INL/CON-24-77431-Revision-0

The Role of Radiation-Induced Non-Equilibrium Plutonium Oxidation States in Solution

April 2024

Changing the World's Energy Future

Gregory Peter Holmbeck

Idaho National Laboratory

INL/CON-24-77431-Revision-0

The Role of Radiation-Induced Non-Equilibrium Plutonium Oxidation States in Solution

Gregory Peter Holmbeck

April 2024

Idaho National Laboratory
Idaho Falls, Idaho 83415

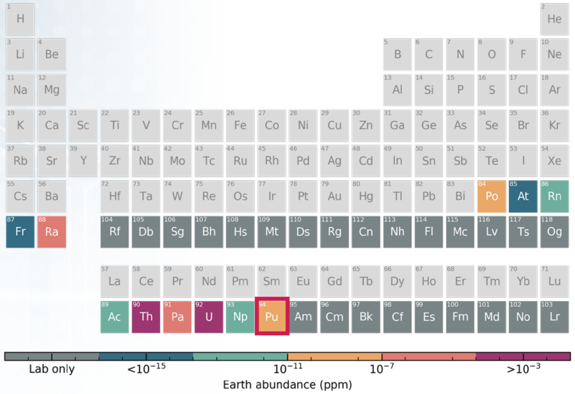
http://www.inl.gov

Prepared for the
U.S. Department of Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

Gregory P. Holmbeck
Center for Radiation Chemistry Research

The Role of Radiation-Induced Non-Equilibrium Plutonium Oxidation States in Solution

INL/CON-24-77431



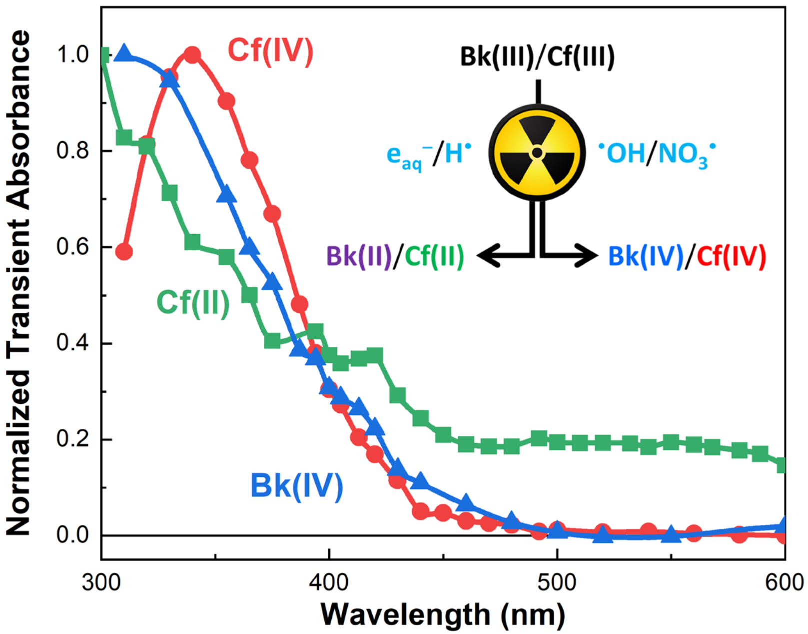
E.M. Holmbeck *et al.*, *The European Physical Journal A* **2023**, *59 (28)*.

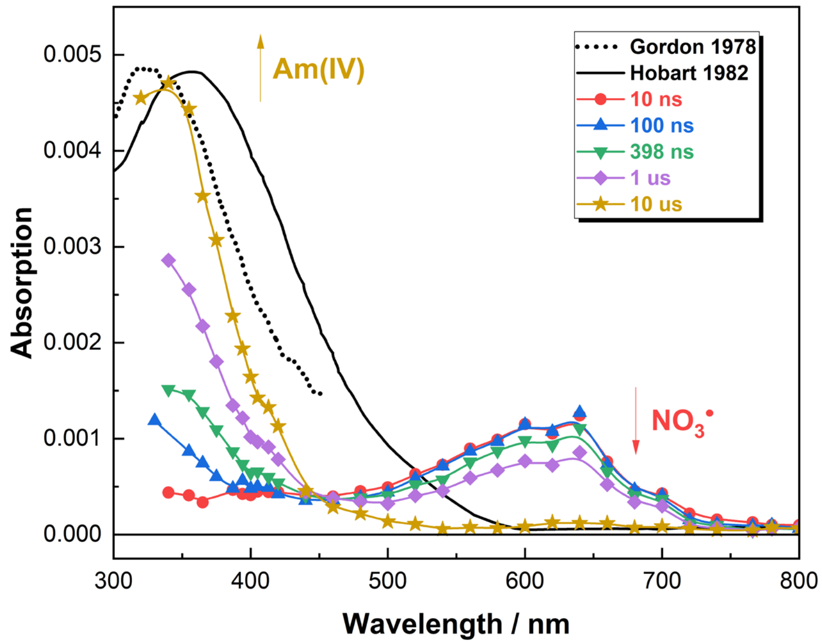
Materials Research Society - SF02.07: Radiation Effects
April 24th 2024 | Seattle, Washington, USA

Idaho National Laboratory

Radiation-Induced Non-Equilibrium Actinide Species

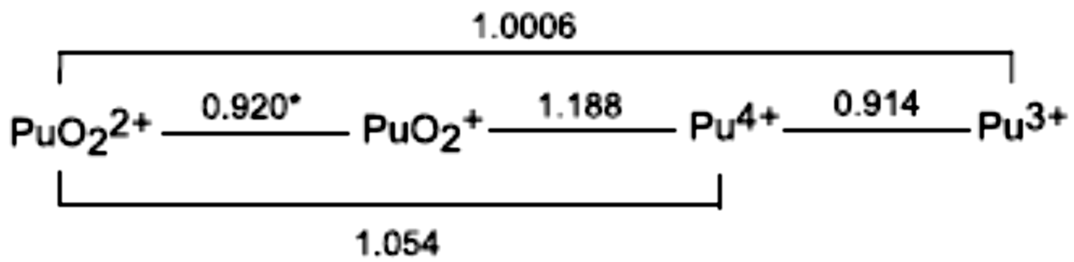
"Short-lived (≤ seconds) atoms or ions formed by the atomistic/molecular-level interaction of radiation-induced radical and molecular products with actinide ion oxidation states in aqueous solution."





- 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**, In Review.

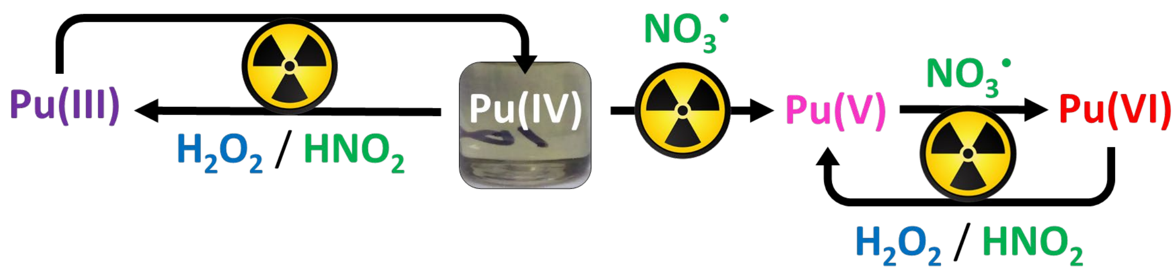
Plutonium Redox Chemistry



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}			

- Gordon, Sullivan, and Ross, *J. Phys. Chem. Ref. Data* **1986**, *15*, 1357.
- Pikaev, Gogolev, and Shilov, *Isotopenpraxis* **1990**, 26, 465.
- **Horne**, Gregson, Sims, Orr, Taylor, and Pimblott, *J. Phys. Chem. B* **2017**, *121 (4)*, 883.
- Perrin, Venault, Broussard, Vandenborre, Blain, Fattahi, and Nikitenko, *Radiochimica Acta* **2022**, *110 (5)*, 3012022.

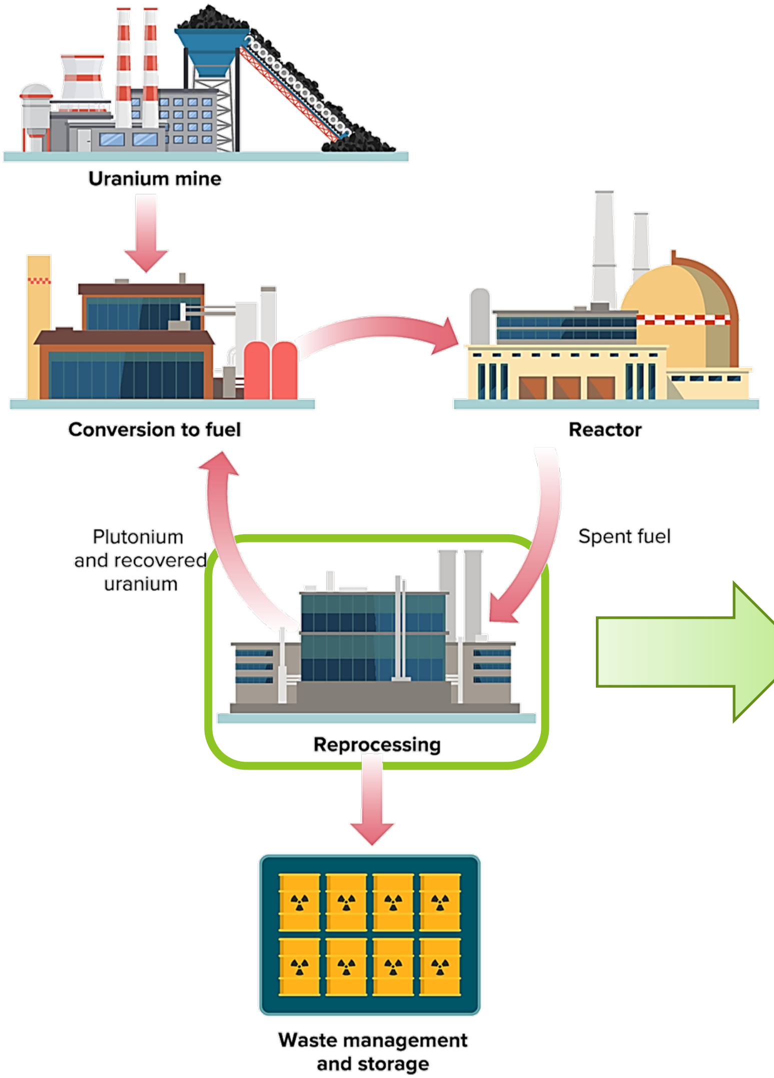
Radiation-Induced Plutonium Redox Chemistry

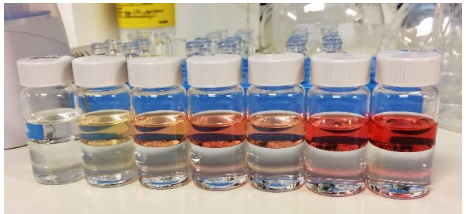


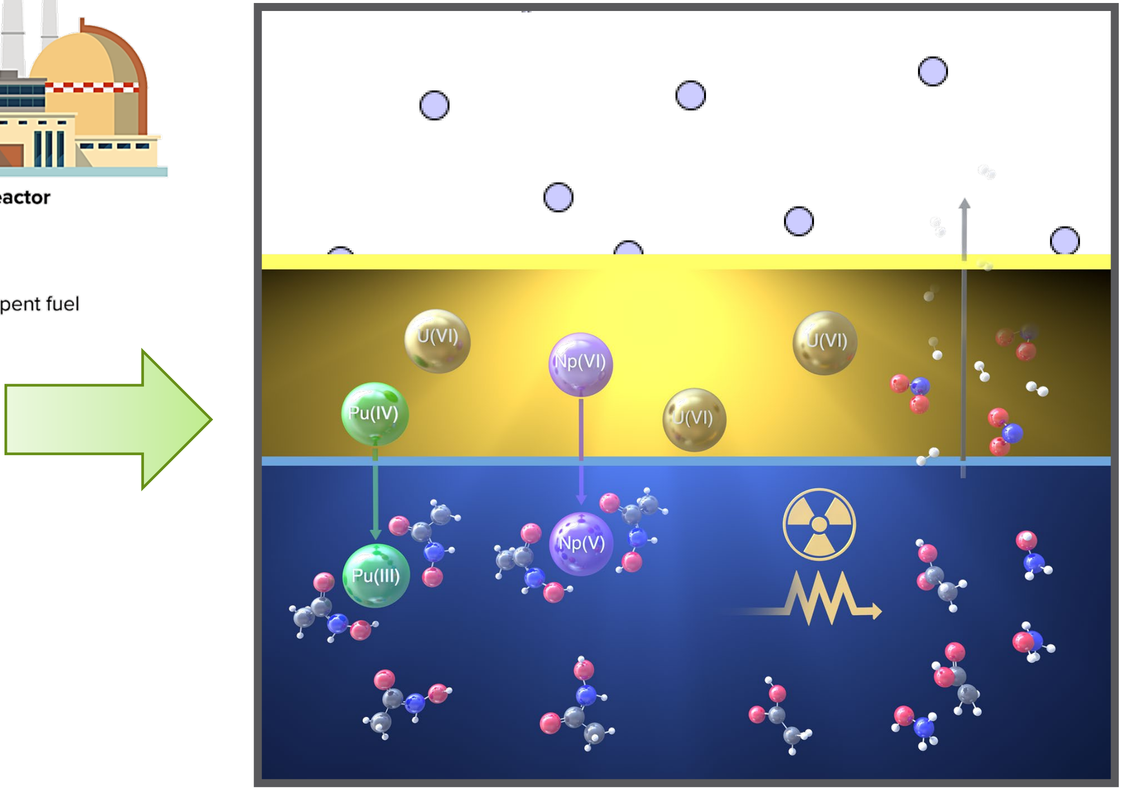
Radiolysis Product	Plutonium Oxidation State Rate Coefficients (k, M^{-1} s^{-1})			
	Pu(III)	Pu(IV)	Pu(V)	Pu(VI)
e_{aq}^{-}		2.0×10^{10}	$1.9–6.4 \times 10^{10}$	3.50×10^{10}
$H^{\bullet}$	$< 1.0 \times 10^{6}$	2.0×10^{7}	2.0×10^{8}	
$^{\bullet}OH$	$1.8–4.2 \times 10^{8}$			
$NO_3^{\bullet}$	2.5×10^{8}			

- Gordon, Sullivan, and Ross, *J. Phys. Chem. Ref. Data* **1986**, *15*, 1357.
- Pikaev, Gogolev, and Shilov, *Isotopenpraxis* **1990**, 26, 465.
- **Horne**, Gregson, Sims, Orr, Taylor, and Pimblott, *J. Phys. Chem. B* **2017**, *121 (4)*, 883.
- Perrin, Venault, Broussard, Vandenborre, Blain, Fattahi, and Nikitenko, *Radiochimica Acta* **2022**, *110 (5)*, 3012022.

Used Nuclear Fuel Reprocessing







- Conrad, Mezyk, Isherwood, Baidak, Pilgrim, Whittaker, Orr, Pimblott, and **Horne**, *ChemPhysChem* **2022**, e20220074.

Reprocessing Radiation Chemistry

Water Radiolysis

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

Indirect Radiation Effects

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

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

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

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

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

$N_2O_4 \rightarrow HNO_2 + HNO_3$

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

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

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

Reprocessing Radiation Chemistry

Water Radiolysis

Direct Radiation Effects

Key Radiolysis Products

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

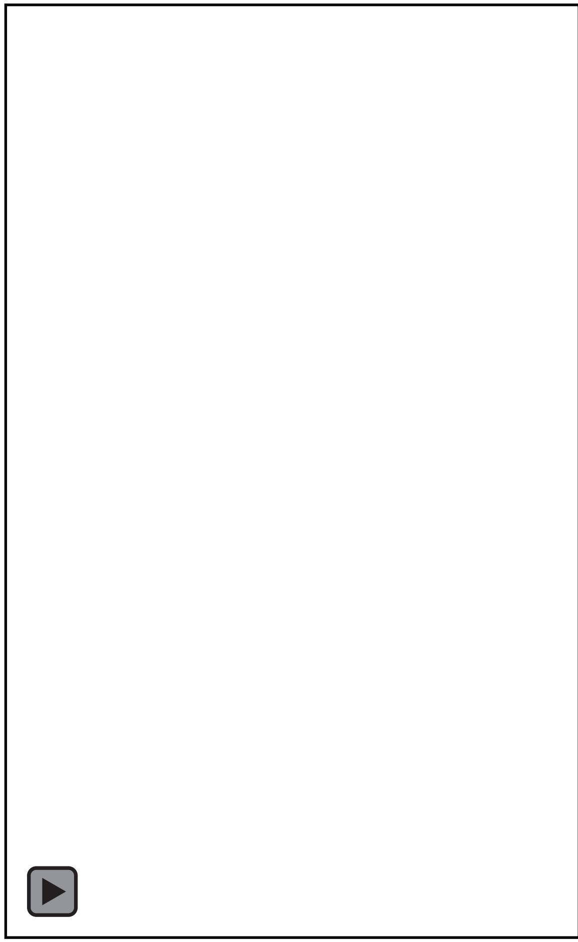
$NO_3^{\bullet}$ and HNO_3 from HNO_3

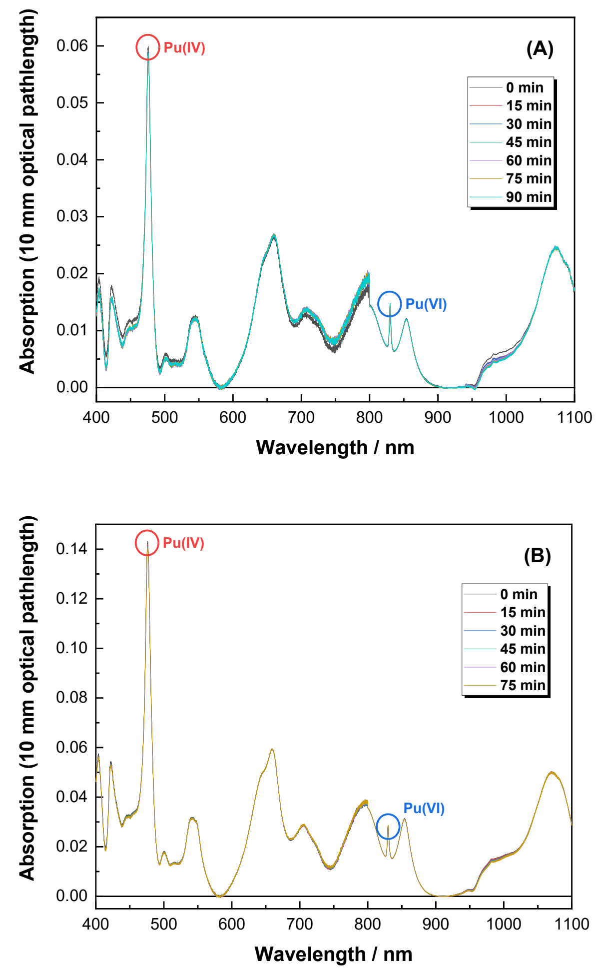
$RH^{\bullet+}$ from *n*-dodecane

$N_2O_4 \rightarrow HNO_2 + HNO_3$

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

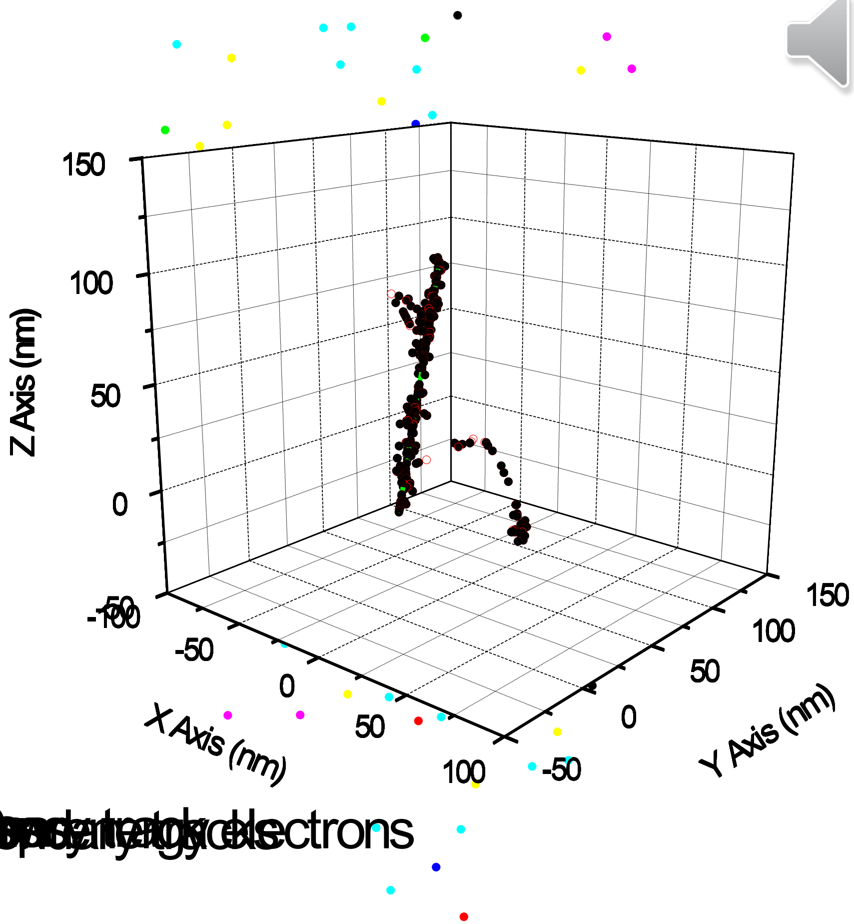
Tetravalent Plutonium Gamma Irradiations

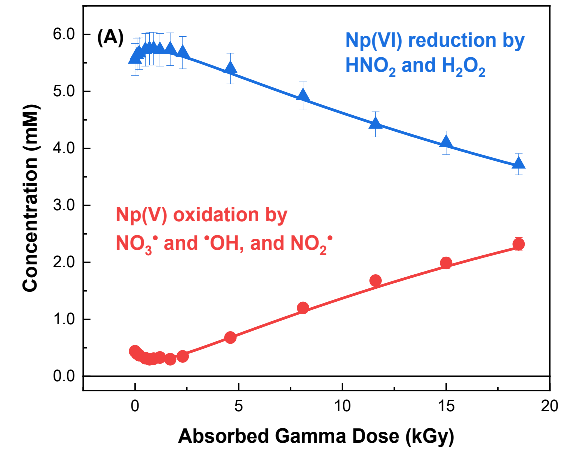


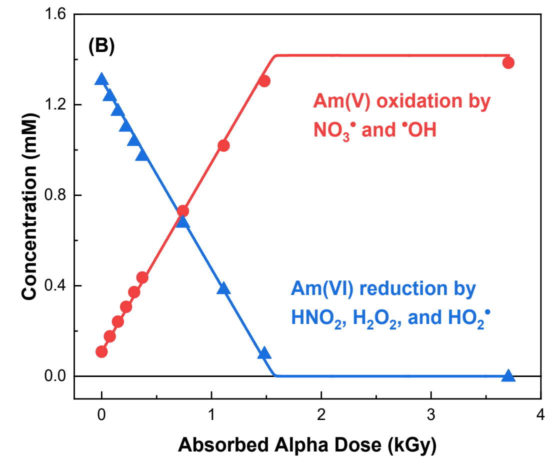


- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

Multiscale Radiation Chemistry Modeling

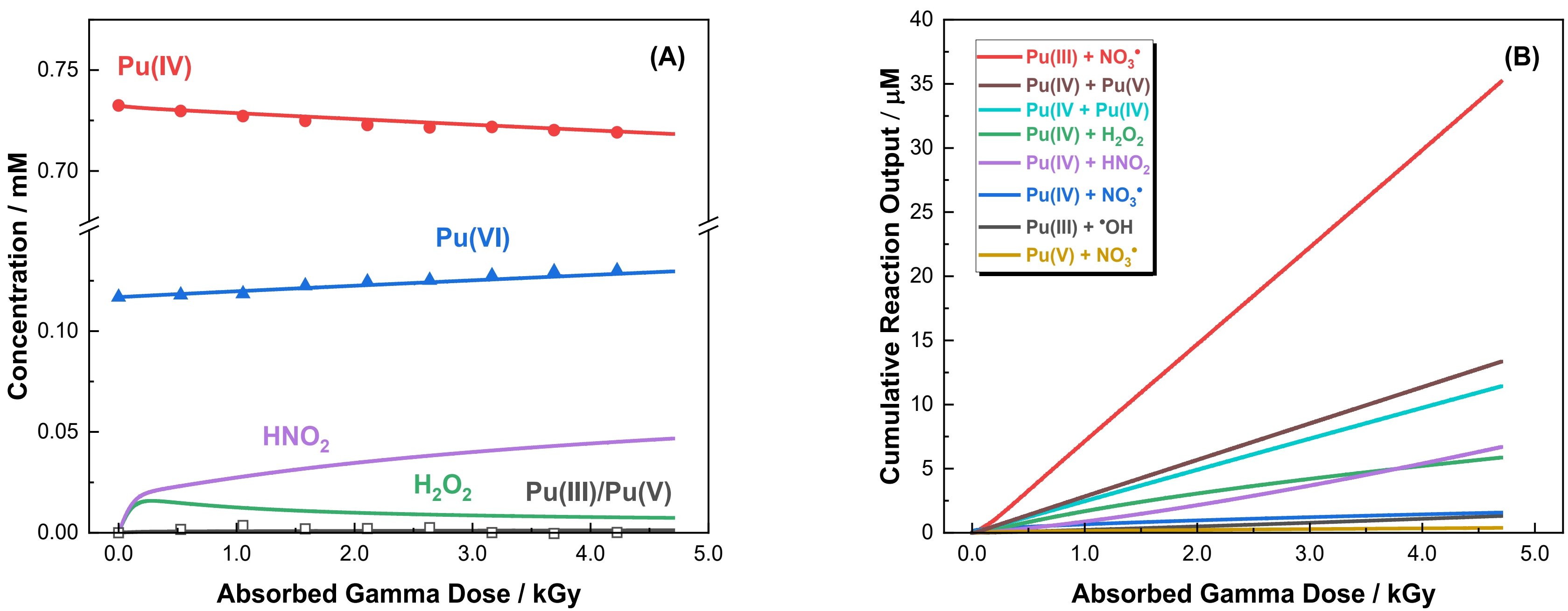






- Clifford, Green, Oldfield, Pilling, and Pimblott, *J. Chem. Soc., Faraday Trans.*, **1986**, *82*, 2673.
- Pimblott, LaVerne, and Mozumder, *J. Phys. Chem.*, **1996**, *100*, 8595.
- **Horne**, Grimes, Mincher, and Mezyk, *J. Phys. Chem. B* **2016**, *120 (49)*, 12643.
- **Horne**, Grimes, Bauer, Dares, Pimblott, Mezyk, and Mincher, *Inorg. Chem*. **2019**, *58*, 8551.
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorganic Chemistry* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

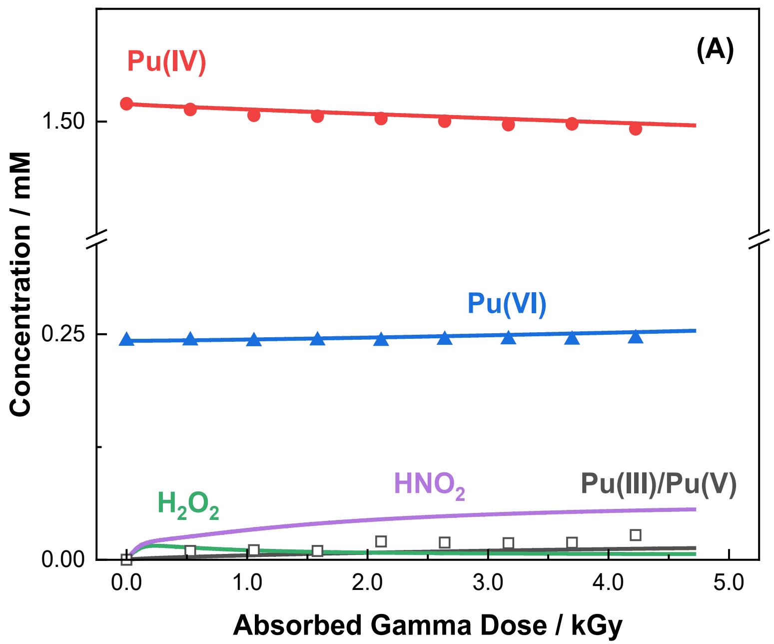
The Role of Radiation-Induced Non-Equilibrium Plutonium Oxidation States in Solution (1.0 M HNO_3)

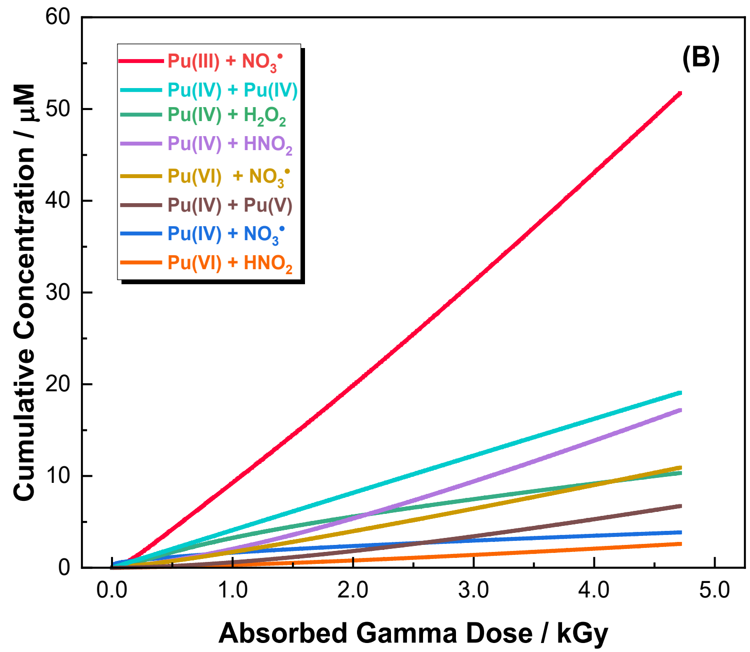


- **Pu(IV)** is transiently reduced to **Pu(III)** by its reactions with H_2O_2 and HNO_2.
- Oxidation of **Pu(IV)** is in competition with the scavenging of $NO_3^{\bullet}$ radicals by **Pu(III)**.
- Remaining G($NO_3^{\bullet}$) partially accounts for the accumulation of **Pu(VI)** via the oxidation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

- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorg. Chem.* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

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

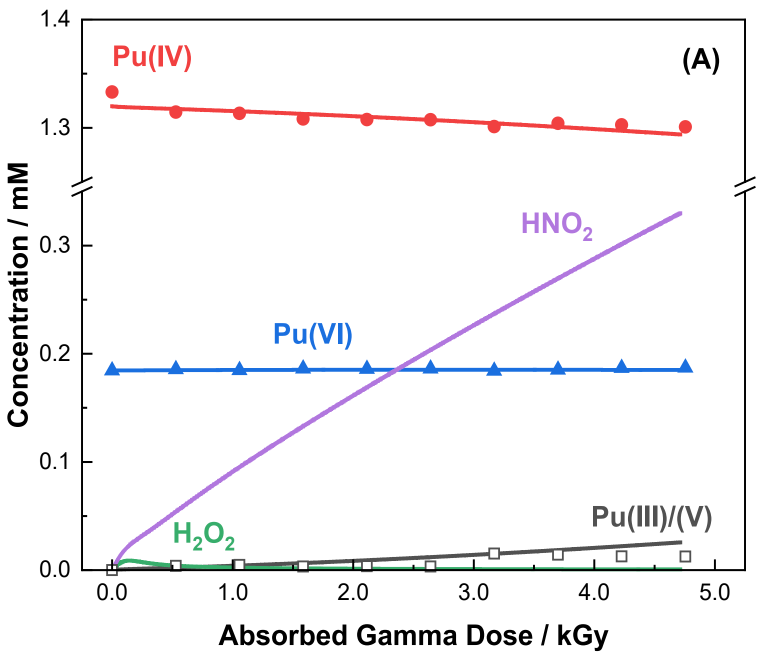


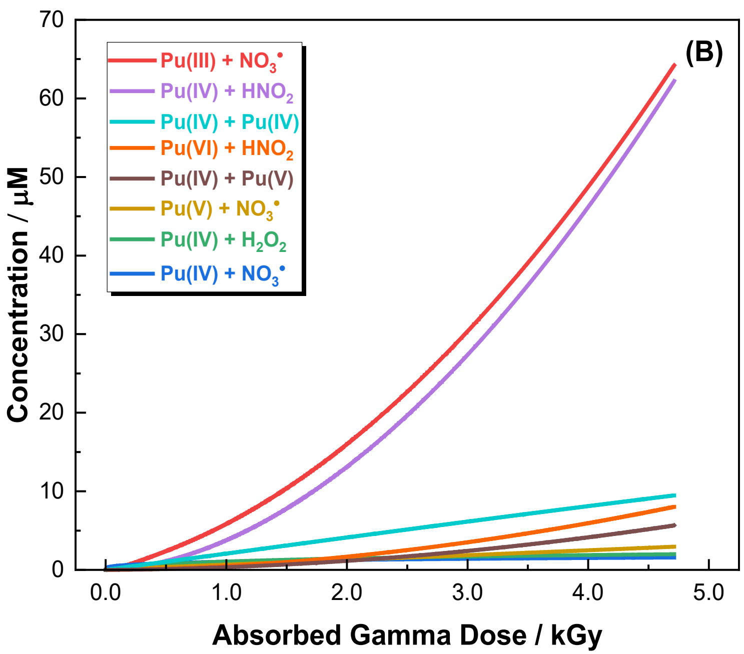


- **Pu(III)** oxidation by **•OH** inhibited by HNO_3.
- Contribution of **HNO_2** to **Pu(IV)** reduction becomes greater than that afforded by **H_2O_2**.
- Less **Pu(VI)** is accumulated because of a shift in the position of the Pu-equilibria with acidity.
- Model predicts the formation of a low (µM),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

- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorg. Chem.* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

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

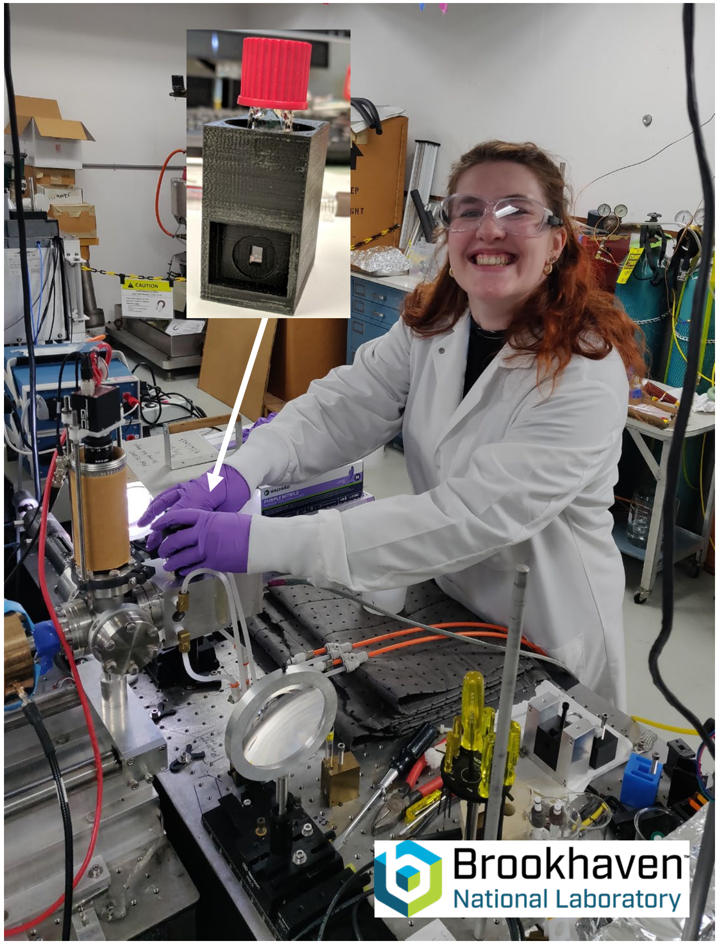


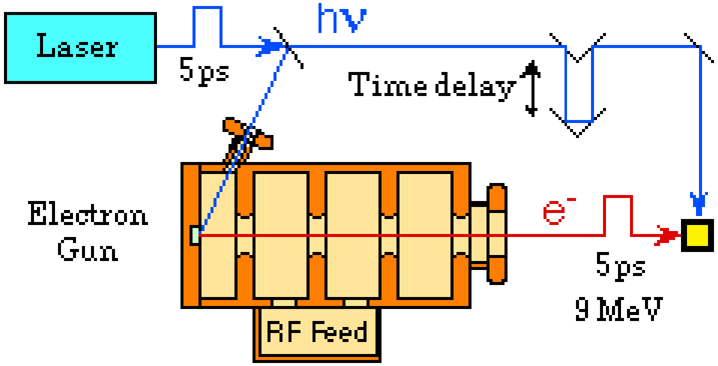


- Radiation-induced redox chemistry of Pu is dominated by three processes: the reduction of **Pu(IV)** and **Pu(VI)** by HNO_2, and the oxidation of **Pu(III)** by $NO_3^{\bullet}$ radicals to regenerate **Pu(IV)**.
- Calculations again predict the accumulation (10s µM) of **Pu(III)** and **Pu(V)**.

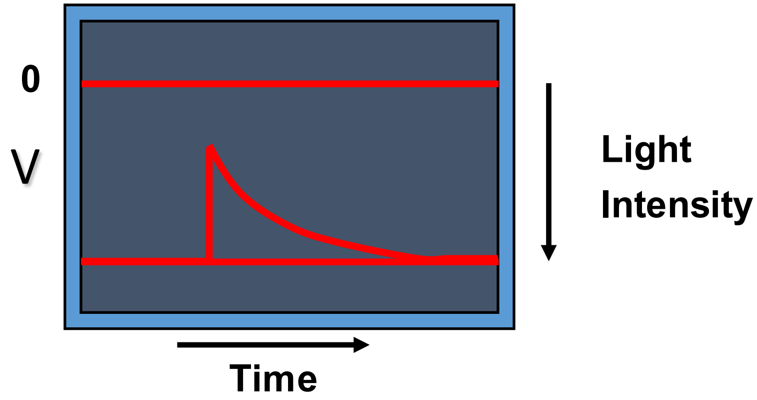
- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorg. Chem.* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

Time-Resolved Electron Pulse Radiolysis



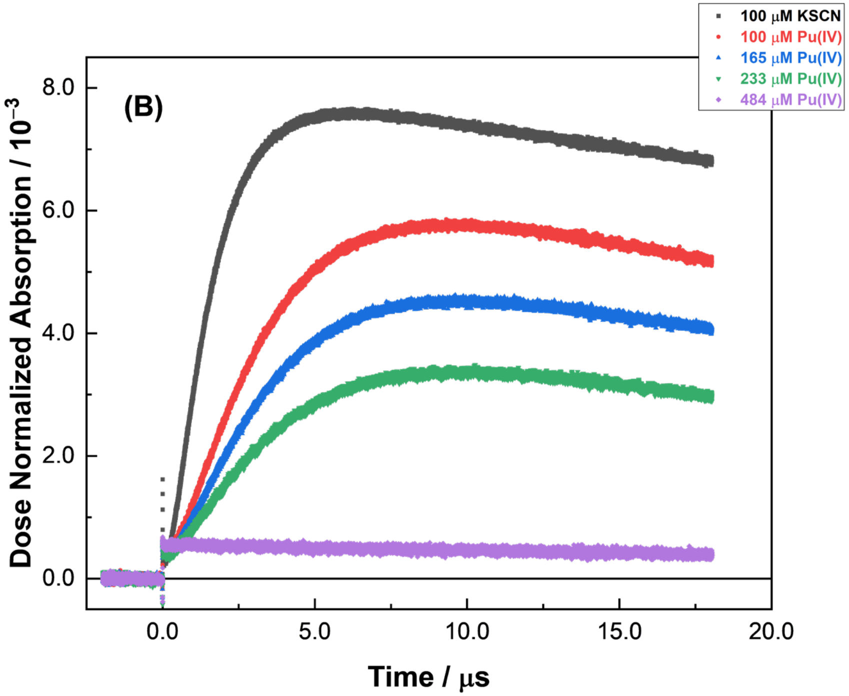


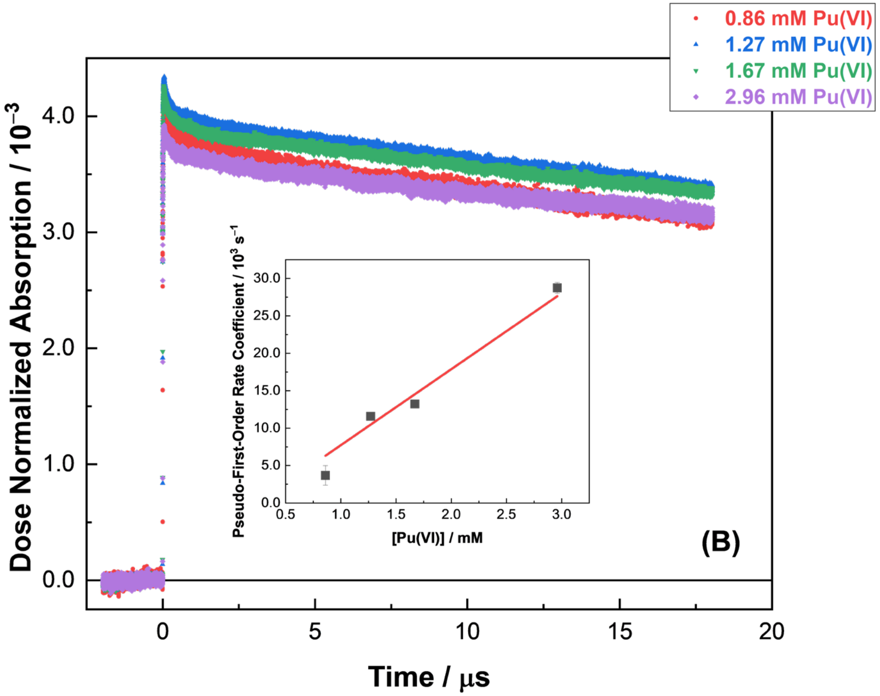
Transients are detected by optical absorption changes.



- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php.
- Kynman, Grimes, Mezyk, Layne, Cook, Rotermund, and **Horne**, *Dalton Trans.* **2024**, *In Review*.

Missing Radiation-Induced Plutonium Kinetics





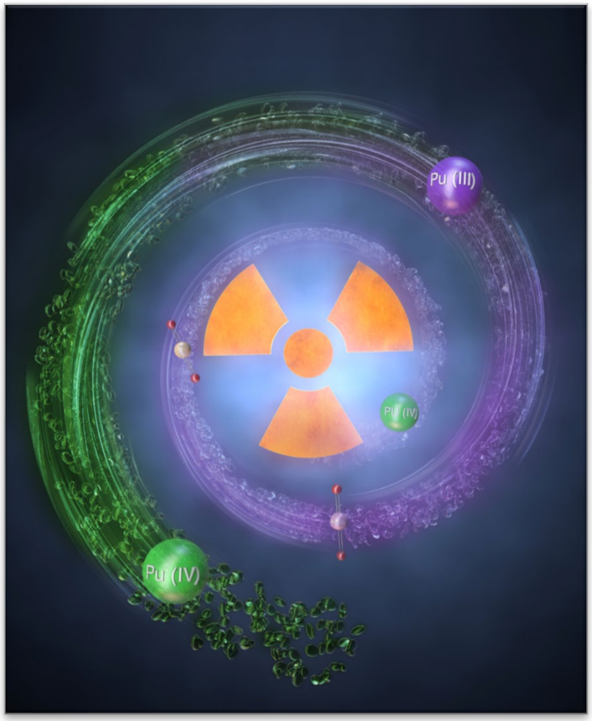
- Oxidation of **Pu(IV)** by **$^{\bullet}$OH** (E ° = +2.7 V) afforded a ***k*** **= (6.31 ± 1.15) × 10^9 M^{-1} s^{-1}**, R^2 = 0.94,
- Oxidation of **Pu(VI)** by **$NO_3^{\bullet}$** (E° = +2.3–26 V) afforded a ***k*** **= (1.02 ± 0.18) × 10^7 M^{-1} s^{-1}**, R^2 = 0.91.

- Kynman, Grimes, Layne, Cook, Mezyk, and **Horne**, *PCCP* **2024**, *In Preparation*.

Conclusions

GLENN T. SEABORG INSTITUTE
Idaho National Laboratory

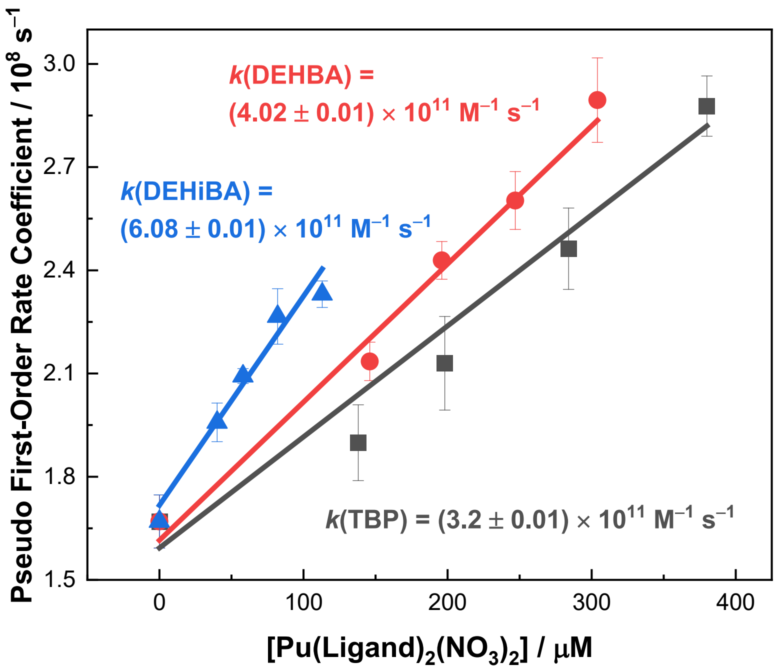
- A multiscale model has been developed and used to elucidate the fundamental gamma radiation-induced behavior of Pu in concentrated HNO_3.
- Gamma irradiation of Pu(IV)/Pu(VI) solutions afforded negligible (<12%) net change in redox distribution.
- Calculations indicate that observations are a consequence of:
  - redox cycling between **Pu(IV)** and **Pu(III)**, as mediated $^{\bullet}OH$/$NO_3^{\bullet}$ radical oxidation of **Pu(III)**;
  - H_2O_2/HNO_2 driven reduction of **Pu(IV)**.
  - oxidation of **Pu(V)** by the $NO_3^{\bullet}$ radical and **Pu(IV)**.
- These radiation-induced process are augmented by Pu equilibria, which were predicted to facilitate the additional accumulation of **Pu(III)** and **Pu(V)** with increasing HNO_3 concentration.



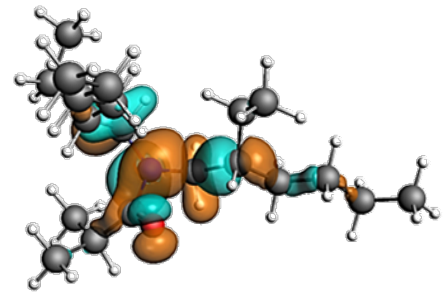
Cover artwork designed by Rett Tyler Longmore, Idaho National Laboratory.

- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorg. Chem.* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.

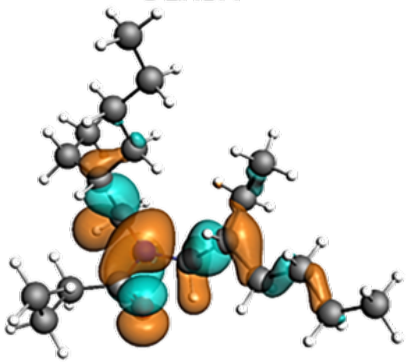
What's Next? Complexation Effects



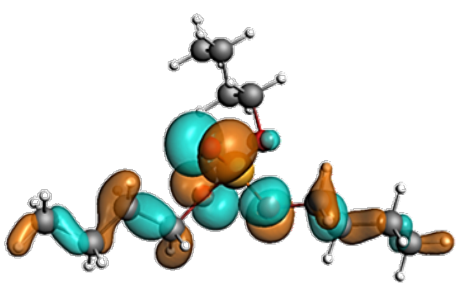
DEH*i*BA$^{\bullet+}$



DEHBA$^{\bullet+}$



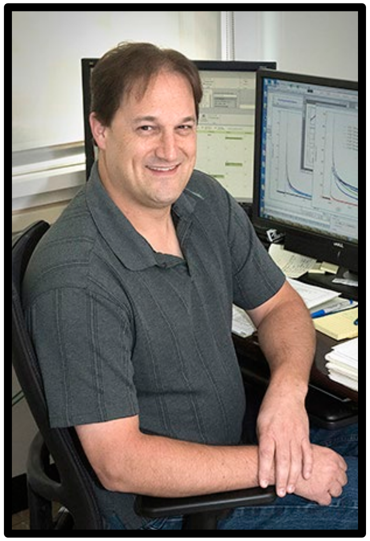
TBP$^{\bullet+}$



- Pu(VI) 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?

- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and **Horne**, *PCCP*, **2021**, *23*, 24589.
- Culbertson, Celis-Barros, Pilgrim, McLachlan, Cook, Mezyk, and **Horne**, *Inorg. Chem.* **2024**, *In Preparation*.

Acknowledgements



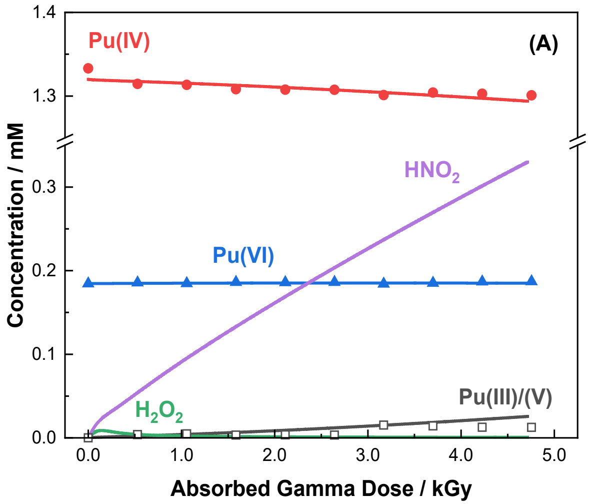
Brookhaven™
National Laboratory

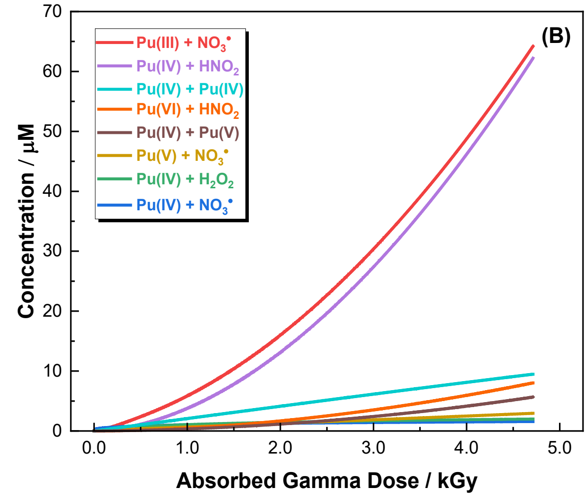
GLENN T.
SEABORG
INSTITUTE
Idaho National Laboratory

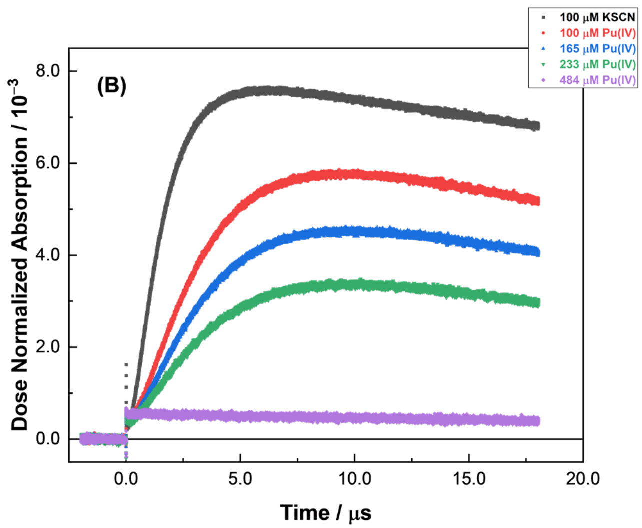
Idaho National Laboratory

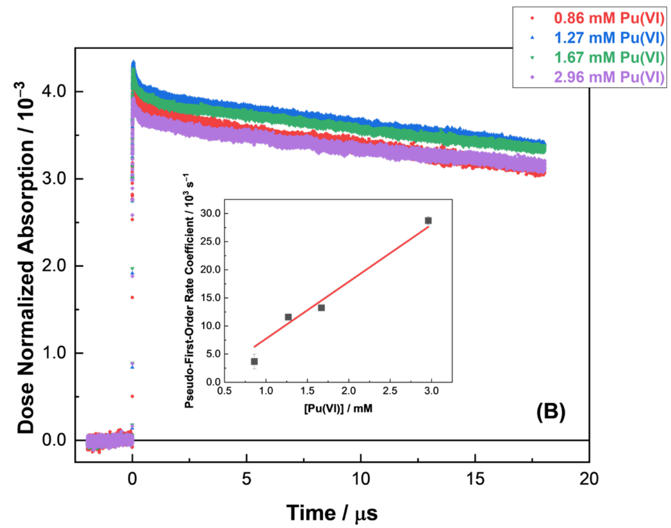
Questions?

GLENN T. SEABORG INSTITUTE
Idaho National Laboratory









- Kynman, Grimes, Conrad, Pimblott, and **Horne**, *Inorg. Chem.* **2024**. DOI: https://doi.org/10.1021/acs.inorgchem.4c00138.