INL/CON-22-66322-Revision-0

Recent Advances in Actinide Radiation Chemistry

April 2022

Changing the World's Energy Future

Gregory P Horne

Idaho National Laboratory

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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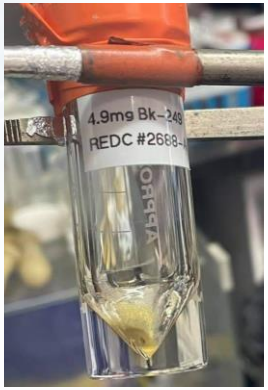
March 30th 2022

Gregory P. Horne

Center for Radiation Chemistry Research

Recent Advances in Actinide Radiation Chemistry

INL/CON-22-02069



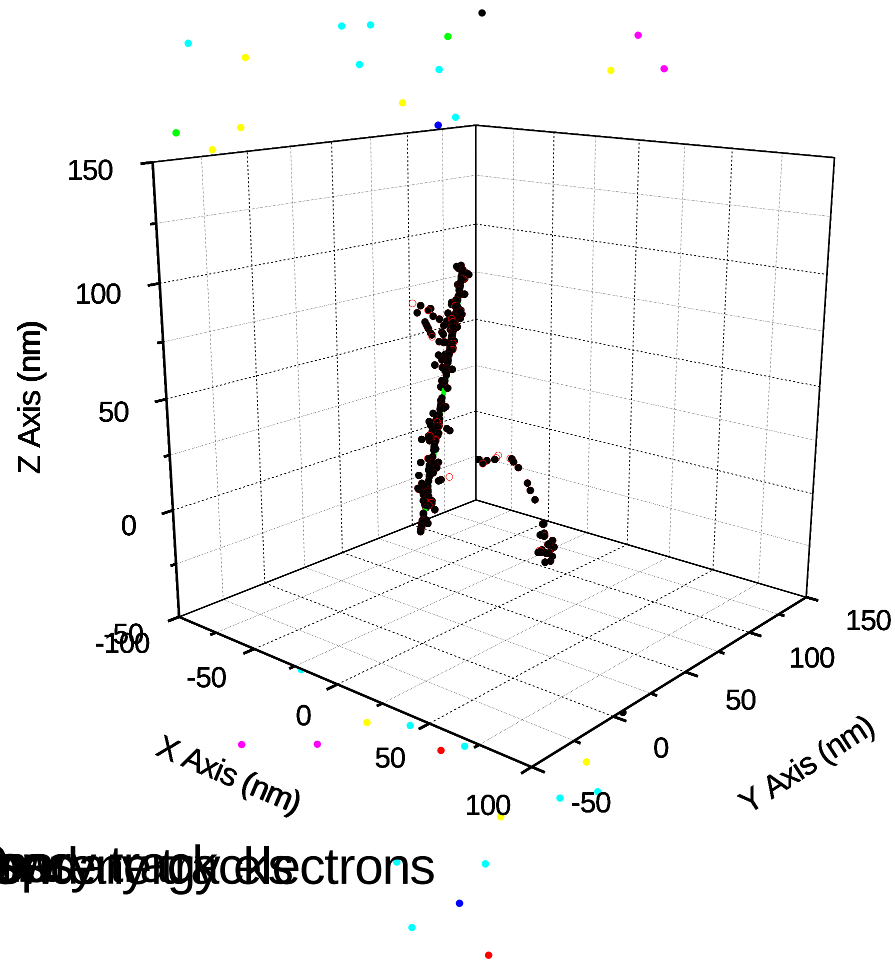
Los Alamos National Laboratory

G. T. Seaborg Institute Seminar Series

INL Idaho National Laboratory

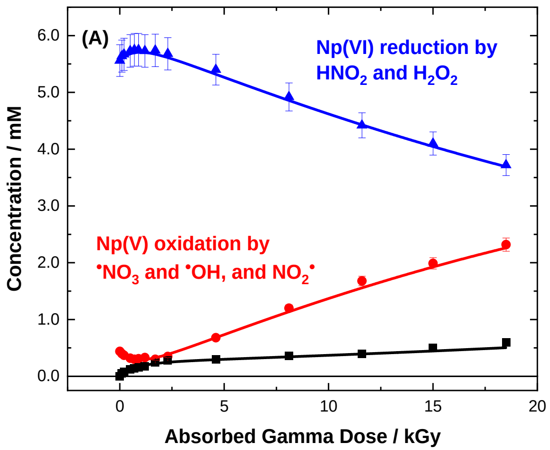
Radiation Chemistry

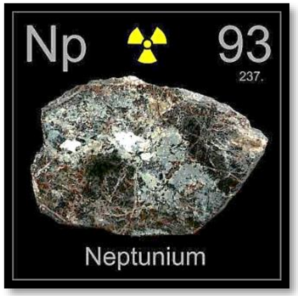
- Radiation chemistry is the study of **chemistry induced by the absorption of ionizing radiation** by matter.
- Radiation is the propagation of energy through space.
- The passage of radiation through matter results in a series of energy transfer events.

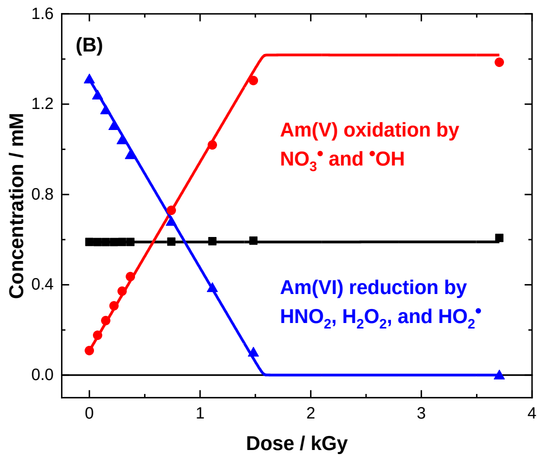


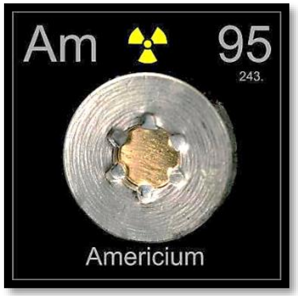
- Pimblott, LaVerne, and Mozumder, A. *J. Phys. Chem.*, **1996**, 100, 8595.
- Clifford, Green, Oldfield, Pilling, and Pimblott, S. M., *J. Chem. Soc., Faraday Trans.*, **1986**, 82, 2673.

Actinide Radiation Chemistry





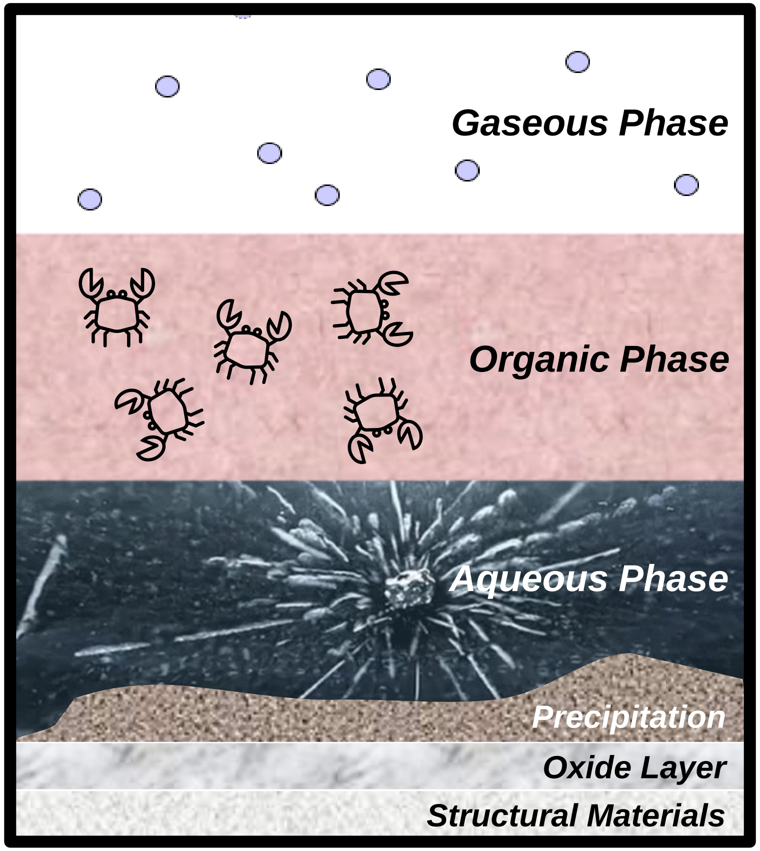




Solvent Extraction Reprocessing

Ligands/organic diluent:HNO_3/H_2O

(± additives)



- Horne, Grimes, Mincher, and Mezyk, *J. Phys. Chem. B* **2016**, *120 (49)*, 12643.
- Grimes, Horne, Dares, Pimblott, Mezyk, and Mincher, *Inorg. Chem.* **2017**, *56 (14)*, 8295.
- Horne, Grimes, Bauer, Dares, Pimblott, Mezyk, and Mincher, *Inorg. Chem*. **2019**, *58*, 8551.

Actinide Chemistry

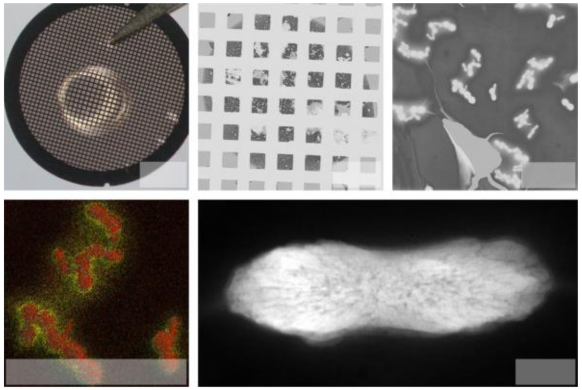


Fig. 1. Investigation of a dropcast Cf-containing sample from Müller, Deblonde, Ercius, Zeltmann, Abergel, and Minor, Probing electronic structure in berkelium and californium via an electron microscopy nanosampling approach. *Nature Communications*, **2021**, *12 (948)*, 1−6.

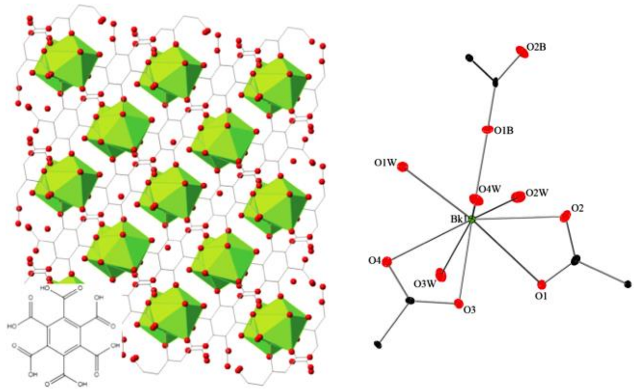


Fig. 2. The extended structure and coordination environment of Bk-carboxylate from Sperling, Beck, Scheibe, Bai, Brannon, Gomez-Martinez, Grödler, Johnson, Lin, Rotermund, and Albrecht-Schönzart, Synthesis, characterization, and high-pressure studies of a 3D berkelium(III) carboxylate framework material. *Chem. Commun.*, **2022**, *58*, 2200-2203.

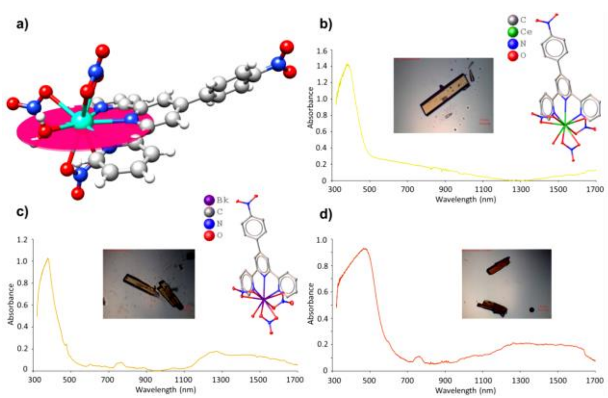


Fig. 3. Characterization of Ce(III) and Bk(III) terpyridine complexes from Gaiser, Celis-Barros, White, F.D. *et al.*, Creation of an unexpected plane of enhanced covalency in cerium(III) and berkelium(III) terpyridyl complexes. *Nature Communications*, **2021**, *12 (7230)*, 1−9.

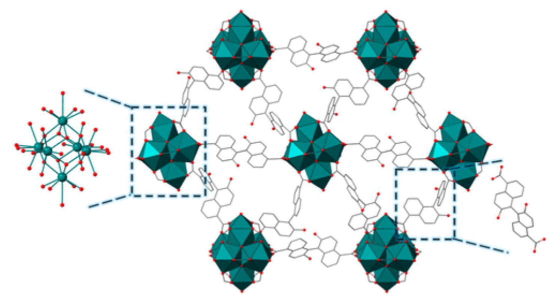


Fig. 4. . Structure of TOF-16, the binaphthol linker, and the hexameric thorium-oxo SBU from Gilson, Fairley, Julien, Oliver, Hanna, Arntz, Farha, LaVerne, and P.C. Burns, Unprecedented Radiation Resistant Thorium-Binaphthol Metal-Organic Framework. *J. Am. Chem. Soc.*, **2020**, *142 (31)*, 13299-13304.

Reprocessing 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

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

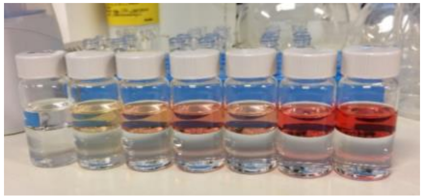
$HNO_3 \rightsquigarrow HNO_3^* \longrightarrow HNO_2 + O$

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

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

Alkane Radiolysis

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



- Buxton, 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 Transient Species

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

$^\bullet NO_3$ from HNO_3

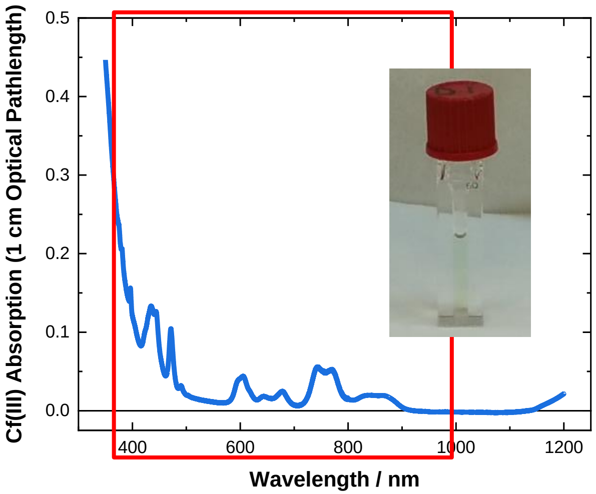
$RH^{\bullet +}$ from *n*-dodecane

$N_2O_4 \rightarrow HNO_2 + HNO_3$

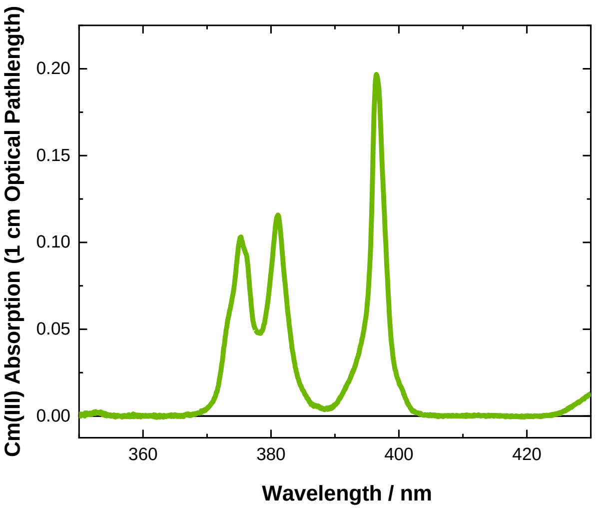
- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

Actinide Sample Preparation

^{249}Cf(III)



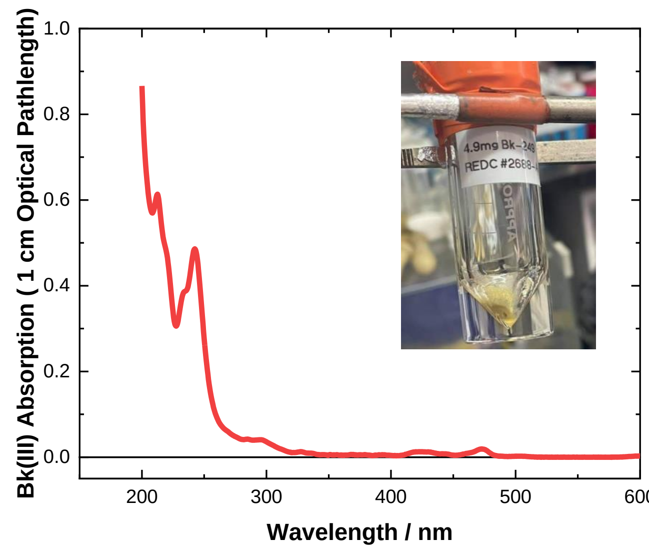
^{248}Cm(III)



- Carnall, Fields, Stewart, and Keenan, *J. Inorg. Nucl. Chem*. **1958**, *6*, 213.
- Conway, Fried, Latimer, McLaughlin, Gutmacher, Carnall, and Gields, *Inorg. Nucl. Chem.* **1966**, 28, 3064.

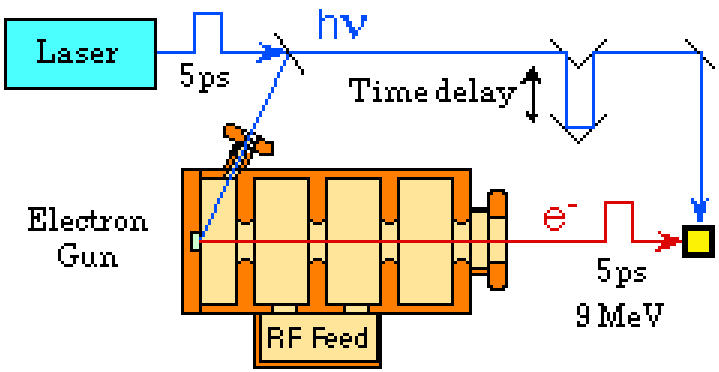
Actinide Sample Preparation

^{249}Bk(III)

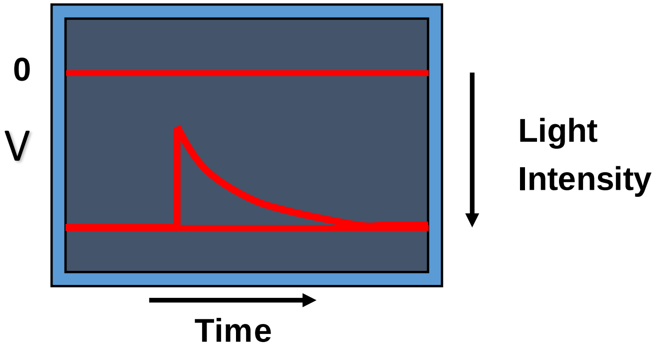


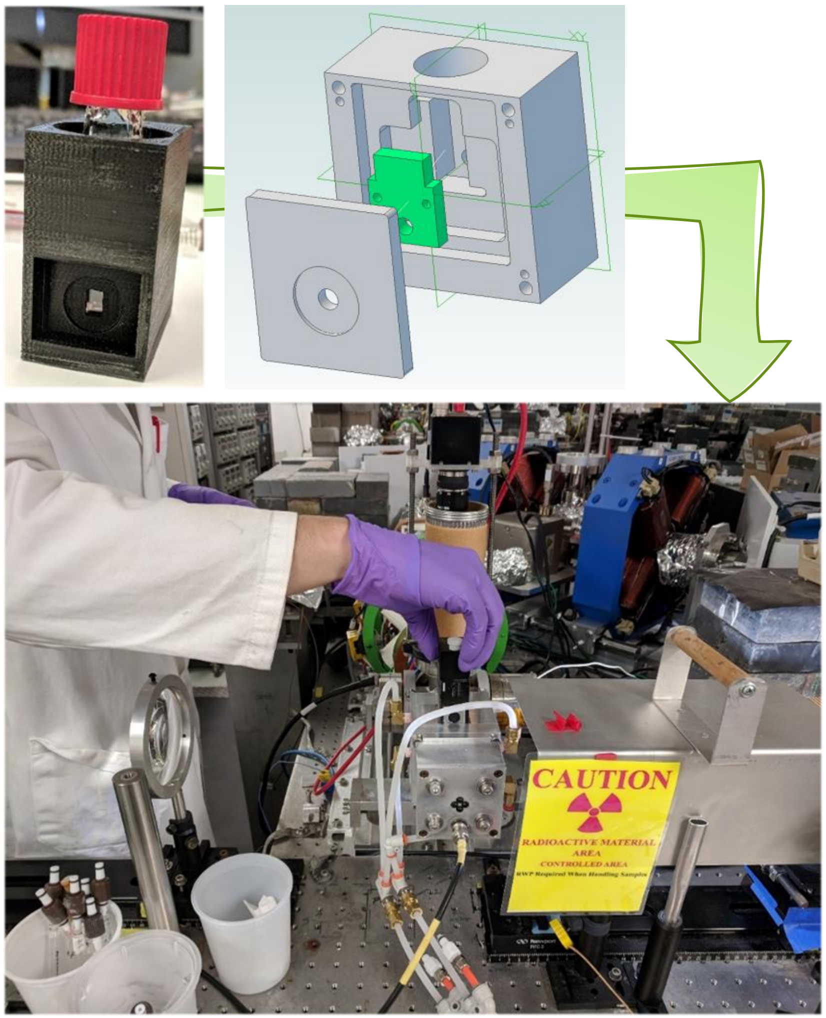
- Gutmacher, Hulet, Lougheed, Conway, Carnall, Cohen, Keenan, and Baybarz, *et al.*, *J. Inorg. Nucl. Chem.*, **1967**, *29*, 2341.

Pulsed Electron Radiolysis



Transients are detected by optical absorption changes.

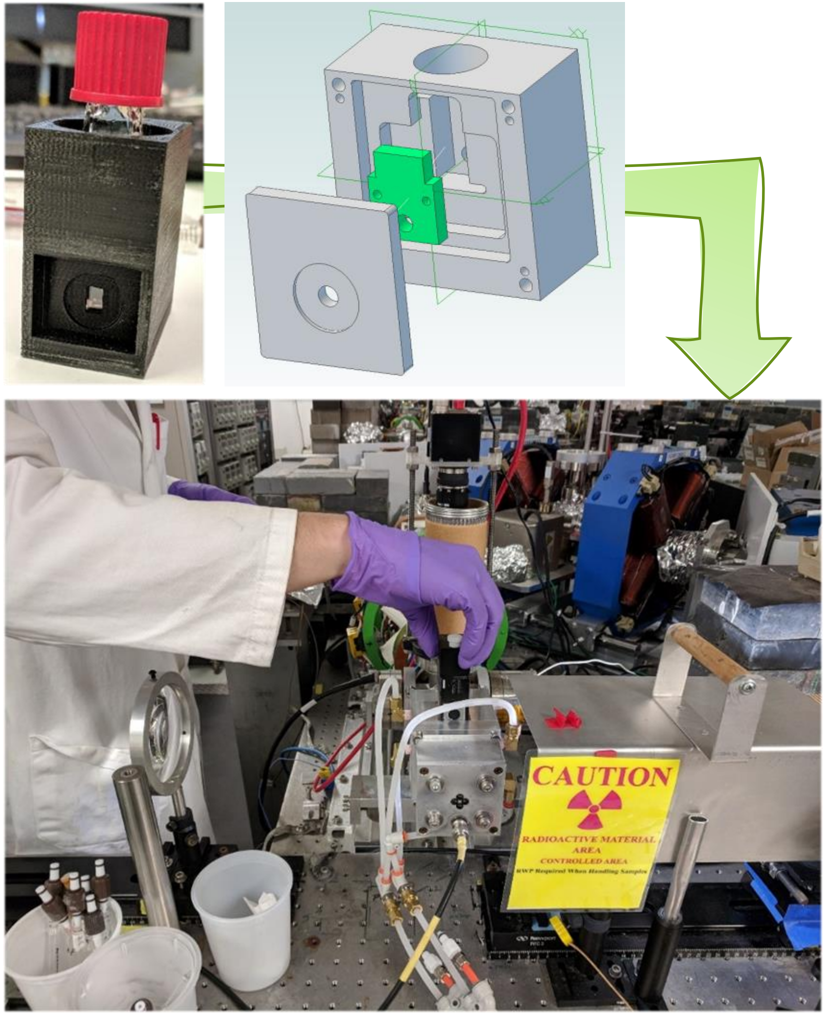




- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- https://www.bnl.gov/chemistry/EPIP/instrumentation.php

Pulsed Electron Radiolysis

- Hydrated Electron (**e_{aq}^{-}**): $HClO_4$/0.5 M tBuOH/N_2-saturated.
- Hydrogen Atom (**$H^{\bullet}$**): 100 µM PCB/$HClO_4$/50 mM tBuOH/N_2-saturated.
- Hydroxyl Radical (**$^{\bullet}OH$**): 100 µM KSCN/10 mM $HClO_4$/N_2O-saturated.
- Nitrate Radical (**$^{\bullet}NO_3$**): 6 M HNO_3/N_2O-saturated.
- Dodecane Radical Cation (**$RH^{\bullet+}$**): 0.5 M DCM/n-dodecane.



- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data*, **1988**, *17*, 513.

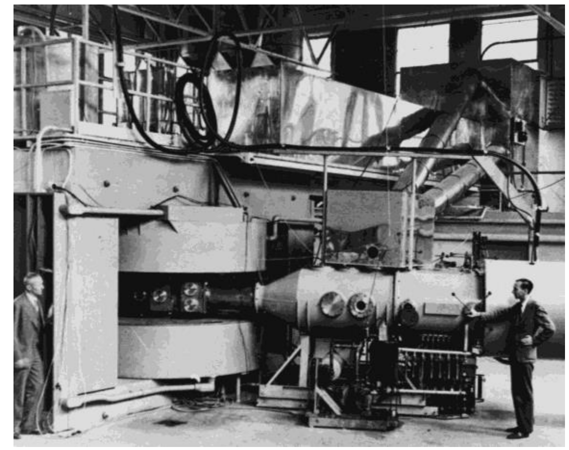
Radiation-Induced Curium(III) Redox Chemistry

- Sullivan, Gordon, Mulac, Schmidt, Cohen, and Sjoblom, *Inorg. Nucl. Chem. Let.* **1976**, *12*, 599.
- Horne, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Trans.* **2021**, *50*, 10853.

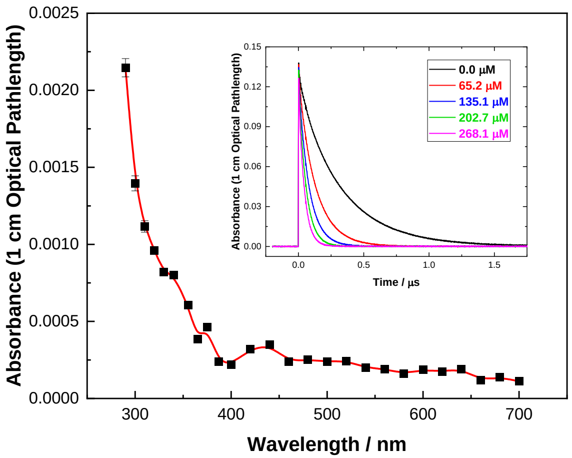
Cm(III) Radiation Chemistry

The results obtained with Cm(III) are of importance in the evaluation of redox potentials estimated from spectra. The values for the potentials of OH (-1.90V)(9) and e^-_{aq} (2.86V)(6) are not consistent with the estimates of -3.25V (10) for the Cm(IV)/(III) couple and +5.0V (11) for the Cm(III)/(II) couple.

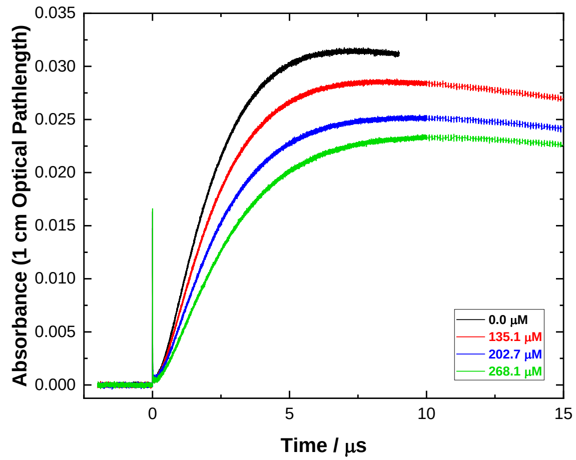
An	λ_{max}(nm)	$t_{1/2}$(sec)
Cm(II)[d]	240	∿12 x 10^{-6}
Cm(IV)	260	∿20 x 10^{-6}



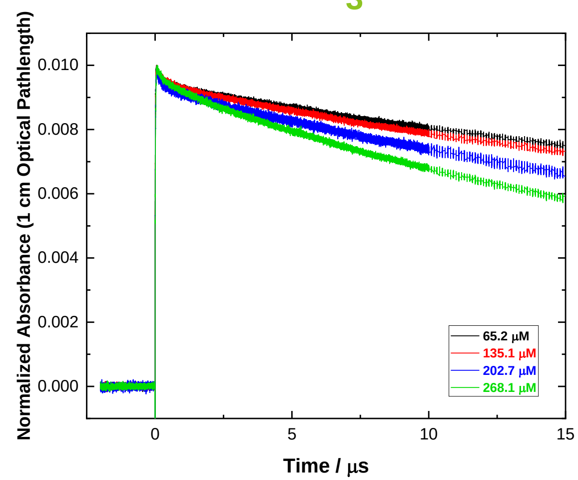
e_{aq}^-



•OH



$^•NO_3$

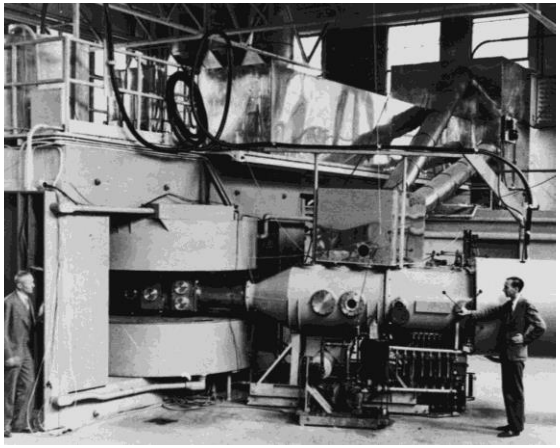


- Sullivan, Gordon, Mulac, Schmidt, Cohen, and Sjoblom, *Inorg. Nucl. Chem. Let.* **1976**, *12*, 599.
- Horne, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Trans.* **2021**, *50*, 10853.

Cm(III) Radiation Chemistry

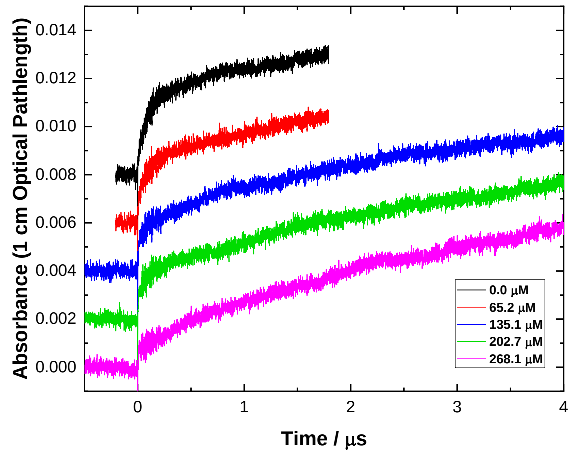
The results obtained with Cm(III) are of importance in the evaluation of redox potentials estimated from spectra. The values for the potentials of OH (-1.90V)(9) and e^-_{aq} (2.86V)(6) are not consistent with the estimates of -3.25V (10) for the Cm(IV)/(III) couple and +5.0V (11) for the Cm(III)/(II) couple.

An	λ_{max}(nm)	$t_{1/2}$(sec)
Cm(II)[d]	240	∿12 x 10^{-6}
Cm(IV)	260	∿20 x 10^{-6}



Radical Species	***k*** ($M^{-1}\ s^{-1}$)
e_{aq}^{-}	$(1.25 \pm 0.03) \times 10^{10}$
$H^{\bullet}$	$(5.16 \pm 0.37) \times 10^{8}$
$^{\bullet}OH$	$(1.69 \pm 0.24) \times 10^{9}$
$NO_3^{\bullet}$	$(4.83 \pm 0.09) \times 10^{7}$

$H^{\bullet}$

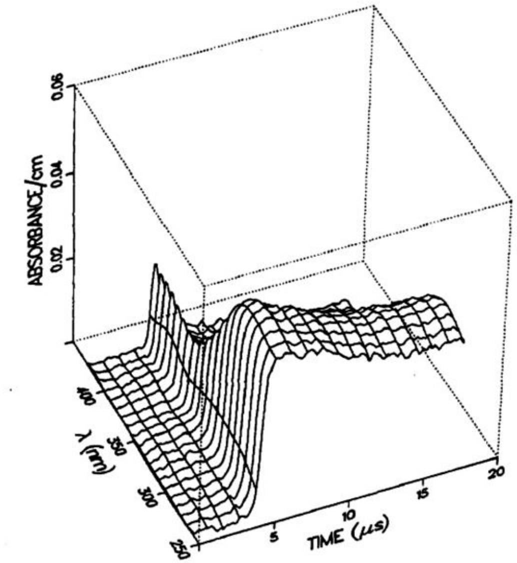


- Sullivan, Gordon, Mulac, Schmidt, Cohen, and Sjoblom, *Inorg. Nucl. Chem. Let.* **1976**, *12*, 599.
- Horne, Grimes, Zalupski, Meeker, Albrecht-Schönzart, Cook, and Mezyk, *Dalton Trans.* **2021**, *50*, 10853.

Radiation-Induced Berkelium(III) Redox Chemistry

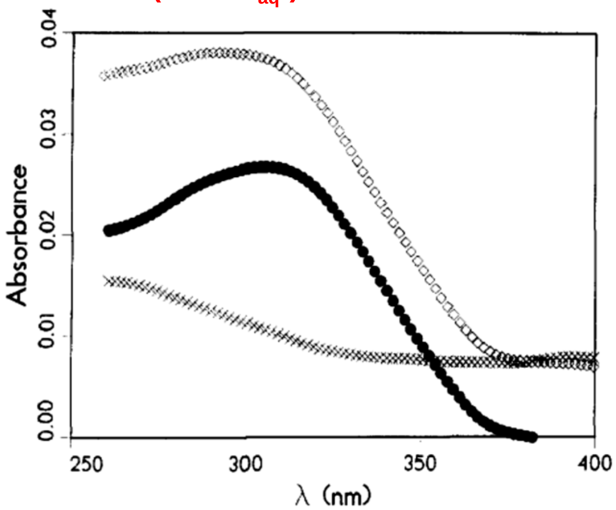
- Sullivan, Schmidt, Morss, Pippin, and Williams, *Inorg. Chem.*, **1988**, *27*, 597.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Layne, Cook, Albrecht-Schönzart, and Mezyk, *in preparation*.

Bk(III) Radiation Chemistry



Transient Absorption Signal of Bk(II)

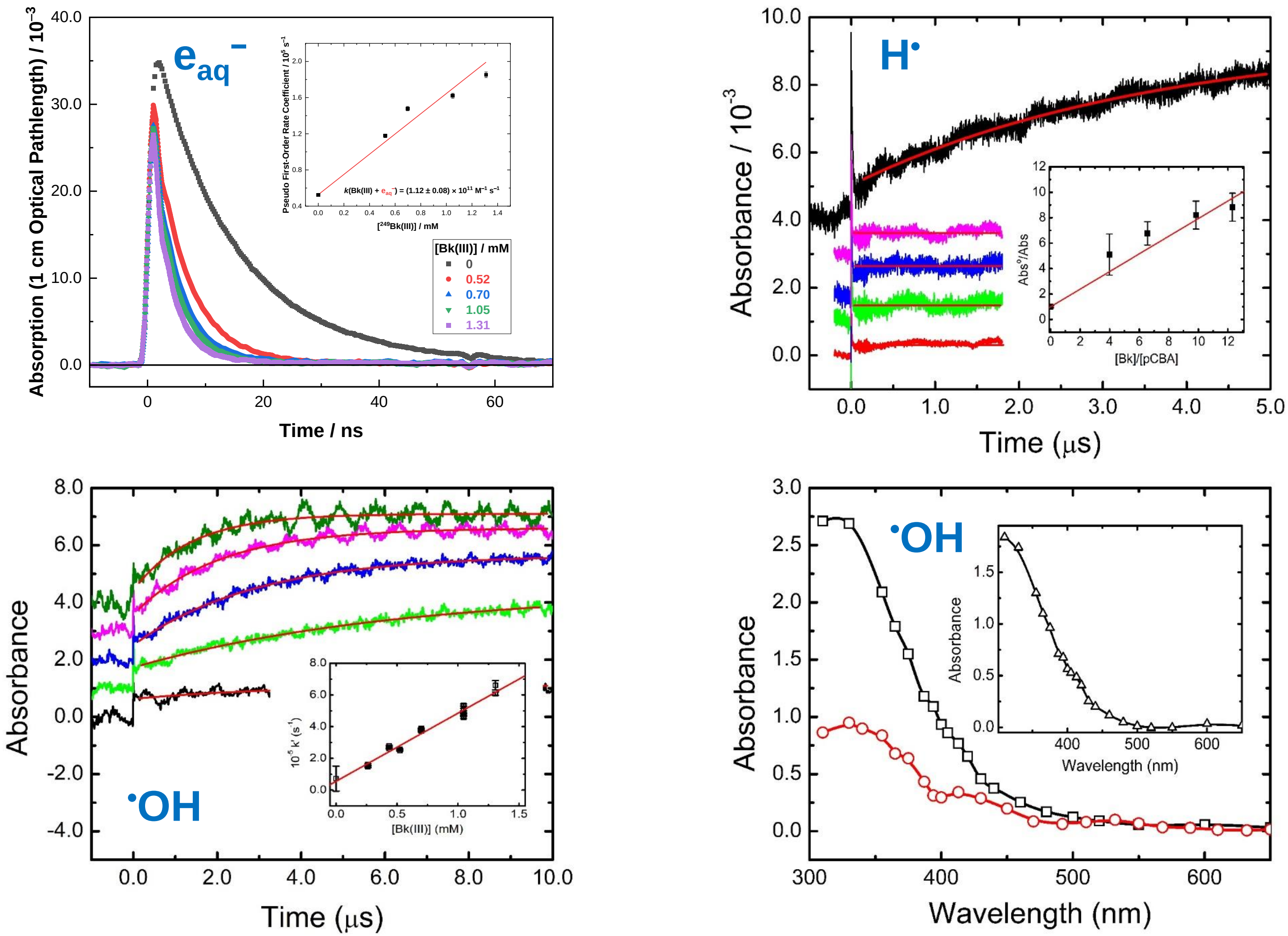
$k(Bk^{3+} + e_{aq}^{-}) = 1.12 \times 10^{9}\ M^{-1}\ s^{-1}$



Radical Species	***k*** ($M^{-1}\ s^{-1}$)
e_{aq}^{-}	$(1.12 \pm 0.08) \times 10^{11}$
$H^{\bullet}$	$(9.14 \pm 1.40) \times 10^{8}$
$^{\bullet}OH$	$(4.69 \pm 0.56) \times 10^{8}$

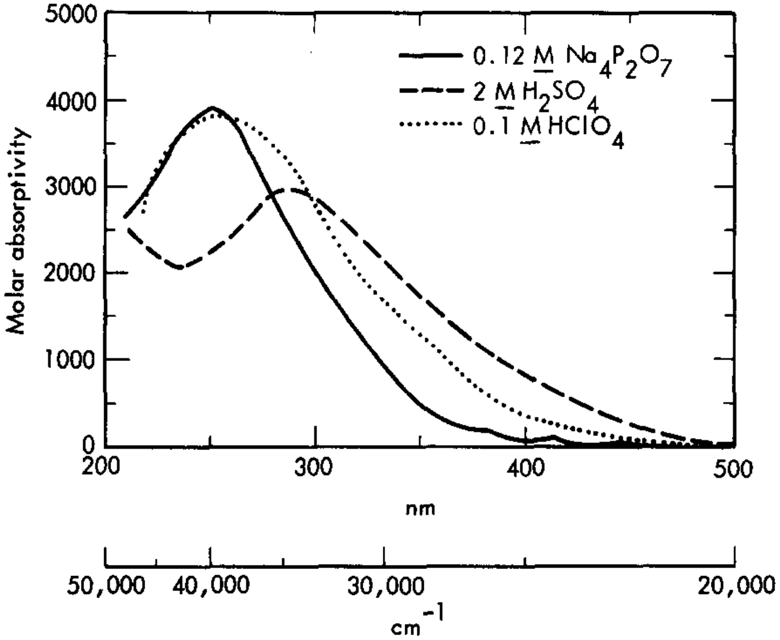
- Sullivan, Schmidt, Morss, Pippin, and Williams, *Inorg. Chem.*, **1988**, *27*, 597.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Layne, Cook, Albrecht-Schönzart, and Mezyk, *in preparation*.

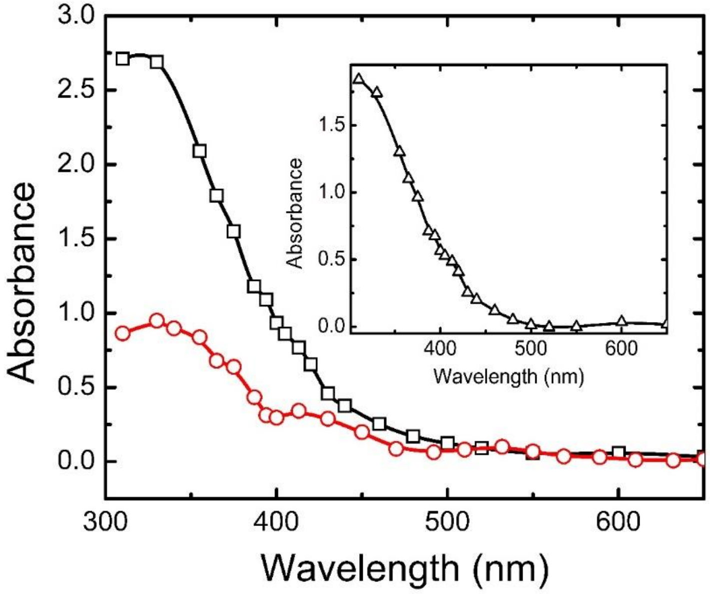
Bk(III) Radiation Chemistry



• Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Layne, Cook, Albrecht-Schönzart, and Mezyk, *in preparation*.

Bk(III) Radiation Chemistry





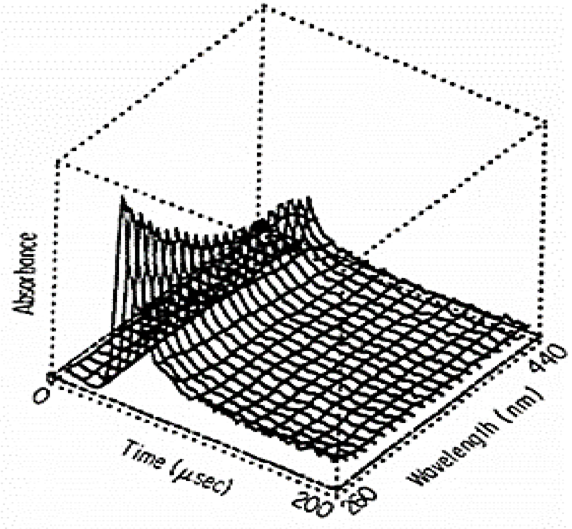
- From single-exponential fits of Bk(IV) decay, a **Bk(IV) lifetime = 29.9 ± 1.1 μs** was estimated.

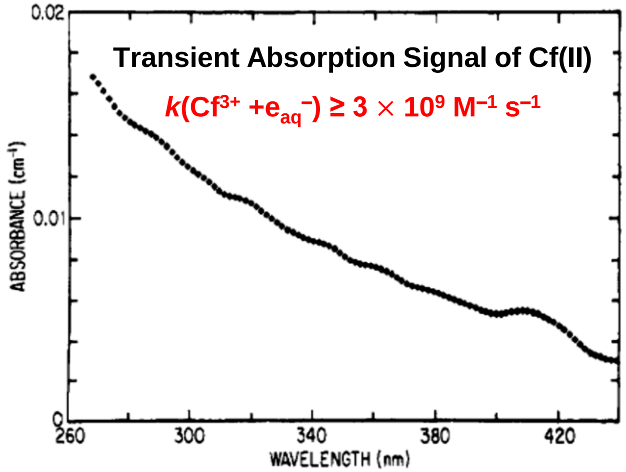
- Gutmacher, Bode, Lougheed, and Hulet, *J. Inorg. Nucl. Chem.*, **1973**, *35*. 979.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Layne, Cook, Albrecht-Schönzart, and Mezyk, *in preparation*.

Radiation-Induced Californium(III) Redox Chemistry

- Sullivan, Morss, Schmidt, Mulac, and Gordon, *Inorg. Chem.* **1983**, *22*, 2338.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Layne, Cook, Albrecht-Schönzart, and Mezyk, *in preparation*.

Cf(III) Radiation Chemistry

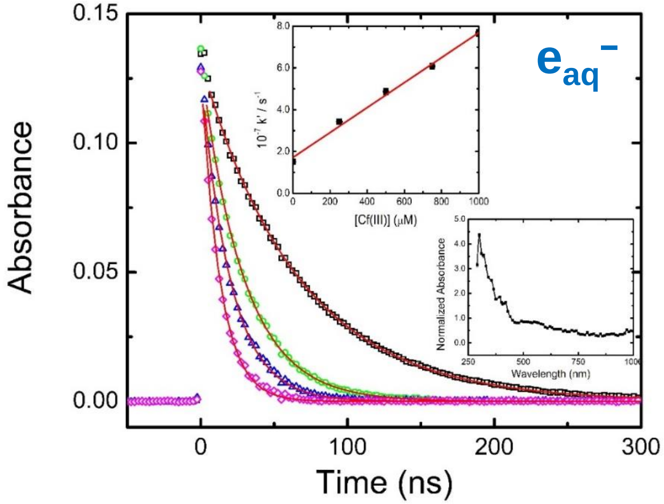


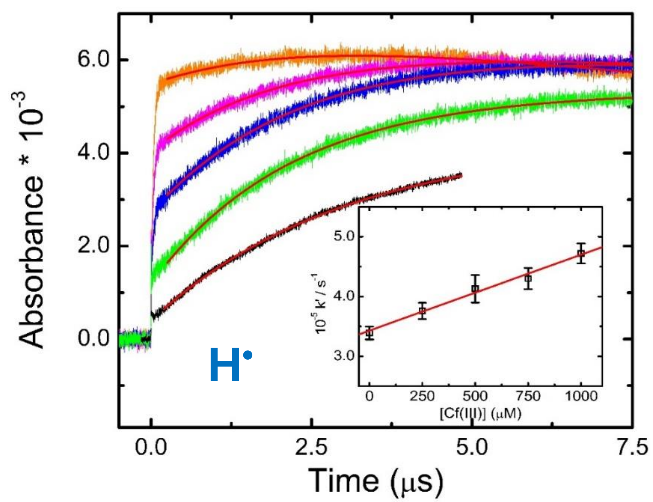


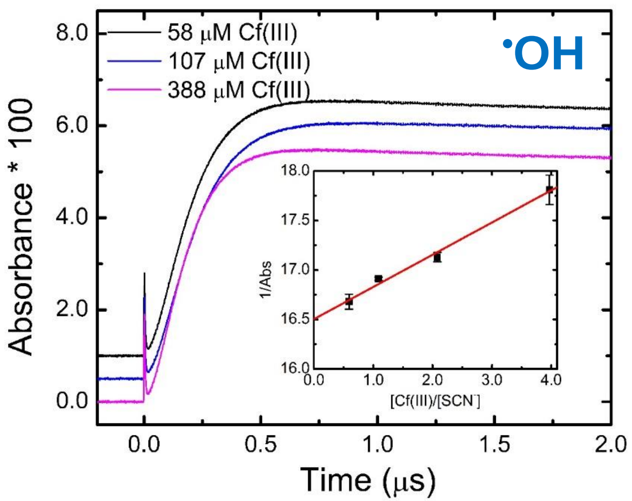
Radical Species	***k*** $(M^{-1}\ s^{-1})$
e_{aq}^{-}	$(5.97 \pm 0.10) \times 10^{10}$
$H^{\bullet}$	$(1.28 \pm 0.15) \times 10^{8}$
$^{\bullet}OH$	$(2.07 \pm 0.24) \times 10^{8}$
$NO_3^{\bullet}$	$(1.78 \pm 0.19) \times 10^{8}$

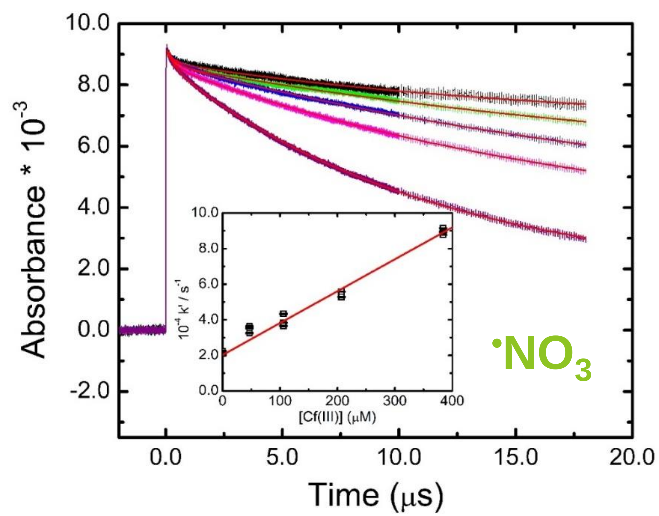
- Sullivan, Morss, Schmidt, Mulac, and Gordon, *Inorg. Chem.* **1983**, *22*, 2338.
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Cook, Wishart, Albrecht-Schönzart, and Mezyk, *ChemComm.*, **2022**, in review.

Cf(III) Radiation Chemistry









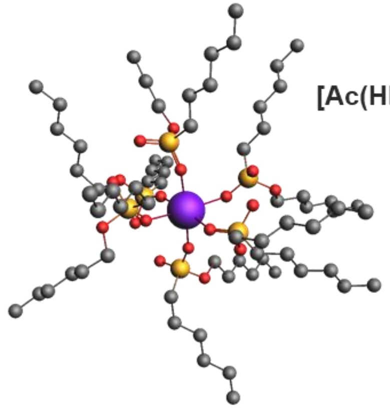
- Horne, Rotermund, Grimes, Sperling, Meeker, Zalupski, Peterman, Layne, Cook, Albrecht-Schönzart, and Mezyk, *in preparation*.

f-element Complexation

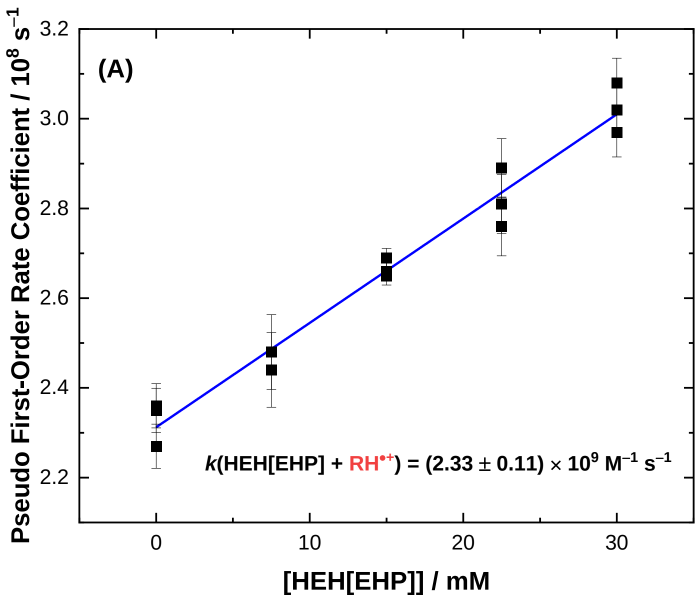
"To what extent does metal ion complexation influence the radiation chemistry of the coordinating ligand?"

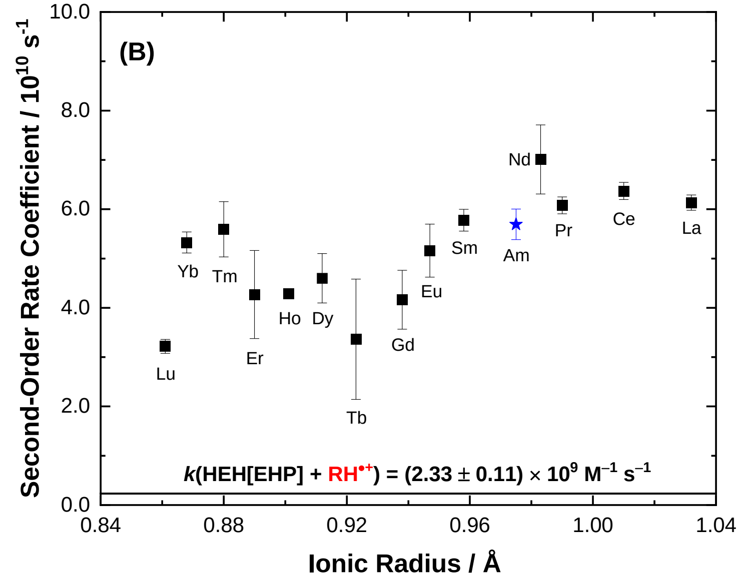
- Bhattacharyya and Kundu, Int. *J. Radiat. Phys. Chem.*, **1971**, *3*, 1.
- Kundu and Matuura, *Int. J. Radiat. Phys. Chem.*, **1975**, *7*, 565.
- Ilan and Czapski, *Biochimica et Biophysica Acta*, **1977**, *498*, 386.
- Buettner, Doherty, and Patterson, *Fed. Euro. Biochem. Soc.*, **1983**, *158 (1)*, 143.
- Toigawa, Peterman, Meeker, Grimes, Zalupski, Mezyk, Cook, Yamashita, Kumagai, Matsumura, Horne, *PCCP*, **2021**, *23*, 1343.

Size Matters



[Ac(HEH[EHP])$_6$]

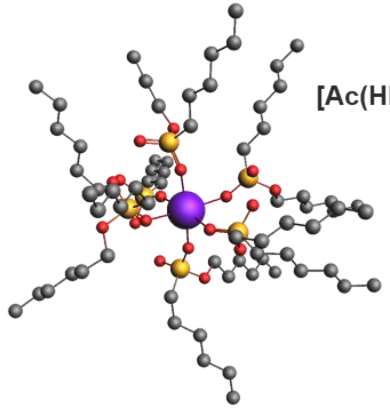




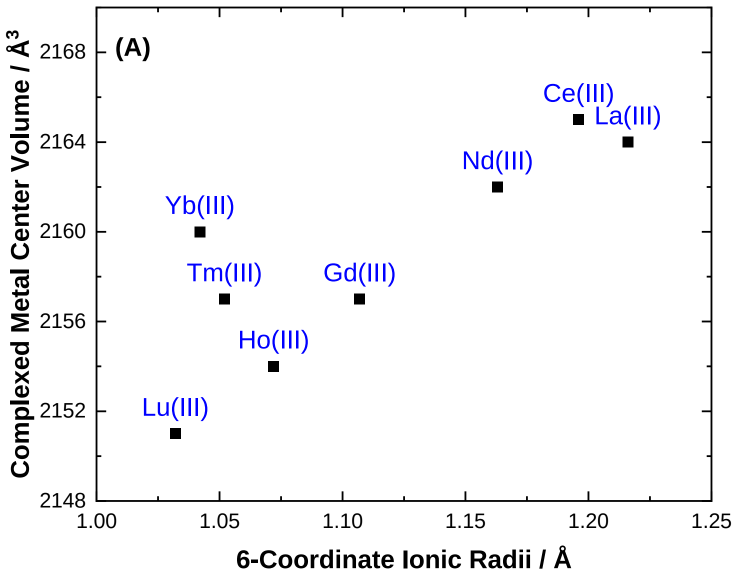
- **Methodology:** Δ[**HEH[EHP]**]/[**M{(HEH[EHP])$_2$}$_3$**] in 0.5 M DCM/*n*-dodecane; **RH•$^+$** decay measured at 800 nm over 200 ns using the *Brookhaven National Laboratory* (BNL) *Laser Electron Accelerator Facility* (LEAF).

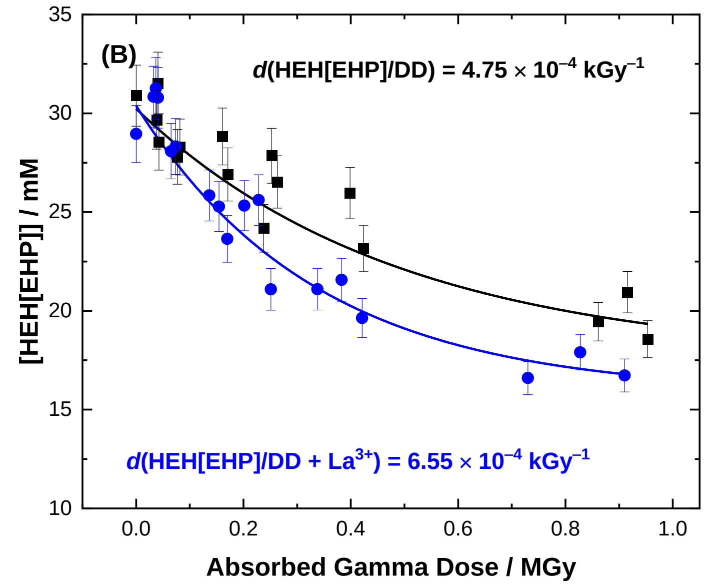
- Baxter, Cellis-Baros, Pilgrim, Cook, Grimes, *et al.*, *Dalton Trans.*, **2022**, under review.
- Tagawa, Hayashi, Yoshida, Washio, and Tabata, *Int. J. Radiat. Appl. Instrum., Part C*, **1989**, *34(4)*, 503.
- Yoshida, Ueda, Kobayashi, Shibata, and Tagawa, *Nucl. Instrum. Methods Phys. Res.*, *Sect. A*, **1993**, *327(1)*, 41.
- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.

Size Matters



[Ac(HEH[EHP])$_6$]





- **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-Baros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *Dalton Trans.*, **2022**, *in review*.

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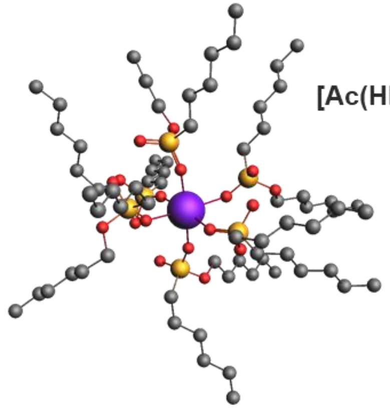

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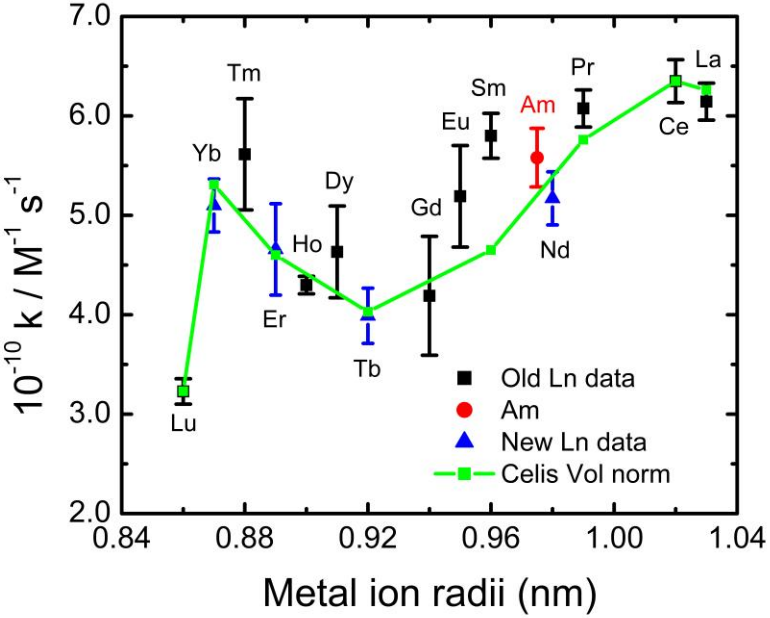

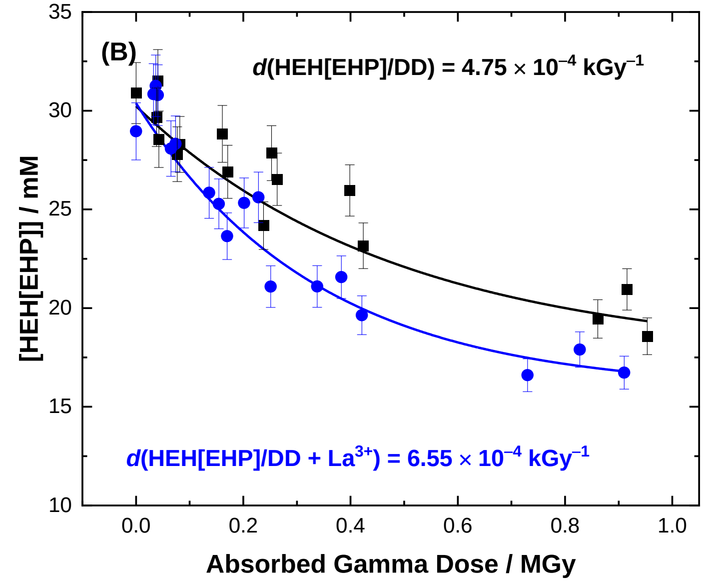

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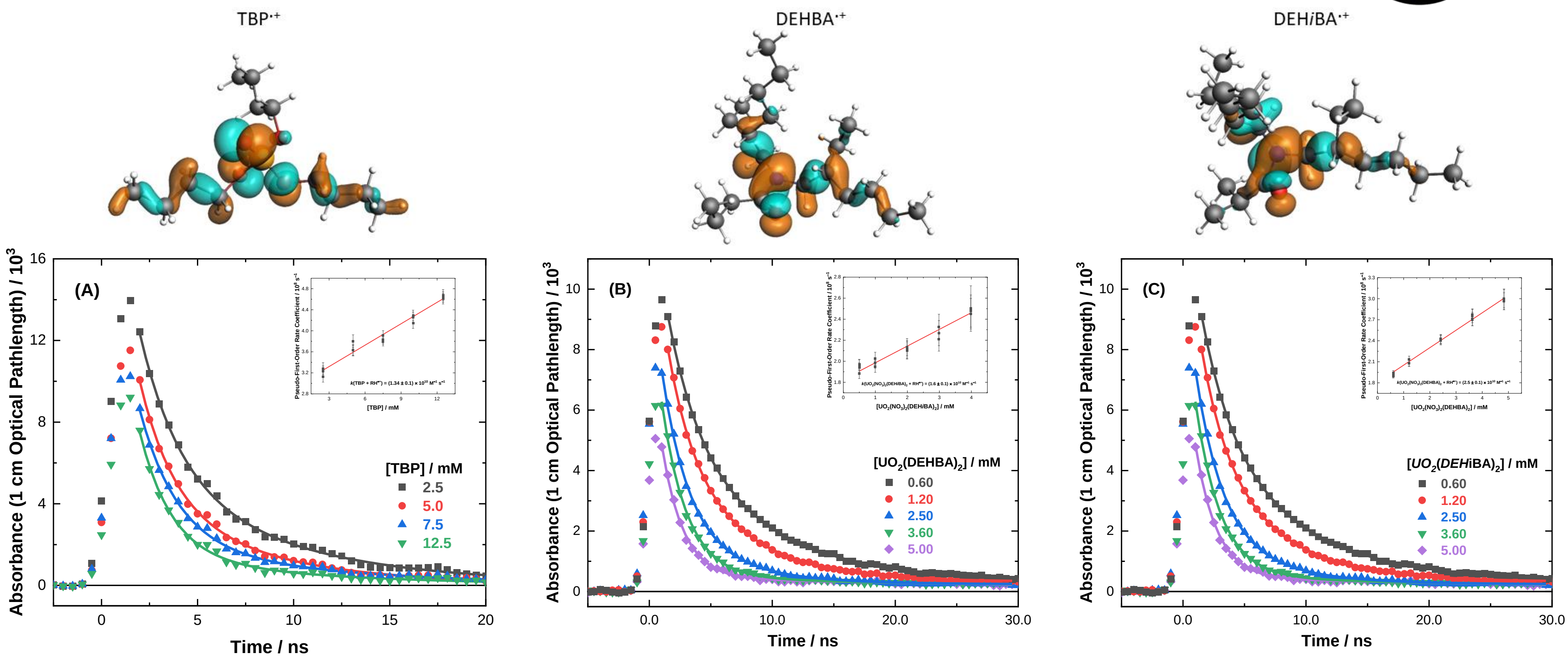
Structural Dependence



- UO_2^{2+} complexation had negligible effect on the reaction of **TBP** with **RH•⁺**, *k*(**TBP** + **RH•⁺**) = **(1.3 ± 0.1) × 10¹⁰ M⁻¹ s⁻¹**.
- For **DEHBA** and **DEHiBA**, UO_2^{2+} complexation afforded a **2.6x** and **1.4x** increase in their respective rate coefficients, respectively.

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Structural Dependence

$[UO_2(NO_3)_2(TBP)_2]^{\cdot+}$ $[UO_2(NO_3)_2(DEHBA)_2]^{\cdot+}$ $[UO_2(NO_3)_2(DEH\textit{i}BA)_2]^{\cdot+}$

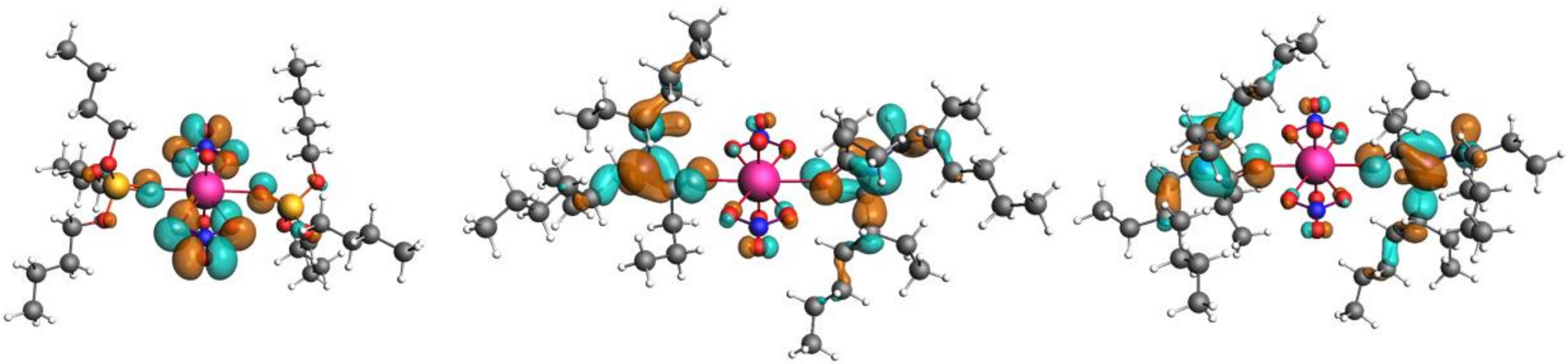

Table 1 Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet+}$ with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

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 + $[\text{Ligand}]^{\bullet+}$

Proton Transfer

$RH^{\bullet+}$ + Ligand → R• + $[\text{Ligand(+H)}]^{+}$

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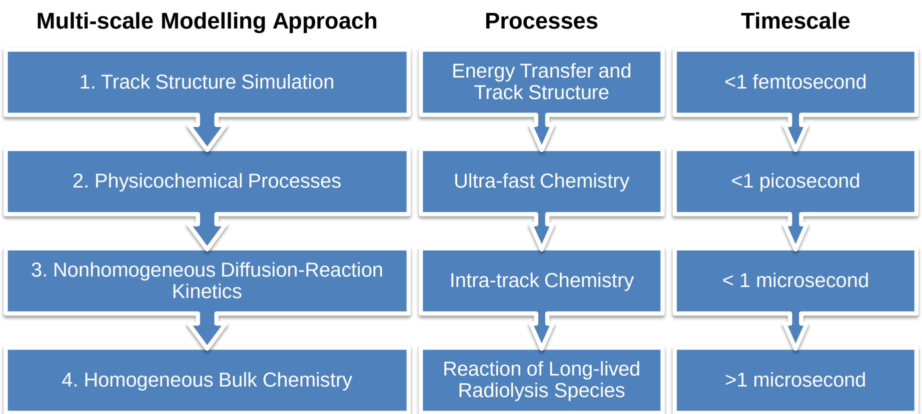
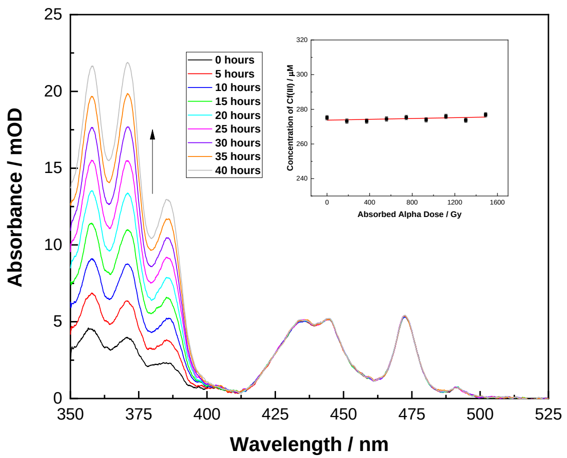
Conclusions

- Chemical kinetics were measured for **Cm(III)**/**Bk(III)**/**Cf(III)** redox reactions with highly reactive radiation-induced transients for the development of predictive, **multiscale models**.
- *f*-element ions have a profound effect on reaction kinetics, from changes in electron distribution to size.
- **The presented chemical reaction kinetics data provide important missing information that will augment current and future studies into the unique chemistry of these elements and their periodicity.**





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Acknowledgements

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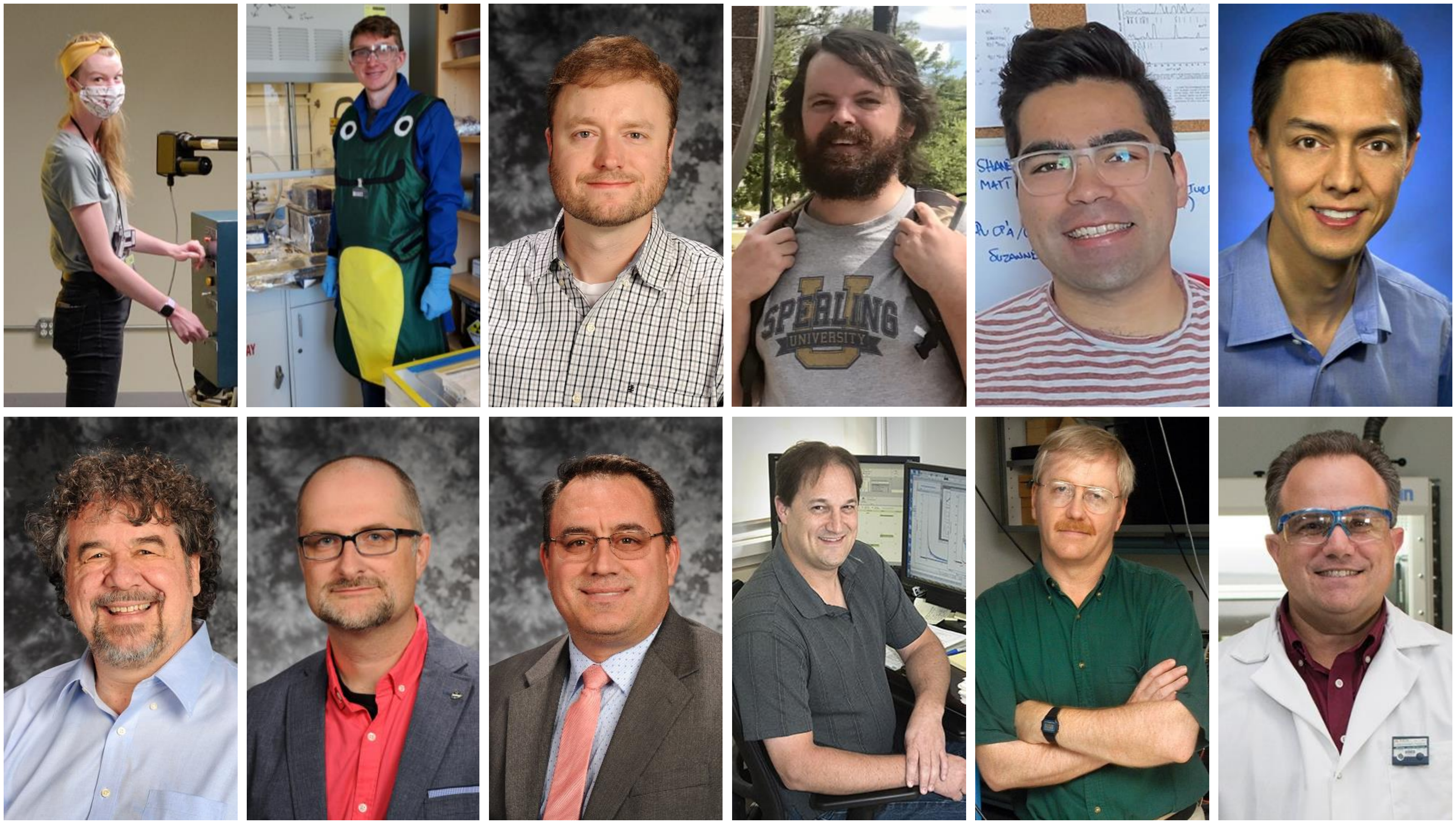

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