INL/CON-25-83193-Revision-0

Investigating Radiation-Induced Actinide Species in Solution

March 2025

Changing the World's Energy Future

Amy Elizabeth Kynman, Gregory Peter Holmbeck, Travis S Grimes

Idaho National Laboratory

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Investigating Radiation-Induced Actinide Species in Solution

Amy E. Kynman

Idaho National Laboratory

Center for Radiation Chemistry Research | Radiochemical Separations & Radiation Science

About the Presenter

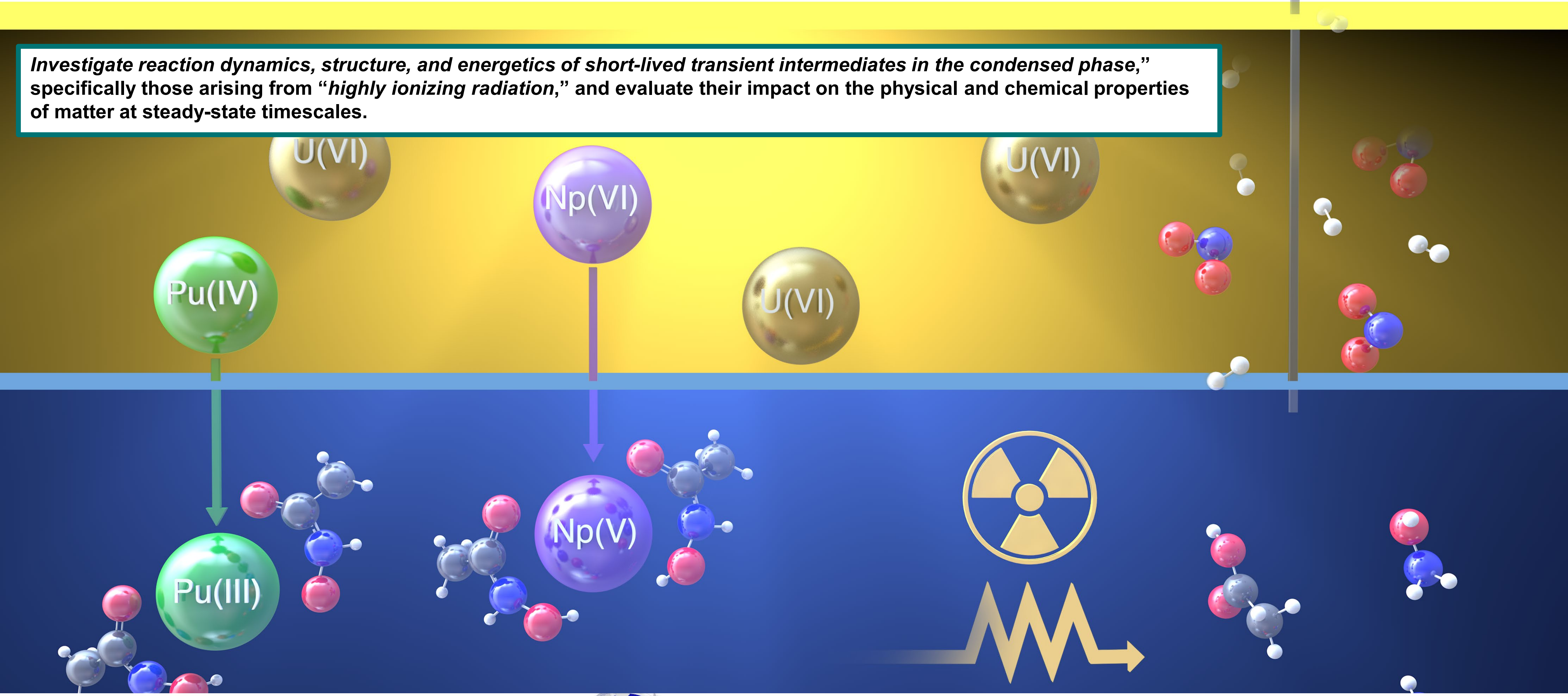
- INL Glenn T. Seaborg Distinguished Postdoctoral Research Associate
  - Director of the INL Postdoc Association
  - Ph.D. in Chemistry, University of California, Berkeley (2023)
  - M.Sc. in Chemistry (by Research), University of Warwick (2019)
  - B.Sc. in Chemistry, University of Warwick (2018)

- Principal Investigator of two independent Laboratory Directed Research and Development (LDRD) projects in actinide science at INL.

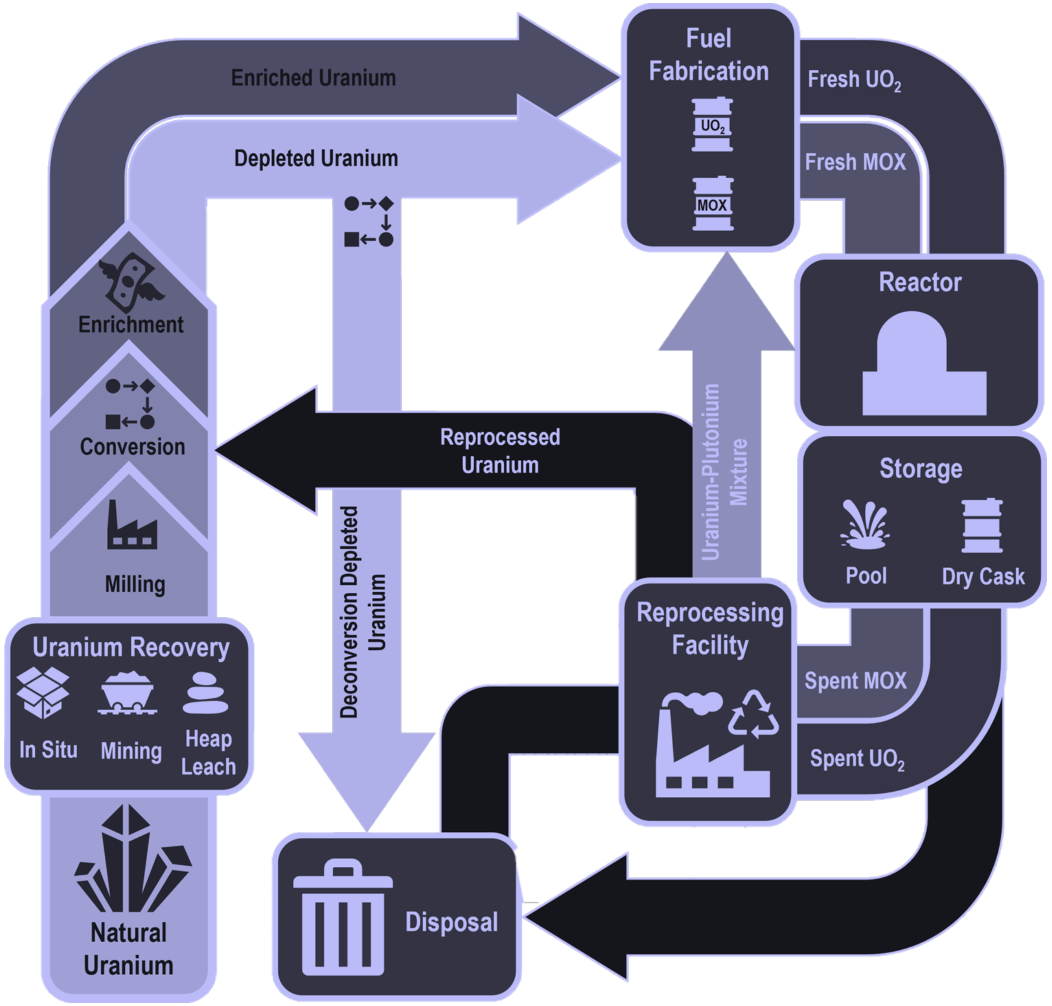
- Co-authors: Gregory P. Holmbeck, Travis S. Grimes, Steven P. Mezyk, Andrew R. Cook, Bobby Layne, Simon M. Pimblott, Brian M. Rotermund and Jacy K. Conrad.

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.**



Closing the Nuclear Fuel Cycle



- **Closing the nuclear fuel cycle has several benefits:**
  - ✓ **Minimize final high-level waste for disposal or storage.**
  - ✓ **Recover additional energy from fuel.**
  - ✓ **Reduce impact on the environment and natural resources.**
- **To make reprocessing more cost-effective, greater fundamental understanding of actinide behavior under radiation fields is needed.**

Radiation Chemistry Under Reprocessing Conditions

Water Radiolysis

Direct Radiation Effects

H_2O

+ O

Indirect

HNO_3

NO_3^-

$NO_3^\bullet$

NO_3^-

CH_3, $H^\bullet$, H_2

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

$N_2O_4 \rightarrow HNO_2 + HNO_3$

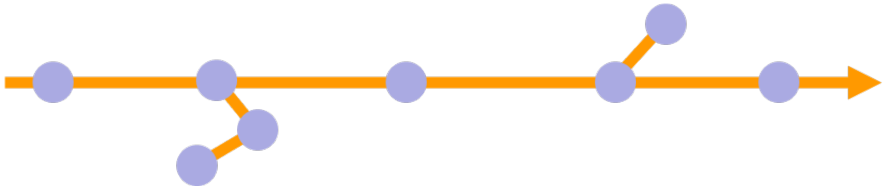
Key Radiolysis Products

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

$NO_3^\bullet$ and HNO_2 from HNO_3

Ex-situ Gamma Irradiations

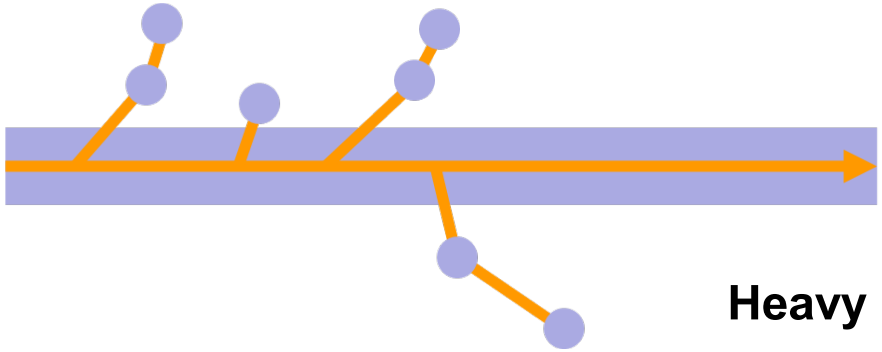
- **Actinide-containing solutions irradiated and changes in oxidation state monitored over time.**
- **Absorbed dose calculated from the irradiator dose rate.**
- **Radical products dominate.**



Fast electron track

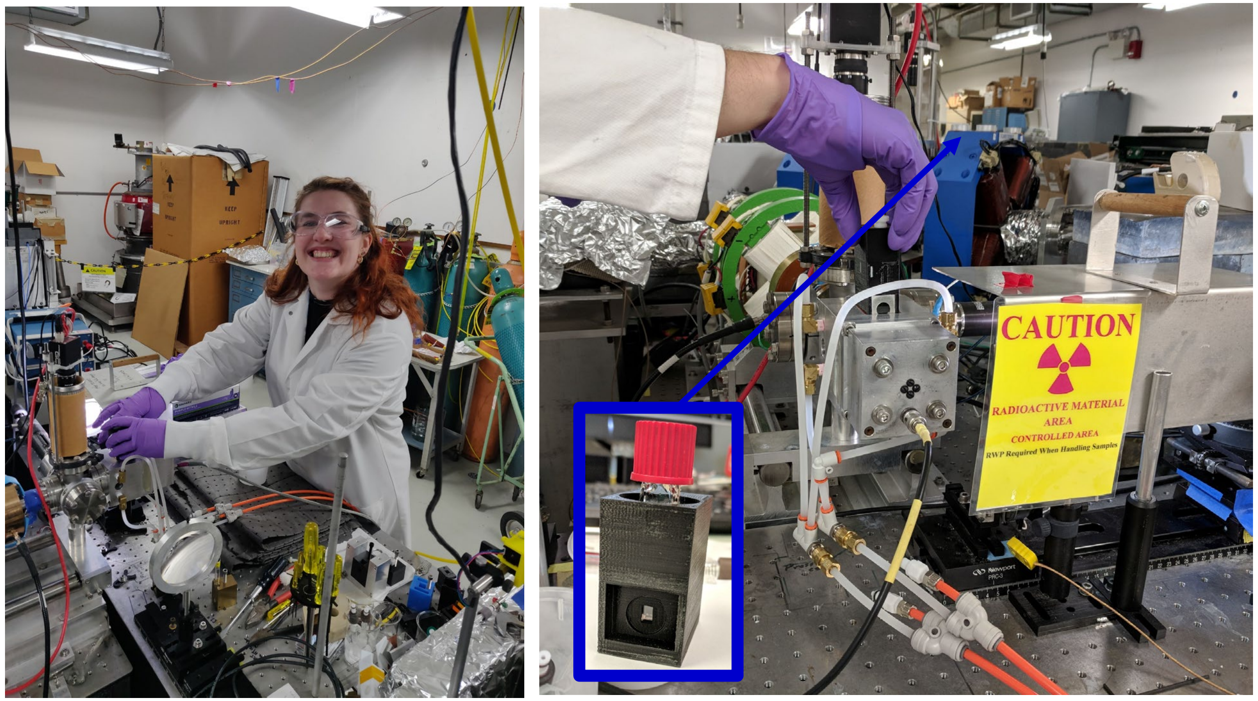
In-situ Alpha Irradiations

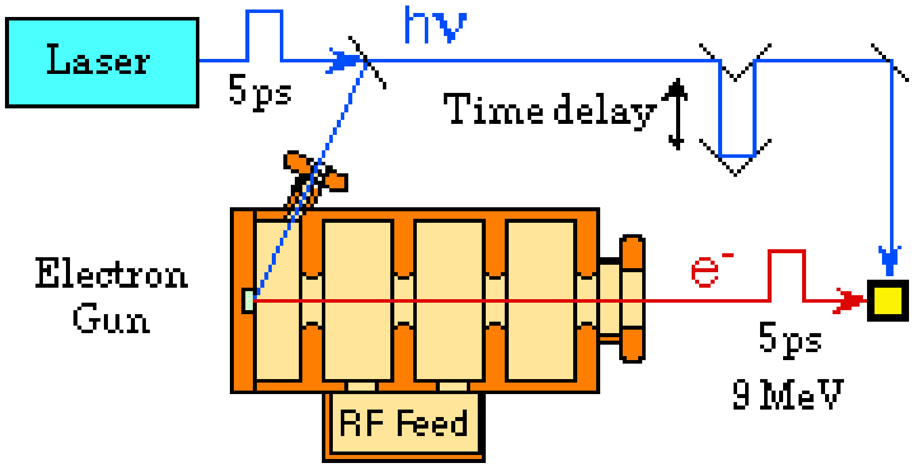
- **Source of radiation is the inherent decay of the actinide element.**
- **Absorbed dose calculated from quantity and specific activity of alpha emitter, and time exposed.**
- **Molecular products dominate.**



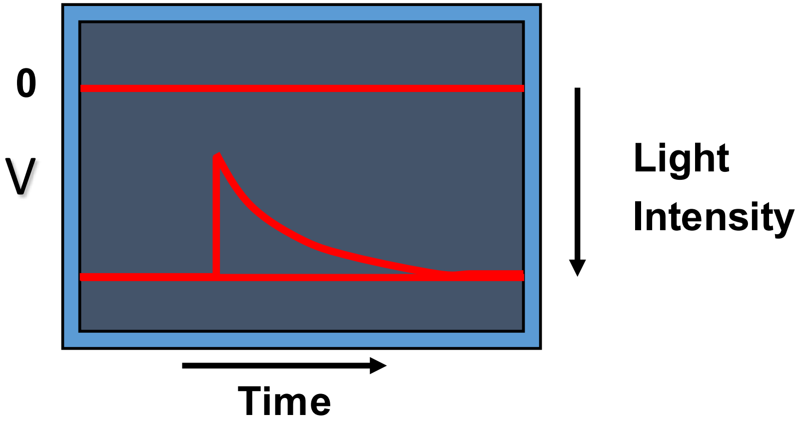
Heavy ion track

Time-resolved Electron Pulse Radiolysis



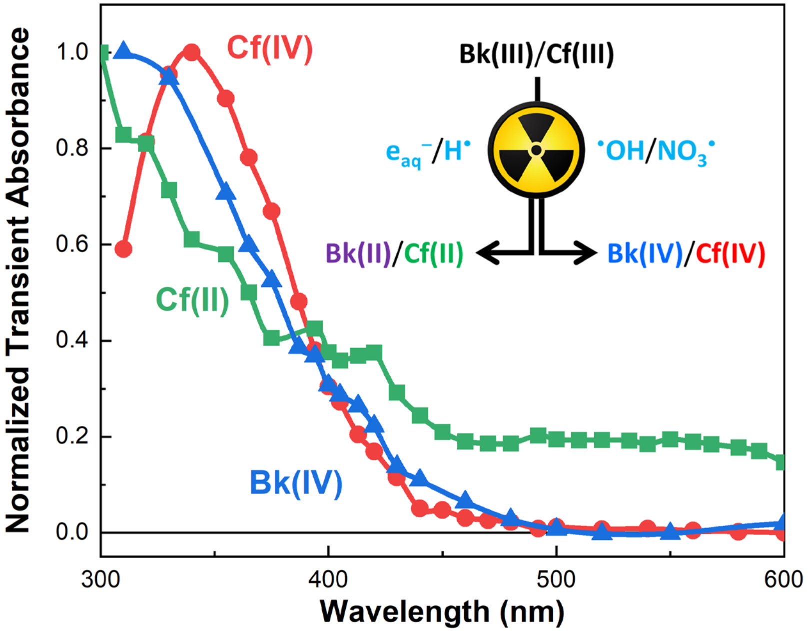


Transients are detected by optical absorption changes.

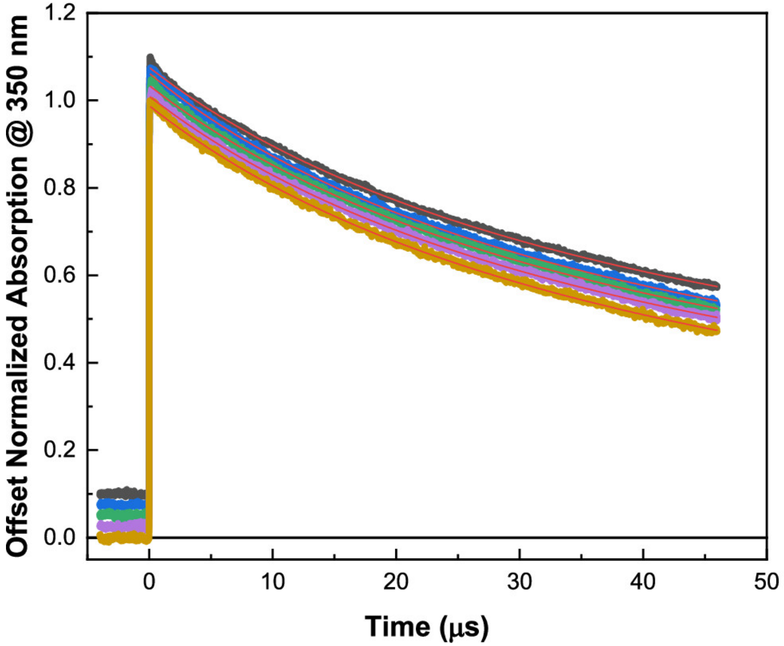


Radiation-induced Actinide Redox Chemistry

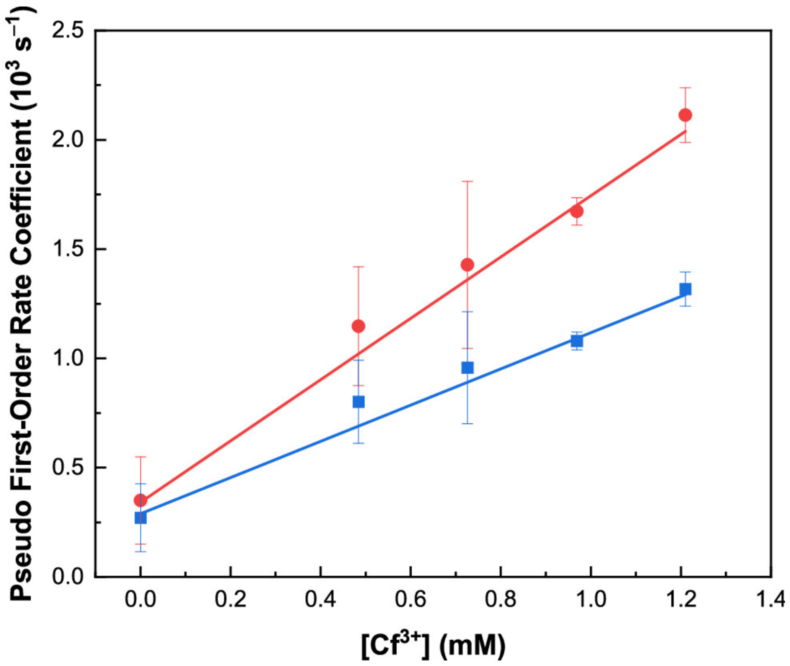
“Short-lived (≤ seconds) atoms or ions formed by the atomistic/molecular-level interaction of radiation-induced radical and molecular products with actinide ion oxidation states in aqueous solution.”



Dose Normalized Absorption Spectrum



Absorption-normalized $Cl_2^{\bullet-}$ decays in Cf^{3+} containing solutions

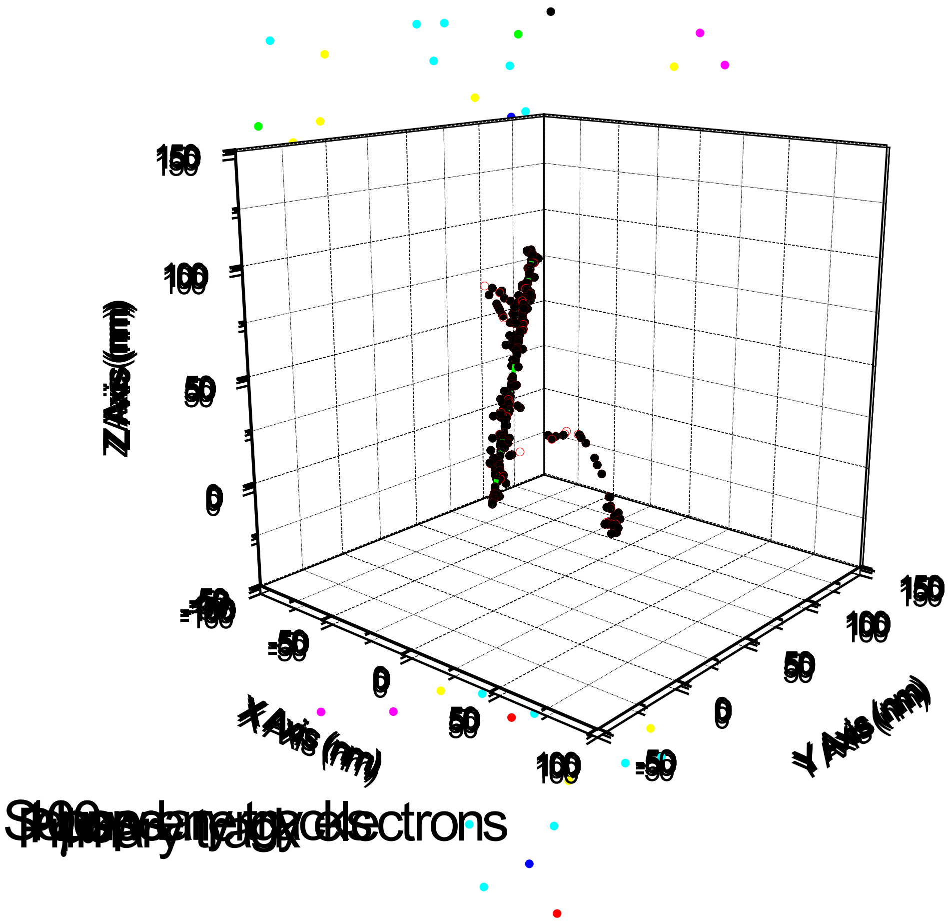


Derived second order rate coefficients

- 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.

Predicting Radiation-induced Actinide Redox Chemistry

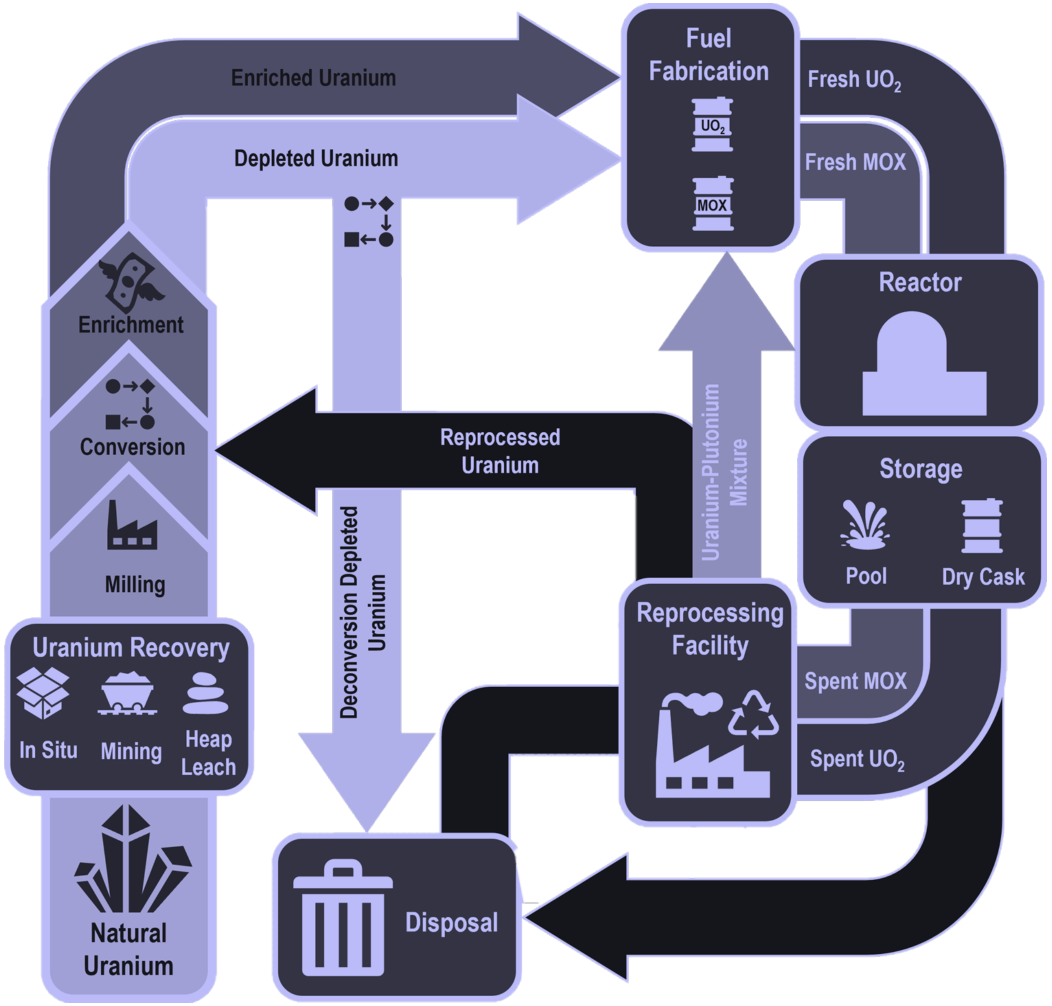
- **Generation of a multiscale model.**
- **Inputs of radiation track yields and reaction kinetics.**



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

Predicting Radiation-induced Plutonium Redox Chemistry Using Multiscale Modeling Methods

Plutonium in the Nuclear Fuel Cycle

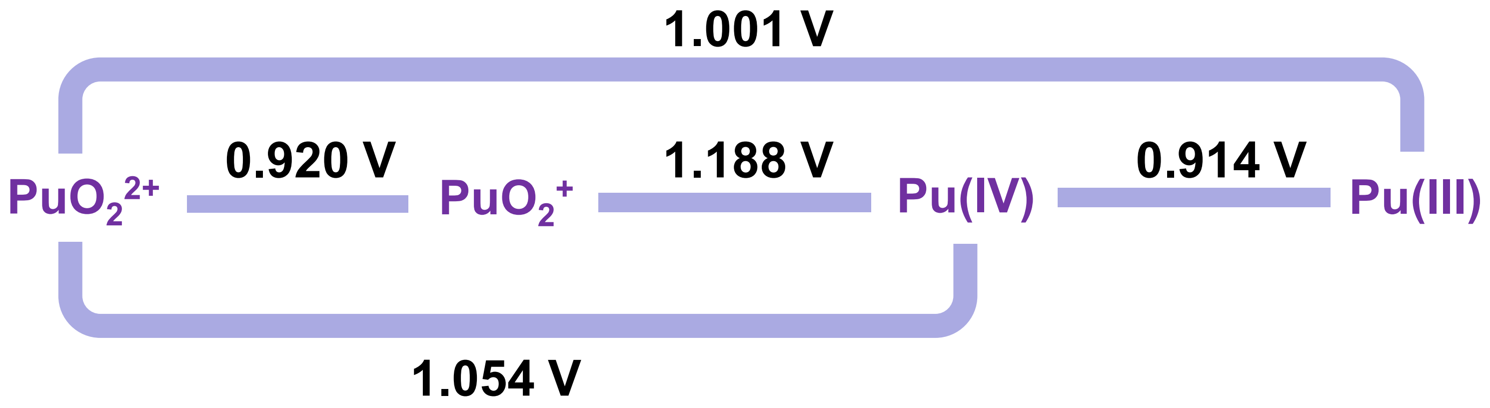


$$Pu^{4+} + PuO_2^{+} \rightleftharpoons Pu^{3+} + PuO_2^{2+}$$

PUREX Chemistry

- Pu(IV) and U(VI) co-extracted as neutral nitrate complexes by tributyl phosphate (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.

The Starting Point for a Plutonium Multiscale Model



1.001 V

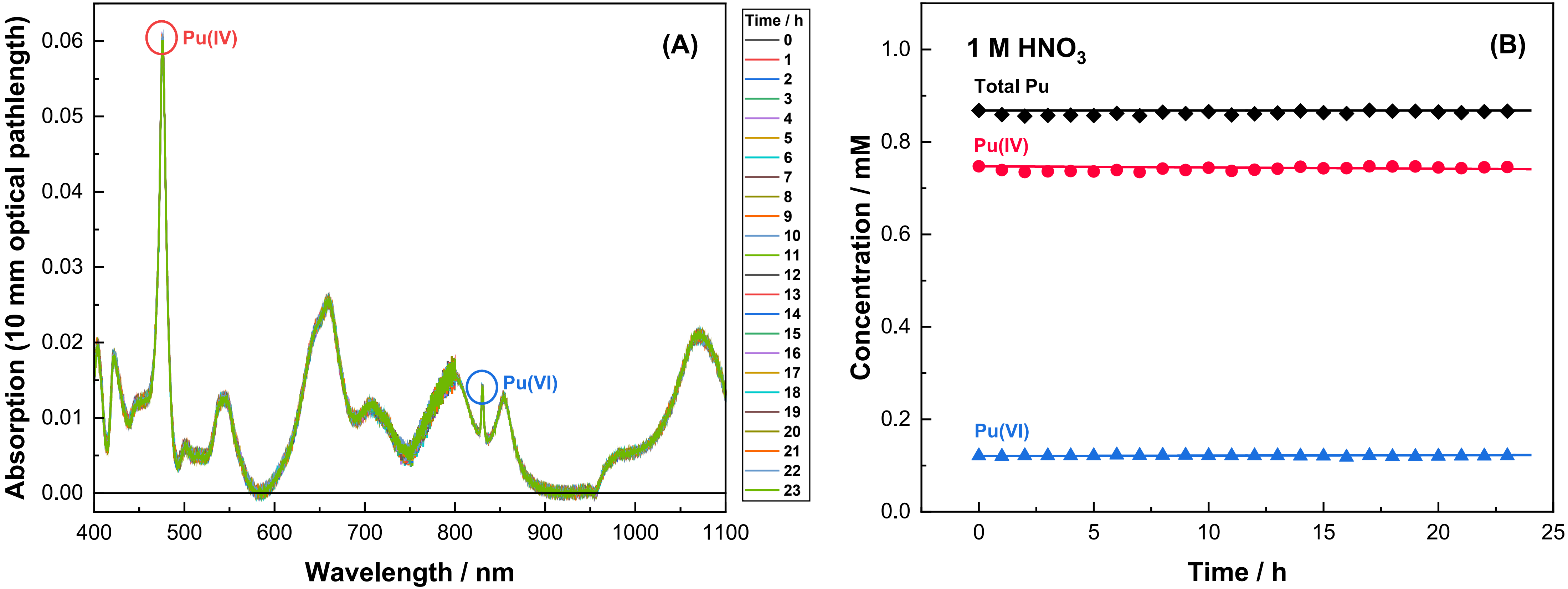
PuO_2^{2+} 0.920 V PuO_2^{+} 1.188 V Pu(IV) 0.914 V Pu(III)

1.054 V

Radiolysis Product	Plutonium Oxidation State (k, $M^{-1}s^{-1}$)			
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
e_{aq}^{-}	—	2.1×10^{10}	$1.9\text{-}6.4 \times 10^{10}$	3.5×10^{10}
$H^{\cdot}$	$< 1 \times 10^{6}$	2.0×10^{7}	2.0×10^{8}	—
$^{\cdot}OH$	$1.8\text{-}4.2 \times 10^{8}$	—	—	—
$NO_3^{\cdot}$	2.5×10^{8}	—	—	—

- Gordon, Sullivan, and Ross, *J. Phys. Chem. Ref. Data* 1986, *15*, 1357.
- Pikaev, Gogolev, Shilov, and Fedoseev, *Isotopenpraxis: Isot. Environ. Health Stud.,* 1990, 26, 465.
- Mincher and Mezyk, *Radiochim. Acta* 2009, *97*, 519.

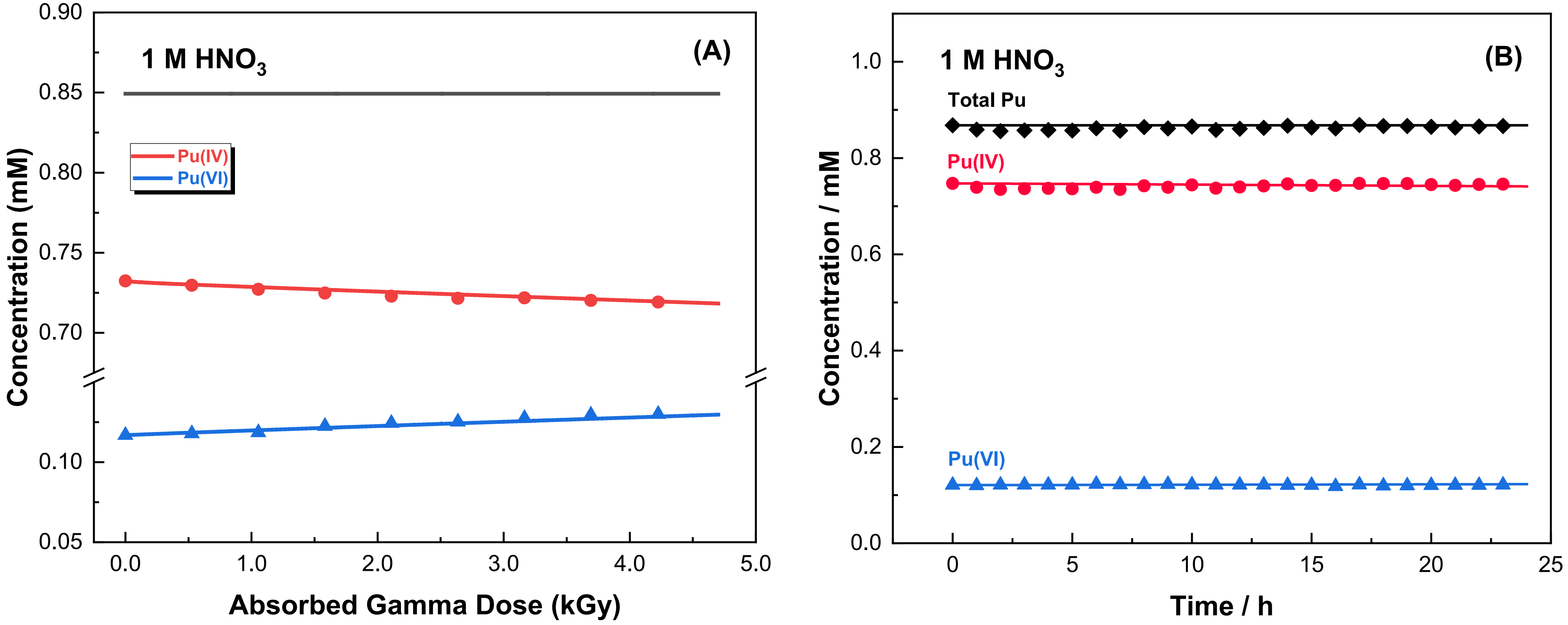
Control Reactions



(A) Absorption spectra for Pu-239 in aerated, aqueous 1.0 M HNO3 solution over 23 hours with no gamma irradiation.
(B) Corresponding concentrations of Pu(IV), Pu(VI), and total plutonium.

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.,* 2024, *68*, 18, 8092-8098.

Cobalt-60 Gamma Irradiations

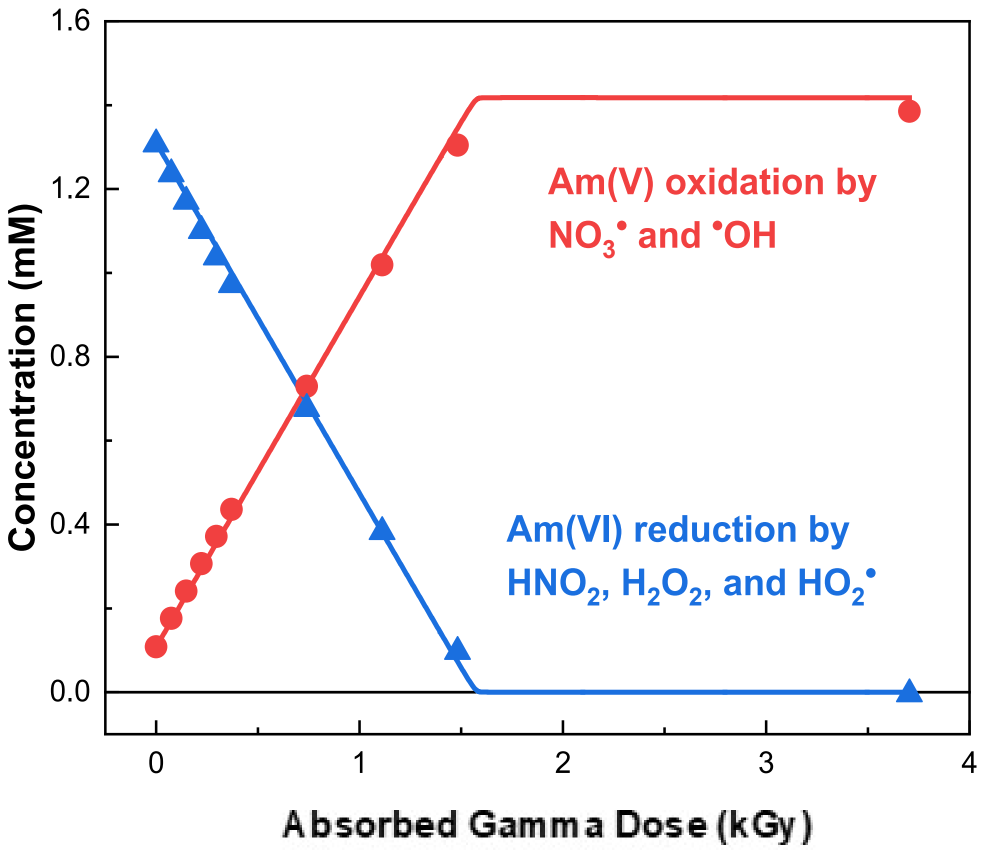


(A) Concentration of Pu oxidation state as a function of dose in aqueous 1.0 M HNO$_3$ solution over 23 hours with gamma irradiation.
(B) Control

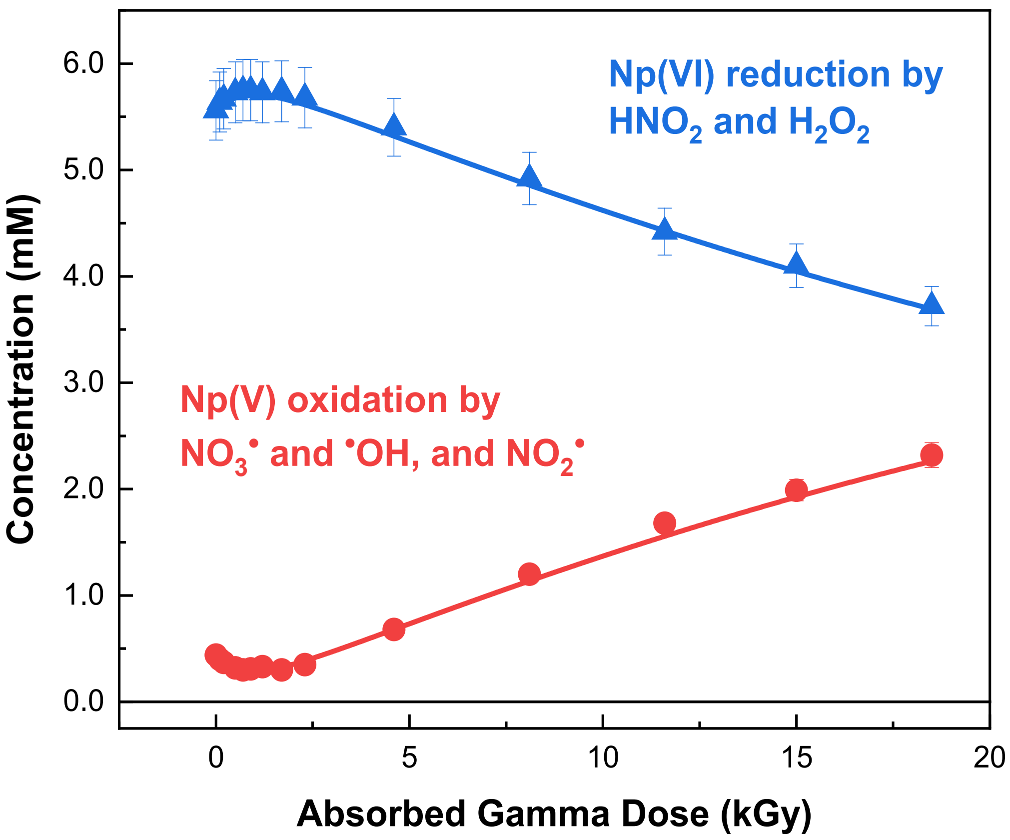
- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.,* 2024, *68*, 18, 8092-8098.

Comparison to Neptunium and Americium Models

Americium

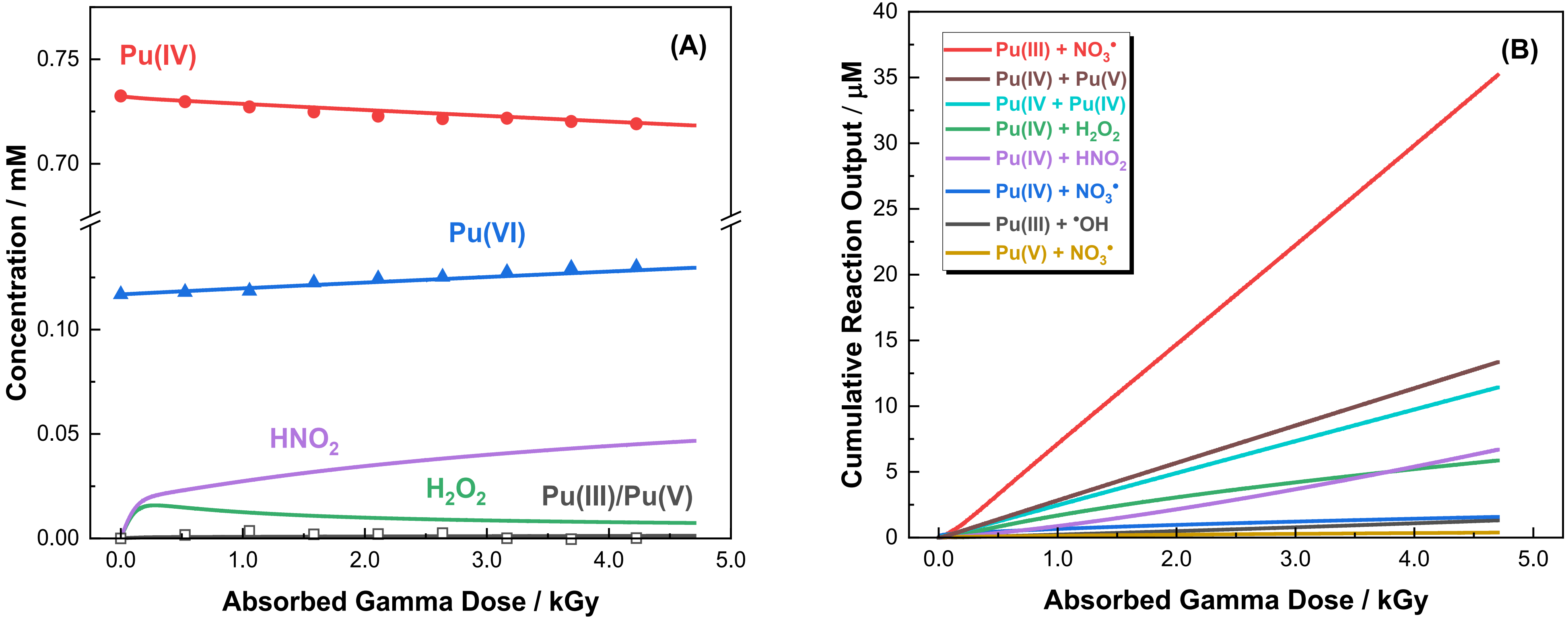


Neptunium



- Horne, Grimes, Mincher and Mezyk, *J. Phys. Chem. B.* 2016, *120*, *49*, 12643-12649.
- Horne, Grimes, Bauer, Dares, Pimblott, Mezyk and Mincher, *Inorg. Chem.* 2019, *58*, 13, 8551-8559

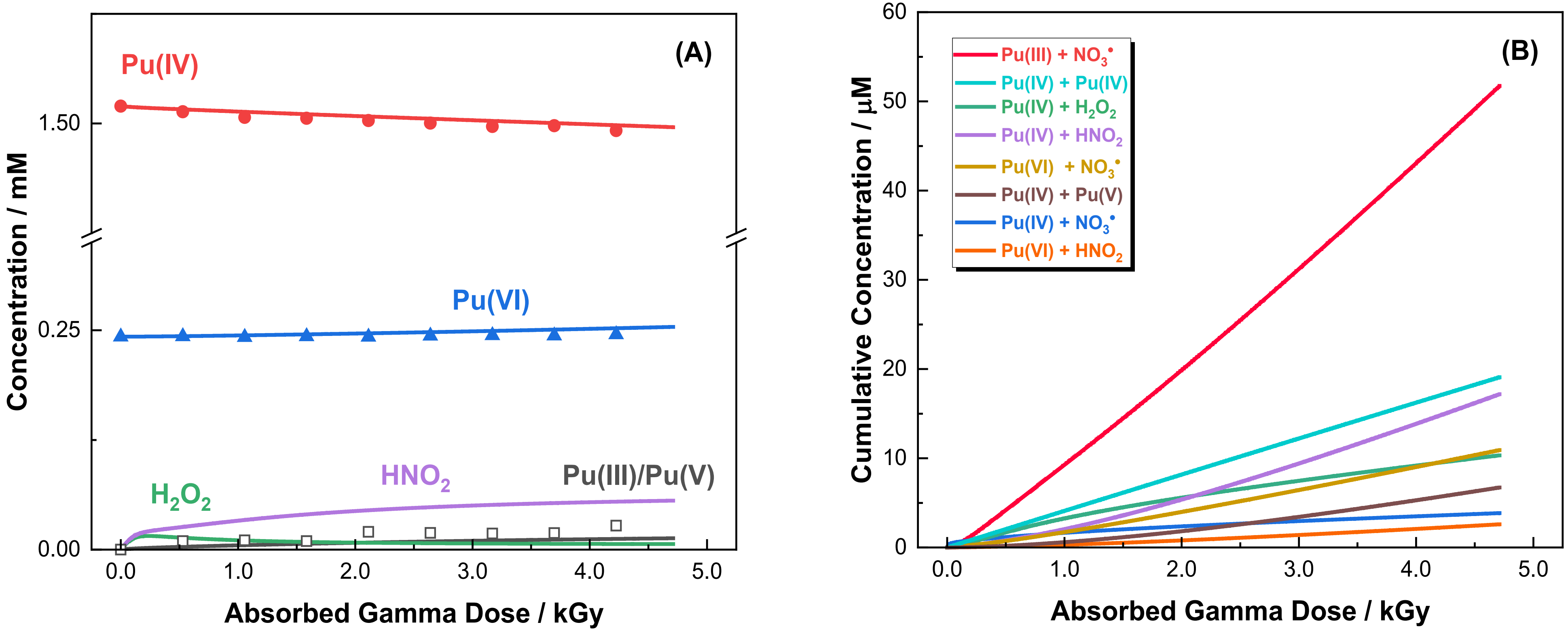
Radiation-induced Plutonium Oxidation States in 1.0 M HNO_3



- 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 $NO_3^•$ radicals by Pu(III).
- Remaining G($NO_3^•$) partially accounts for the accumulation of Pu(VI) via the oxidation of Pu(V).

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.,* 2024, *68*, 18, 8092-8098.

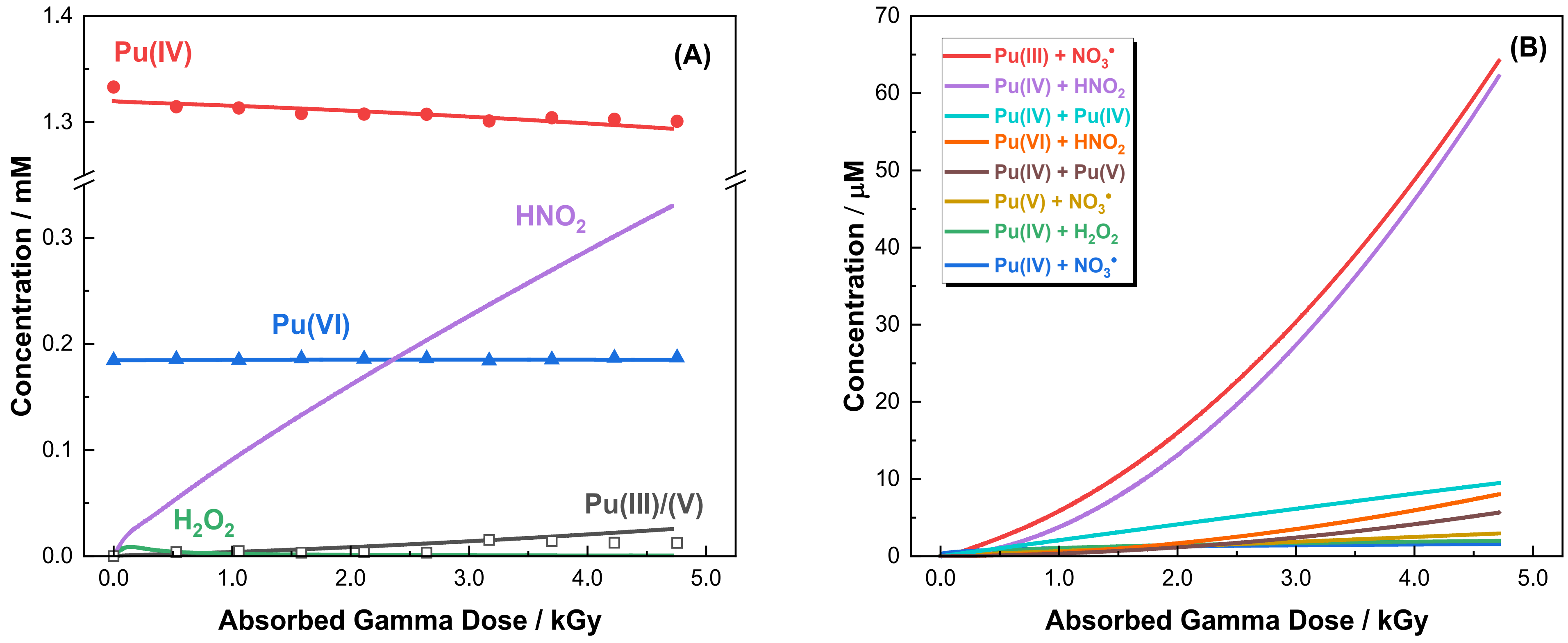
Radiation-induced Plutonium Oxidation States in 3.0 M HNO_3



- 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).

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.,* 2024, *68*, 18, 8092-8098.

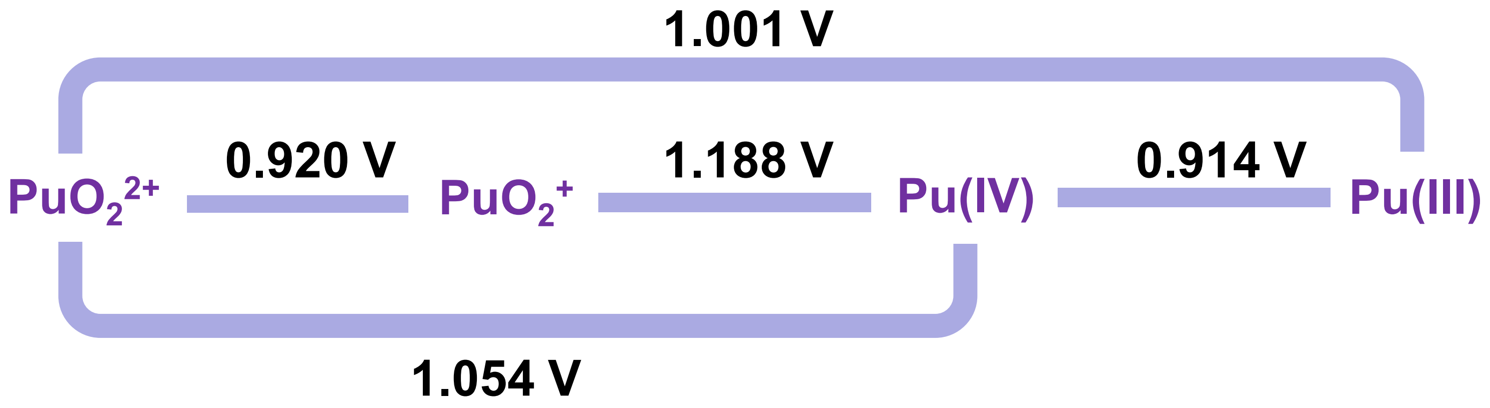
Radiation-induced Plutonium Oxidation States in 6.0 M HNO_3



- **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).**

- **Kynman**, Grimes, Conrad, Pimblott and Horne, *Inorg. Chem.,* 2024, *68*, 18, 8092-8098.

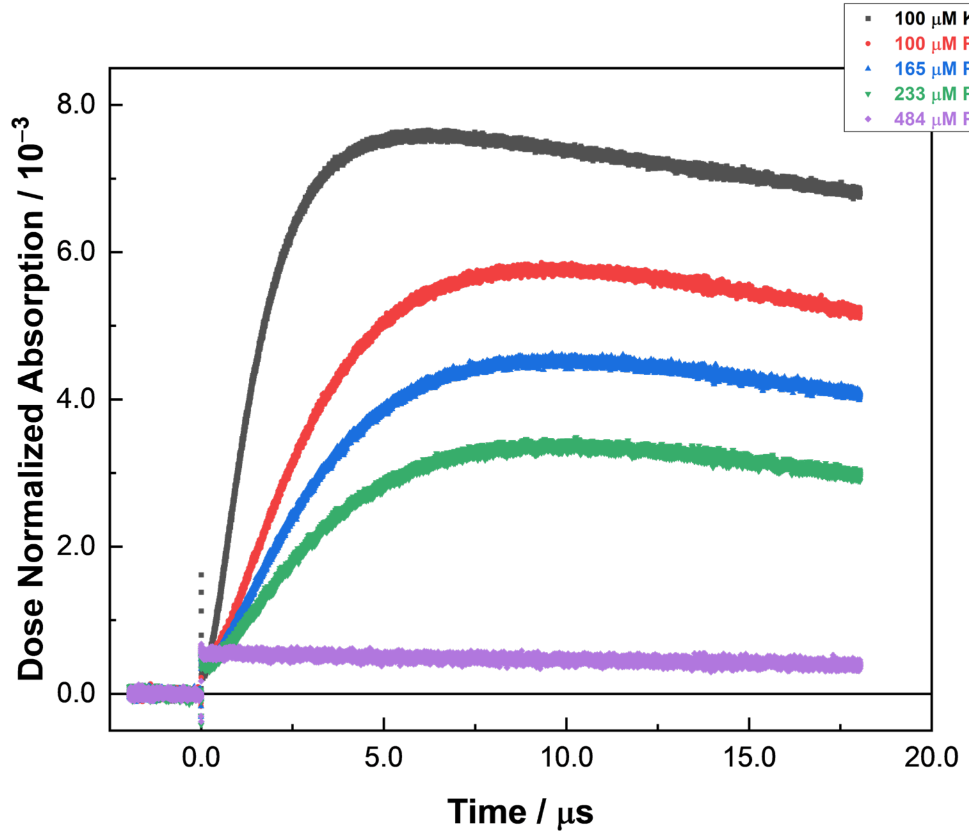
Missing Plutonium-Radical Reaction Kinetics

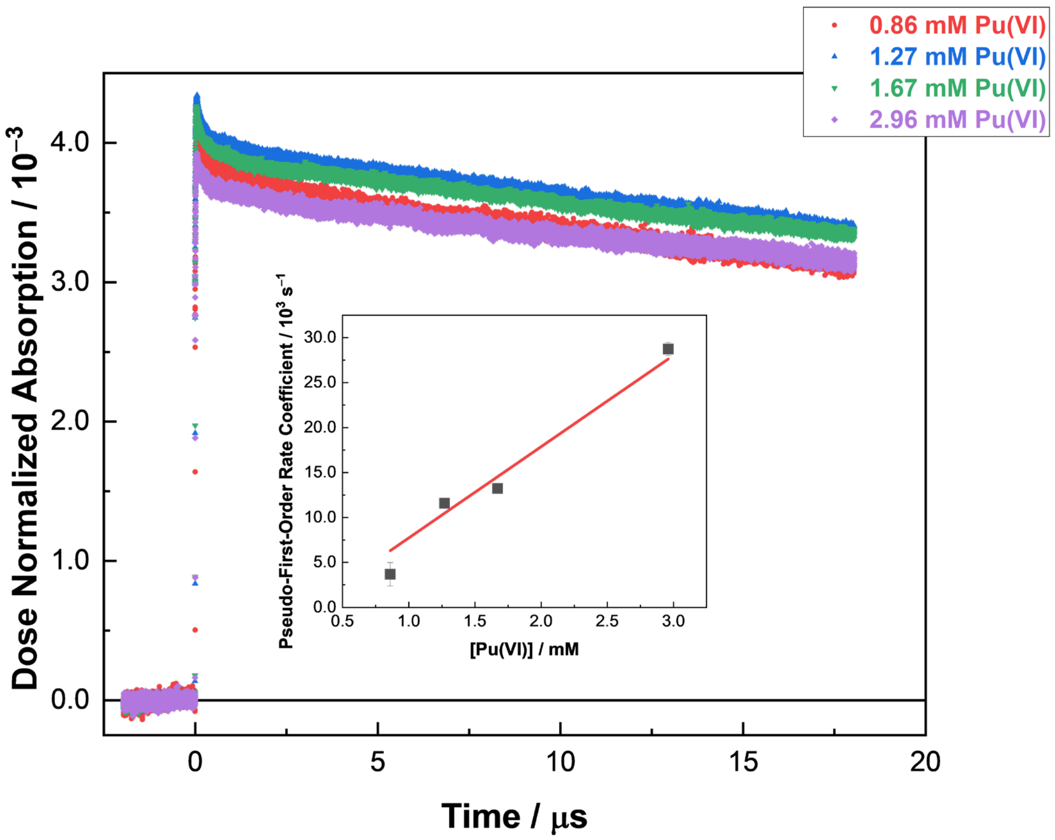


Radiolysis Product	Plutonium Oxidation State (k, $M^{-1}s^{-1}$)			
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
e_{aq}^{-}	—	2.1×10^{10}	$1.9\text{-}6.4 \times 10^{10}$	3.5×10^{10}
$H^{\cdot}$	$< 1 \times 10^{6}$	2.0×10^{7}	2.0×10^{8}	—
$^{\cdot}OH$	$1.8\text{-}4.2 \times 10^{8}$	—	—	—
$NO_3^{\cdot}$	2.5×10^{8}	—	—	—

- Gordon, Sullivan, and Ross, *J. Phys. Chem. Ref. Data* 1986, *15*, 1357.
- Pikaev, Gogolev, Shilov, and Fedoseev, *Isotopenpraxis: Isot. Environ. Health Stud.,* 1990, 26, 465.
- Mincher and Mezyk, *Radiochim. Acta* 2009, *97*, 519.

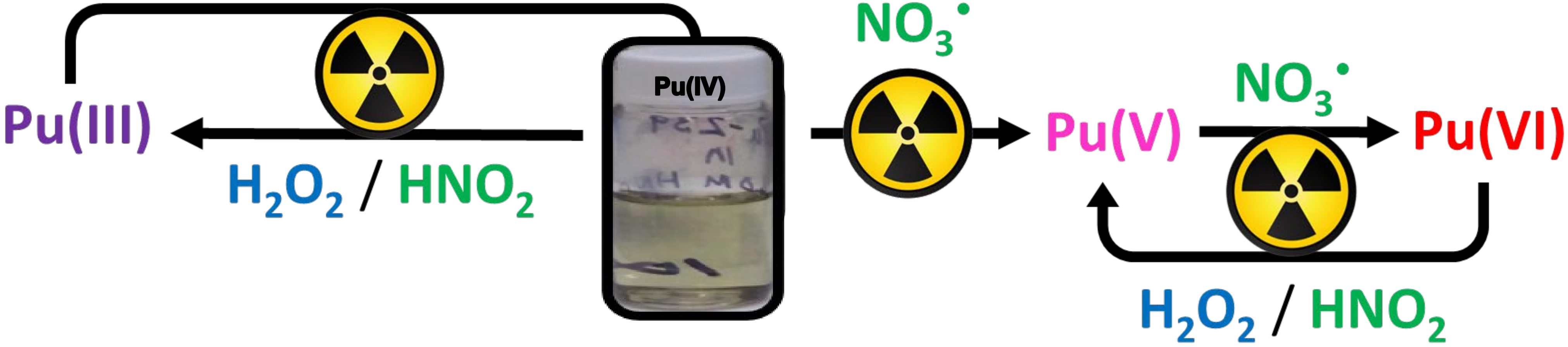
Missing Plutonium-Radical Reaction Kinetics





- **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° = +2.3–2.6 V) afforded a *k* = (1.02 ± 0.18) × 10^7 M^{-1} s^{-1}, $R^2 = 0.91$.**

Ongoing Plutonium Studies



Pu(III)

H_2O_2 / HNO_2

Pu(IV)

$NO_3^{\bullet}$

Pu(V)

$NO_3^{\bullet}$

Pu(VI)

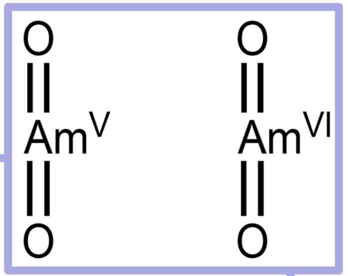
H_2O_2 / HNO_2

- ✓ Pu(IV) alpha irradiations
- ✓ Pu(VI) gamma and alpha irradiations
- ☐ Validate model!

Generation and Study of Am(IV) by Temperature-controlled Electron Pulse Radiolysis

Separation of Americium from Fission Products

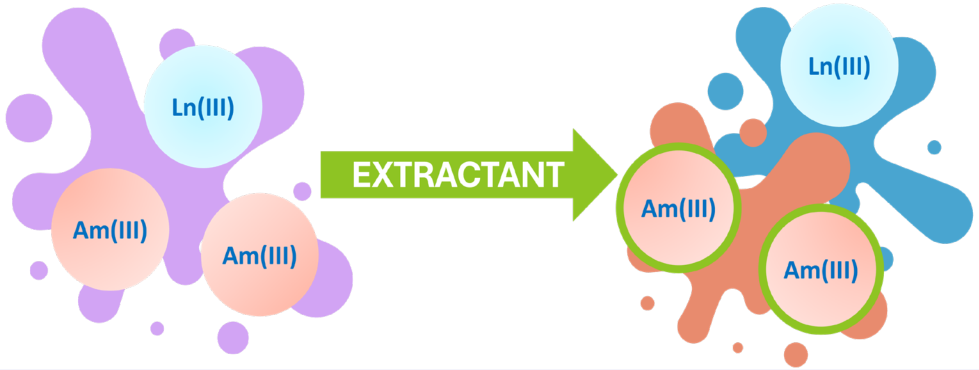
- **Minor actinides and fission products remain after the removal of actinides for fuel fabrication.**
- **Important to remove americium from trivalent lanthanides.**



$O=Am^{V}=O$ $O=Am^{VI}=O$

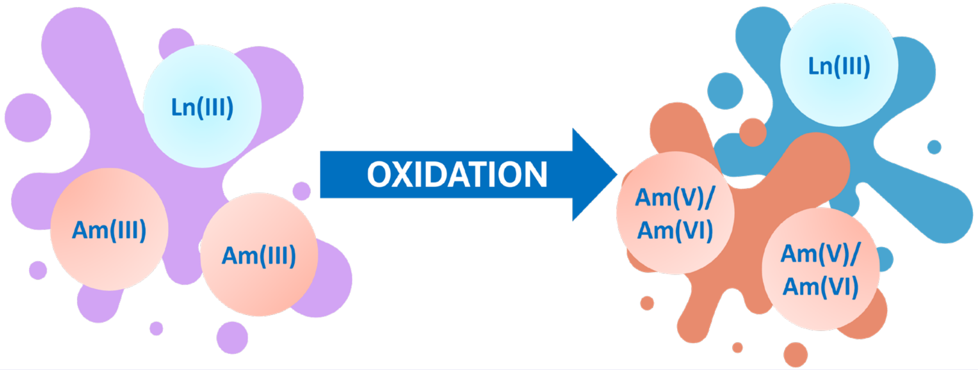
Trivalent Americium

- **Separation achieved by preferential binding of organic ligands to Am(III) or Ln(III).**
- **Exploits chemical bonding differences between Am(III) and Ln(III)**
- **Difficult because Am(III) and Ln(III) are very chemically similar.**

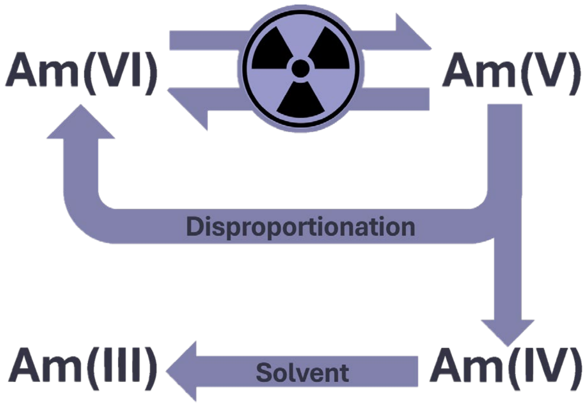


High Valent Americium

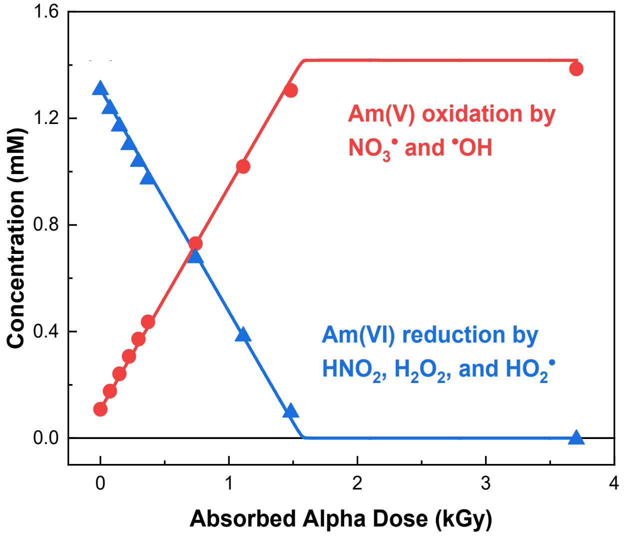
- **Penta- and hexavalent oxidation states (MO_2^{+}, MO_2^{2+}) are not accessible for Ln.**
- **Am(V) and Am(VI) are not easily extracted by organic ligands.**
- **The chemistry of Am(V) and Am(VI) need to be better understood.**



Radiation-induced Americium Redox Chemistry


Am(VI)
Am(V)
Disproportionation
Am(III)
Solvent
Am(IV)

- Under alpha and gamma irradiation, Am(VI) is converted to Am(V) by nitric acid radiolysis products (HNO_2, H_2O_2, $HO_2^{\bullet}$).
- Prolonged irradiation of the Am(V)/Am(III) system eventually leads to the reduction of Am(V) and quantitative ingrowth of Am(III).



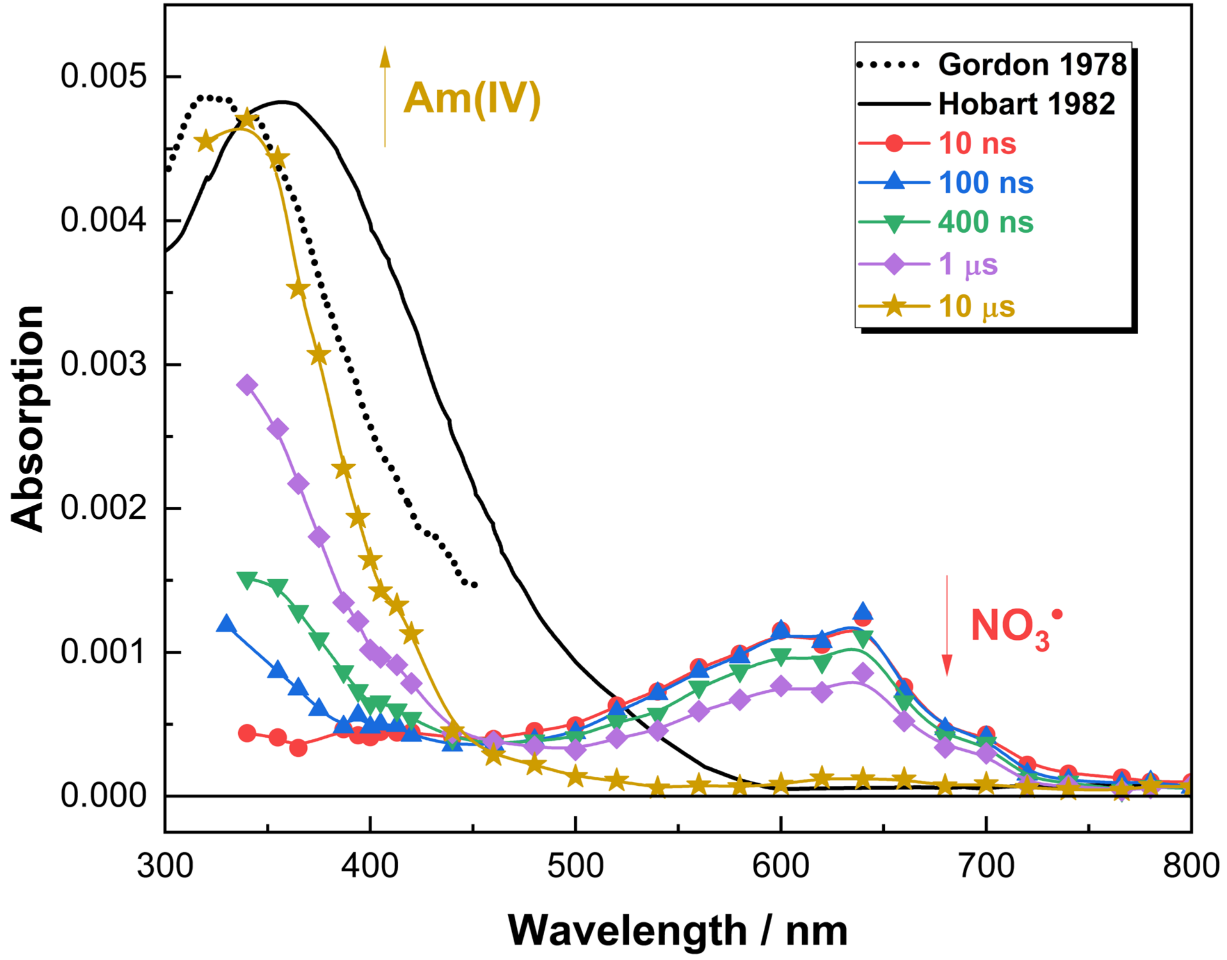
$$2AmO_2^{+} + 4H_{aq}^{+} \longrightarrow Am^{4+} + AmO_2^{2+} + H_2O$$

$$AmO_2^{+} + Am^{4+} \longrightarrow AmO_2^{2+} + Am^{3+}$$

$$2Am^{4+} + H_2O \longrightarrow Am^{V}O_2^{+} + Am^{3+} + 4H_{aq}^{+}$$

- Grimes, Horne, Dares, Pimblott, Mezyk and Mincher, *Inorganic Chemistry* 2017, *56*, 8295.
- Horne, Grimes, Bauer, Dares, Pimblott, Mezyk and Mincher, *Inorganic Chemistry* 2019, *58*, 8551.

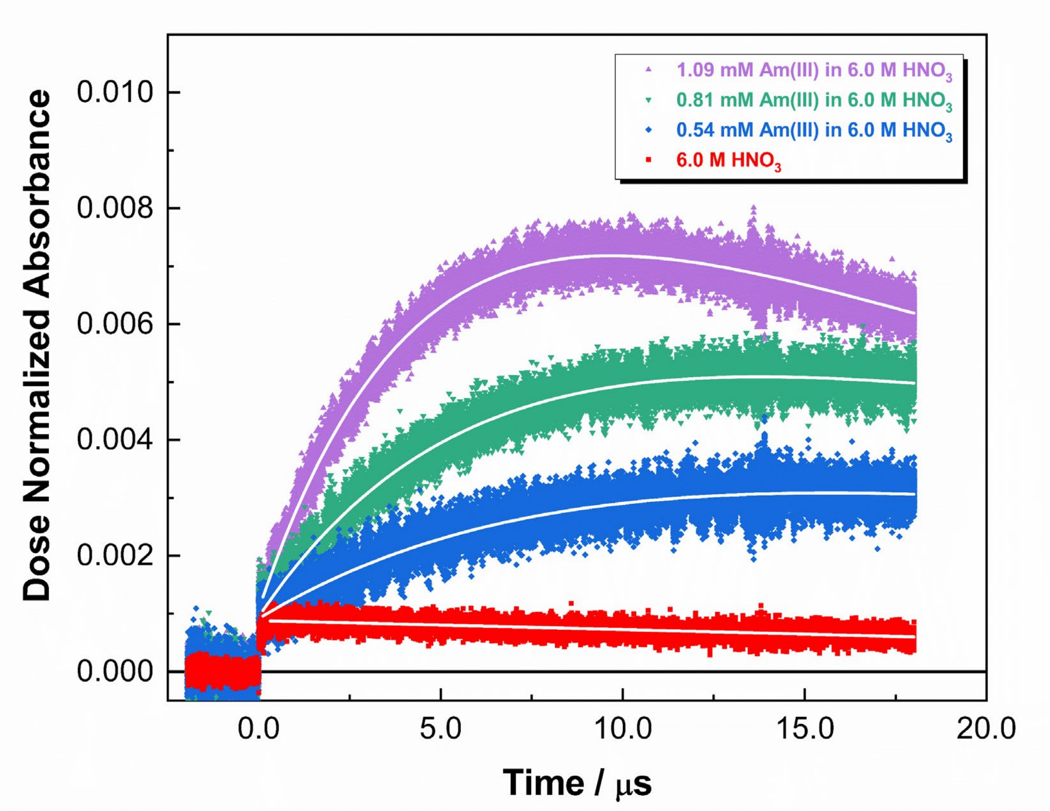
Transient Am(IV) Absorption Spectra

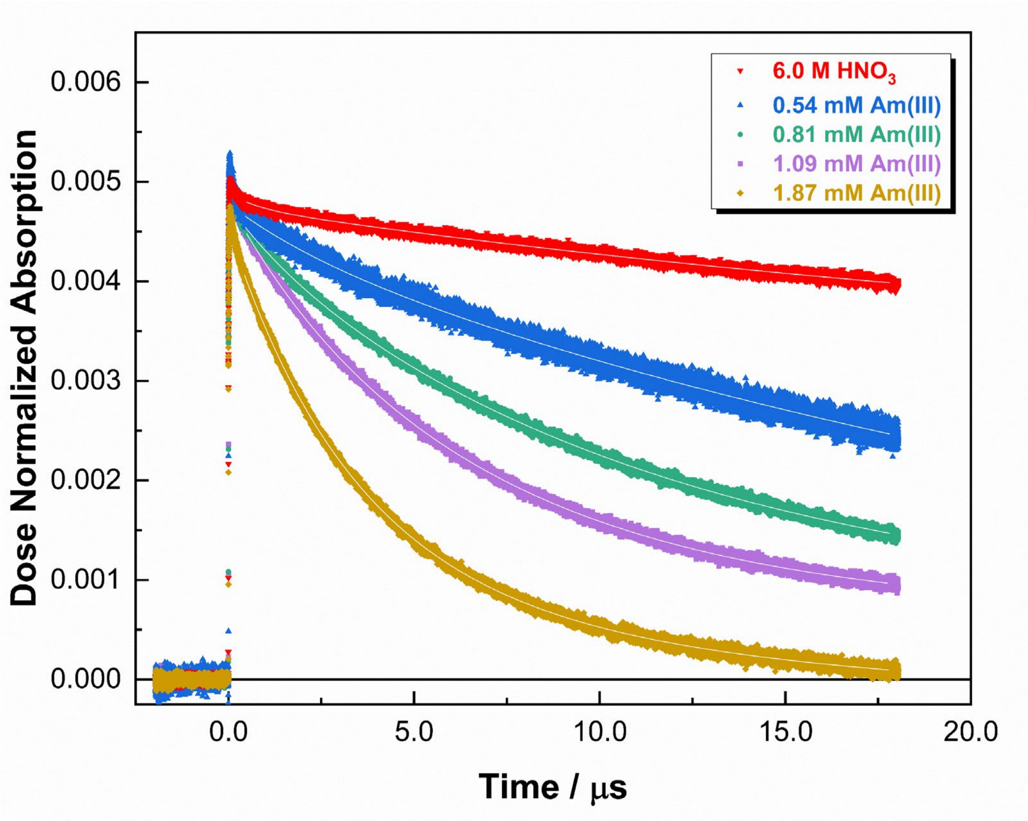


- **Am(IV) in the absence of strong complexing agents observed in HNO_3 for the first time.**
- **Results consistent with previous reports of Am(IV) in solution.**

- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* 2024, *53*, 9262.

Ambient Temperature Am(III) + $NO_3^{\bullet}$ Kinetics



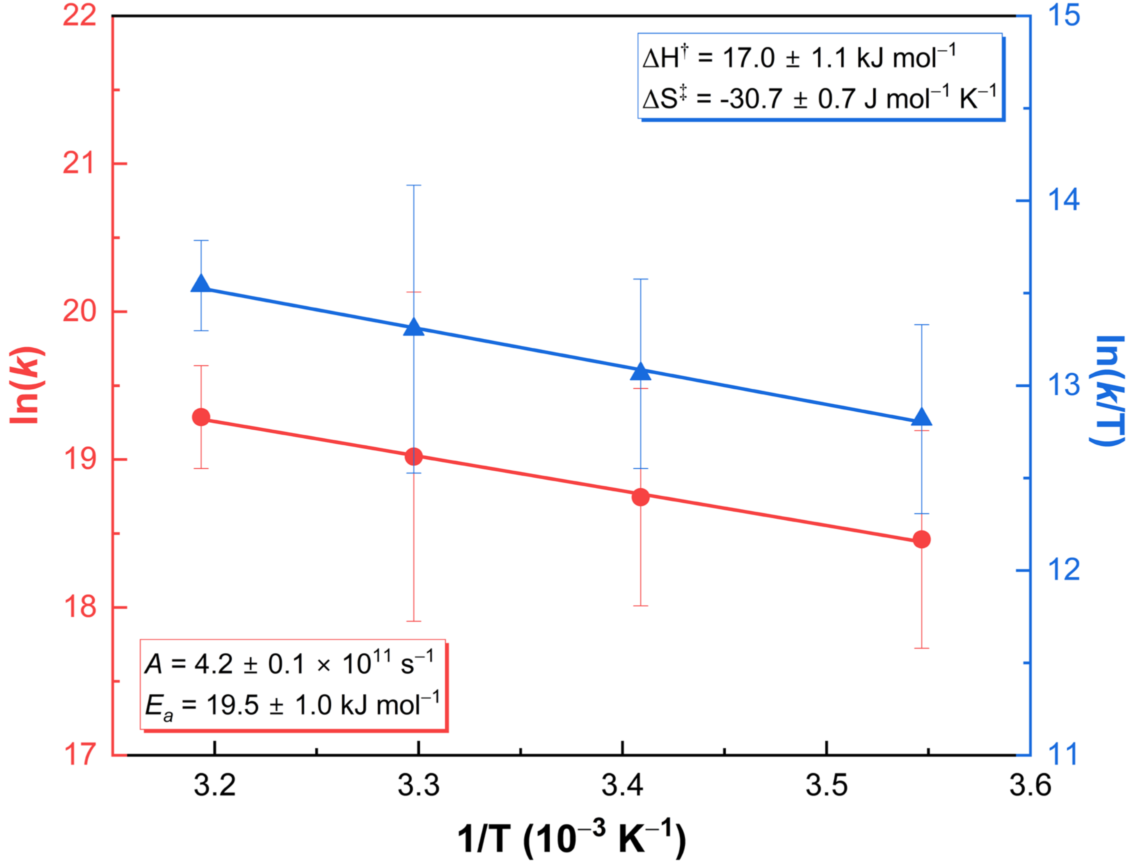


- **Rate coefficient = (1.35 ± 0.05) × 10^8 M^{-1} s^{-1}**
- **Am(IV) lifetime in 6 M HNO_3 is approximately 16 µs.**

- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* 2024, *53*, 9262.

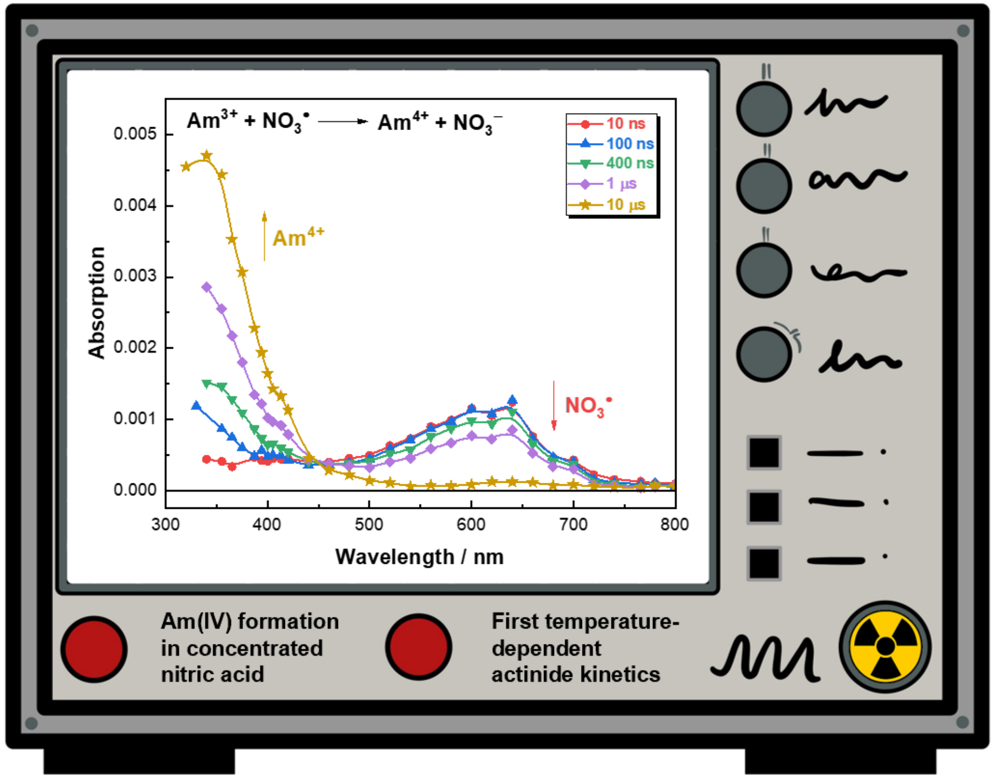
Temperature-dependent Am(III) + $NO_3^{\bullet}$ Kinetics

- **First radiation-induced temperature-dependent kinetics for any actinide element.**
- **Oxidation of Am(III) to Am(IV) occurs via an associative mechanism with some perturbation of its coordination sphere by $NO_3^{\bullet}$.**



- **Kynman**, Grimes, Mezyk, Layne, Cook, Rotermund, and Horne, *Dalton Transactions* 2024, *53*, 9262.

Ongoing Americium Work



Am(IV) formation in concentrated nitric acid

First temperature-dependent actinide kinetics

- **Further investigation of temperature-dependent actinide kinetics under varied conditions.**
- **Radiation chemistry studies of americium complexes**
- **Continued development of multiscale models to predict Am chemistry.**

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- Idaho National Laboratory, Laboratory Directed Research & Development Program under Department of Energy Idaho Operations Office Contract DE-AC07-05ID14517.
- U.S. DOE, SC, BES, Solar Photochemistry Program under award DE-SC0024191
- U.S. DOE, BES, Division of Chemical Sciences, Geosciences, and Biosciences under contract DE-SC0012704.

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