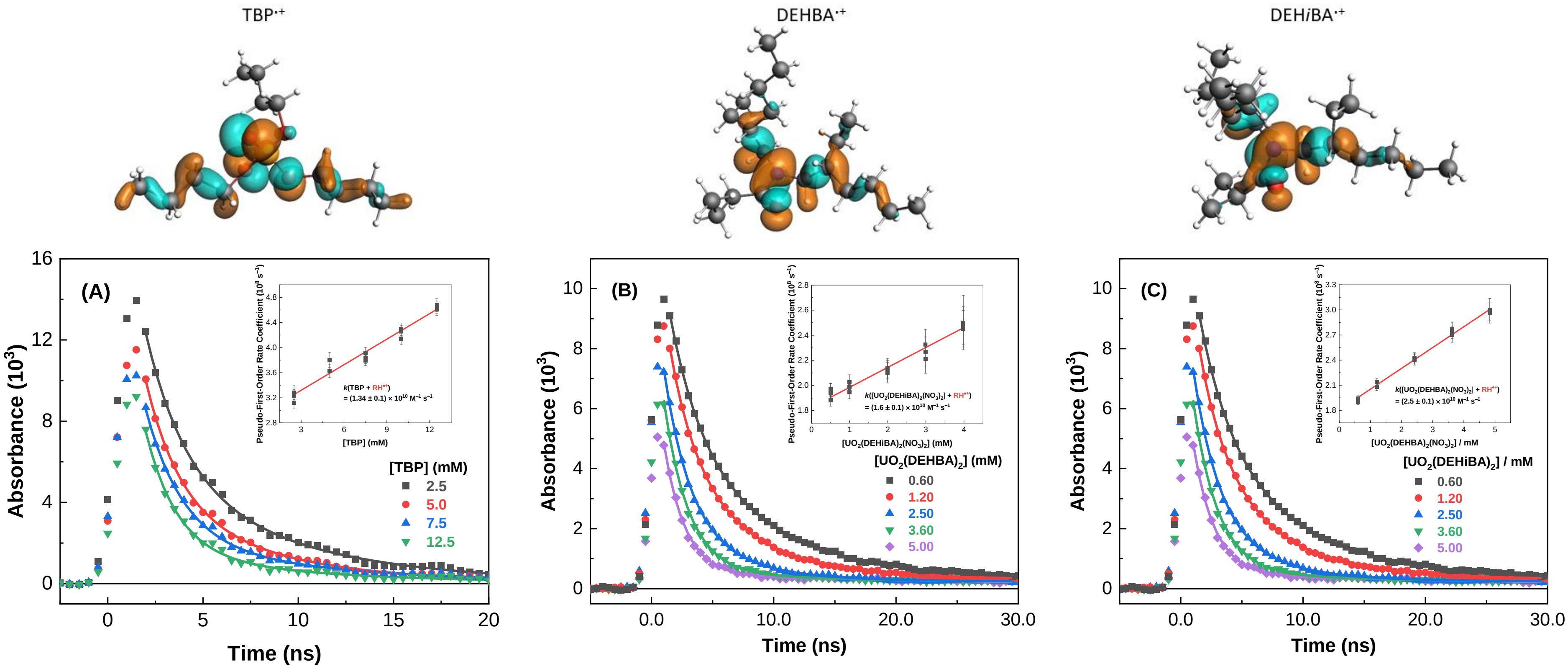
Steady-State Impact?



- **Steady-State Gamma Irradiations:** Cobalt-60 irradiation of 30 mM HEH[EHP] under organic only (■) and loaded with 2.5 mM La(III) from PIPPS/HNO_3 solution (●). Dose constants (d) were calculated from linear fits to [[La(([HEH[EHP]])$_2$)$_3$)] *vs.* absorbed gamma dose.

- Baxter, Cellis-Barros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *in preparation*.

Uranyl Complexes of TBP, DEHBA, and DEHiBA



- UO_2^{2+} complexation had negligible effect on the reaction of **TBP** with **RH•$^+$**, k(**TBP** + **RH•$^+$**) = **(1.3 ± 0.1) × 10^{10} M^{-1} s^{-1}**.
- For **DEHBA** and **DEHiBA**, UO_2^{2+} complexation afforded a **2.6×** and **1.4×** increase in their respective rate coefficients, respectively.

• Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.

Changes in Reaction Mechanism

$[UO_2(NO_3)_2(TBP)_2]^{\bullet+}$ $[UO_2(NO_3)_2(DEHBA)_2]^{\bullet+}$ $[UO_2(NO_3)_2(DEH\textit{i}BA)_2]^{\bullet+}$

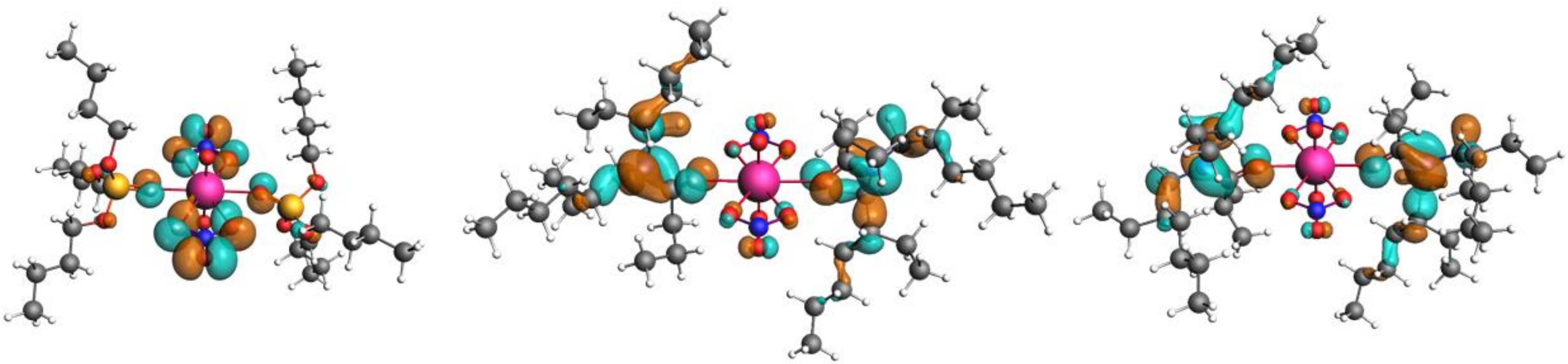


Table 1 Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet+}$ with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

Ligand	$\Delta G_{\text{electron/hole transfer}}$ (eV)	$\Delta G_{\text{proton transfer}}$ (eV)
TBP	0.16	−0.36
DEHBA	−0.88	−0.60
DEHiBA	−0.90	−0.57

Electron/Hole Transfer

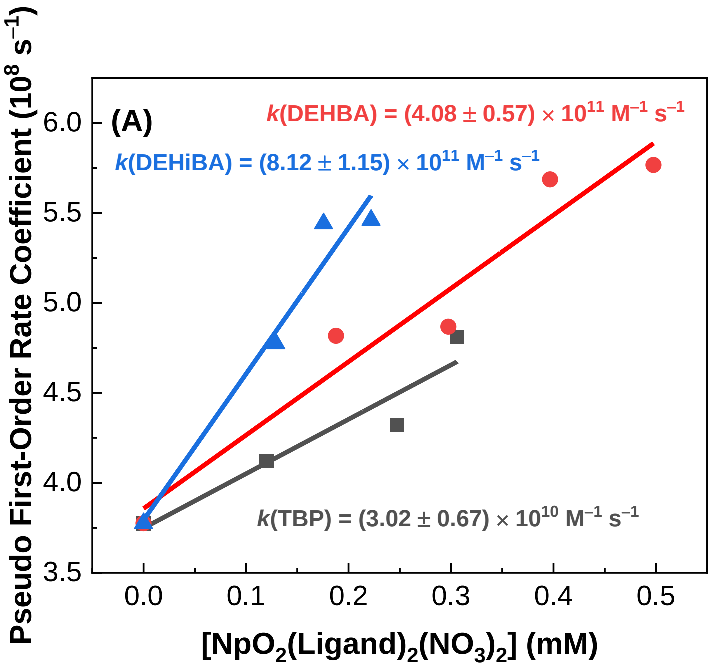
$$RH^{\bullet+} + \text{Ligand} \rightarrow RH + [\text{Ligand}]^{\bullet+}$$

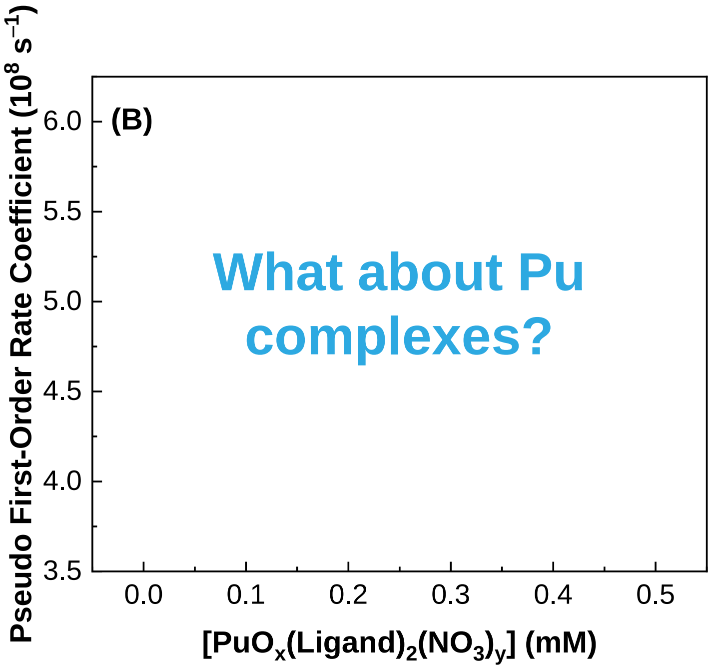
Proton Transfer

$$RH^{\bullet+} + \text{Ligand} \rightarrow R^{\bullet} + [\text{Ligand(+H)}]^{+}$$

- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.
- Frisch, Trucks, Schlegel, Scuseria, Robb, *et al.*, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.
- ADF 2021.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

Transuranic Complexation…





- **NpO_2^{2+}** complexation by **TBP** afforded **~3×** faster rate of reaction with **$RH^{\bullet +}$**, and over an order of magnitude increase for complimentary **DEHBA** and **DEHiBA** complexes.
- Evidence for electron transfer with the complexed metal center?

- Pilgrim, Celis-Barros, Grimes, Cook, Mezyk, and Horne, *in preparation*.

Conclusions

- Actinide radiation chemistry is as fundamental to the actinides as their 5*f* electrons.
- “Unbound” actinides attain exotic radiation-induced transient oxidation states with lifetimes sufficient to propagate chemistry.
- Actinide complexation has significant effects on the radiation robustness of their complexes.
- **Overall, the presented data provide important missing information that will augment current and future studies into the unique chemistry of these elements and their periodicity.**

Acknowledgements

U.S. DEPARTMENT OF ENERGY

CALIFORNIA STATE UNIVERSITY LONG BEACH

FLORIDA STATE UNIVERSITY

BROOKHAVEN NATIONAL LABORATORY

Material Recovery & Waste Form Development

NTRD Nuclear Technology Research & Development

Idaho National Laboratory

New Postdoctoral/Staff Scientist Position(s)

- **The INL *Aqueous Separations and Radiochemistry* group and the *Center for Radiation Chemistry Research* are seeking to add an enthusiastic, self-motivated Post-Doctoral Research Fellow and/or Staff Scientist to their team.**
- An ideal candidate(s) would have previous experience with:
  - **organic and/or inorganic synthesis as well as characterization techniques used for validation;**
  - **previous familiarity with vitrification, radiation, and/or actinide chemistry is favorable;**
  - **and seeking funds through grant proposal writing.**

- If interested, please contact either **Colt Heathman** (colt.heathman@inl.gov), **Corey Pilgrim** (corey.pilgrim@inl.gov), **Melissa Warner** (melissa.warner@inl.gov), and/or myself (gregory.horne@inli.gov) for more information.