November 16th 2023

Gregory P. Holmbeck
Center for Radiation Chemistry Research

Understanding Ionizing Radiation-Induced Speciation, Chemistry, and Transport in Nuclear Materials

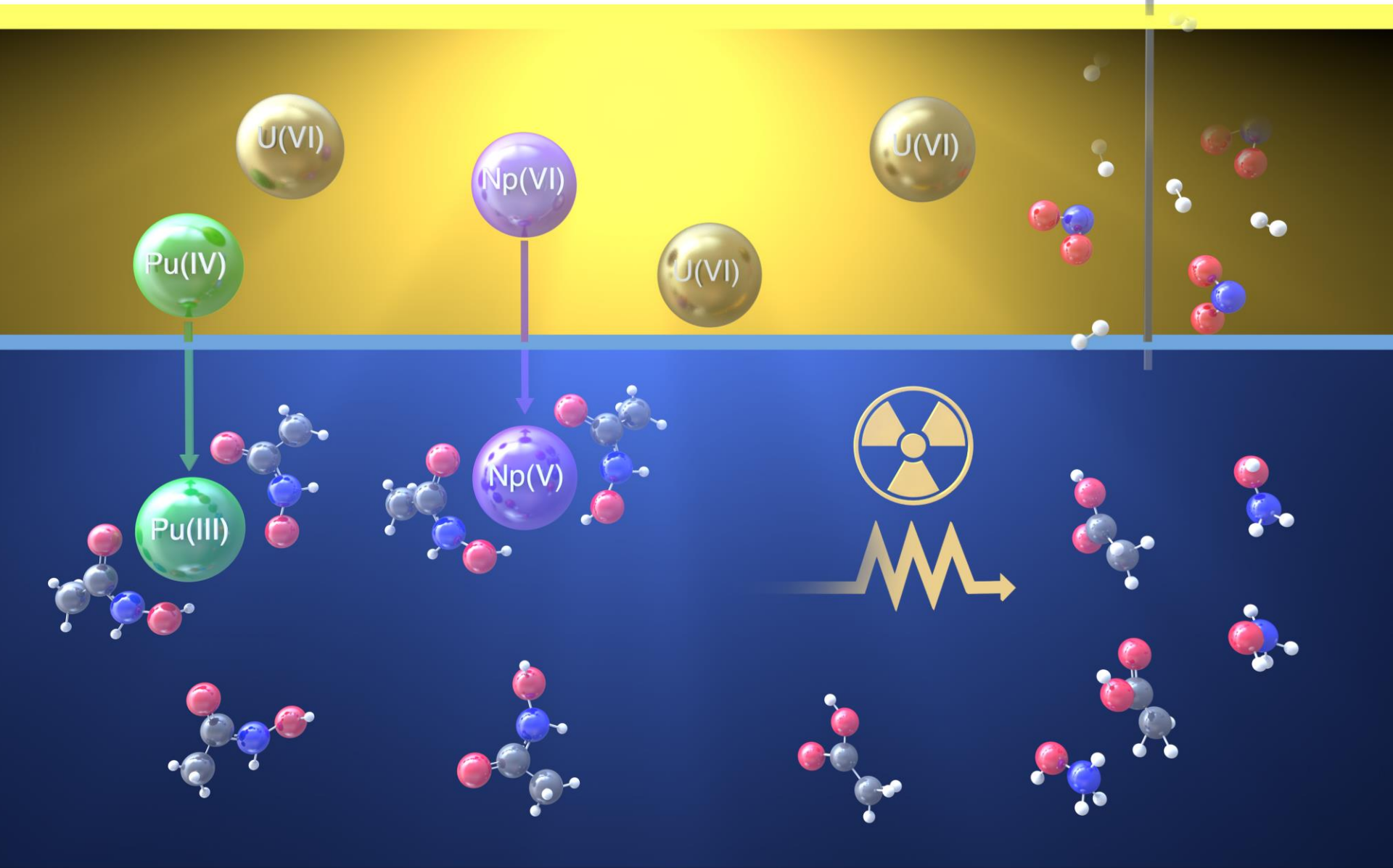
INL/MIS-23-03966

2023 Condensed Phase and Interfacial Molecular Science (CPIMS) Principal Investigators' Research Meeting

Idaho National Laboratory

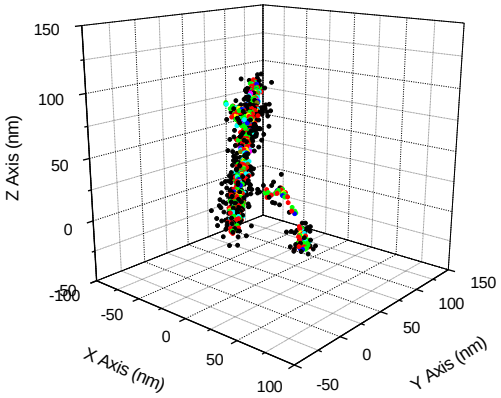
The INL Center for Radiation Chemistry Research

"*Investigate reaction dynamics, structure, and energetics of short-lived transient intermediates in the condensed phase*," specifically those arising from "*highly ionizing radiation*," and evaluate their impact on the physical and chemical properties of matter at steady-state timescales.

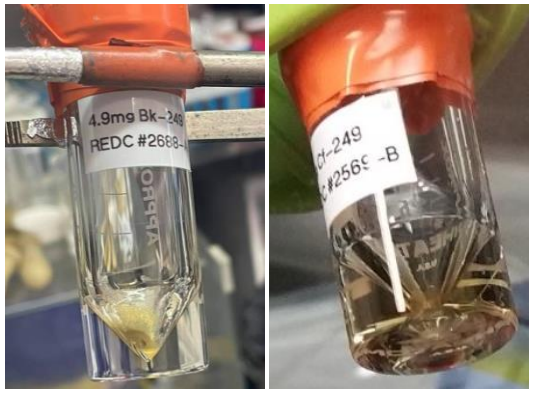


Techniques Employed

Multiscale Modeling

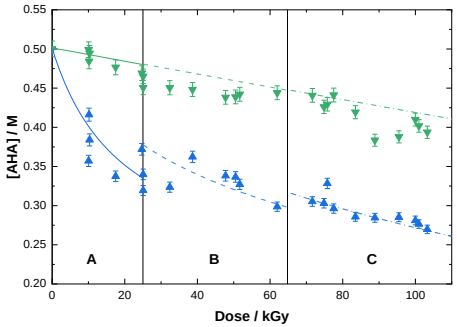


***In Situ* Steady-State Self-Irradiation**



***Ex Situ* Steady-State Cobalt-60 Gamma Irradiation**

Time-Resolved Electron Pulse Irradiation



- Wishart *et al.*, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- **Horne** *et al.*, *J. Phys. Chem. B* **2016**, *120 (49)*, 12643.
- Phillips *et al.*, *Rev. Sci. Instrum.* **2020**, *91(8)*, 083105.

Radiation-Induced Late Actinide Redox Chemistry

2019–2022

Reprocessing Actinide Radiation Chemistry

Water Radiolysis

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

Indirect Radiation Effects

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

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

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

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

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

$$N_2O_4 \rightarrow HNO_2 + HNO_3$$

Direct Radiation Effects

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

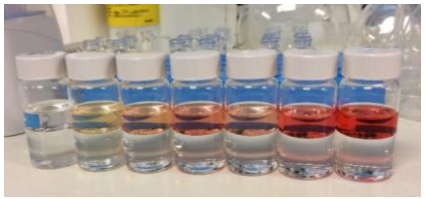
$$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + O$$

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

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

Alkane Radiolysis

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



- Buxton *et al.*, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Reprocessing Actinide Radiation Chemistry

Water Radiolysis

Direct Radiation Effects

Key Transient Species

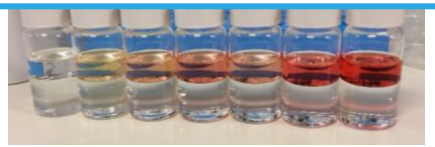
e_{aq}^-, $H^\bullet$, and $^\bullet OH$ from H_2O

$^\bullet NO_3$ from HNO_3

$RH^{\bullet+}$ from ***n*-dodecane**

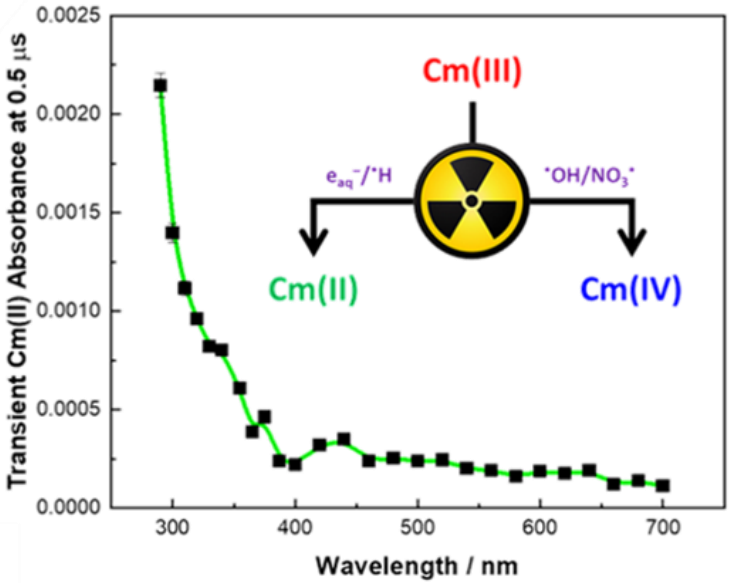
H_2

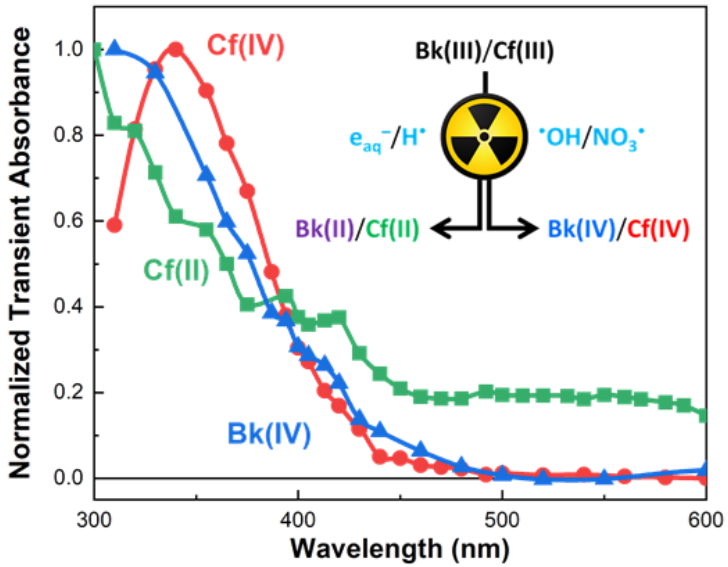
$N_2O_4 \rightarrow HNO_2 + HNO_3$



- Buxton *et al.*, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Non-equilibrium Actinide Oxidation States





- Fast, radical-driven, redox processes yielded non-equilibrium oxidation states that exhibited transient lifetimes on the order of 10–100s of microseconds.
- Chemical kinetics were measured for **Cm(III)**/**Bk(III)**/**Cf(III)** ion redox reactions with highly reactive radiation-induced transients for the development of predictive, multi-scale models.

- **Horne** *et al.*, *Dalton Trans.* **2021**, *50*, 10853.
- **Horne** *et al.*, *Inorg. Chem.* **2022**, *61 (28)*, 10822.

Radiation-Induced Chemistry of Nuclear Materials

2023–2026

Complexation Effects

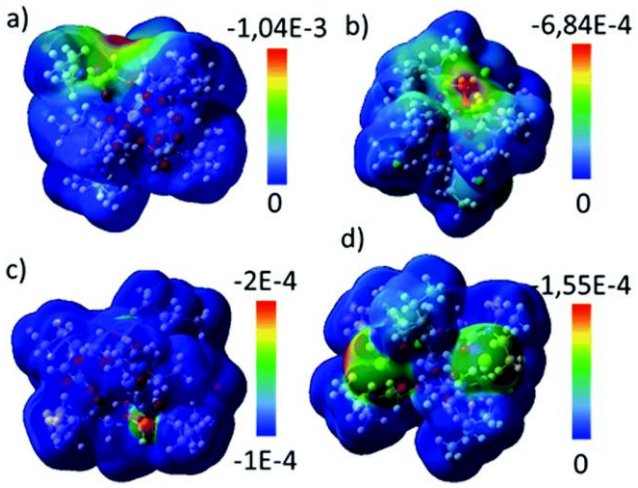
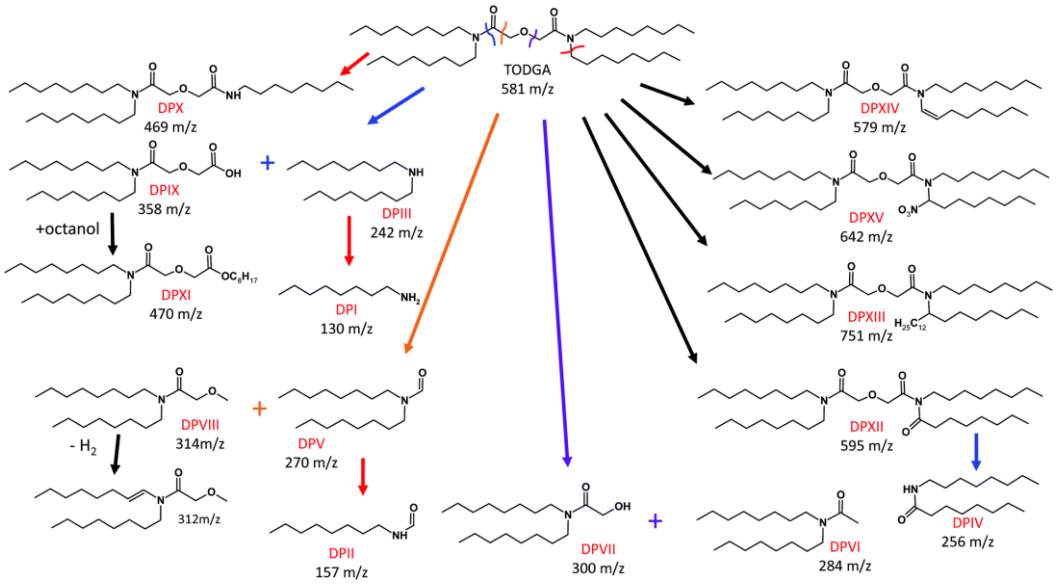
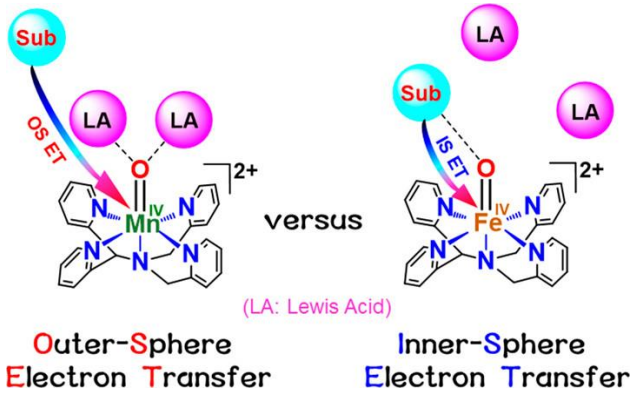


Fig 1. Results of the Fukui function calculations performed on M-TEDGA complexes. Color scales depict the values of the Fukui function calculated in Å^3. **(a)** $[Nd(TEDGA)_3](NO_3)_3$, **(b)** $[Nd(TEDGA)_3]Cl_3$, **(c)** $[Am(TEDGA)_3](NO_3)_3$, and **(d)** $[Am(TEDGA)_3]Cl_3$.



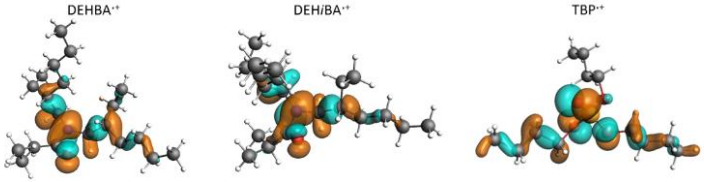
"…in the presence of macroconcentration of lanthanides and actinides, TODGA degradation by radiolysis is minimal and does not generate problematic degradation products." Kimberlin *et al. PCCP,* **2022**, *24*, 9213.

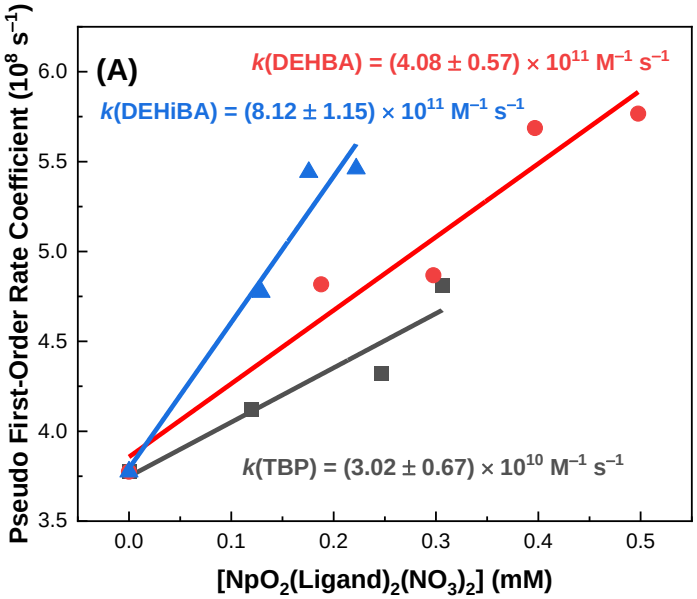


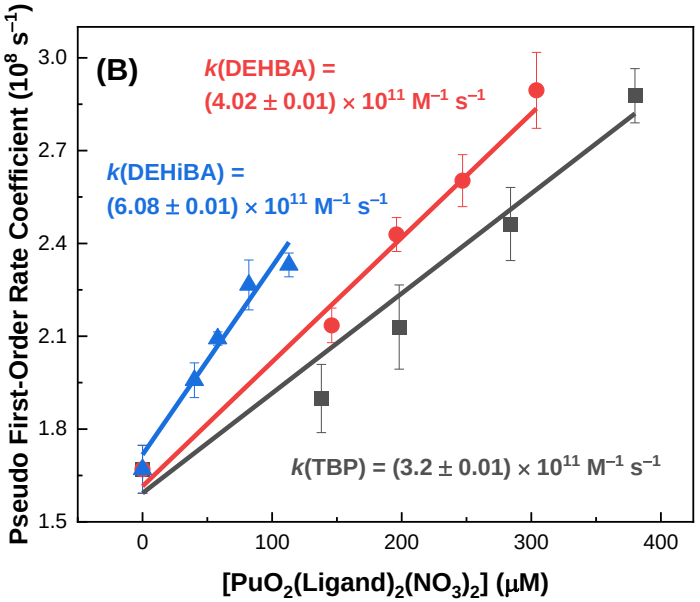
Sharma, Lee, Li, Nam, and Fukuzumi, *Inorg. Chem.*, **2019**, *58 (20)*, 13761.

- Kimberlin *et al.*, *PCCP* **2022**, *24*, 9213.
- Celis-Barros *et al.*, *PCCP* **2021**, *23*, 24589.
- **Horne** *et al.*, *PCCP* **2023**, *25*, 16404

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.
- UO_2^{2+} complexation had negligible effect on the reaction rate for **TBP** with $RH^{\bullet+}$. Evidence for electron transfer with the complexed metal center?

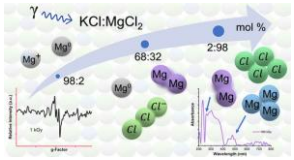
- Celis-Barros *et al.*, *PCCP* **2021**, *23*, 24589.
- Culbertson *et al.*, *Inorg. Chem.* **2024**, In Preparation.

Understanding Radiation-Induced Iodine Speciation, Chemistry, and Transport in High Temperature Molten Salts

2022–2025

Understanding Radiation-Induced Iodine Speciation, Chemistry, and Transport in High Temperature Molten Salts (2022–2025)

Brookhaven National Laboratory



I^-

$M^+ Cl^-$

Initial Species

$M^+ + Cl^\bullet \xleftarrow{Cl^-} M^{2+} + e^-$

$e^- + Cl^\bullet$

Transient Species

M^+ M^+ → M

Cl^- → $Cl_2^{\bullet-}$

e_s^- / e_t^-

$Cl_2^{\bullet-}$ → $Cl^- + Cl_3^-$

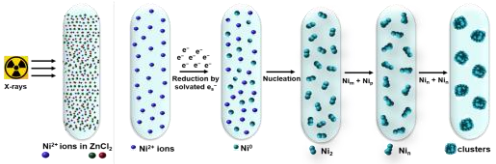
Steady-State Species

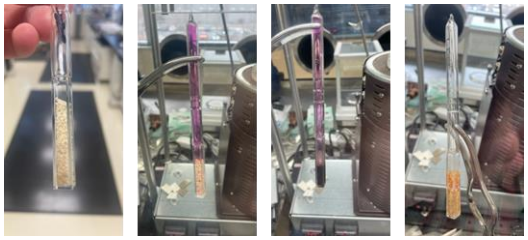
$Cl^- + Cl_2$

$Cl^\bullet + I^- \rightarrow ICl^{\bullet-}$

$ICl^{\bullet-} + ICl^{\bullet-}/Cl_2^{\bullet-} \rightarrow XI_2^-/X_2I^- + Cl$

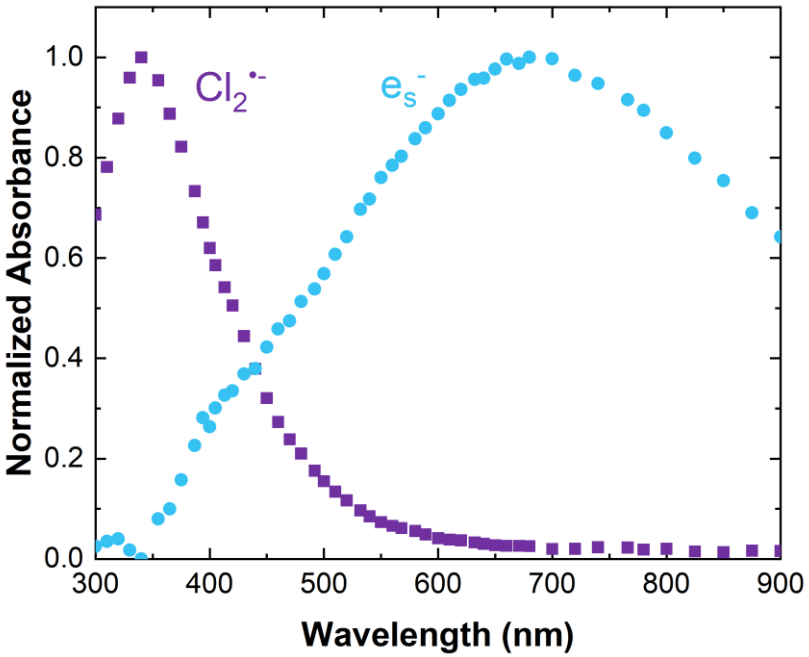
$XI_2^-/X_2I^- \rightleftharpoons ICl + I^-/Cl^-$

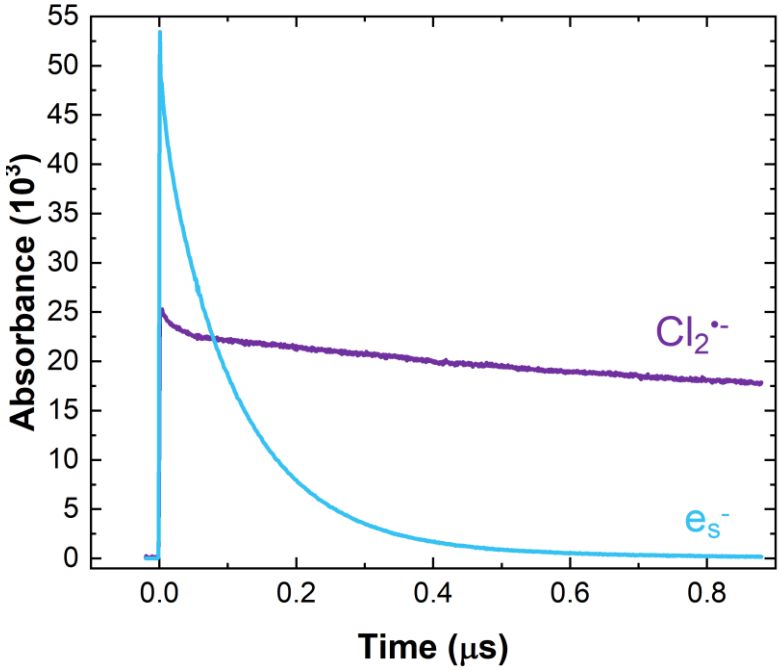




- Ramos-Ballesteros *et al.*, *Phys. Chem. Chem. Phys.* **2021**, *23*, 10384.
- Dias *et al.*, *J. Phys. Chem. Lett.* **2021**, *12*, 157.
- Ramos-Ballesteros *et al.*, *J. Phys. Chem. C* **2022**, *126 (23)*, 9820.
- Iwamatsu *et al.*, *PCCP* **2023**, *25*,16009.

Time-Resolved Molten Salt Irradiations:LiCl-KCl

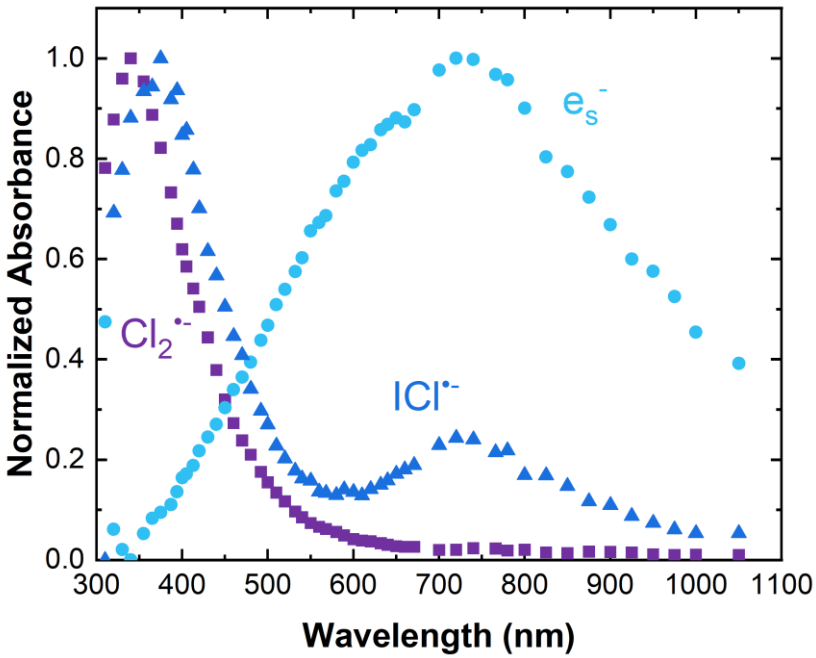


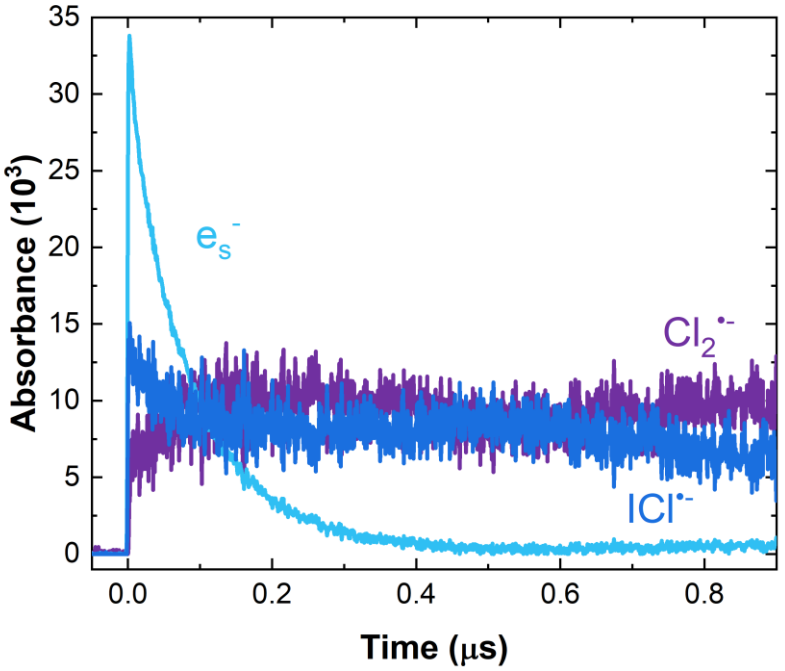


Spectro-Kinetic Analysis (SK-Ana) software was used to deconvolute the overlapping chemical species for the first μs after the electron pulse.

- Pernot, SK-Ana: Analysis of Spectro-Kinetic Data, **2018**
- Iwamatsu *et al.*, *PCCP* **2022**, *24*, 25088.

Time-Resolved Molten Salt Irradiations:10 wt.% KI in LiCl-KCl





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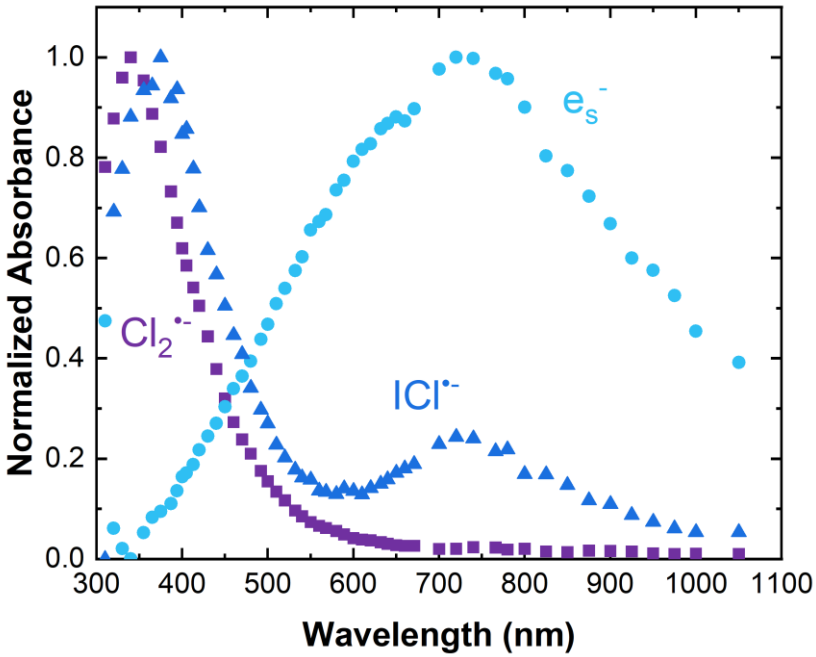
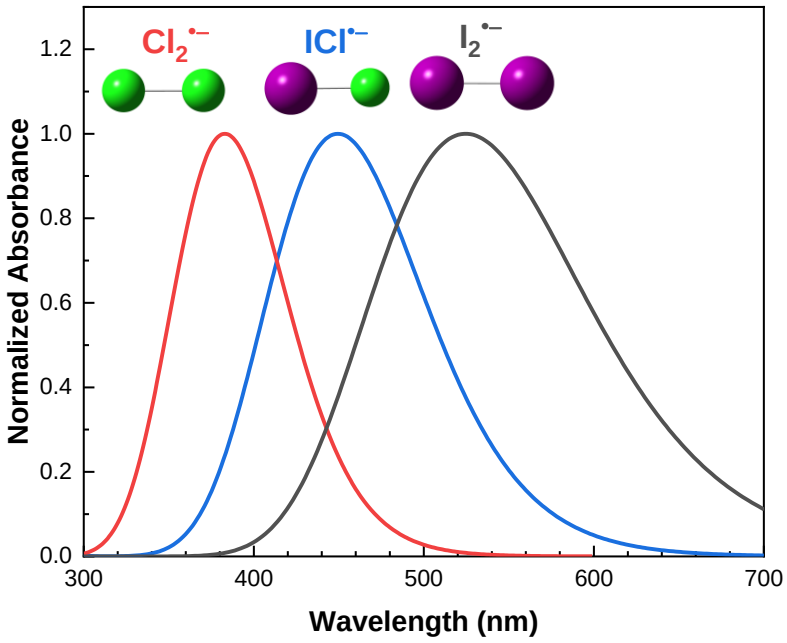
- Pernot, SK-Ana: Analysis of Spectro-Kinetic Data, **2018**
- Conrad *et al.*, *PCCP* **2023**, *25*,16009.

Time-Resolved Molten Salt Irradiations:10 wt.% KI in LiCl-KCl

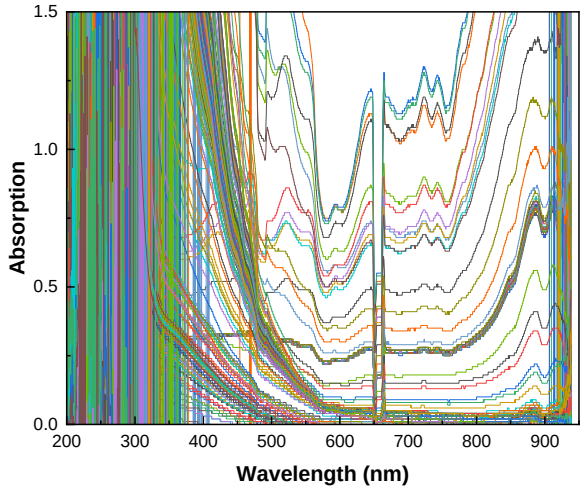


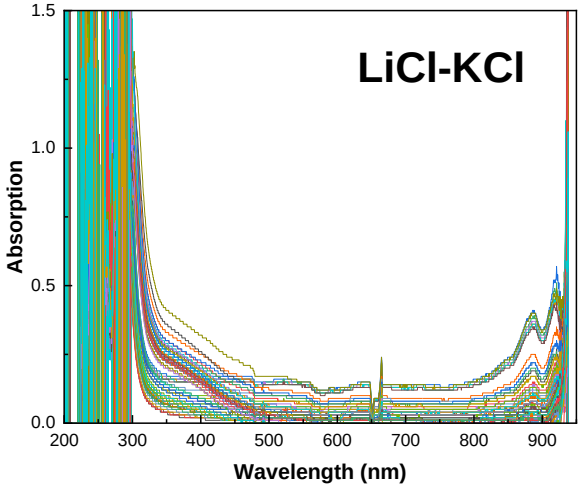


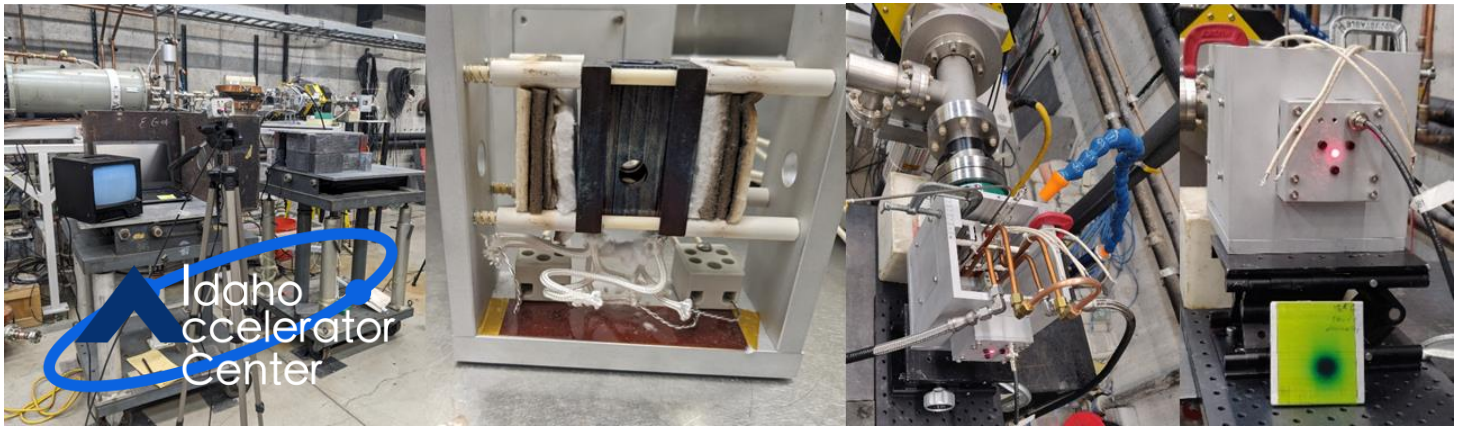
Gaussian 16 was used to run calculations in the gas phase using the *B3LYP/6-311++G(d,p)* level of theory for **Cl**, and the *Def2TZVP* effective core potential basis set for **I**. Optimized geometries were found to be minima on the potential energy surface using harmonic vibrational frequency analysis. Minimum energy structures were analyzed using time-dependent density functional theory to predict electronic absorption spectra.

- Conrad *et al.*, *PCCP* **2023**, *25*,16009.

Steady-State Molten Salt Irradiations:10 wt.% KI in LiCl-KCl







- Phillips *et al.*, *Rev. Sci. Instrum.* **2020**, *91(8)*, 083105.

Summary

1. Irradiation of actinide containing systems promotes the formation of non-equilibrium actinide oxidation states that likely possess new redox chemistry.

2. Metal ion complexation can have profound effects on the steady-state chemistry of nuclear materials by providing additional degrees of reaction freedom.

3. The presence of iodine in irradiated molten chloride salts affords the formation of a transient inter-halide species that likely dictates the fate of iodine in a molten salt reactor system.

- **Horne** *et al.*, *Dalton Trans.* **2021**, *50*, 10853.
- **Horne** *et al.*, *Inorg. Chem.* **2022**, *61 (28)*, 10822.
- Conrad *et al.*, *PCCP* **2023**, *25*,16009.
- Rotermund *et al.*, *Inorg. Chem.* **2023**, *62 (32)* 12905.
- Rotermund *et al.*, *J. Phys. Chem. A* **2023**, Accepted.

ECRP – Unravelling the Role of Non-Equilibrium Radiation-Induced Actinide Oxidation States

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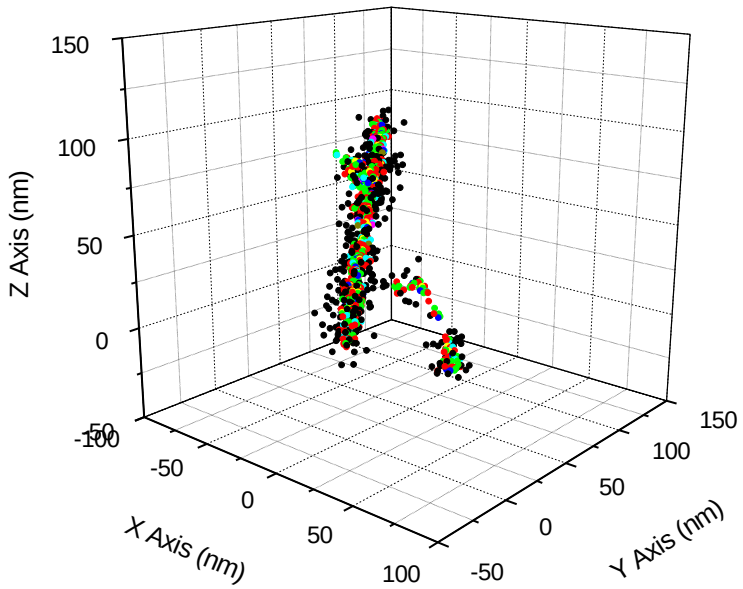
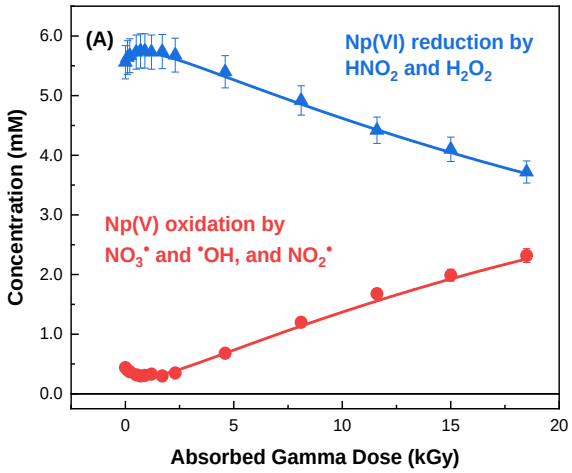
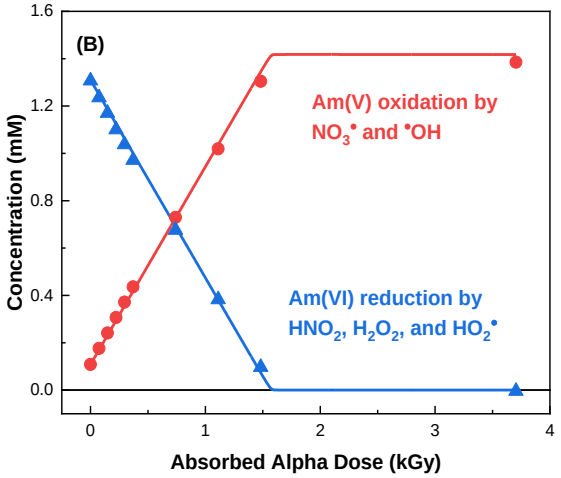


Multi-scale Modelling Approach	Processes	Timescale
1. Track Structure Simulation	Energy Transfer and Track Structure	<1 femtosecond
2. Physicochemical Processes	Ultra-fast Chemistry	<1 picosecond
3. Nonhomogeneous Diffusion-Reaction Kinetics	Intra-track Chemistry	< 1 microsecond
4. Homogeneous Bulk Chemistry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





- Pimblott *et al.*, *J. Phys. Chem.* **1996**, *100*, 8595.
- Clifford *et al.*, *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 2673.
- **Horne** *et al.*, *J. Phys. Chem. B* **2016**, *120 (49)*, 12643.
- **Horne** *et al.*, *Inorg. Chem.* **2019**, *58*, 8551.

Acknowledgements

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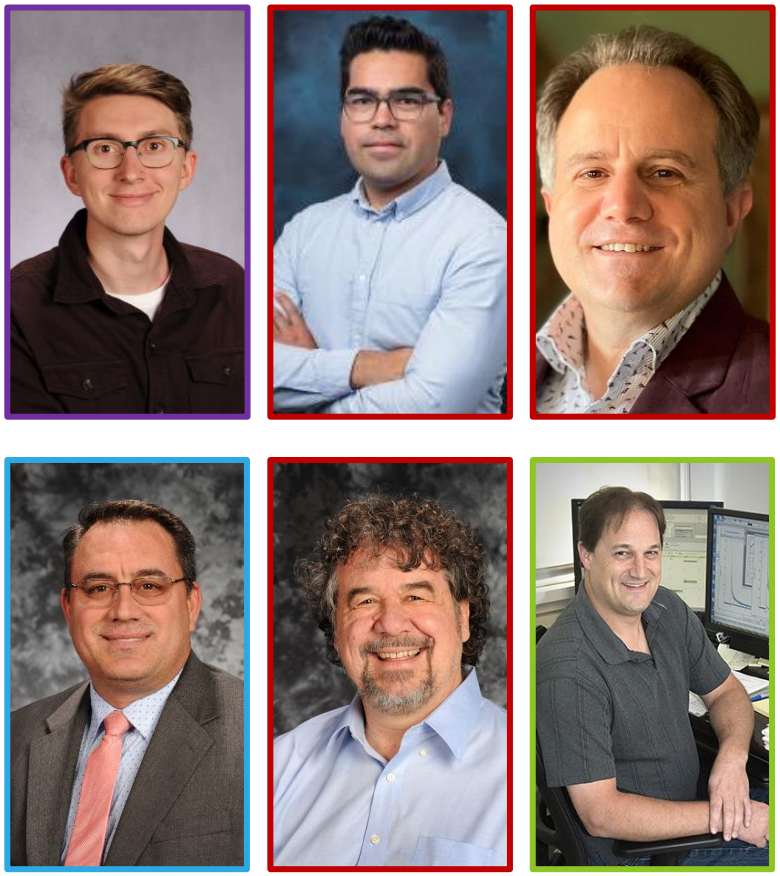

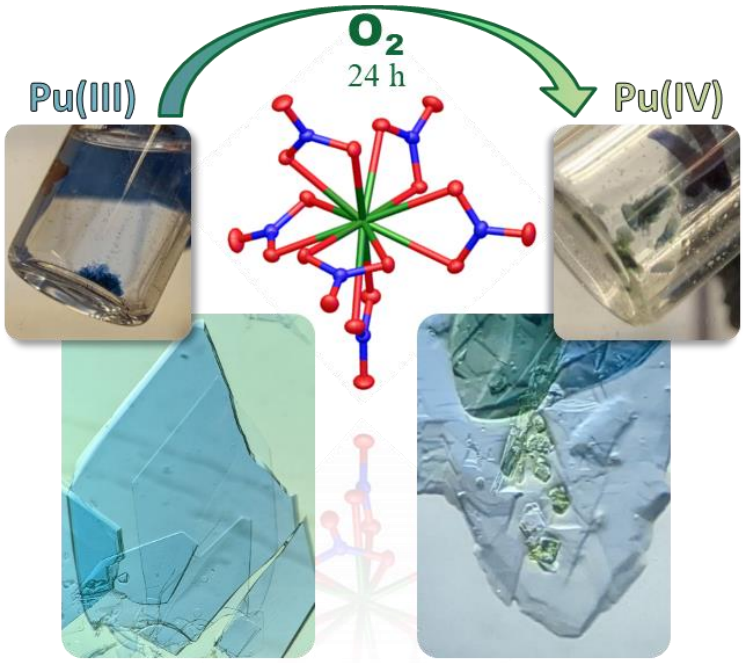

INL, BNL, Universities, and Graduate Students

Brookhaven National Laboratory | Colorado School of Mines | California State University Long Beach | Florida State University | Idaho National Laboratory

Acknowledgements

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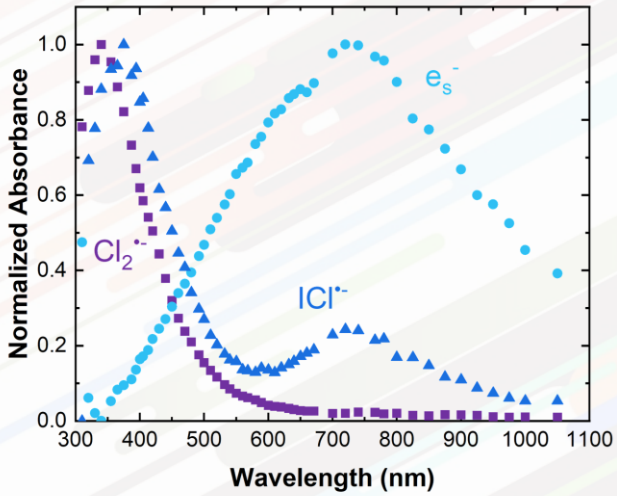
INL, BNL, Postdoctoral Researchers, and Graduate Students

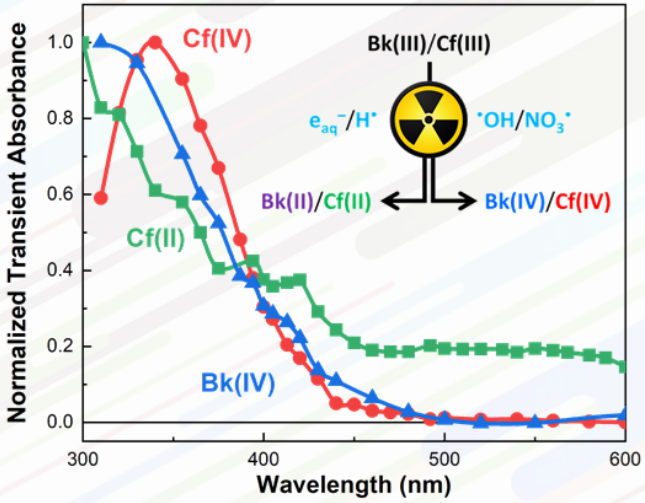
Brookhaven National Laboratory

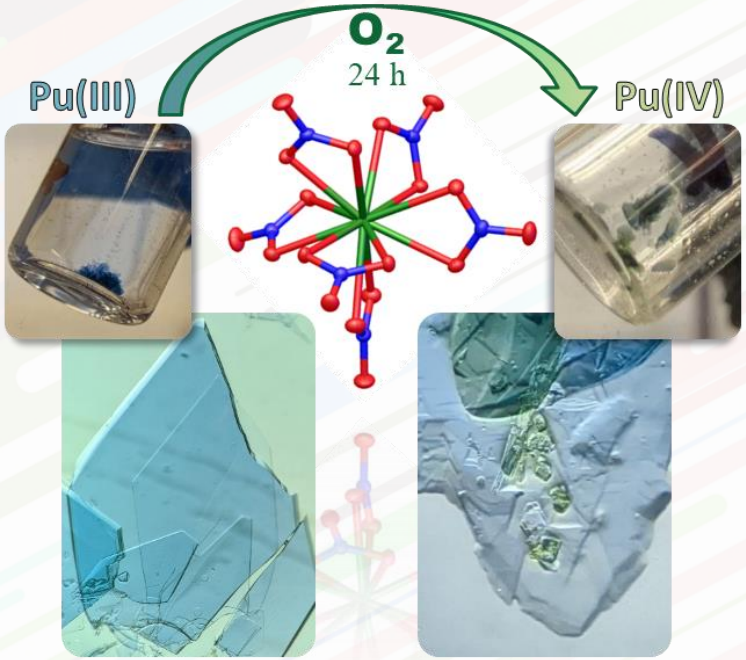
IDAHO NATIONAL LABORATORY

Idaho National Laboratory

Questions?


Normalized Absorbance
Wavelength (nm)
e_s^-
$Cl_2^{\bullet-}$
$ICl^{\bullet-}$


Normalized Transient Absorbance
Wavelength (nm)
Cf(IV)
Cf(II)
Bk(IV)
Bk(III)/Cf(III)
$e_{aq}^-/H^\bullet$
$^\bullet OH/NO_3^\bullet$
Bk(II)/Cf(II)
Bk(IV)/Cf(IV)


O_2
24 h
Pu(III)
Pu(IV)