INL/CON-23-71510-Revision-0

Actinide Radiation Chemistry and Used Nuclear Fuel Reprocessing

March 2023

Changing the World's Energy Future

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Idaho National Laboratory

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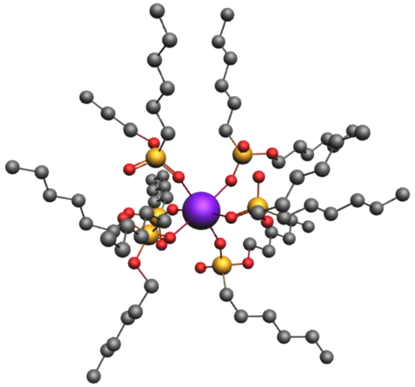

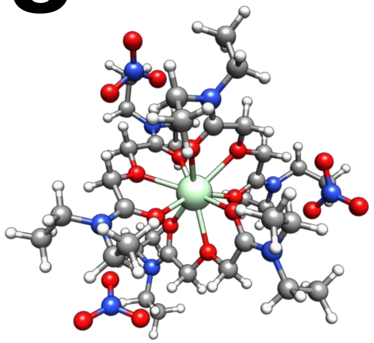

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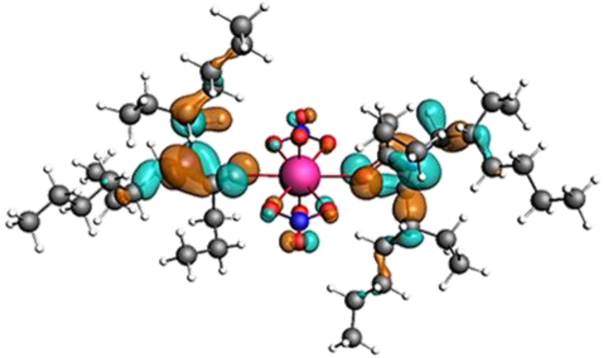
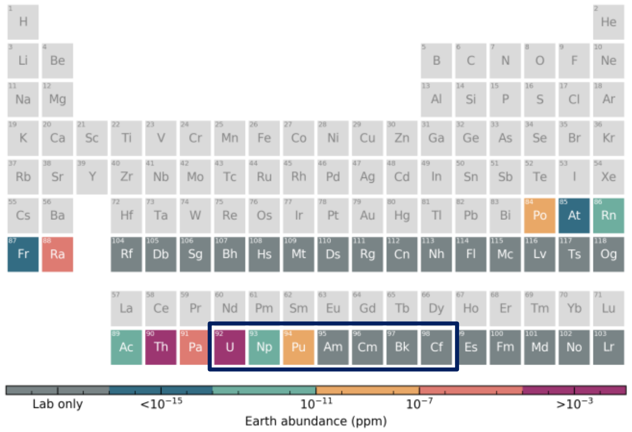
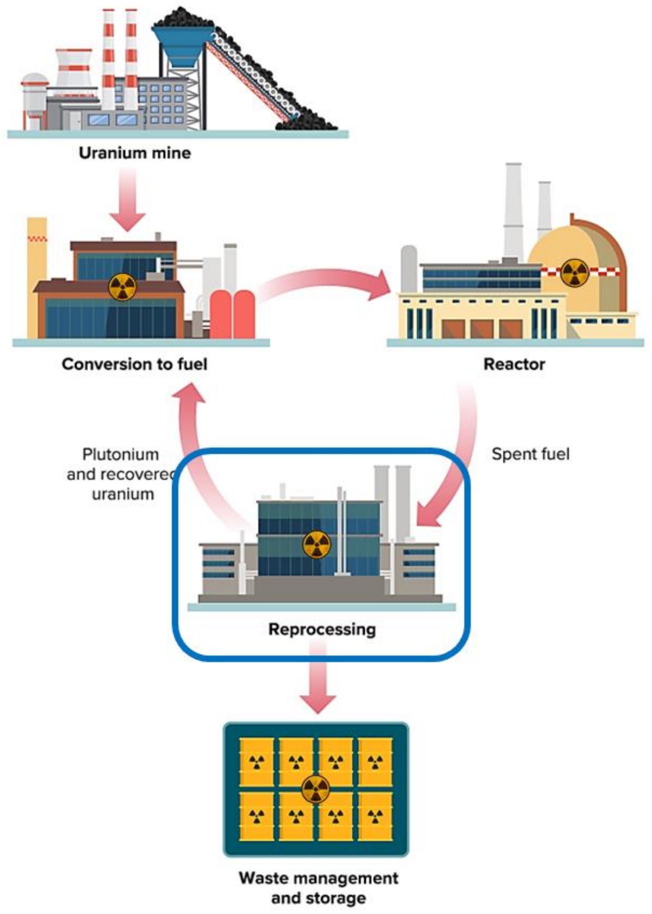


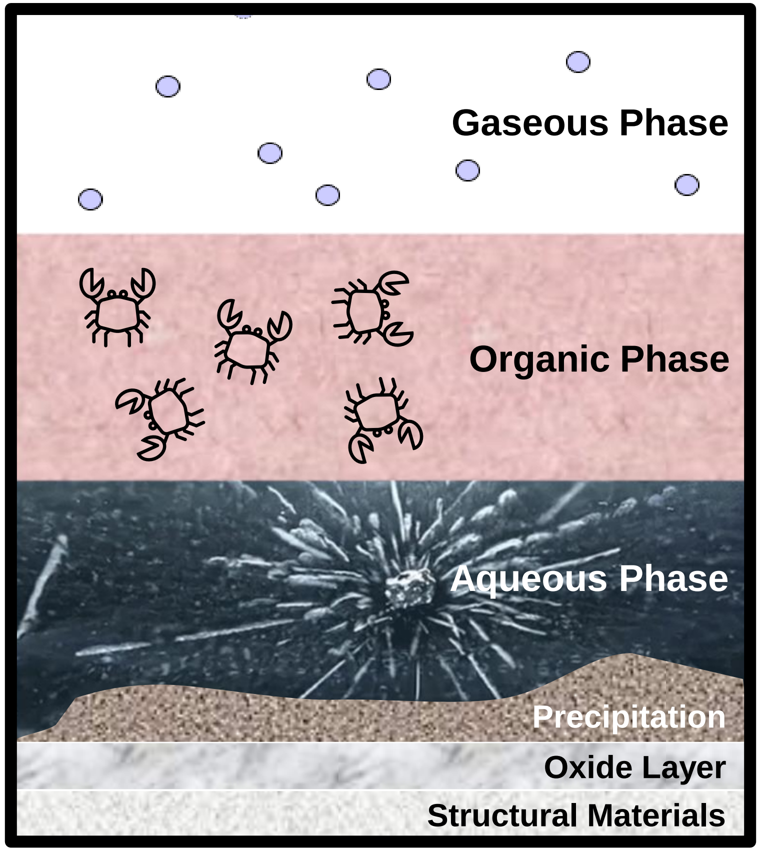


Holmbeck *et al.*, *The European Physical Journal A*, **2023**, *59 (28)*.

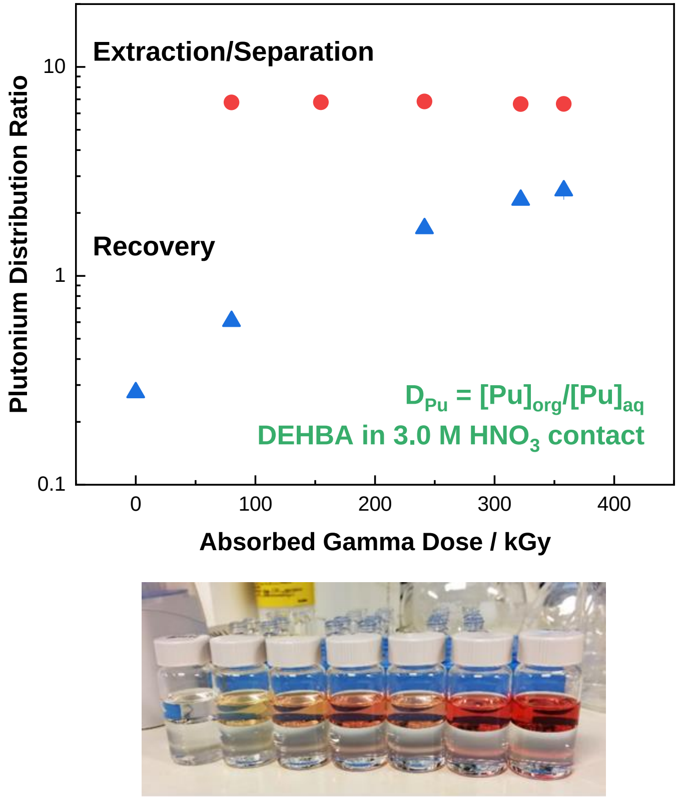
Reprocessing Used Nuclear Fuel



Solvent Extraction Reprocessing
Ligand(s)/organic diluent:HNO_3/H_2O



Horne *et al.*, *Dalton Trans.* **2019**, 48, 14450.



Increasing Gamma Dose

Reprocessing Radiation Chemistry

Water Radiolysis

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

Indirect Radiation Effects

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

$NO_3^- + e^- \rightarrow NO_3^{\bullet 2-}$

$NO_3^{\bullet 2-} + H_2O \rightarrow {}^\bullet NO_2 + 2OH^-$

$NO_3^- + H^\bullet \rightarrow HNO_3^- \rightarrow NO_2^\bullet + OH^-$

$NO_2^\bullet + NO_2^\bullet \rightleftharpoons N_2O_4$

$N_2O_4 \rightarrow HNO_2 + HNO_3$

Direct Radiation Effects

$NO_3^- \rightsquigarrow NO_3^{-*} \rightarrow NO_2^- + O$

$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + O$

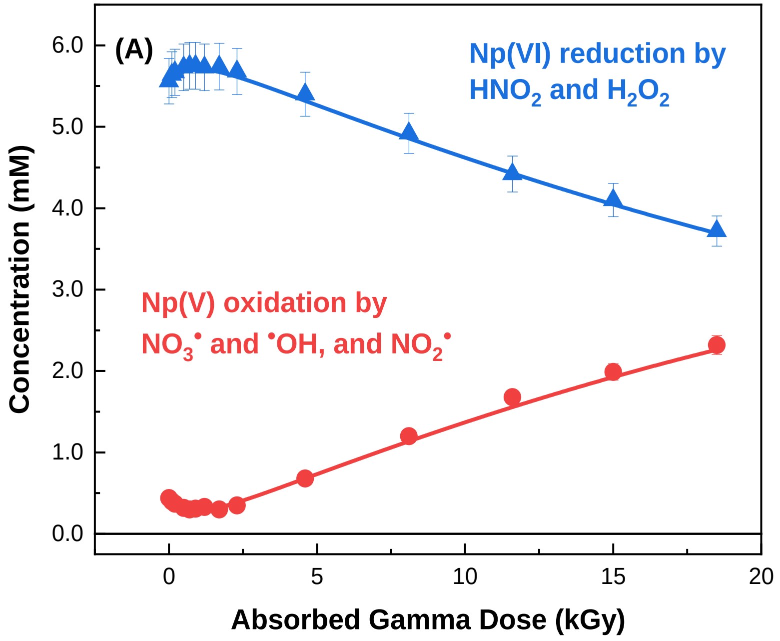
$NO_3^- \rightsquigarrow NO_3^\bullet + e^-$

$HNO_3 \rightsquigarrow NO_3^\bullet + H^\bullet$

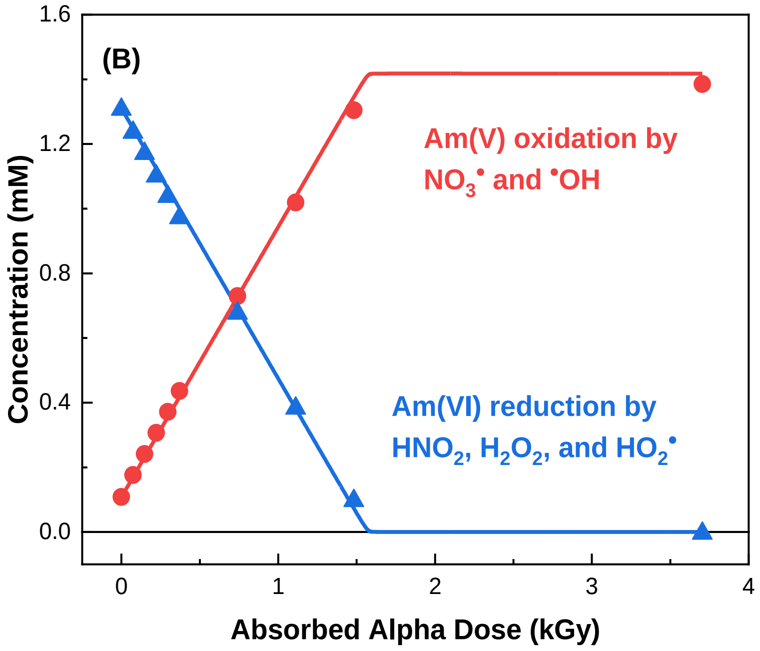
Alkane Radiolysis

$R\text{-}CH_3 \rightsquigarrow e^-, RH^{\bullet +}, RH^\bullet, {}^\bullet CH_3, H^\bullet, H_2$

Radiation-Induced Actinide Redox Chemistry



Horne *et al.*, *J. Phys. Chem. B*
2016, *120 (49)*, 12643.



Horne *et al.*, *Inorg. Chem.*
2019, *58*, 8551.

Complexation Effects

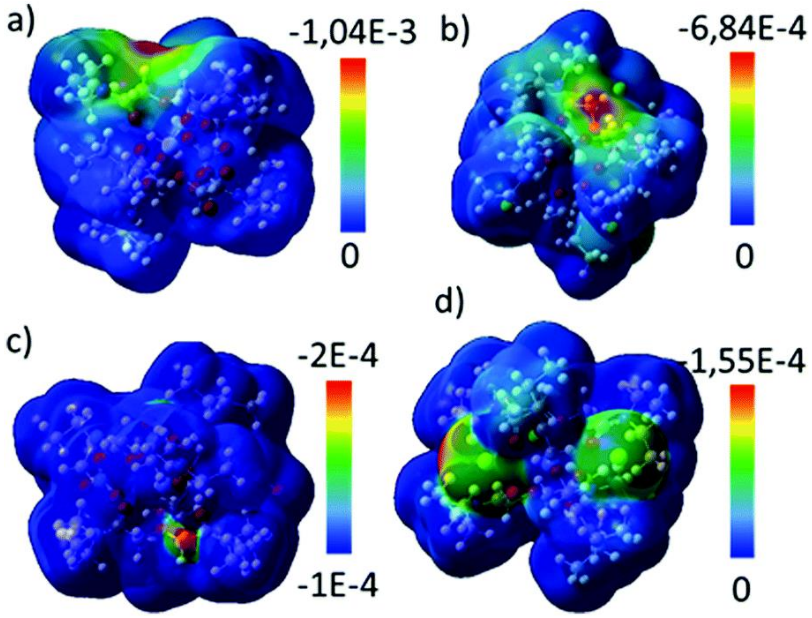
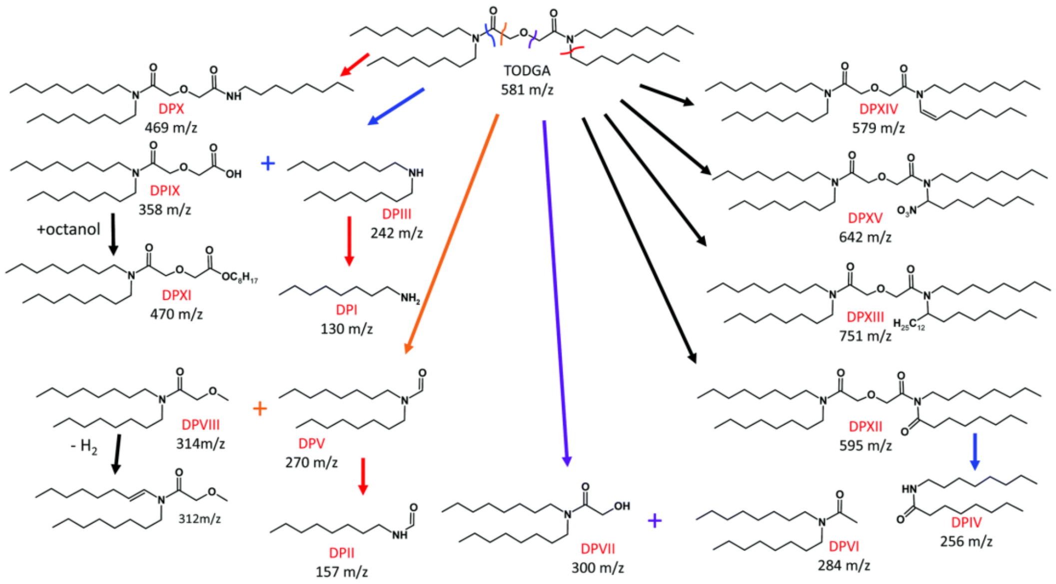


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.



"…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products."

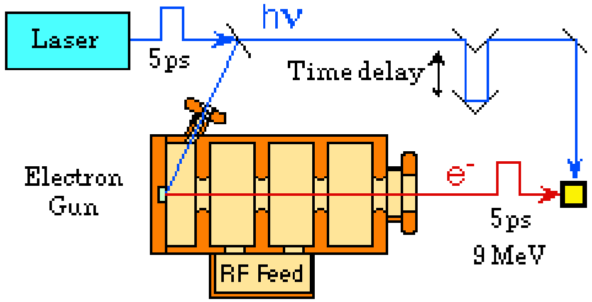
Kimberlin *et al.*, *PCCP,* **2022**, *24*, 9213.

Research Goals

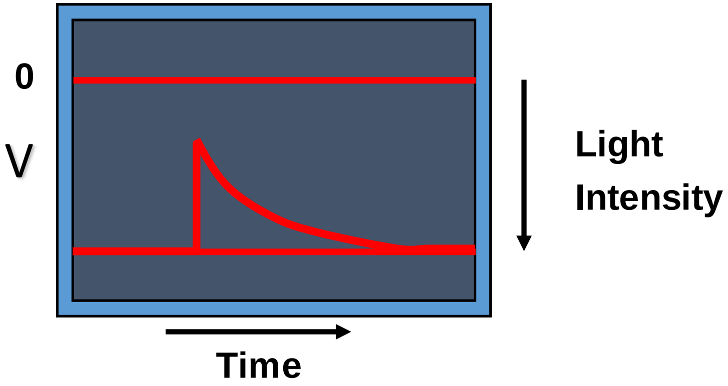
1. Understand the basic radiation chemistry of the actinides in formally non-complexing media.
2. Elucidate the mechanisms underpinning the impact of actinide complexation on ligand radiolysis.
3. Develop multiscale modeling codes for the prediction of radiation-induced chemistry, speciation, and transport of the actinide series in any media.

Research Techniques

Time-resolved Electron Pulse Radiolysis

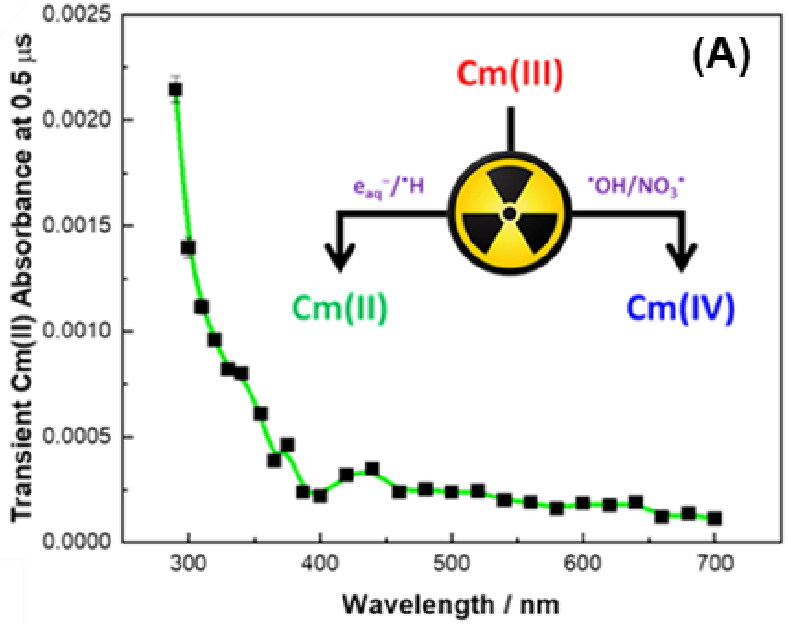


Transients are detected by optical absorption changes.

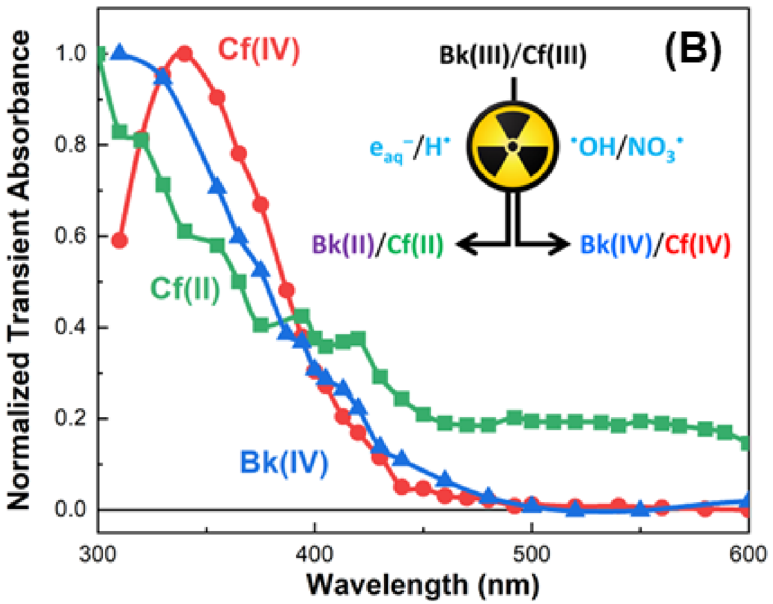


Ex Situ Gamma and *In Situ* Alpha Radiolysis

Radiation-Induced Actinide Redox Chemistry

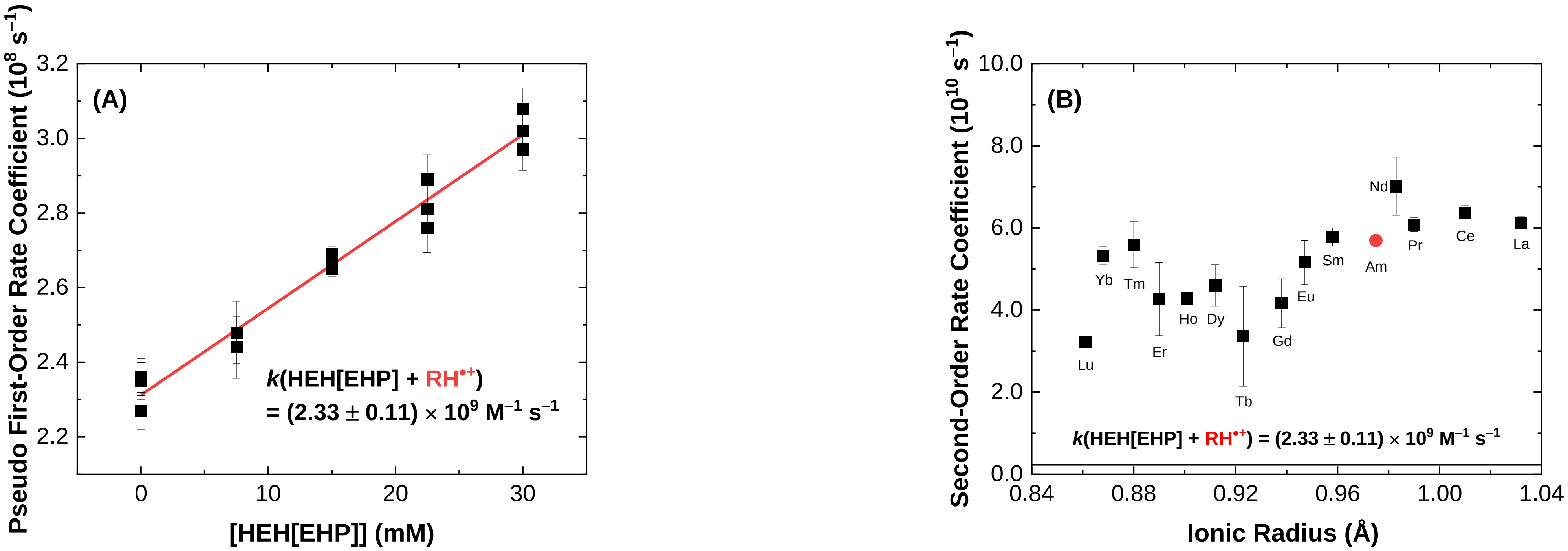


Horne *et al.*, *Dalton Trans.* **2021**, *50*, 10853.



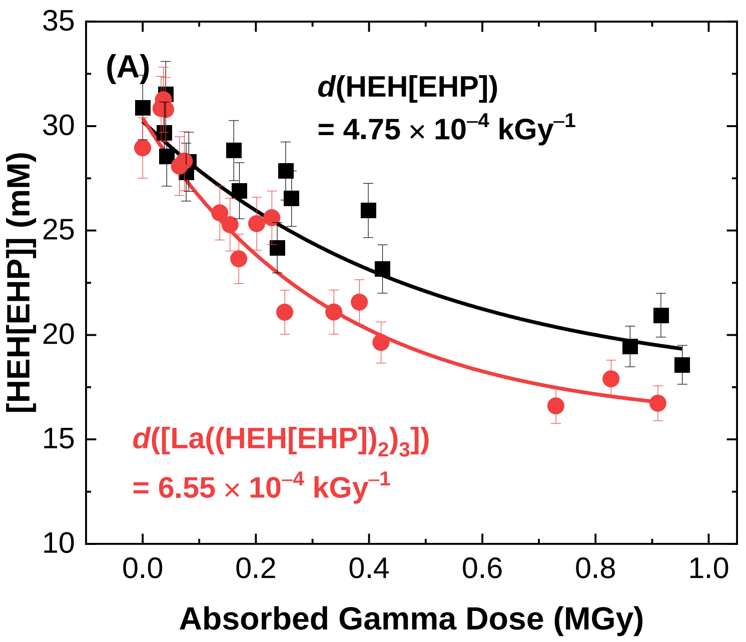
Horne *et al.*, *Inorg. Chem.* **2022**, *61 (28)*, 10822.

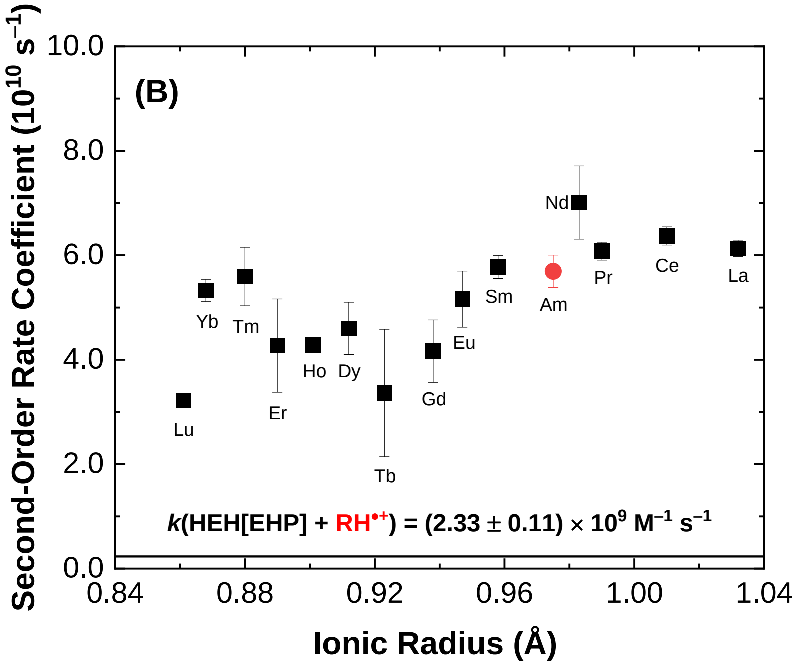
Complexation Effects – HEH[EHP]



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

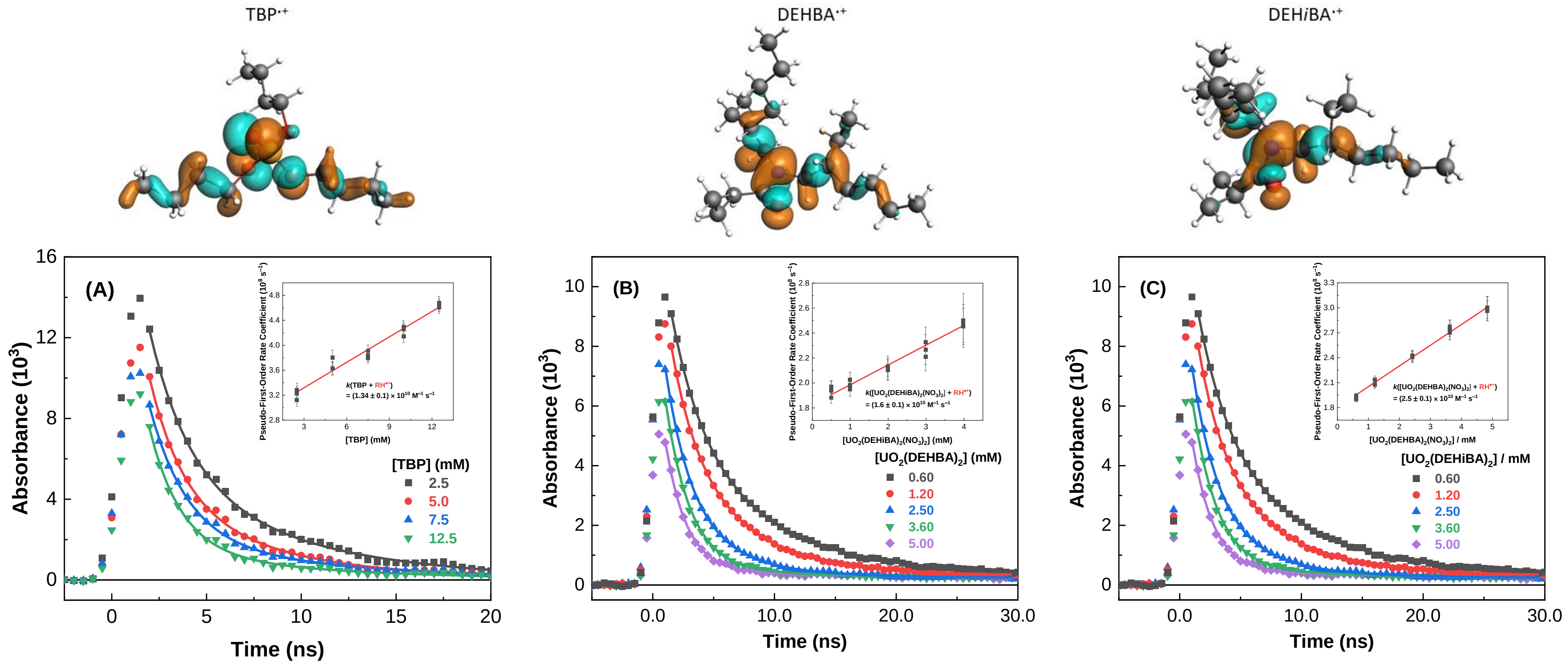
Complexation Effects – HEH[EHP]





- **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.

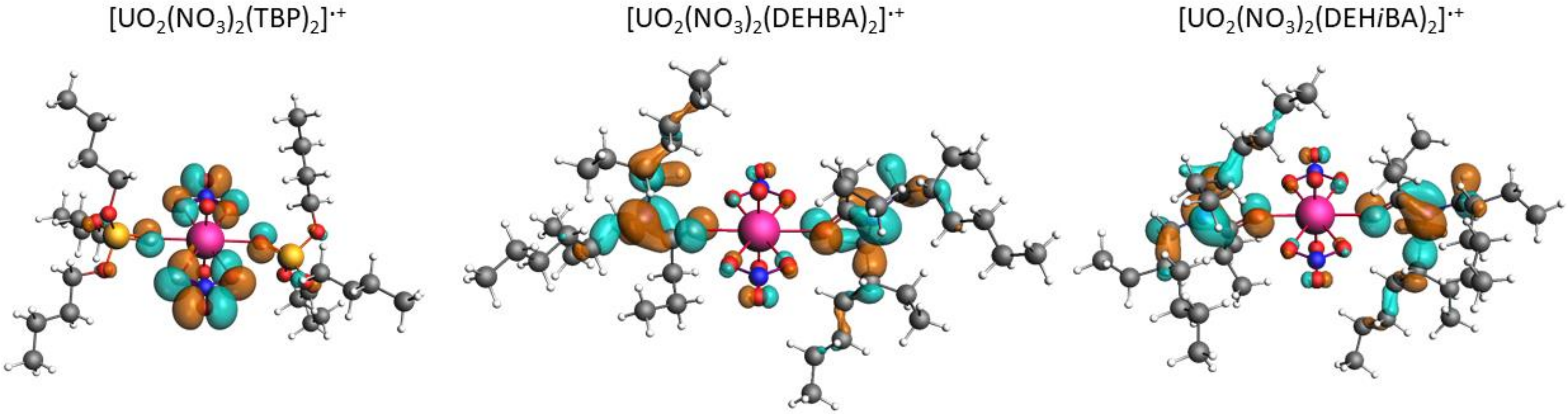
Complexation Effects – TBP, DEHBA, and DEH*i*BA



- UO_2^{2+} complexation had negligible effect on *k*(TBP + $RH^{\bullet +}$).
- For DEHBA and DEH*i*BA, UO_2^{2+} complexation afforded a 2.6× and 1.4× increase in their respective rate coefficients, respectively.

Celis-Barros *et al.*, *PCCP* **2021**, *23*, 24589.

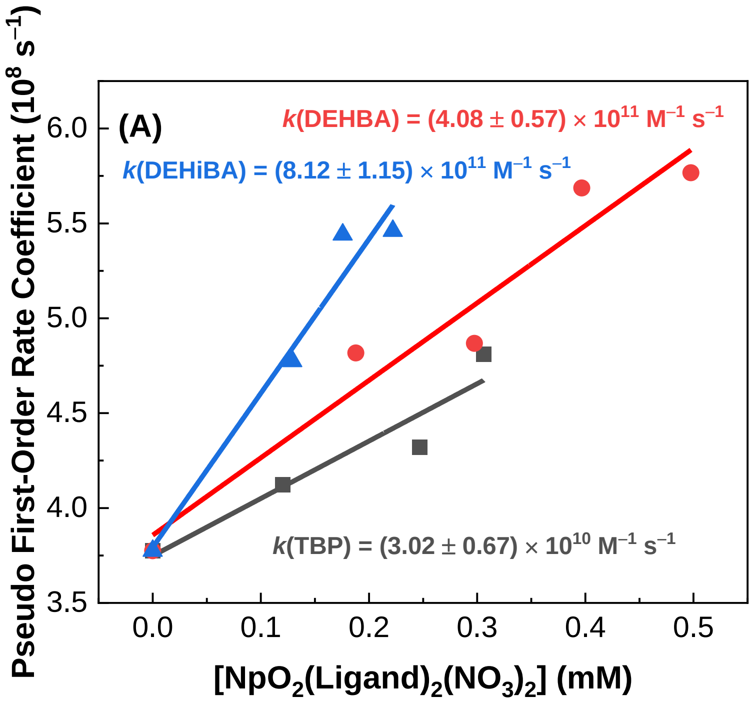
Complexation Effects – TBP, DEHBA, and DEH*i*BA

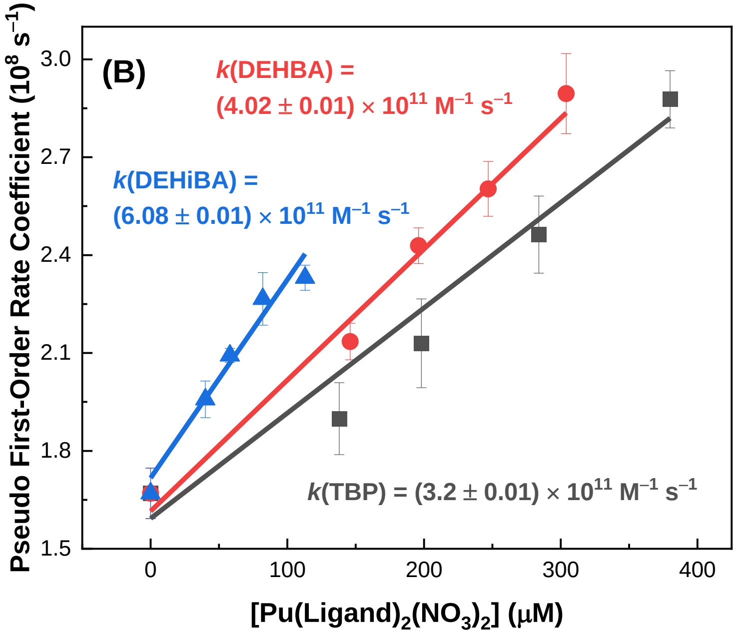


Celis-Barros *et al.*, *PCCP* **2021**, *23*, 24589.

- Coordinated **NO_3^-** protect [**UO_2** (**NO_3**)$_2$(**TBP**)$_2$] complexes.
- Most likely site of attack in **DEHBA**/**DEH*i*BA** remains on the amide functionality in the complex.

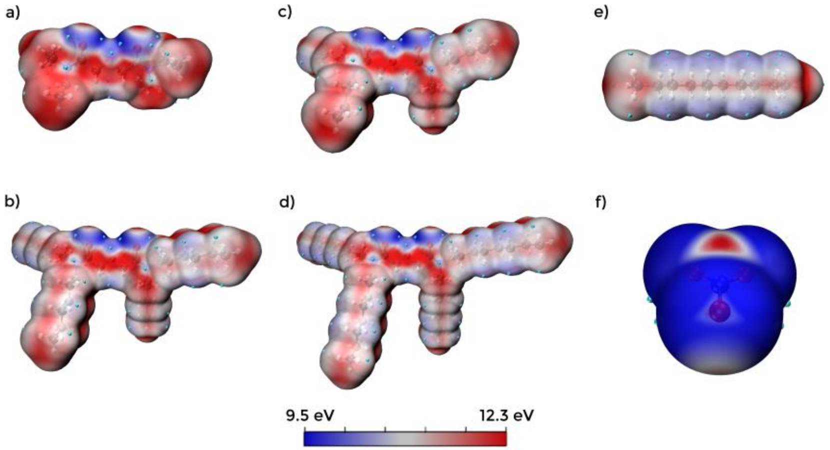
Complexation Effects – TBP, DEHBA, and DEH*i*BA

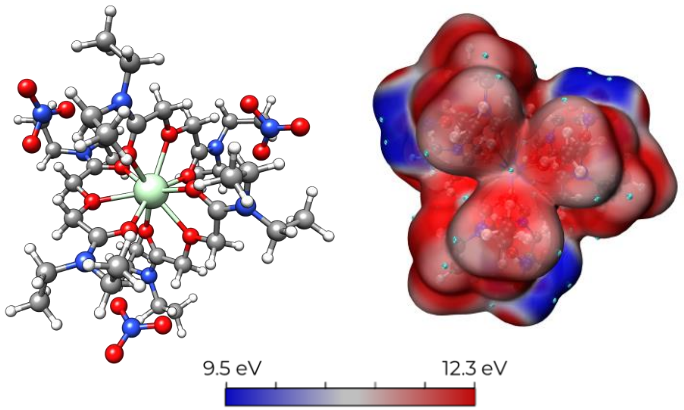


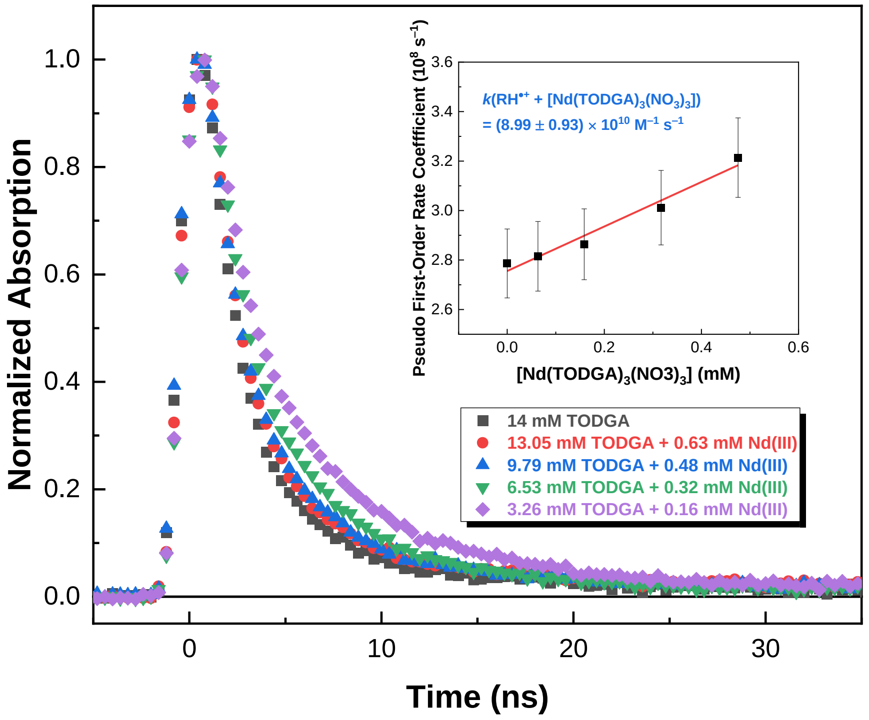


- **NpO_2^{2+}** and **PuO_2^{2+}** complexation afforded significantly faster rates of reaction with **$RH^{\bullet+}$**, then for the non-complexed **TBP**, **DEHBA** and **DEH*i*BA** molecules.
- Evidence for electron transfer with the complexed metal center?

Complexation Effects – TODGA







- **Computations:** average local ionization energy analysis highlights the sites of the molecule susceptible to a radical or electrophilic attack.
- Horne *et al.*, *PCCP* **2023**, *under review*.

Conclusions

- **Understanding radiation chemistry is essential for innovating nuclear energy technologies.**
- Non-traditional actinide oxidation states likely play a large role in redox cycling.
- Actinide complexation has significant effects on the fundamental radiation chemistry of their complexes, owing to ***steric effects***, ***electron distribution differences***, and the ***facilitation of inner vs. outer sphere mechanisms***.

Acknowledgements

U.S. DEPARTMENT OF ENERGY

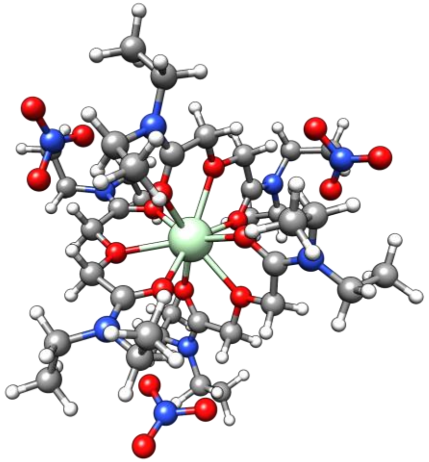
Material Recovery & Waste Form Development

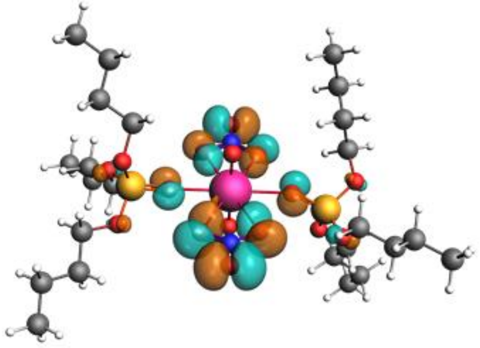
BROOKHAVEN NATIONAL LABORATORY

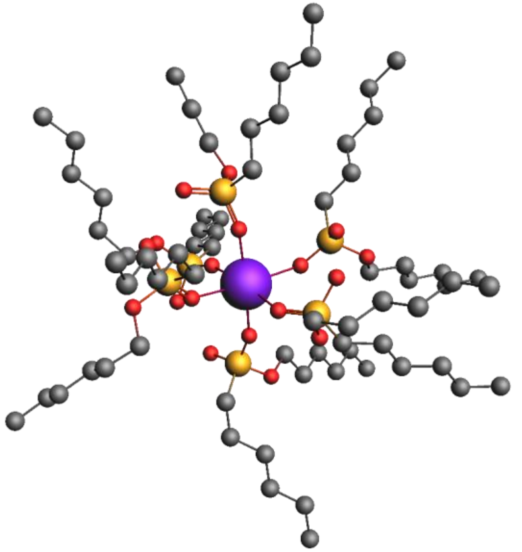
COLORADO SCHOOL OF MINES

NTRD Nuclear Technology Research & Development

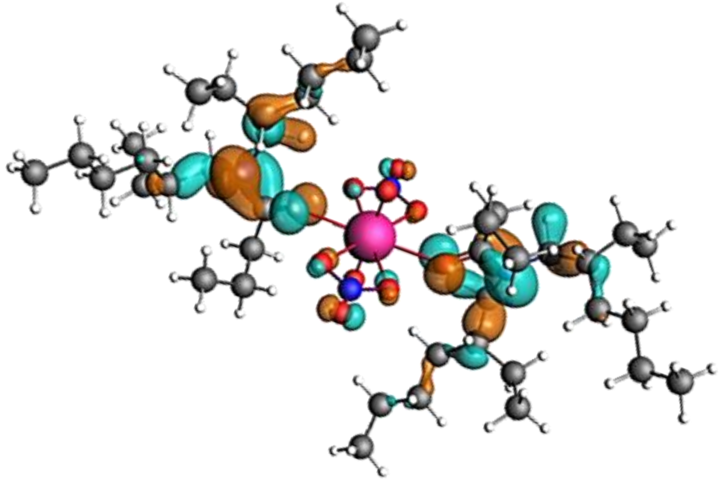
CALIFORNIA STATE UNIVERSITY LONG BEACH

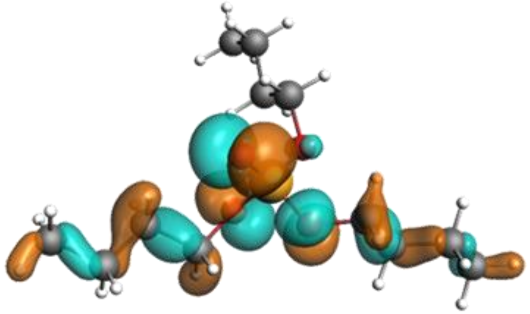


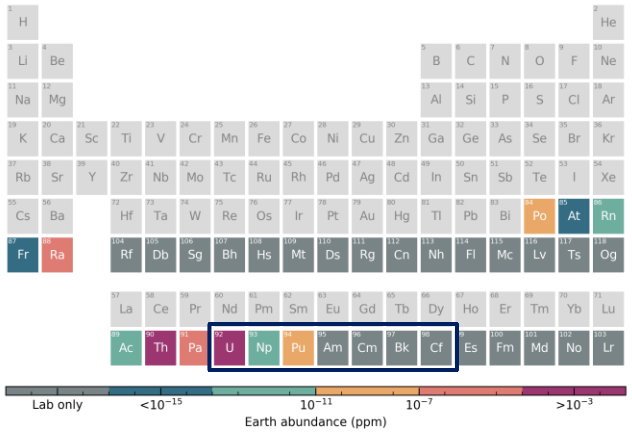




Questions?







Holmbeck *et al.*, *The European Physical Journal A*, **2023**, *59 (28)*.