INL/CON-23-71277-Revision-0

Impact of Actinide Complexation on Ligand Radiolysis

February 2023

Gregory P Horne

Changing the World's Energy Future

Idaho National Laboratory

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http://www.inl.gov

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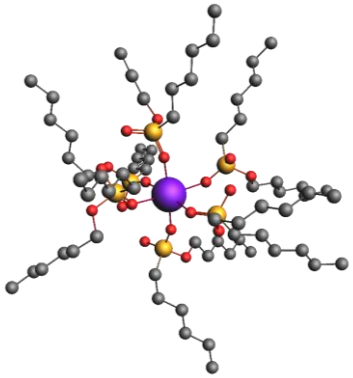
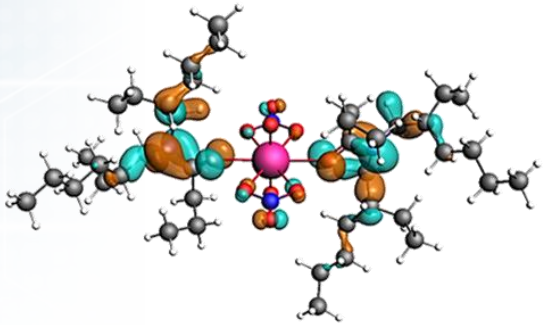
Gregory P. Horne
Center for Radiation Chemistry Research



Impact of Actinide Complexation on Ligand Radiolysis…



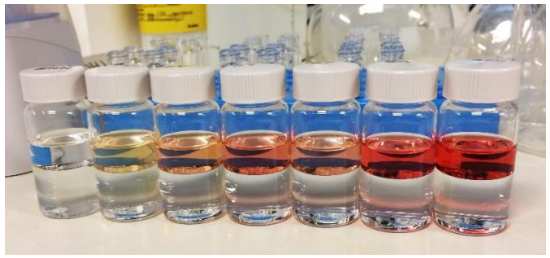
…and how more computation and theory would be nice…

2nd International Workshop on Theory Frontiers in Actinide Science: Chemistry & Materials
February 26th – March 1st, 2023 | Santa Fe, New Mexico, USA

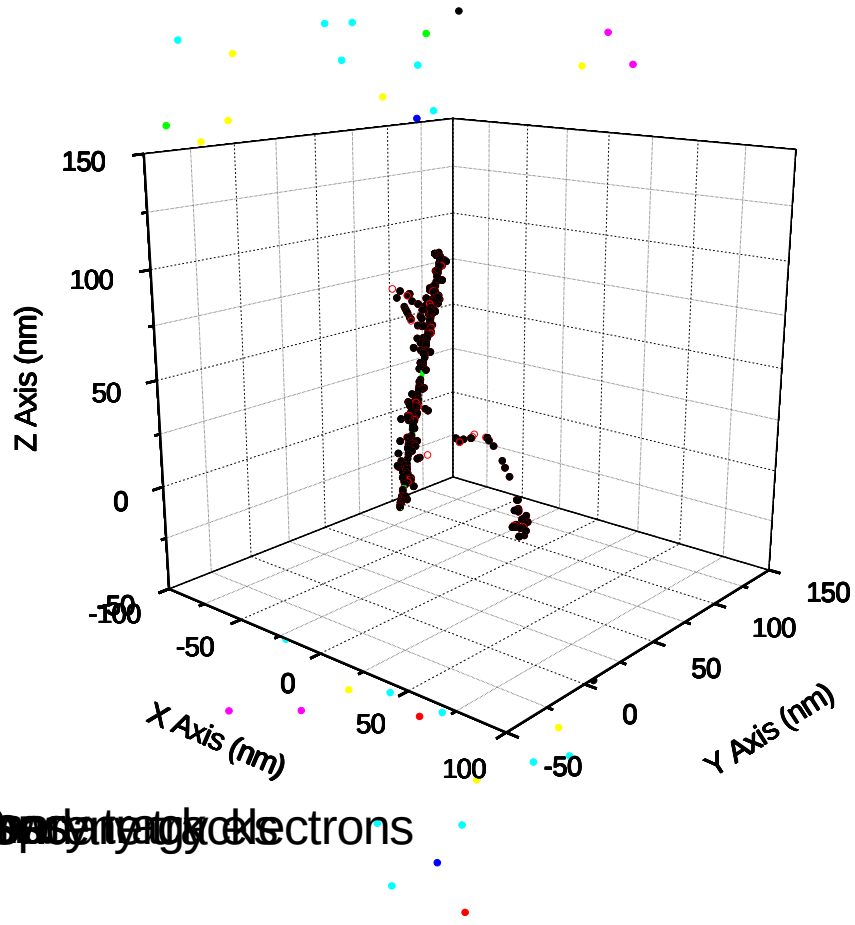
Idaho National Laboratory

What is Radiation Chemistry?

- The study of chemistry induced by the absorption of ionizing radiation.
- The passage of radiation through matter results in a series of energy transfer events.
- Radiolysis products propagate physical and chemical changes in the absorbing medium.



Increasing Gamma Dose ⇝ ⇝



Secondary electrons

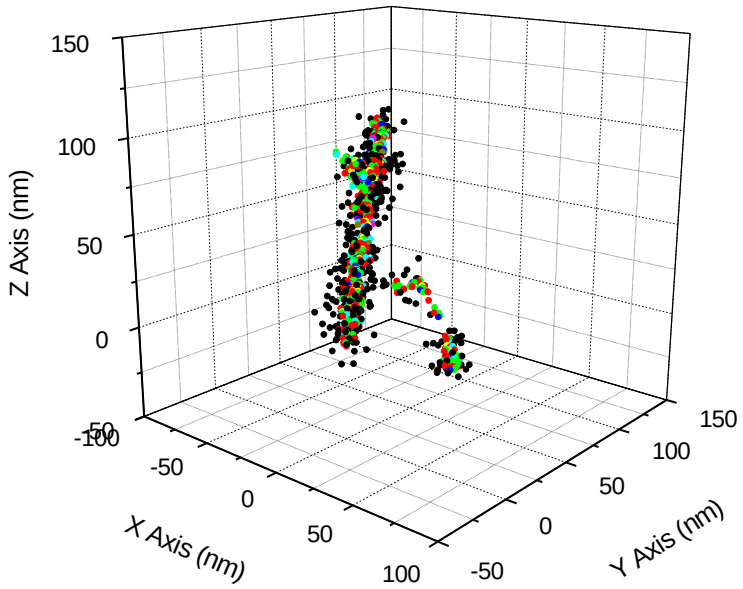
- Spinks and Woods, An Introduction to Radiation Chemistry, 1990.
- Pimblott, LaVerne, and Mozumder, J. Phys. Chem. 1996, 100, 8595.
- Clifford, Green, Oldfield, Pilling, and Pimblott, J. Chem. Soc., Faraday Trans., 1986, 82, 2673.

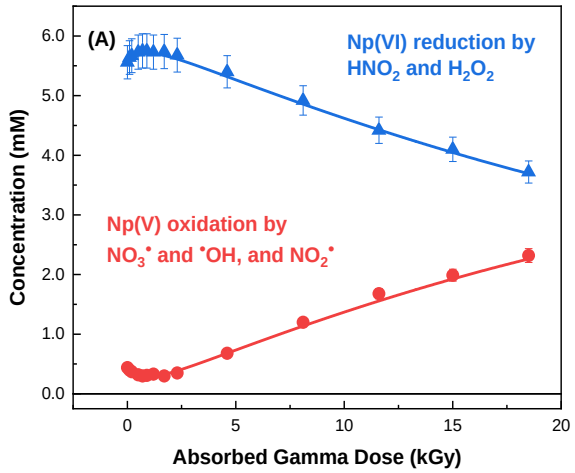
Actinide Radiation Chemistry

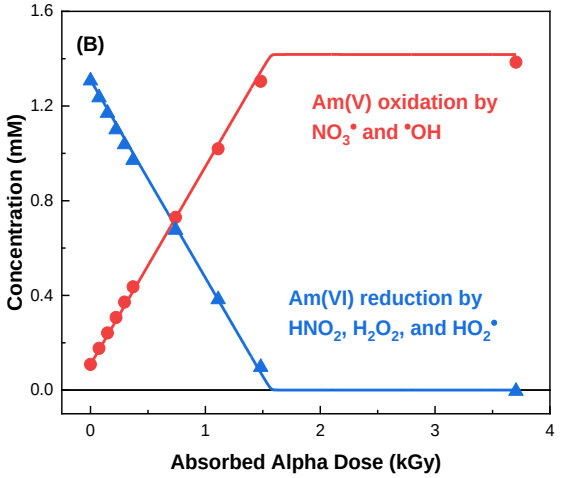
$H_2O \rightsquigarrow e^-, H^\bullet, {}^\bullet OH, H_2, H_2O_2, H_{aq}^+$

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

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







- **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.

Impact of Actinide Complexation

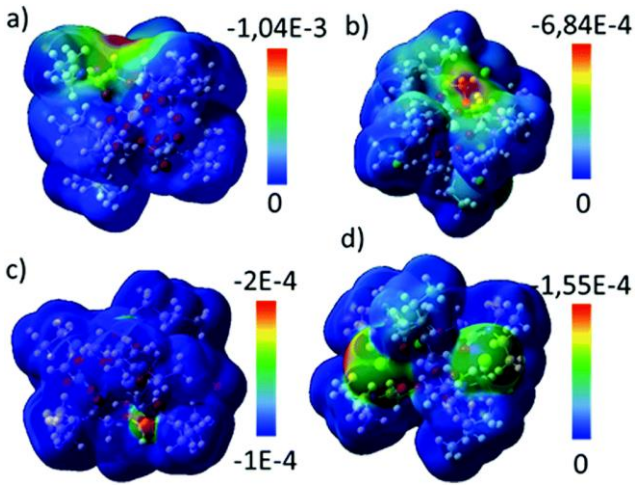
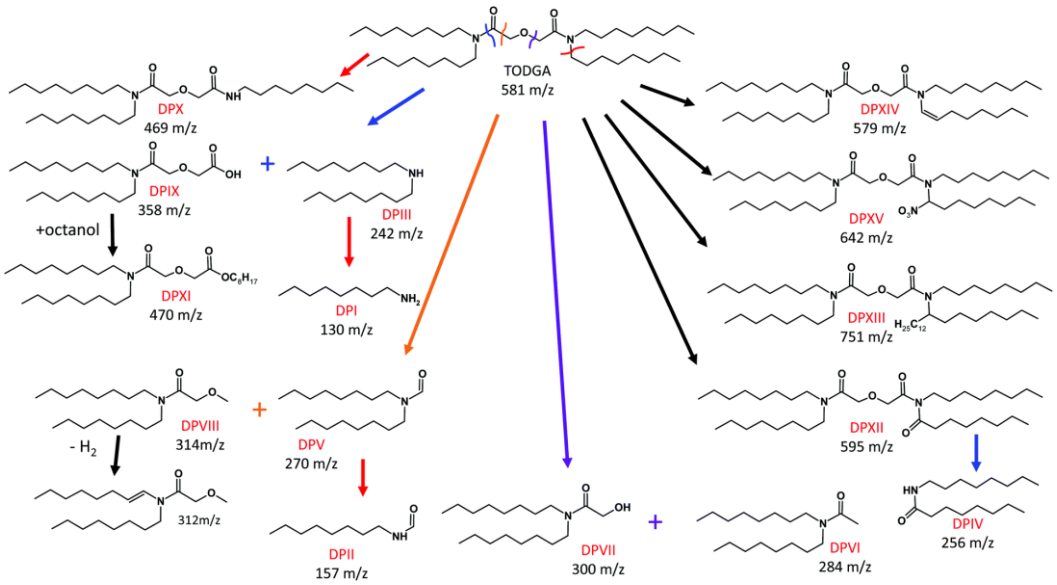


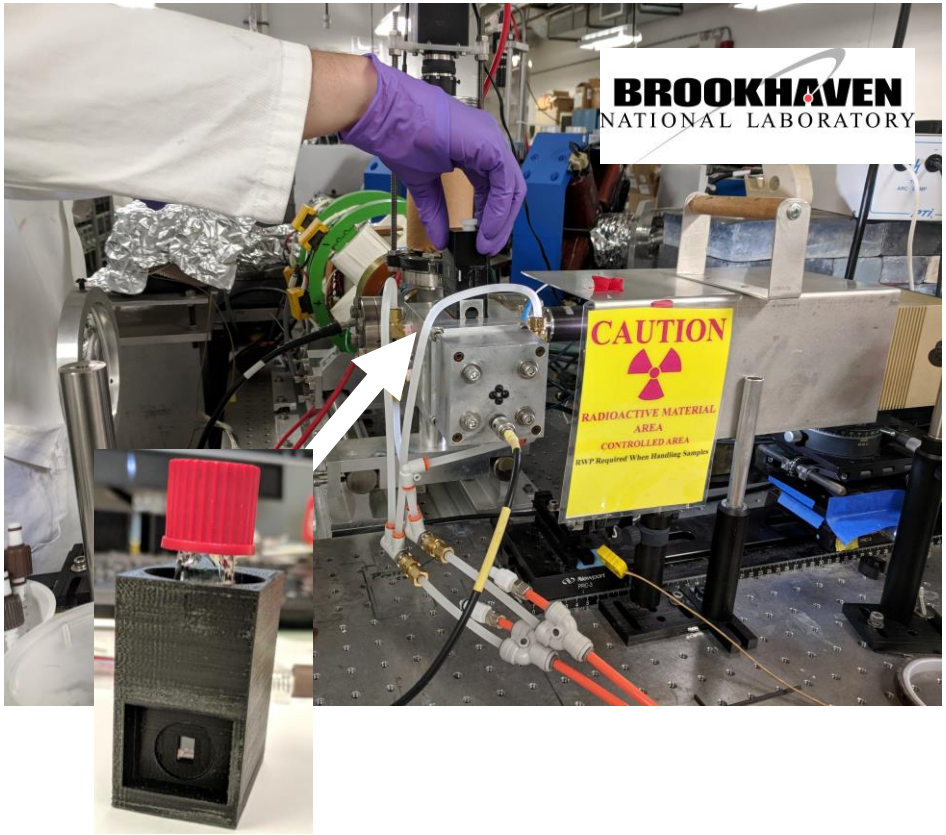
Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** [Nd(TEDGA)$_3$](NO$_3$)$_3$, **(b)** [Nd(TEDGA)$_3$]Cl$_3$, **(c)** [Am(TEDGA)$_3$](NO$_3$)$_3$, and **(d)** [Am(TEDGA)$_3$]Cl$_3$.

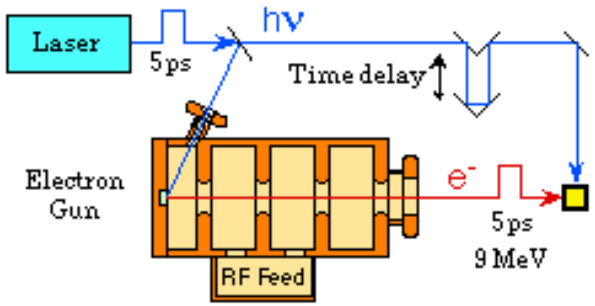


"…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products."
Kimberlin *et al.*, *PCCP,* **2022**, *24*, 9213.

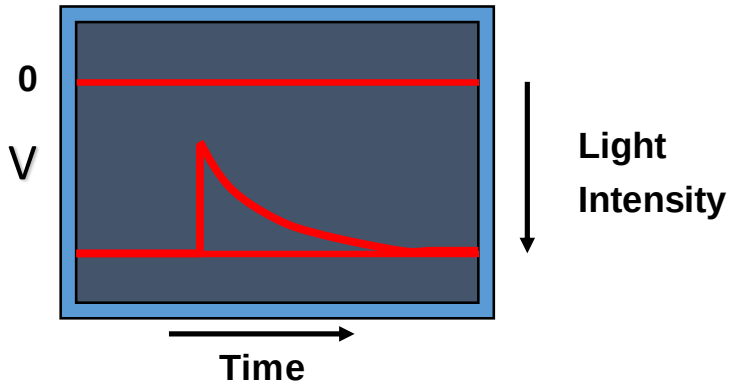
- Bhattacharyya and Kundu, Int. *J. Radiat. Phys. Chem.*, **1971**, *3*, 1.
- Kundu and Matuura, *Int. J. Radiat. Phys. Chem.*, **1975**, *7*, 565.
- Ilan and Czapski, *Biochimica et Biophysica Acta*, **1977**, *498*, 386.
- Buettner, Doherty, and Patterson, *Fed. Euro. Biochem. Soc.*, **1983**, *158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

Chemical Kinetics and Electron Pulse Radiolysis





Transients are detected by optical absorption changes.

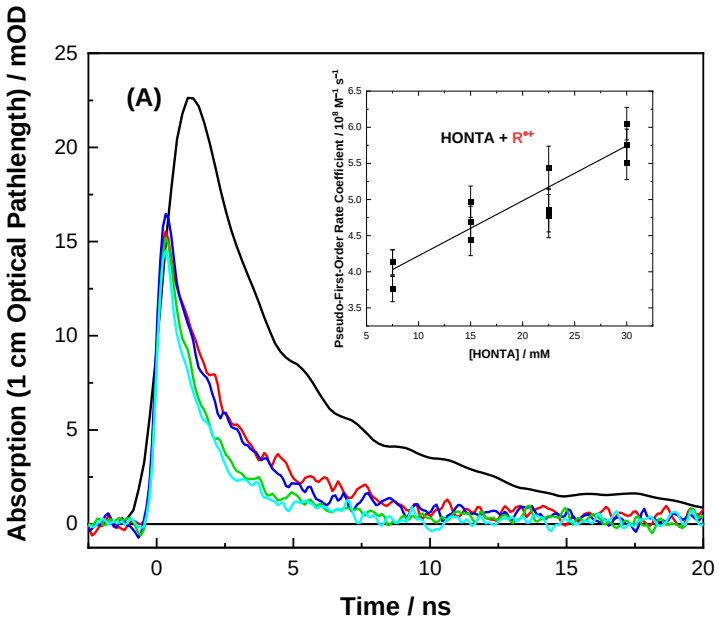


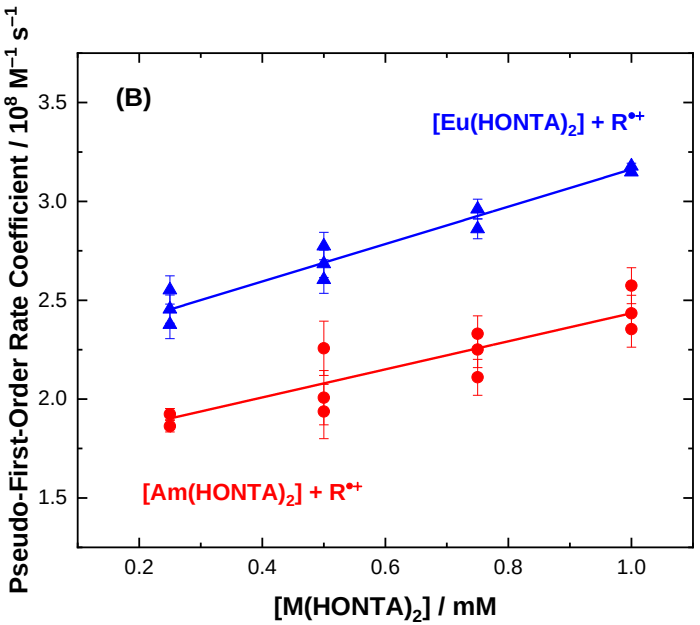
- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

Chemical Kinetics and Electron Pulse Radiolysis

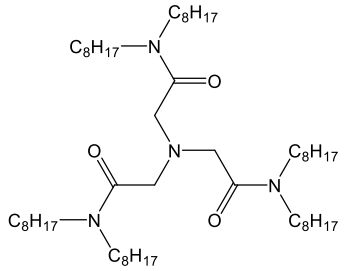
Alkane Radiolysis

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



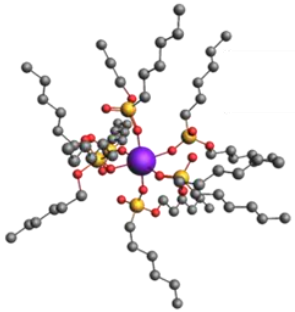


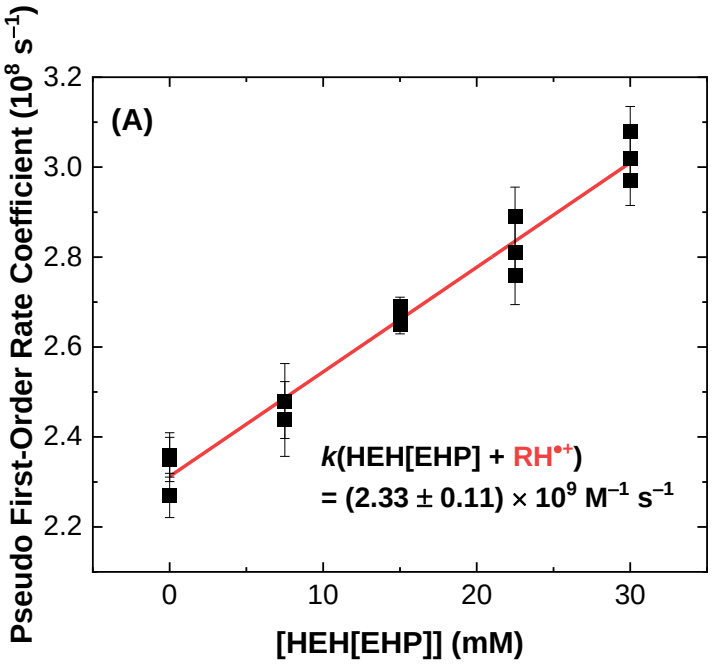
- Complexation of **HONTA** with either **Eu(III)** or **Am(III)** afforded an order of magnitude increase in rate coefficient (*k*):
  - *k*(**HONTA** + **RH•+**) = **(7.6 ± 0.8) × 10^9 M^{-1} s^{-1}.**
  - *k*(**Am(HONTA)$_2$** + **RH•+**) = **(7.1 ± 0.7) × 10^{10} M^{-1} s^{-1}.**
  - *k*(**Eu(HONTA)$_2$** + **RH•+**) = **(9.5 ± 0.5) × 10^{10} M^{-1} s^{-1}.**

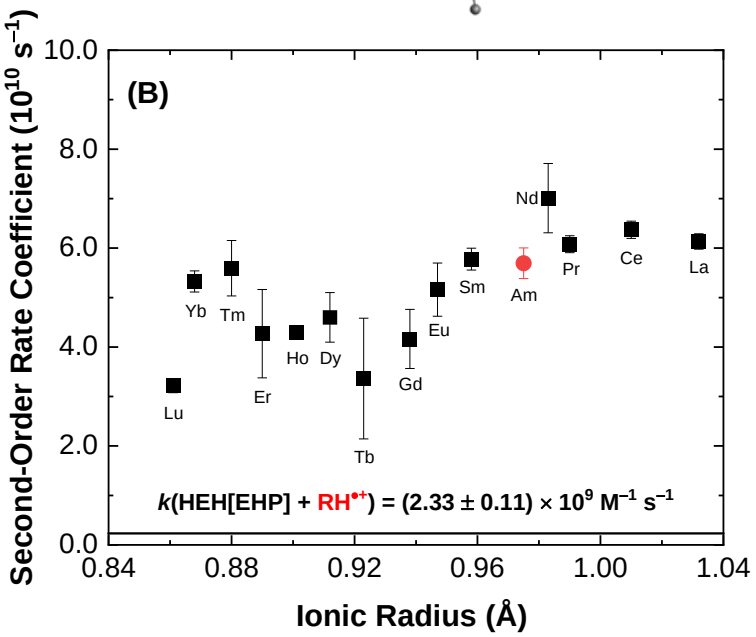


- Toigawa, Peterman, Meeker, Grimes, Zalupski, Mezyk, Cook, Yamashita, Kumagai, Matsumura, and **Horne**, *PCCP* **2021**, *23*, 1343.

f-element Complexes of HEH[EHP]



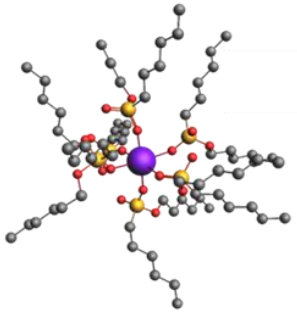


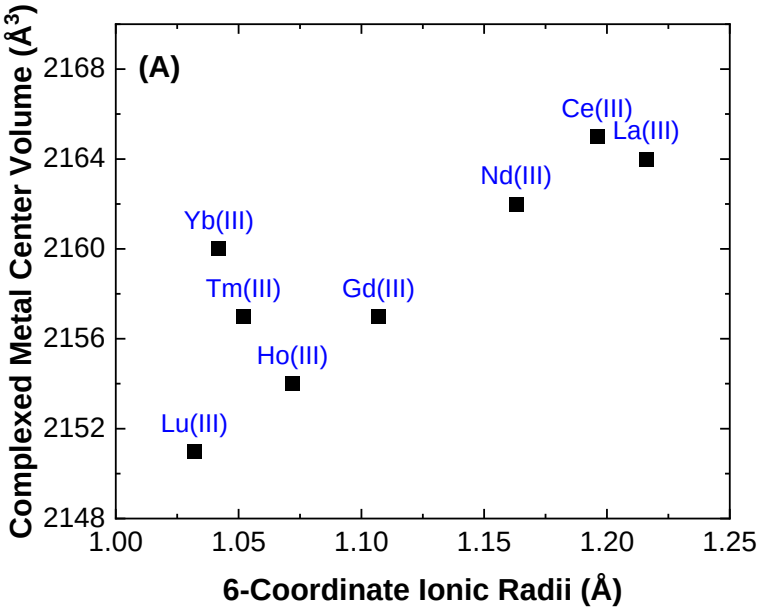


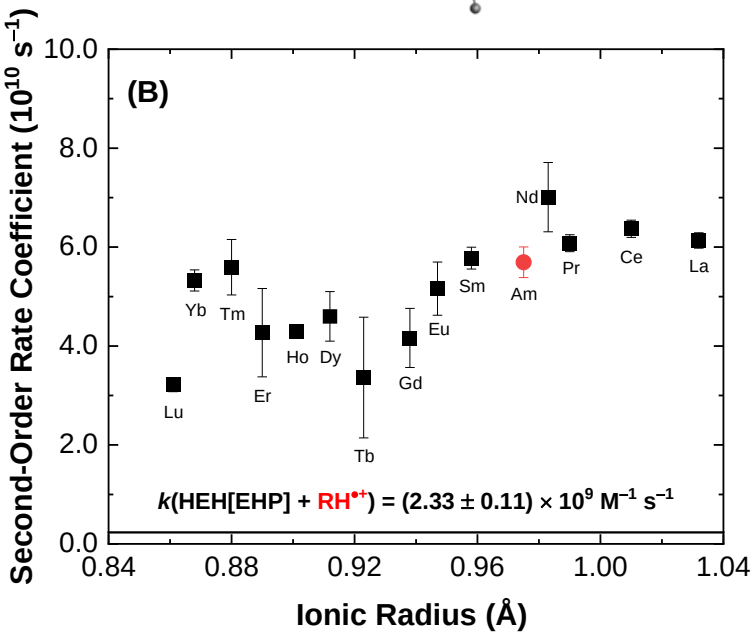
- **Methodology:** Δ[**HEH[EHP]**]/[**M{(HEH[EHP])$_2$}$_3$**] in 0.5 M DCM/*n*-dodecane; **$RH^{\bullet+}$** decay measured at 800 nm over 200 ns using the BNL *Laser Electron Accelerator Facility* (LEAF).

- 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*.

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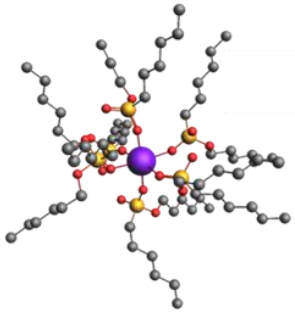

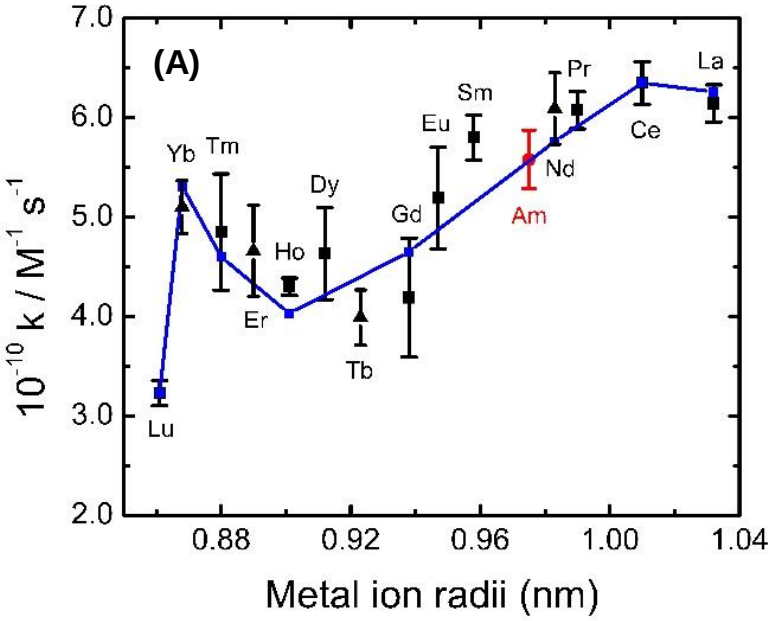

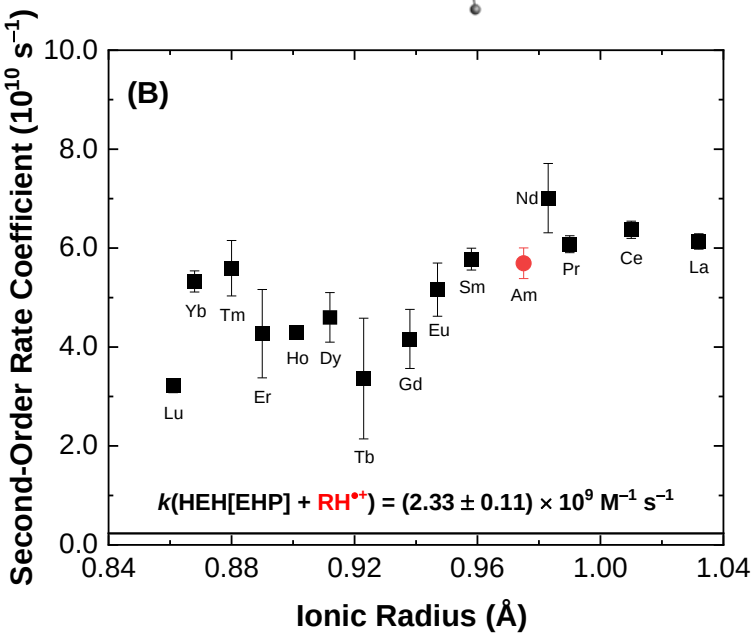

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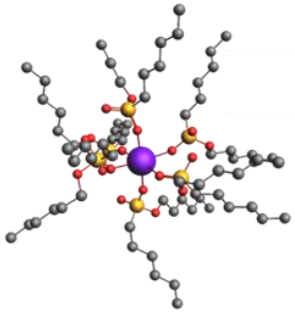
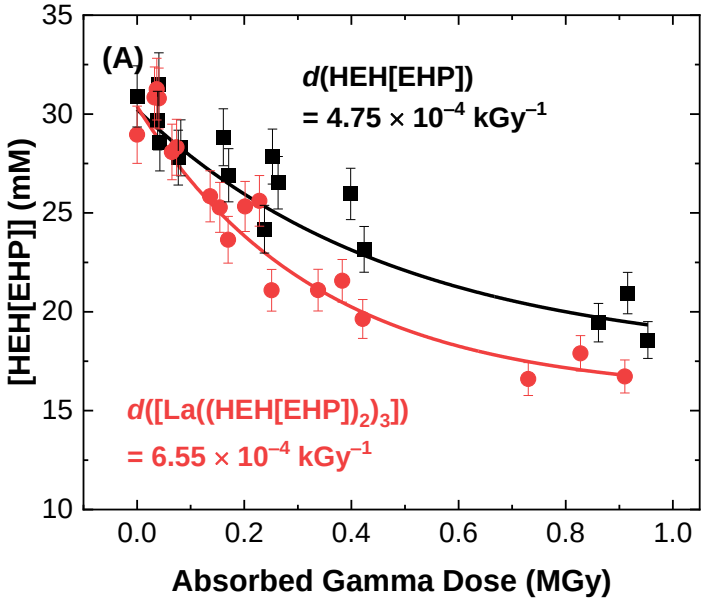
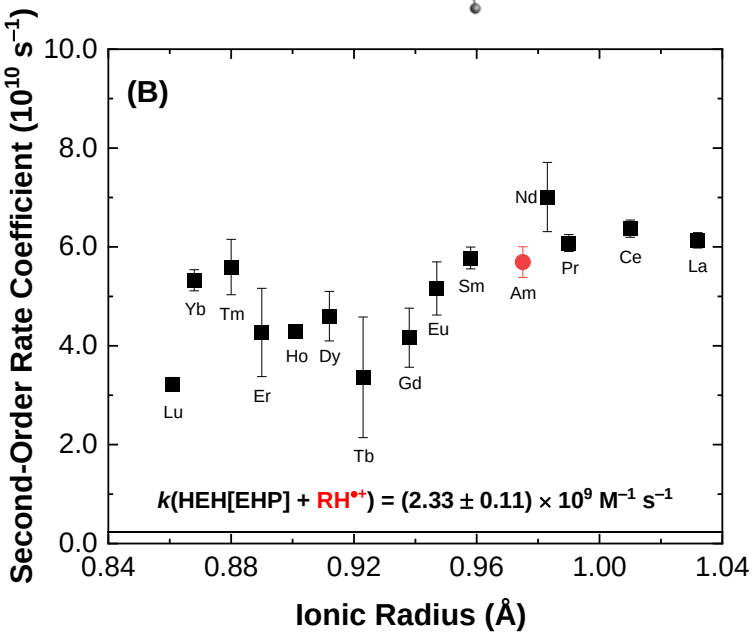
- Baxter, **Cellis-Barros**, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and **Horne**, *in preparation*.

Effect on Steady-State HEH[EHP] Degradation



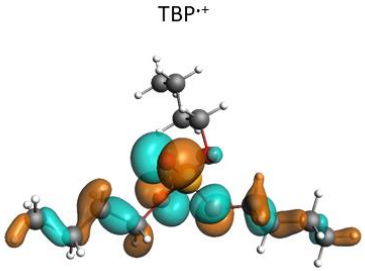


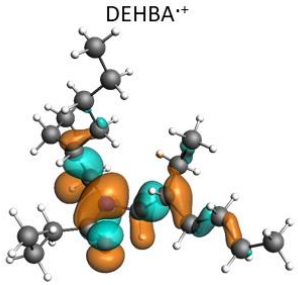


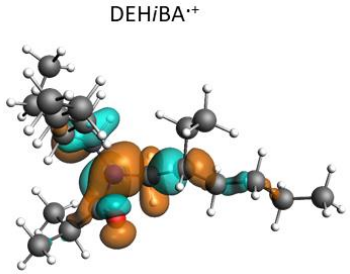
- **Steady-State Gamma Irradiations:** Cobalt-60 irradiation of 30 mM HEH[EHP] under organic only (■) and loaded with 2.5 mM La(III) from PIPPS/HNO_3 solution (●). Dose constants (*d*) were calculated from linear fits to [[La(([HEH[EHP]])$_2$)$_3$)] *vs.* absorbed gamma dose.

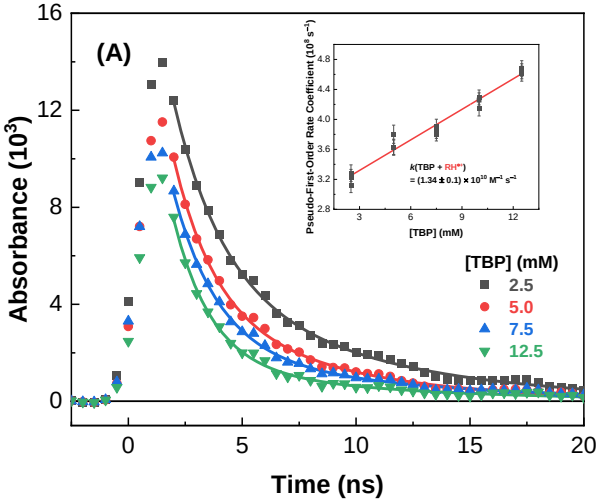
- Baxter, **Cellis-Barros**, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and **Horne**, *in preparation*.

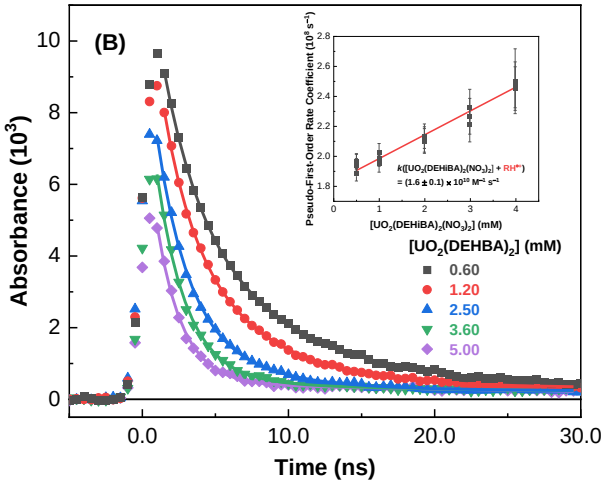
Uranyl Complexes of TBP, DEHBA, and DEH*i*BA

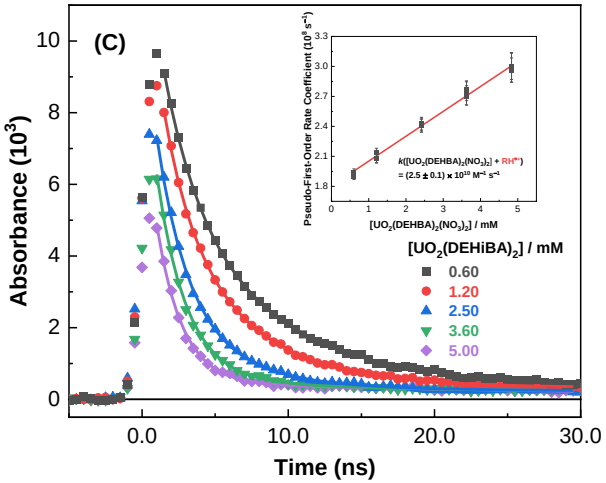










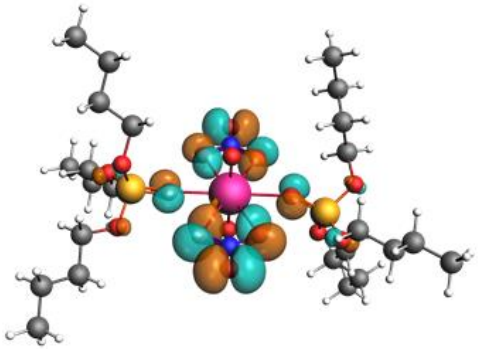


- UO_2^{2+} complexation had negligible effect on the reaction of **TBP** with **RH•+**, *k*(**TBP** + **RH•+**) = **(1.3 ± 0.1) × 10^{10} M^{-1} s^{-1}**.
- For **DEHBA** and **DEHiBA**, UO_2^{2+} complexation afforded a **2.6×** and **1.4×** increase in their respective rate coefficients, respectively.

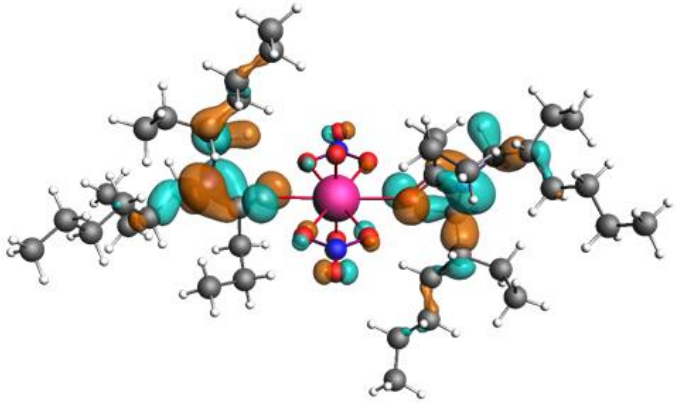
- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and **Horne**, *PCCP*, **2021**, *23*, 24589.

Changes in Reaction Mechanism

$[UO_2(NO_3)_2(TBP)_2]^{\cdot+}$



$[UO_2(NO_3)_2(DEHBA)_2]^{\cdot+}$



$[UO_2(NO_3)_2(DEHiBA)_2]^{\cdot+}$

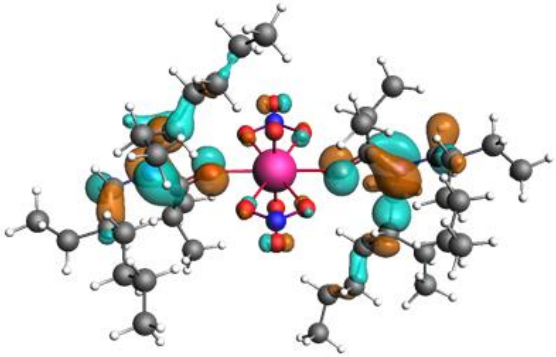


Table 1 Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet+}$ with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

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

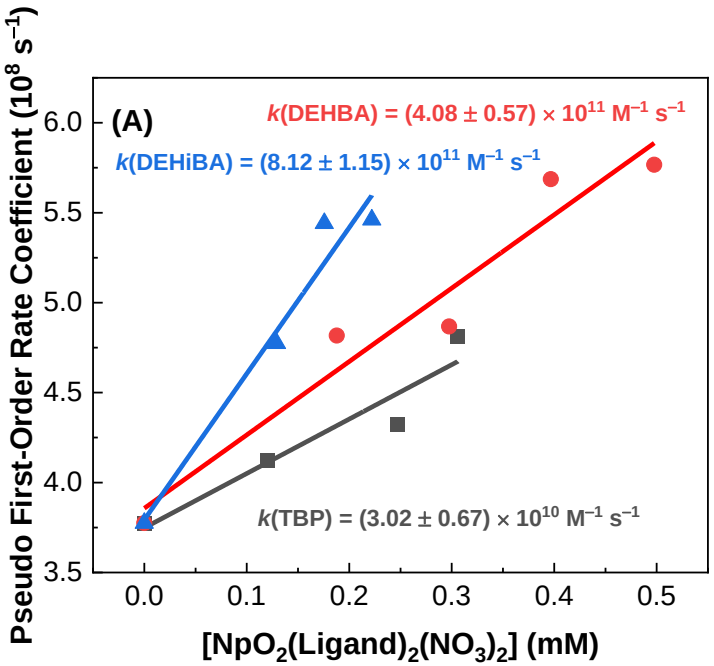
$RH^{\bullet+}$ + Ligand → RH + [Ligand]$^{\bullet+}$

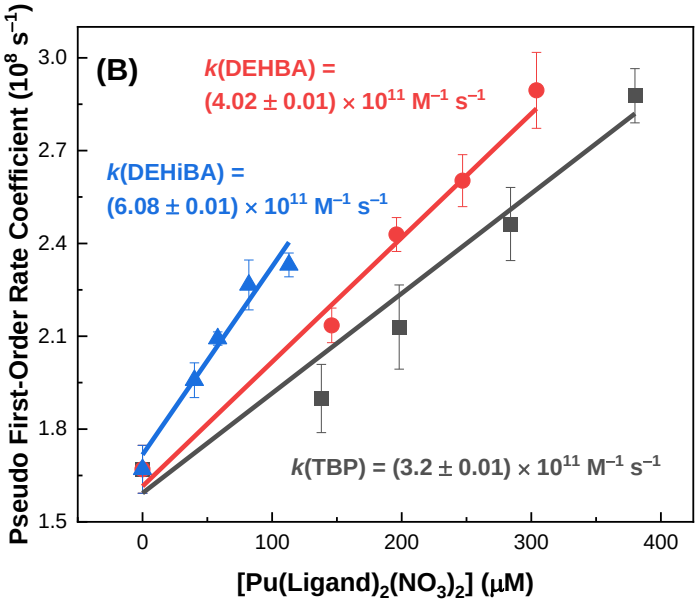
Proton Transfer

$RH^{\bullet+}$ + Ligand → $R^{\bullet}$ + [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.

Impact of Transuranic Complexation

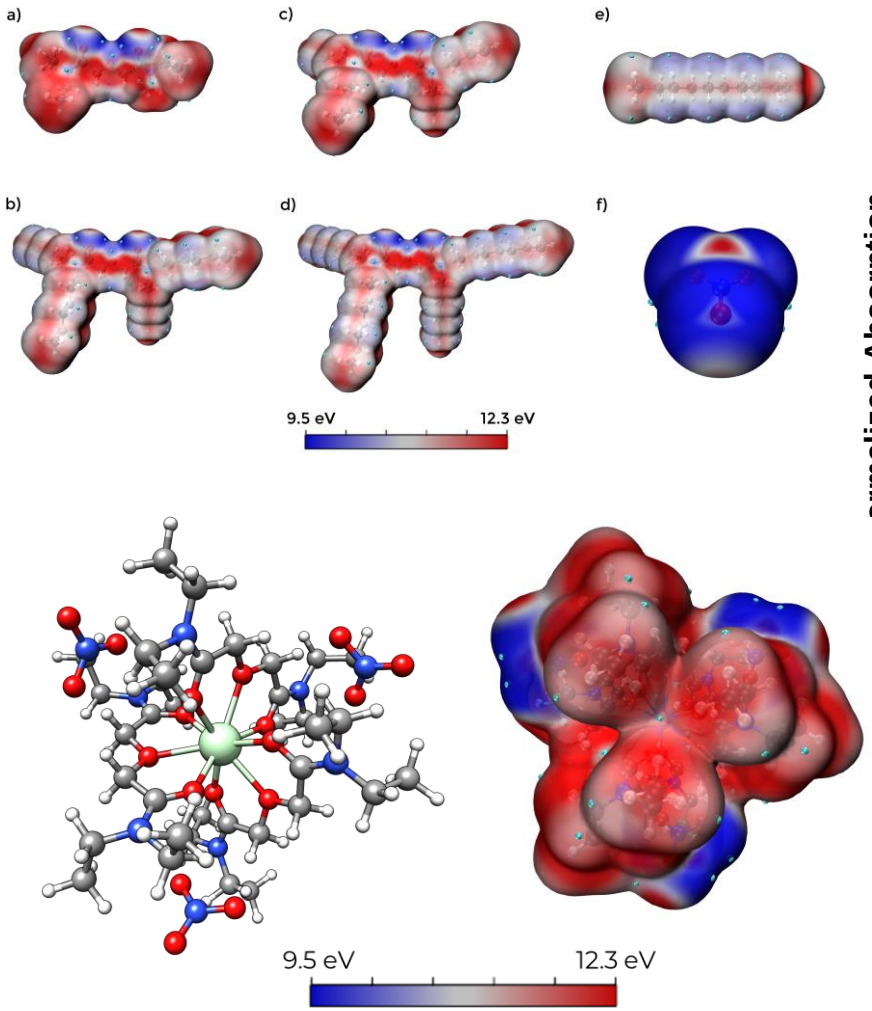


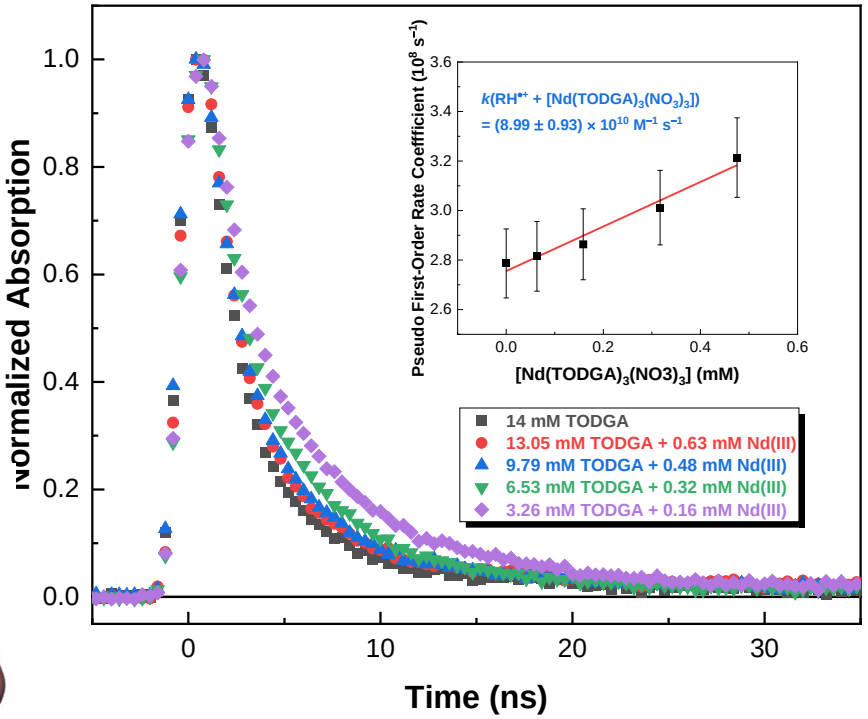


- NpO_2^{2+} and PuO_2^{2+} complexation afforded significantly faster rates of reaction with $RH^{\bullet+}$, then for the non-complexed **TBP**, **DEHBA** and **DEHiBA** molecules.
- Evidence for electron transfer with the complexed metal center?

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

And finally, back to TODGA



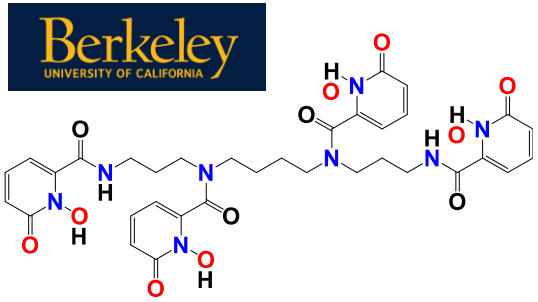


- **Computations:** average local ionization energy analysis highlights the sites of the molecule susceptible to a radical or electrophilic attack.

- **Horne**, **Celis Barros**, Conrad, Grimes, McLachlan, Rotermund, Cook, and Mezyk, *in preparation*

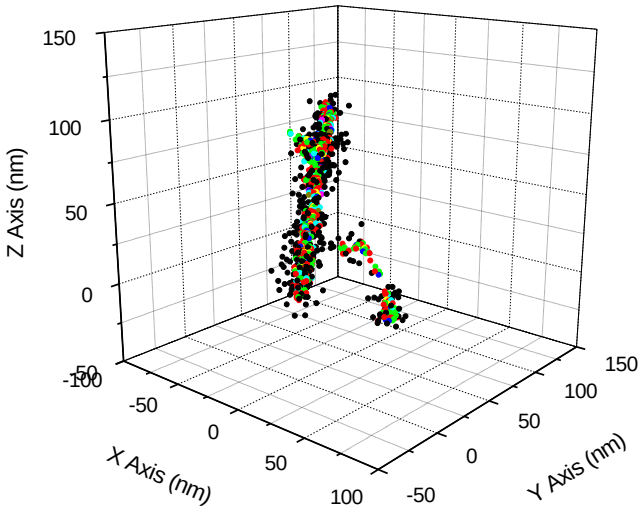
Conclusions

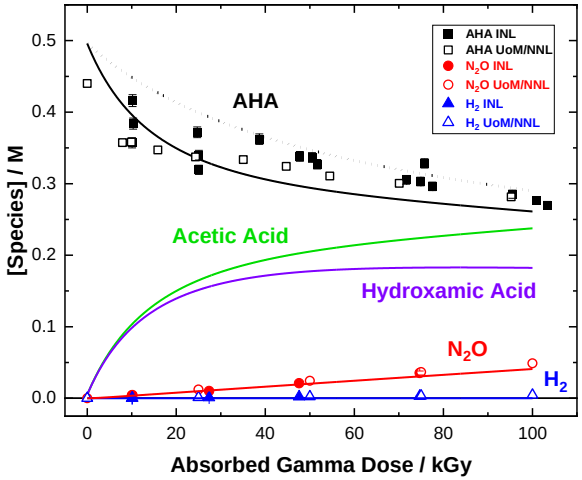
- **Actinide complexation has significant effects on the fundamental radiation chemistry of their complexes, owing to:**
  - steric effects
  - electron distribution differences
  - facilitation of inner *vs.* outer sphere mechanisms
- **Computational and theory needs?**



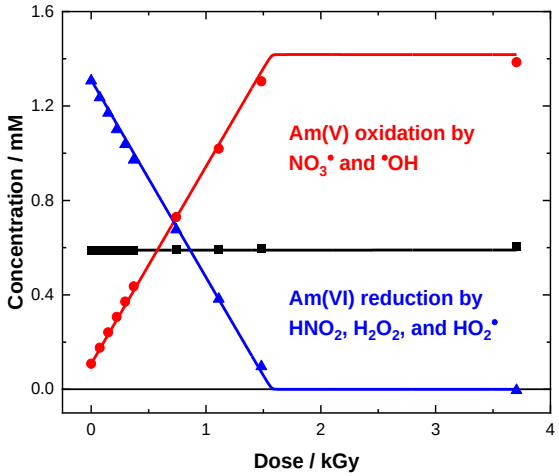
Radical	Rate coefficient (k, M^{-1} s^{-1})	
	HOPO	Nd(HOPO)
e_{aq}^- (10^{10})	3.17 ± 0.04	11.4 ± 0.1
$H^\bullet$ (10^9)	5.5 ± 0.2	5.5 ± 0.2
$^\bullet OH$ (10^{10})	1.66 ± 0.06	1.05 ± 0.02
$^\bullet NO_3$ (10^9)	3.79 ± 0.10	2.61 ± 0.03

The Dream – A Complete Multiscale Model





Multi-scale Modelling Approach	Processes	Timescale
1. Track Structure Simulation	Energy Transfer and Track Structure	<1 femtosecond
2. Physicochemical Processes	Ultra-fast Chemistry	<1 picosecond
3. Nonhomogeneous Diffusion-Reaction Kinetics	Intra-track Chemistry	< 1 microsecond
4. Homogeneous Bulk Chemistry	Reaction of Long-lived Radiolysis Species	>1 microsecond



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Acknowledgements

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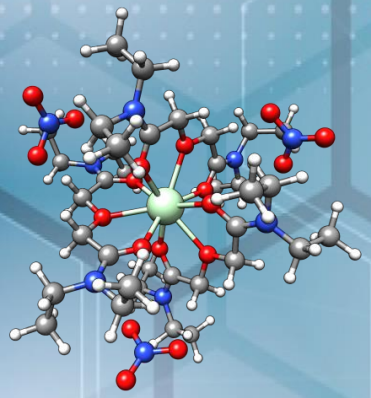

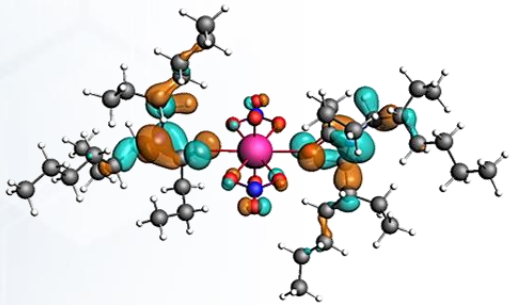

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