INL/CON-24-77098-Revision-1

Predicting Radiation-Induced Plutonium Redox Chemistry using Multi-scale Modeling Methods

September 2024

Changing the World's Energy Future

Amy Elizabeth Kynman, Gregory Peter Holmbeck

Idaho National Laboratory

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Predicting Radiation-Induced Plutonium Redox Chemistry using Multiscale Modeling Methods

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Glenn T. Seaborg Postdoctoral Research Associate

PLUTONIUM FUTURES
THE SCIENCE 2024

Glenn T. Seaborg Institute
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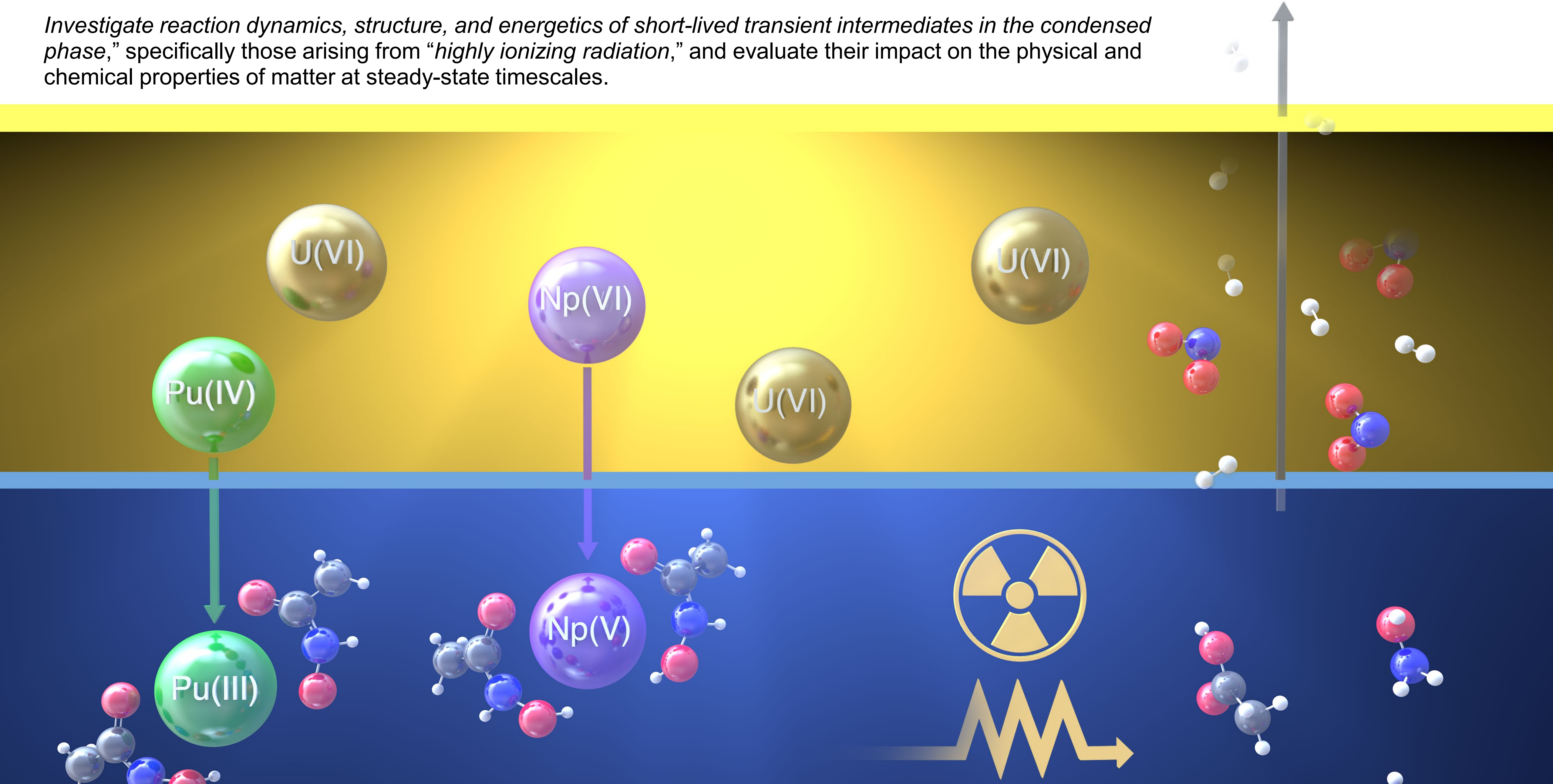
The INL Center for Radiation Chemistry Research

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.



Radiation Chemistry under Reprocessing Conditions

Water Radiolysis

H_2O

H_{aq}^+

Indire

HNO

NO_3^-

$NO_3^{\bullet}$

NO_3

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

$N_2O_4 \rightarrow HNO_2 + HNO_3$

Direct Radiation Effects

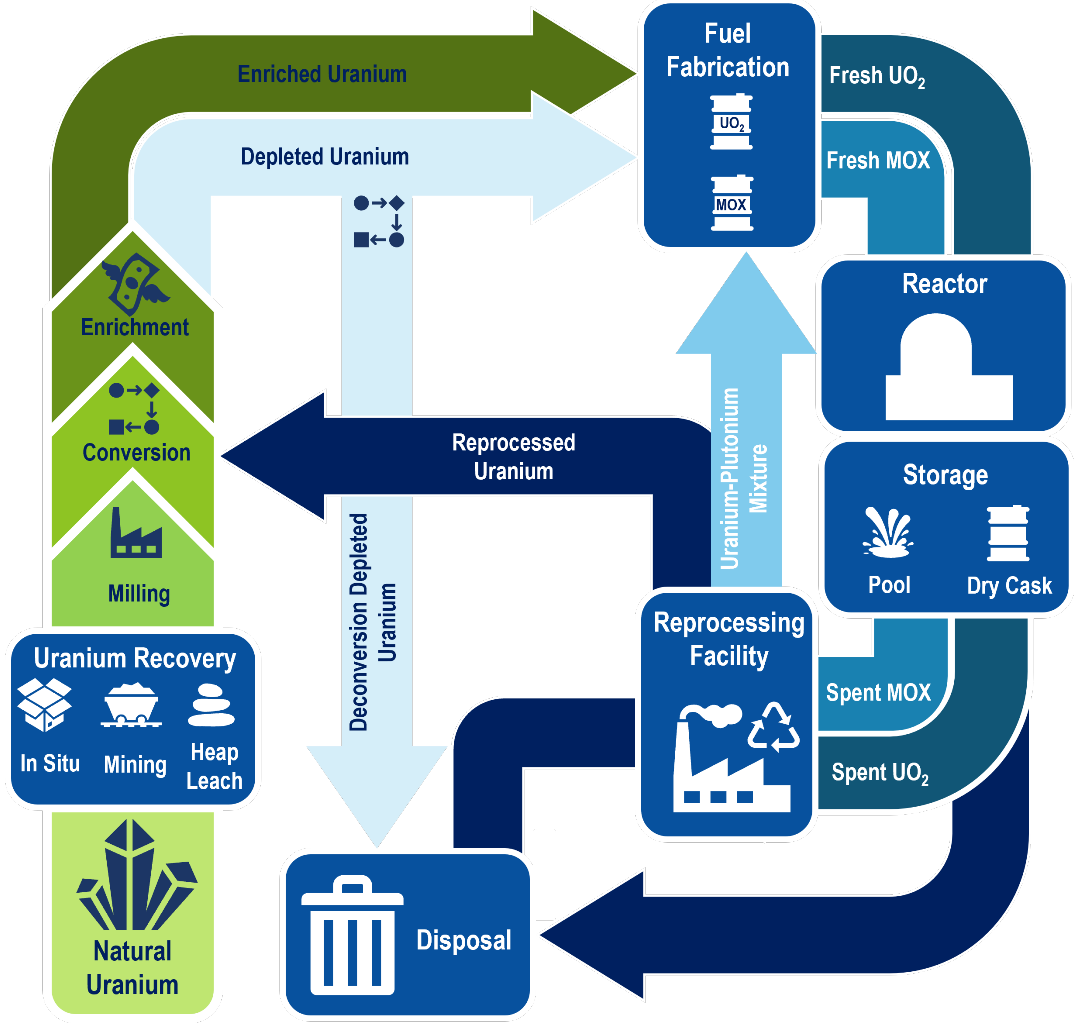
$R\text{-}CH_3$ … H_2

Key Radiolysis Products

e_{aq}^-, $H^{\bullet}$, $^{\bullet}OH$, and H_2O_2 from H_2O

$NO_3^{\bullet}$ and HNO_2 from HNO_3

Plutonium in the Nuclear Fuel Cycle

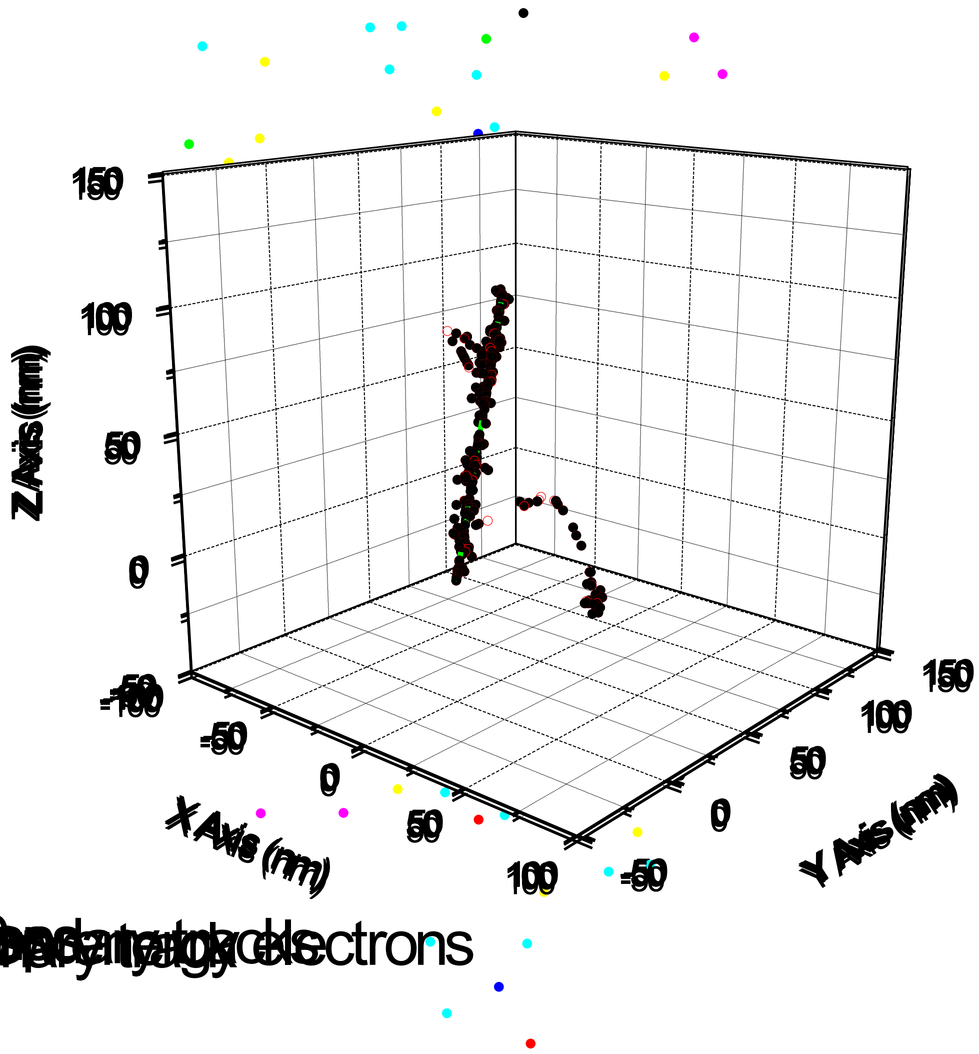


$$Pu^{4+} + PuO_2^{+} \rightleftharpoons Pu^{3+} + PuO_2^{2+}$$

PUREX Chemistry

- Pu(IV) and U(VI) co-extracted as neutral nitrate complexes by TBP.
- Pu(III) generated via reduction and retained in aqueous phase while U(VI) remains in organic phase.
- Understanding and optimizing Pu redox and radiation chemistry is crucial for efficient separation and recovery.

Predicting Radiation-Induced Actinide Redox Chemistry



Species	Radiolytic yield (G-value, molecules 100 eV^{-1})		
	1.0 M HNO_3	3.0 M HNO_3	6.0 M HNO_3
H_{aq}^{+}	4.2017	4.4706	4.3887
e_{aq}^{-}	0.0000	0.0000	0.0000
$^{\bullet}OH$	3.0583	0.0117	0.0000
$H^{\bullet}$	0.0000	0.0000	0.0000
H_2	0.1039	0.0909	0.0543
OH^{-}	0.0000	0.0000	0.0000
H_2O_2	0.6764	0.601	0.5418
$O(^3P)$	0.0173	0.0154	0.0073
O^{-}	0.0000	0.0000	0.0000
O_2	0.0043	0.0081	0.0036
$O_2^{\bullet -}$	0.0000	0.0000	0.0000
$HO_2^{\bullet}$	0.0427	0.4502	0.2997
HO_2^{-}	0.000	0.0000	0.0000
H_2O	0.1180	0.1715	0.1259
$NO_3^{\bullet 2-}$	3.9872	3.1975	3.2376
$NO_3^{\bullet}$	0.0000	3.0839	3.1534
$NO_2^{\bullet}$	0.2310	0.5087	0.6111

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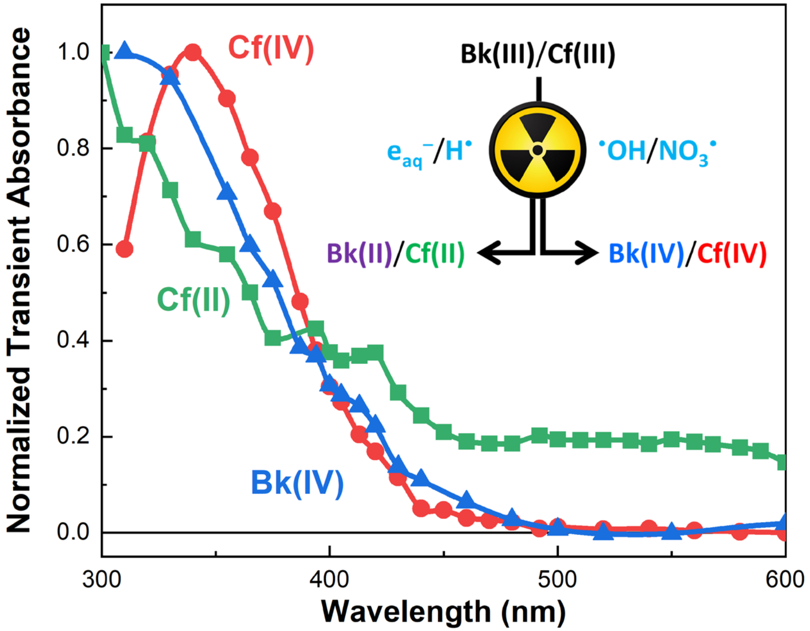
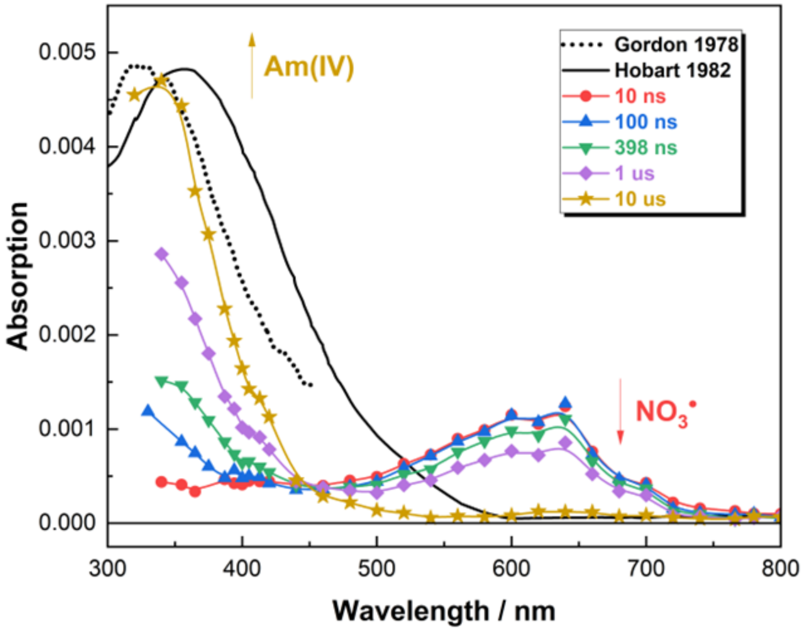
Radiation-Induced Non-Equilibrium Actinide Species

"Short-lived (≤ seconds) atoms or ions formed by the atomistic/molecular-level interaction of radiation-induced radical and molecular products with actinide ion oxidation states in aqueous solution."





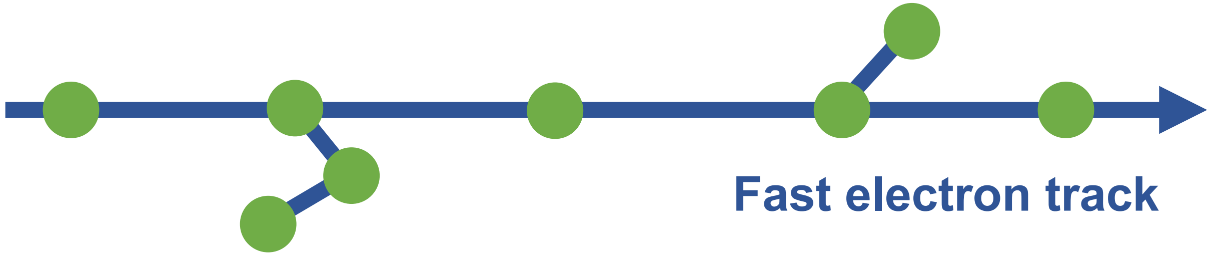
- Gordon, Sullivan, and Ross, J. Phys. Chem. Ref. Data **1986**, *15(4)*, 1357.
- Horne, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Trans.* **2021**, *50*, 10853.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Beck, Gomez Martinez *et al.*, *Inorg. Chem.* **2022**, *61(28)*, 10822.
- Rotermund, Mezyk, Sperling, Beck, Wineinger, Cook, Albrecht-Schönzart, and **Horne**, *J. Phys. Chem. A* **2024**, *128(3)*, 590.
- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and **Horne**, *Dalton Trans.* **2024**, *53*, 9262

In-Situ Alpha and Ex-Situ Gamma Irradiations

Marrale and d'Errico, Gels **2021**, *7(2)*, 74.

Gamma / Beta

- Actinide-containing solutions irradiated and changes in oxidation state monitored over time.
- Absorbed dose calculated from the irradiator dose rate.
- Radical products dominate.



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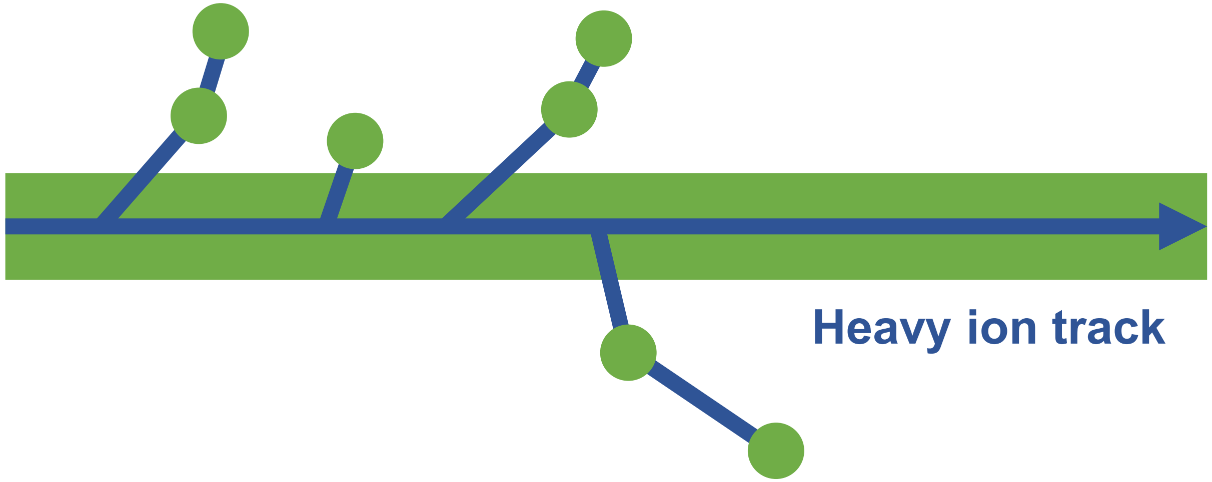
In-Situ Alpha and Ex-Situ Gamma Irradiations

Marrale and d'Errico, Gels **2021**, *7(2)*, 74.

Alpha

- Source of radiation is the inherent decay of the actinide element.
- Absorbed dose calculated from quantity and specific activity of alpha emitter, and time exposed.
- Molecular products dominate.



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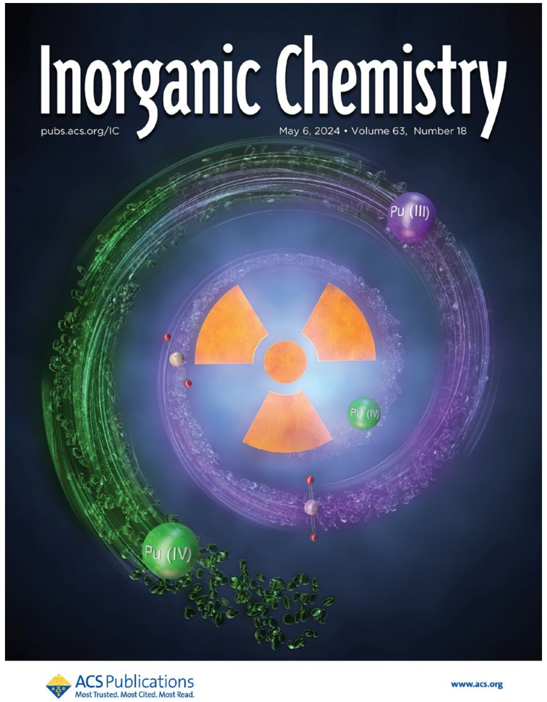
Predicting Radiation-Induced Plutonium Redox Chemistry



Cover artwork designed by
Rett Tyler Longmore,
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Research Goals

Understand plutonium behavior under gamma irradiation

Understand plutonium behavior under alpha irradiation

Use existing and acquired data to create and validate a predictive multiscale model

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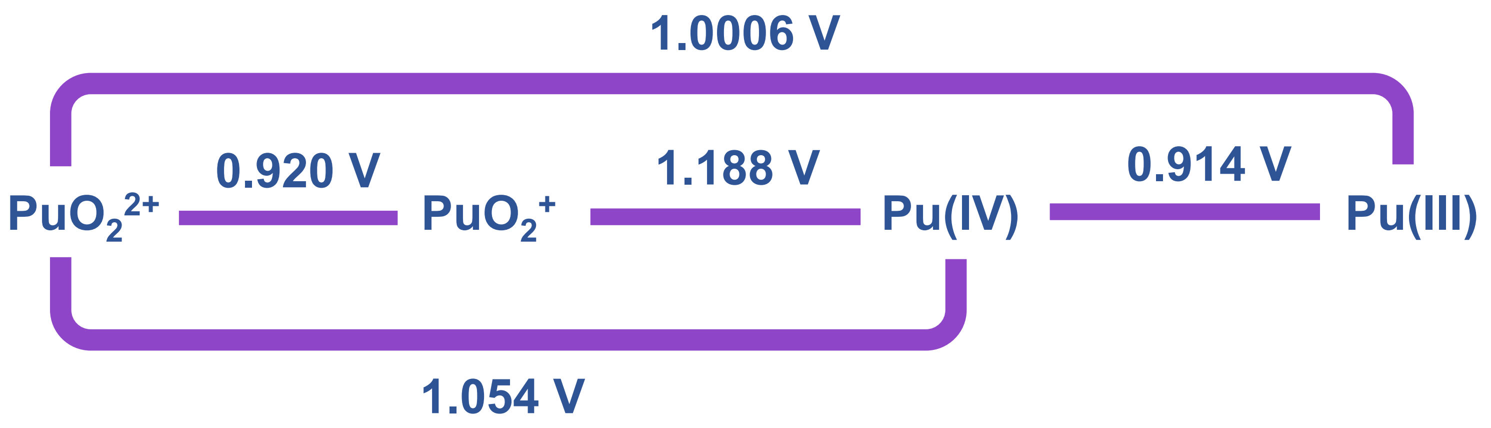
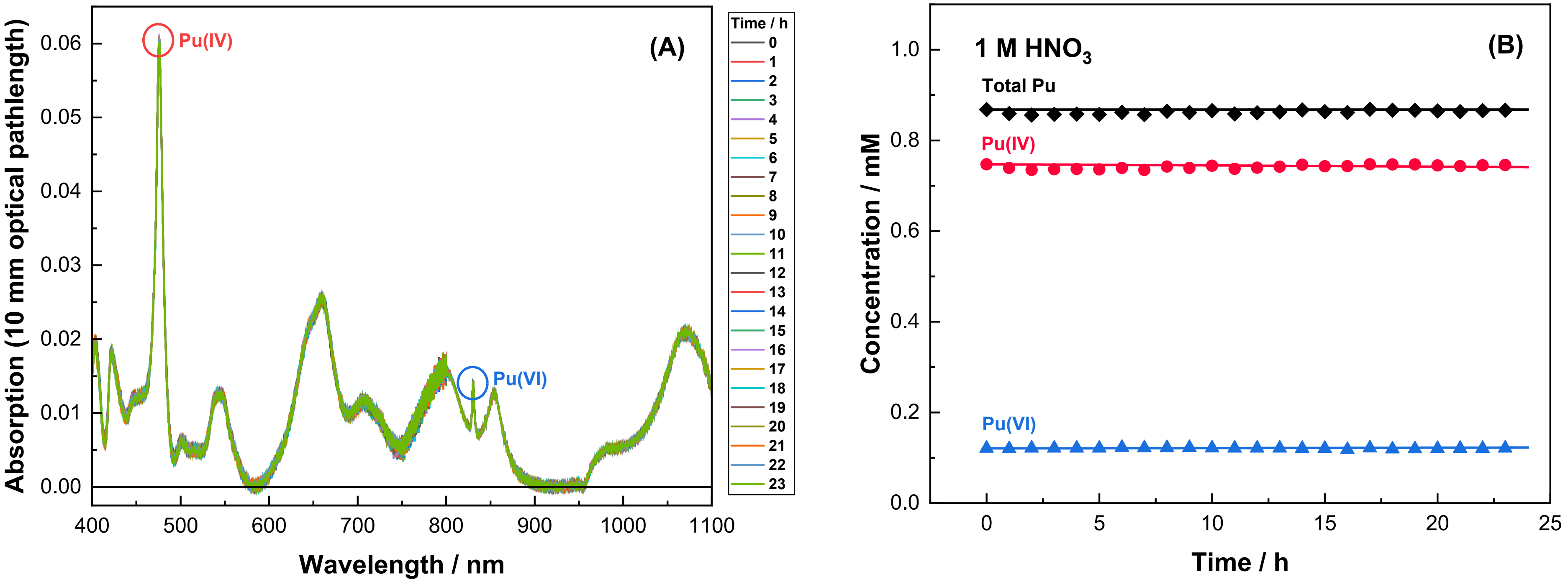
The Starting Point for a Multiscale Model

Radiolysis Product	Plutonium Oxidation State Rate Coefficients (k, $M^{-1}\ s^{-1}$)			
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
e_{aq}^-		2.0×10^{10}	$1.9–6.4 \times 10^{10}$	3.50×10^{10}
$H^\bullet$	$< 1.0 \times 10^6$	2.0×10^7	2.0×10^8	
$^\bullet OH$	$1.8–4.2 \times 10^8$			
$NO_3^\bullet$	2.5×10^8			



Cobalt-60 Gamma Irradiations

Dose Accumulation



(A) Absorption spectra for plutonium in aerated, aqueous 1.0 M HNO_3 solution over 23 hours with no gamma irradiation. **(B)** Corresponding concentrations of Pu(IV), Pu(VI), and total plutonium.

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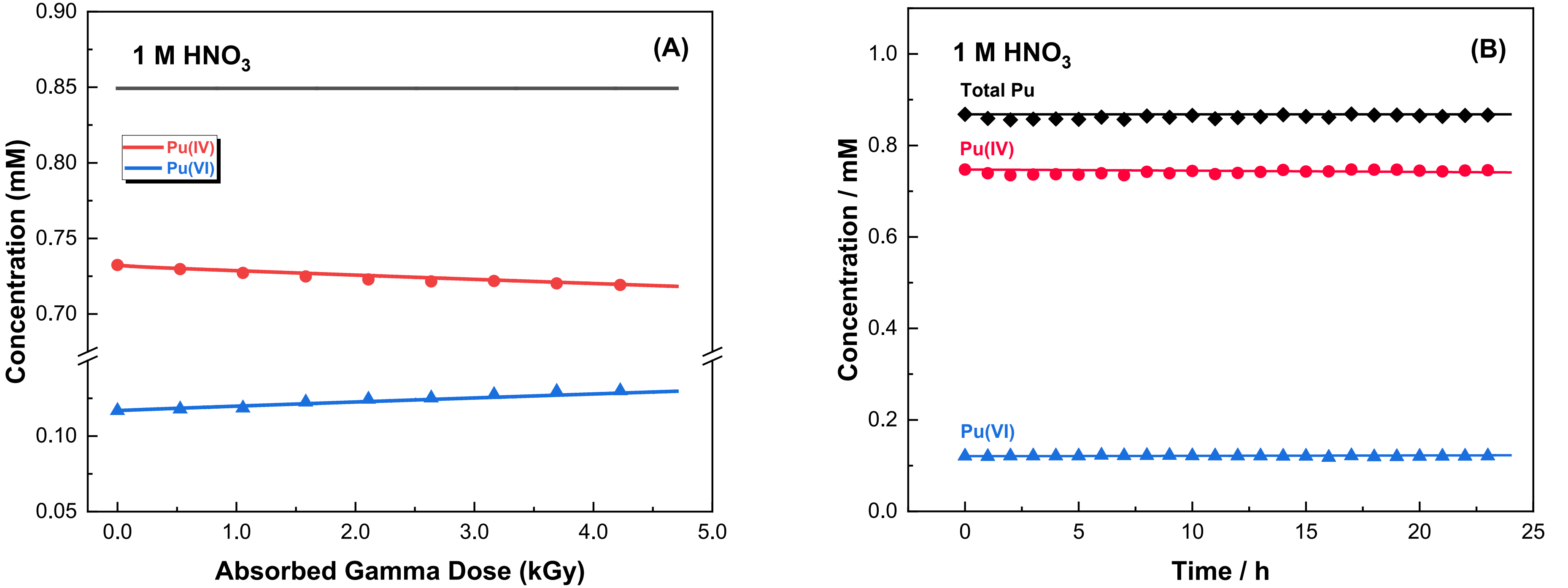
Cobalt-60 Gamma Irradiations



(A) Absorption spectra for plutonium in aerated, aqueous 1.0 M HNO_3 solution over 23 hours with gamma irradiation. **(B)** Corresponding data without irradiation.

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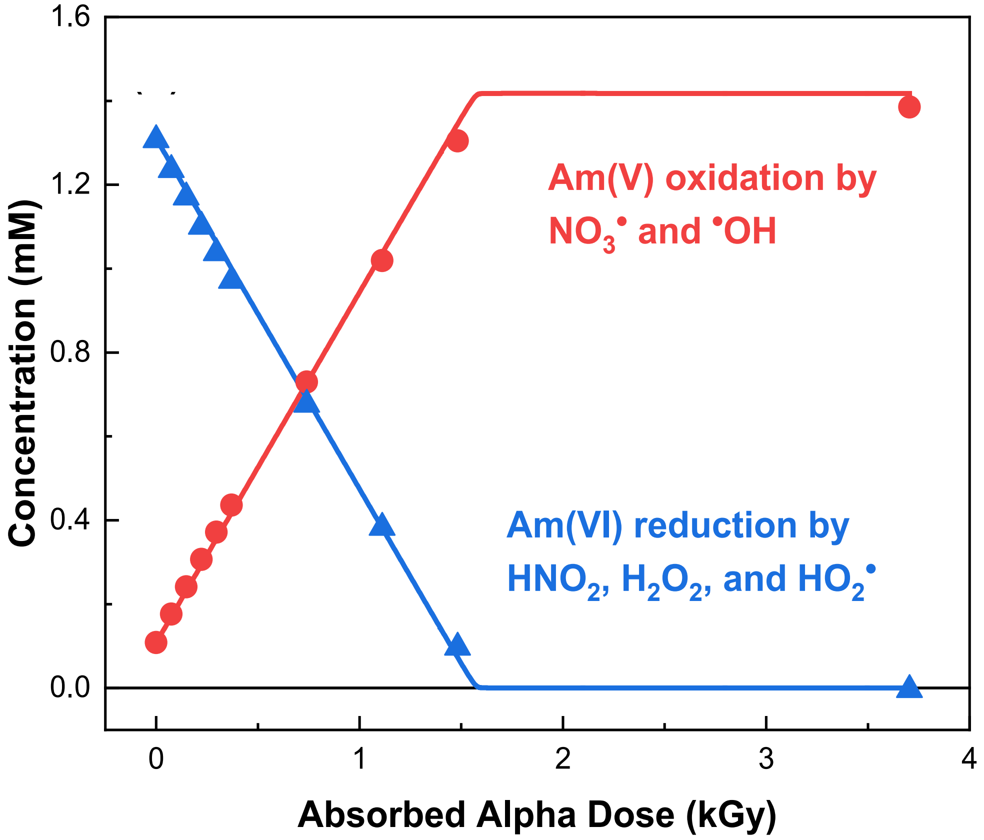
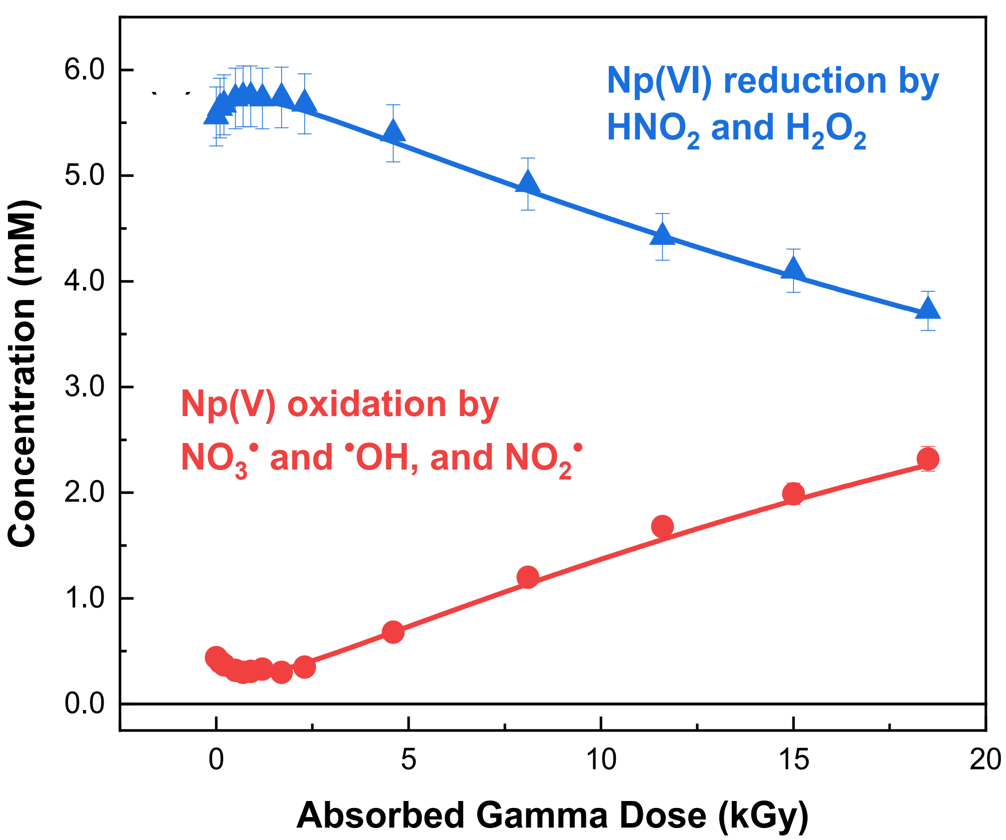
Comparison to Np and Am multiscale models

Americium



Neptunium



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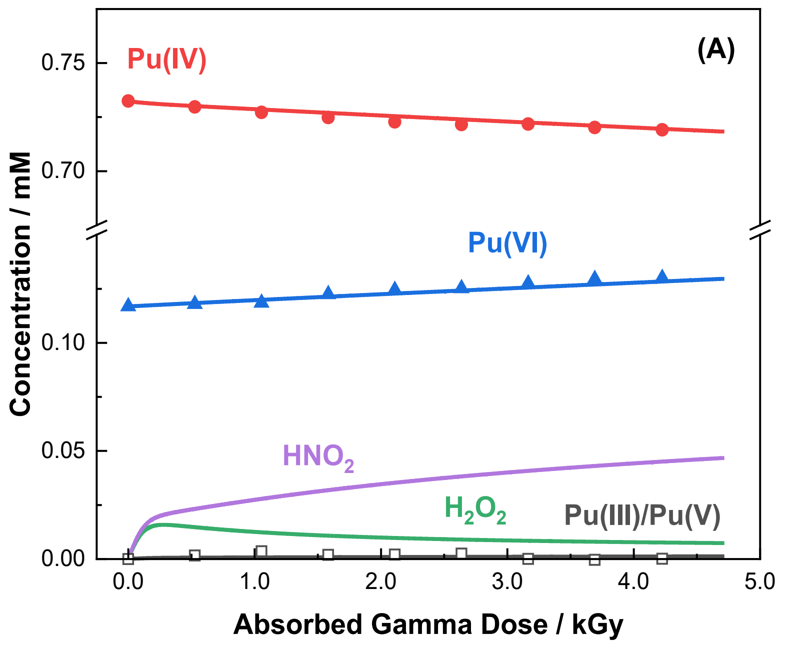
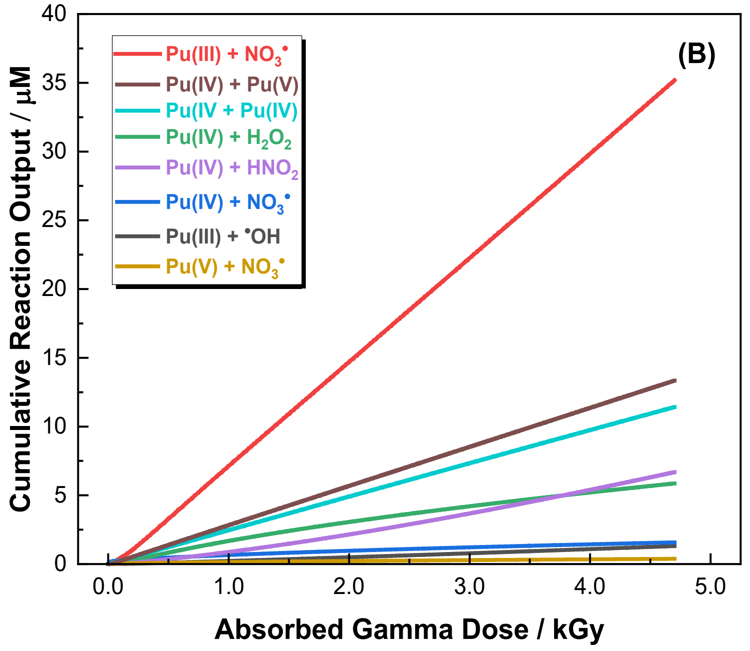
The Role of Radiation-Induced Plutonium Oxidation States in Solution (1.0 M HNO_3)





- **Pu(IV)** is transiently reduced to **Pu(III)** by its reactions with **H_2O_2** and **HNO_2**.
- Oxidation of **Pu(IV)** is in competition with the scavenging of **$NO_3^{\bullet}$** radicals by **Pu(III)**.
- Remaining G(**$NO_3^{\bullet}$**) partially accounts for the accumulation of **Pu(VI)** via the oxidation of **Pu(V)**.

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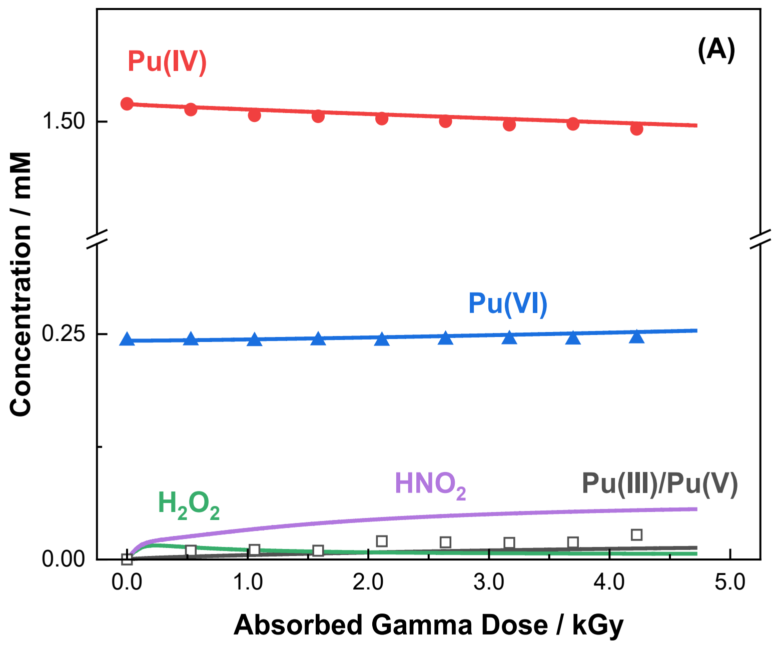
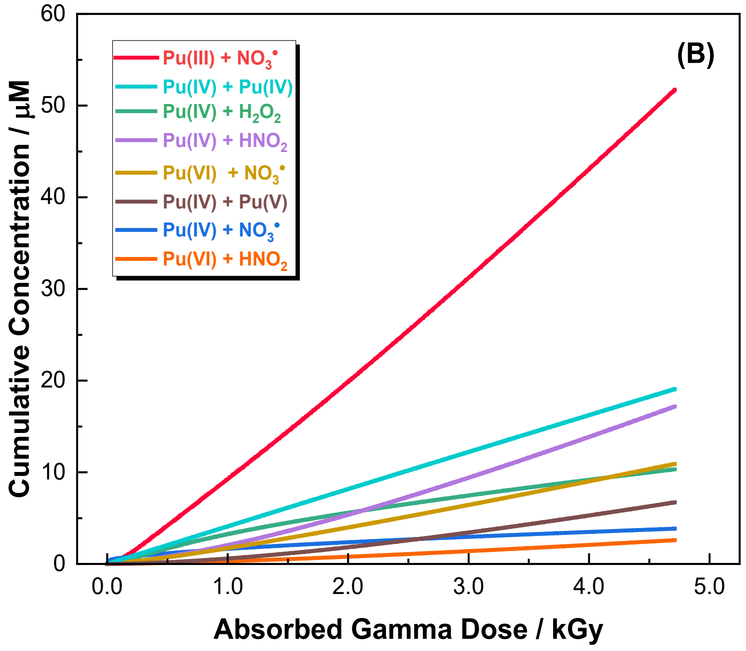
The Role of Radiation-Induced Plutonium Oxidation States in Solution (3.0 M HNO_3)





- **Pu(III)** oxidation by **•OH** inhibited by HNO_3.
- Contribution of **HNO_2** to **Pu(IV)** reduction becomes greater than that afforded by **H_2O_2**.
- Less **Pu(VI)** is accumulated because of a shift in the position of the Pu-equilibria with acidity.
- Model predicts the formation of a low (µM), steady-state concentration of **Pu(III)** and **Pu(V)**.

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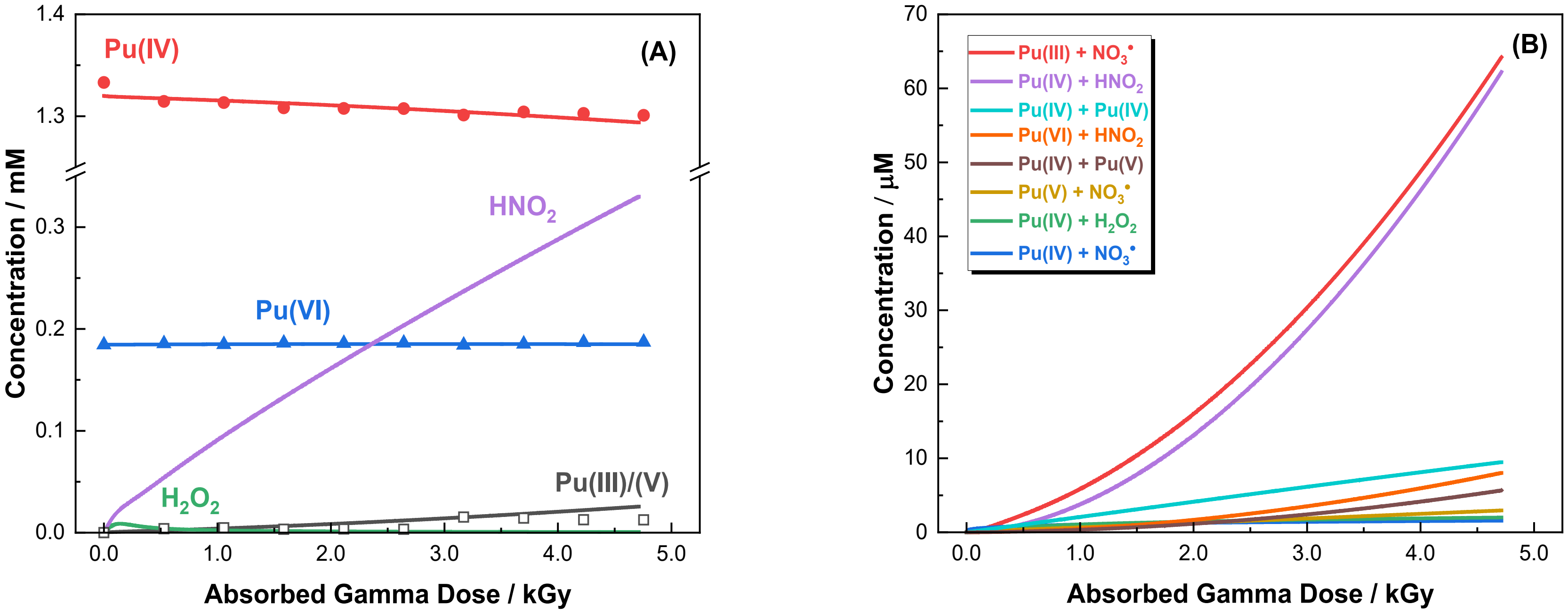
The Role of Radiation-Induced Plutonium Oxidation States in Solution (6.0 M HNO_3)



- Radiation-induced redox chemistry of Pu is dominated by three processes: the reduction of **Pu(IV)** and **Pu(VI)** by HNO_2, and the oxidation of **Pu(III)** by $NO_3^{\bullet}$ radicals to regenerate **Pu(IV)**.
- Calculations again predict the accumulation (10s μM) of **Pu(III)** and **Pu(V)**.

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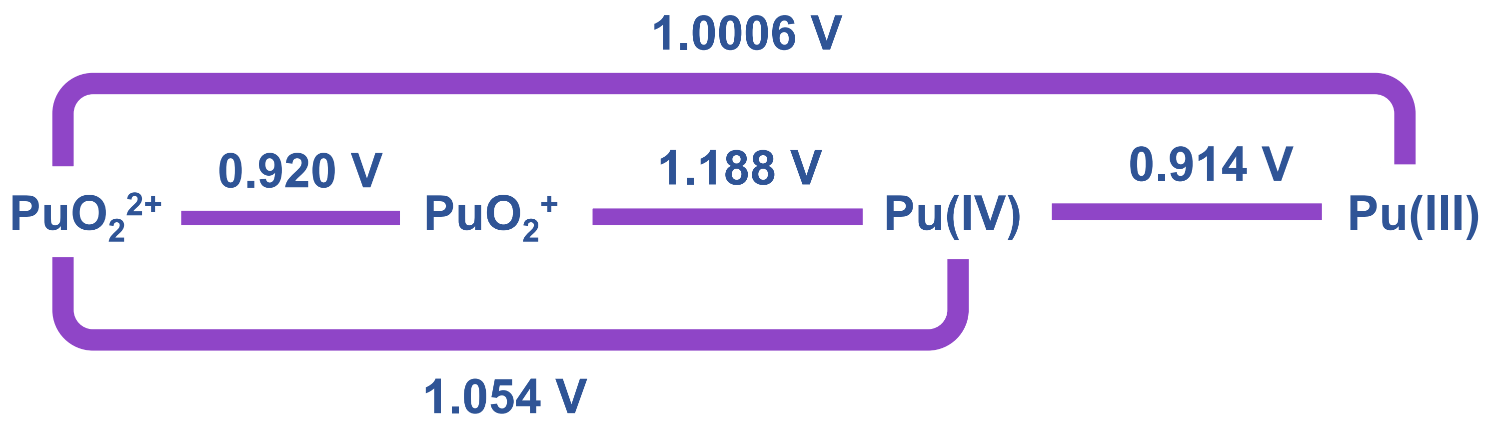
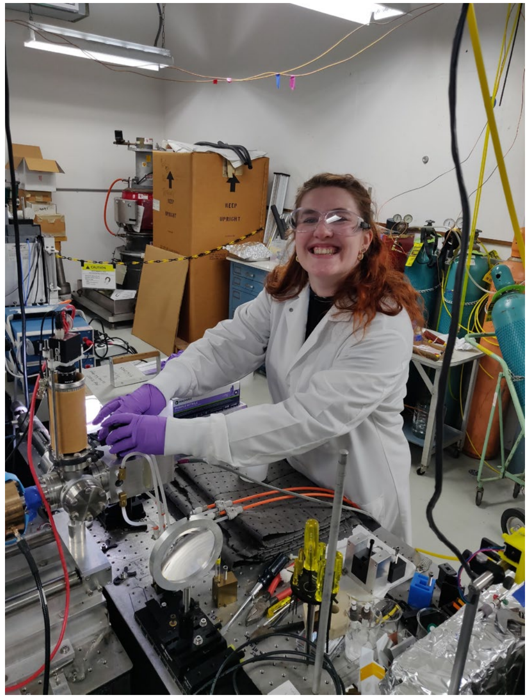
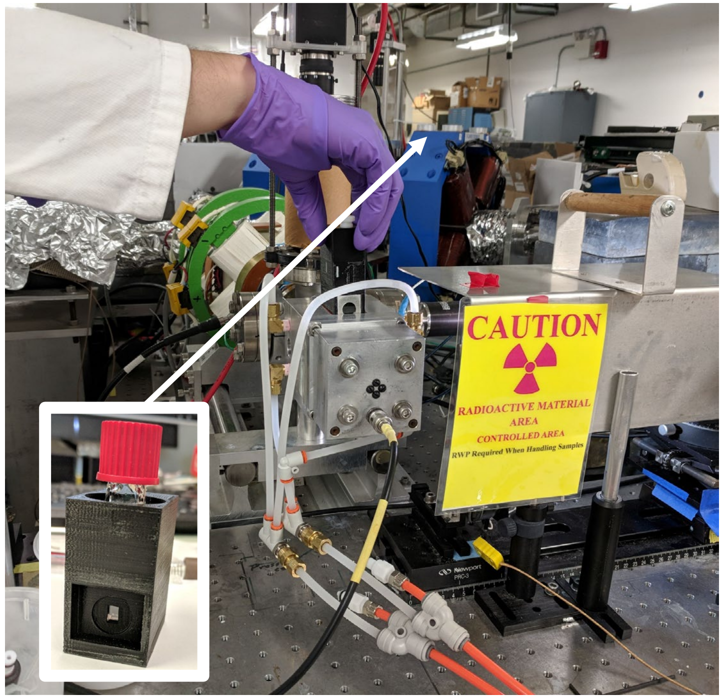
Missing Plutonium Radical Kinetics

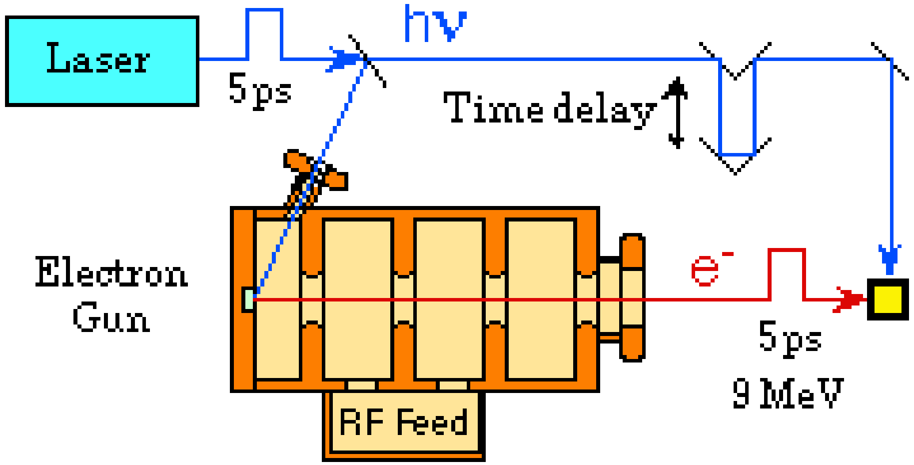
Radiolysis Product	Plutonium Oxidation State Rate Coefficients (k, $M^{-1}\ s^{-1}$) Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
e_{aq}^-		2.0×10^{10}	$1.9–6.4 \times 10^{10}$	3.50×10^{10}
$H^\bullet$	$< 1.0 \times 10^6$	2.0×10^7	2.0×10^8	
$^\bullet OH$	$1.8–4.2 \times 10^8$	?		
$NO_3^\bullet$	2.5×10^8			?



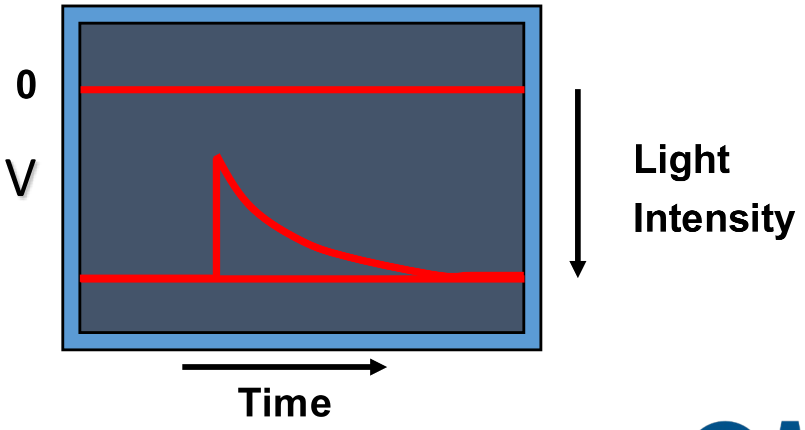
Time-Resolved Electron Pulse Radiolysis







Transients are detected by optical absorption changes.



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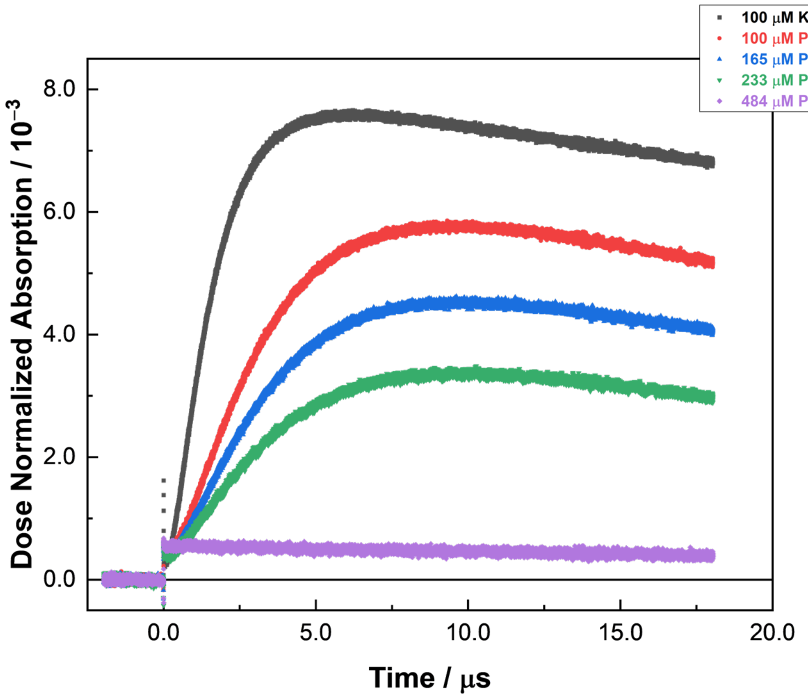
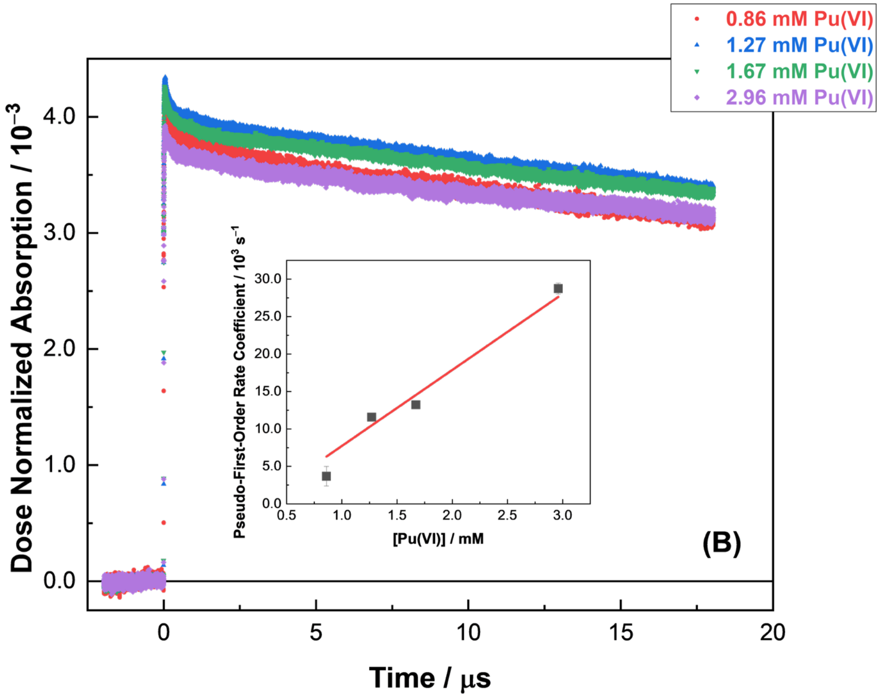
Missing Plutonium Radical Kinetics





- Oxidation of **Pu(IV)** by **$^{\bullet}$OH** (E ° = +2.7 V) afforded a ***k* = (6.31 ± 1.15) × 10^9 M^{-1} s^{-1}**, R^2 = 0.94,
- Oxidation of **Pu(VI)** by **$NO_3^{\bullet}$** (E° = +2.3–26 V) afforded a ***k* = (1.02 ± 0.18) × 10^7 M^{-1} s^{-1}**, R^2 = 0.91.

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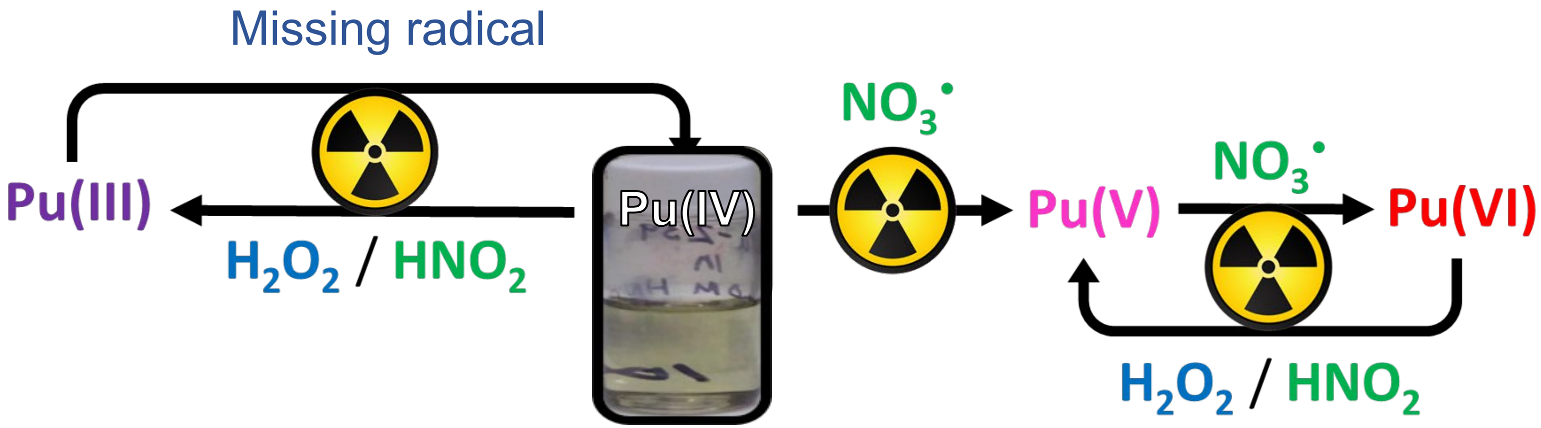
Conclusions and Ongoing Work



- Alpha irradiations
- Additional radical kinetics to deconvolute data.
- Further investigation into plutonium speciation.
- Validation of multiscale model.

Repeat for other oxidation states!

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- **INL Glenn T. Seaborg Institute**

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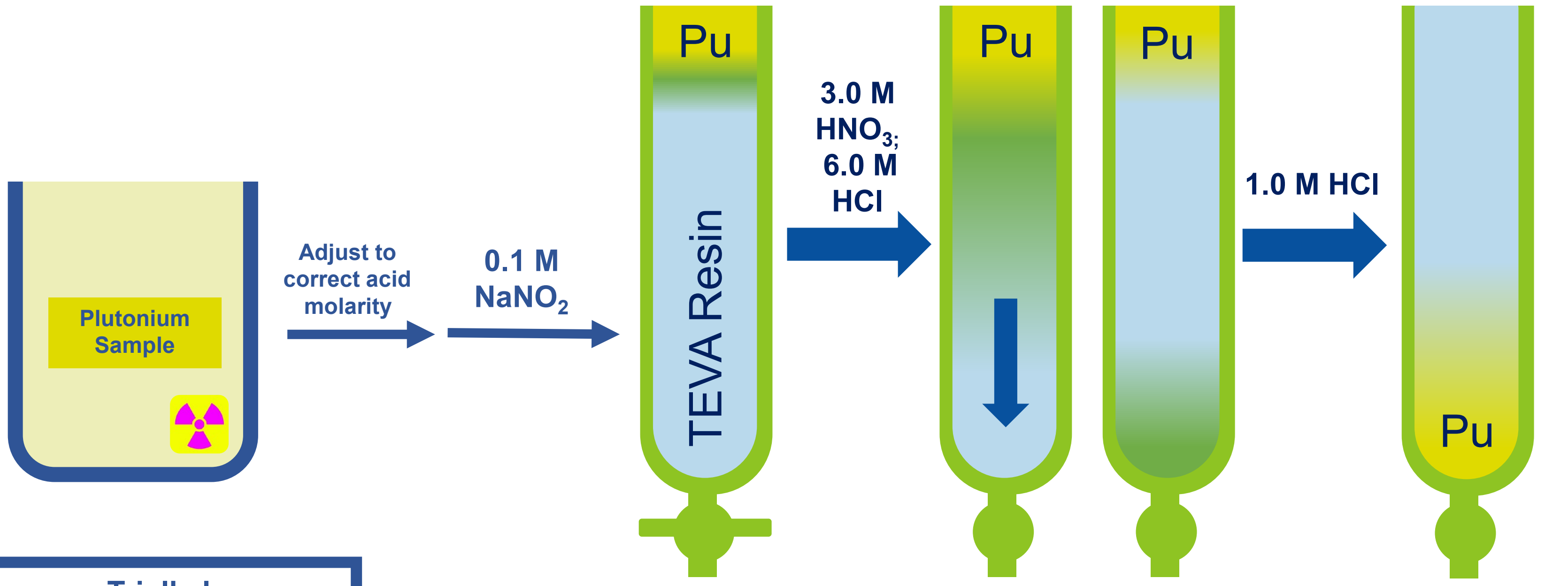
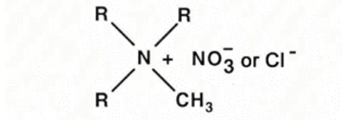
Plutonium-239 Purification



- Anion exchange column needed to change background electrolyte.

Trialkyl Methylammonium Nitrate (or Chloride)

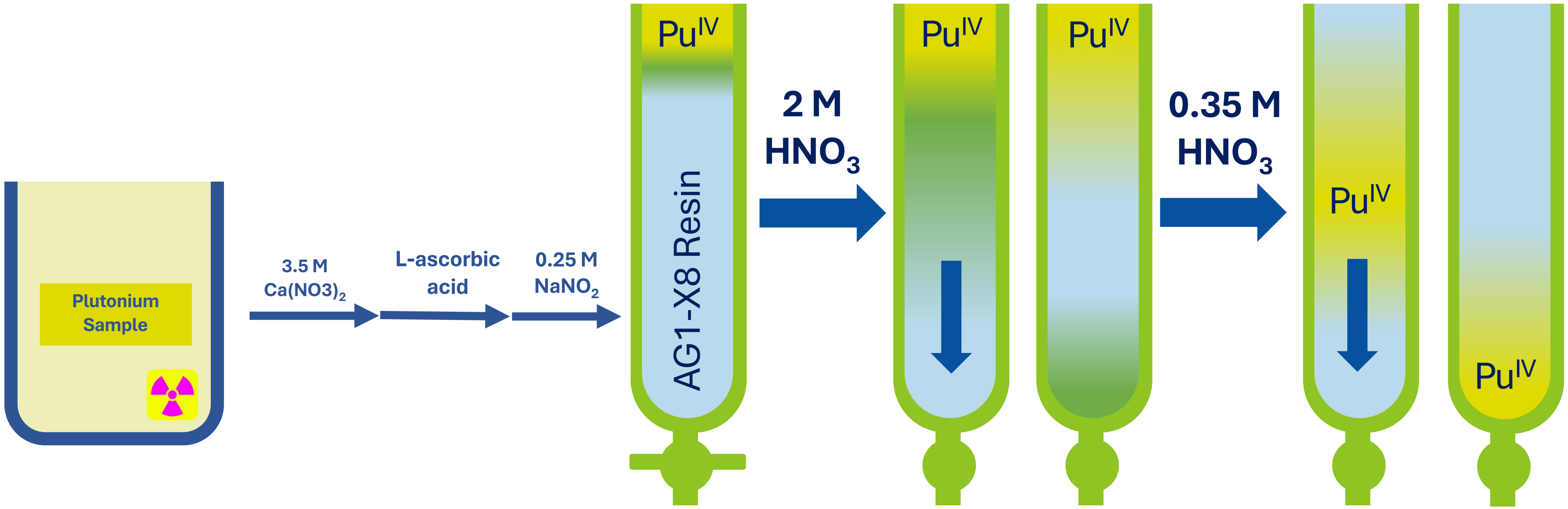


R = C_8H_{17} or $C_{10}H_{21}$

TEtraValent Actinides

- Ryan and Wheelright, *Industrial and Engineering Research* **1959**, *51*, 60.
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

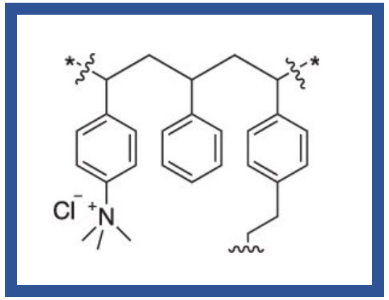
Plutonium-239 Purification



AG1-X8 Resin rinsed with $Ca(NO_3)_2$ in 2 M HNO_3

Converted to nitrate complex

Pu(IV) eluted into HNO_3 reservoir



- Ryan and Wheelright, *Industrial and Engineering Research* **1959**, *51*, 60.
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.