INL/CON-21-65480-Revision-0

Transamericium Radiation-Induced Redox Chemistry

December 2021

Gregory P Horne

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Idaho National Laboratory

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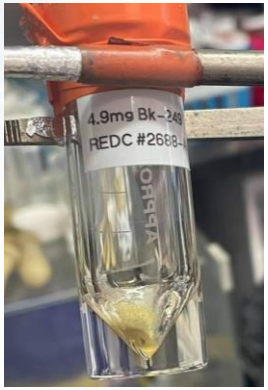
December 17th 2021

Gregory P. Horne
Center for Radiation Chemistry Research

Transamericium Radiation-Induced Redox Chemistry

INL/CON-21-01831



Pacifichem 2021: A Creative Vision for the Future

Team: David S. Meeker, Travis S. Grimes, Peter R. Zalupski, Andrew R. Cook, James F. Wishart, Stephen P. Mezyk, and Thomas E. Albrecht-Schönzart.

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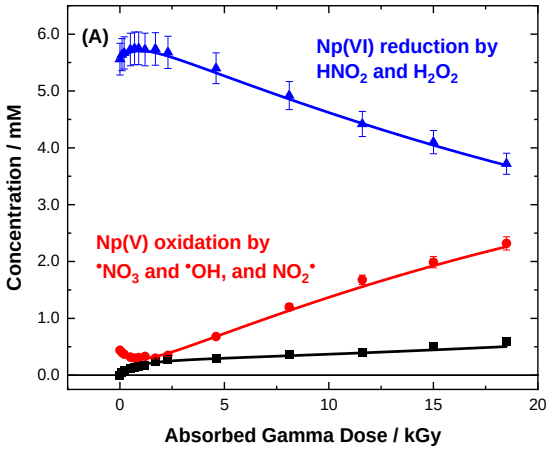
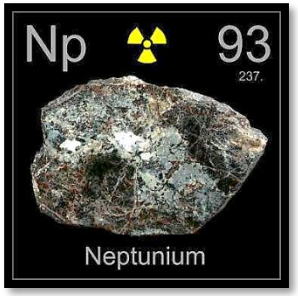
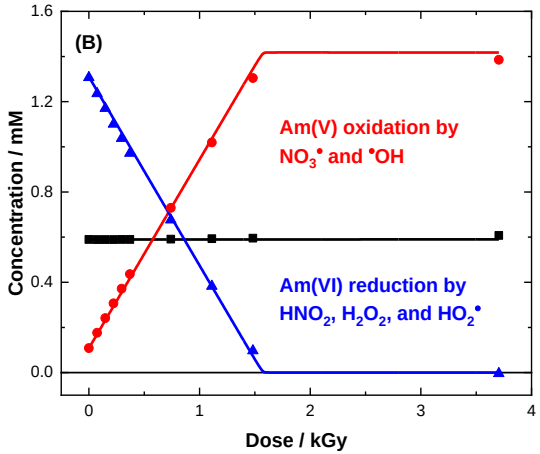
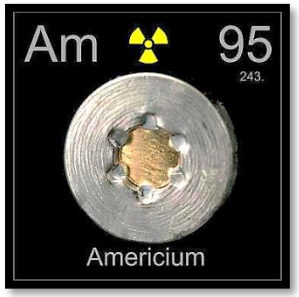
Actinide Radiation Chemistry

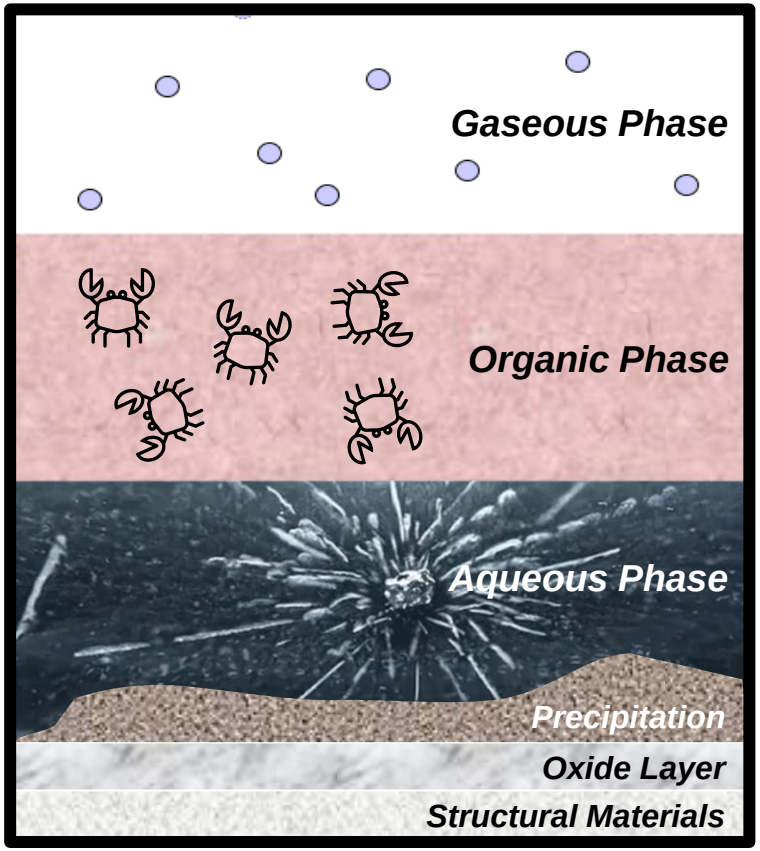








Solvent Extraction Reprocessing
Ligands/organic diluent:HNO_3/H_2O
(± additives)



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- G.P. Horne, T.S. Grimes, W.F. Bauer, C.J. Dares, S.M. Pimblott, S.P. Mezyk, and B.J. Mincher, *Inorg. Chem.* **2019**, *58*, 8551.

Radiation Chemistry in Nitrate and Nitric Acid Solutions

Water Radiolysis

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

Indirect Radiation Effects

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

$$NO_3^- + e_{aq}^- \rightarrow NO_3^{\bullet 2-}$$

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

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

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

$$N_2O_4 \rightarrow HNO_2 + HNO_3$$

Direct Radiation Effects

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

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

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

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

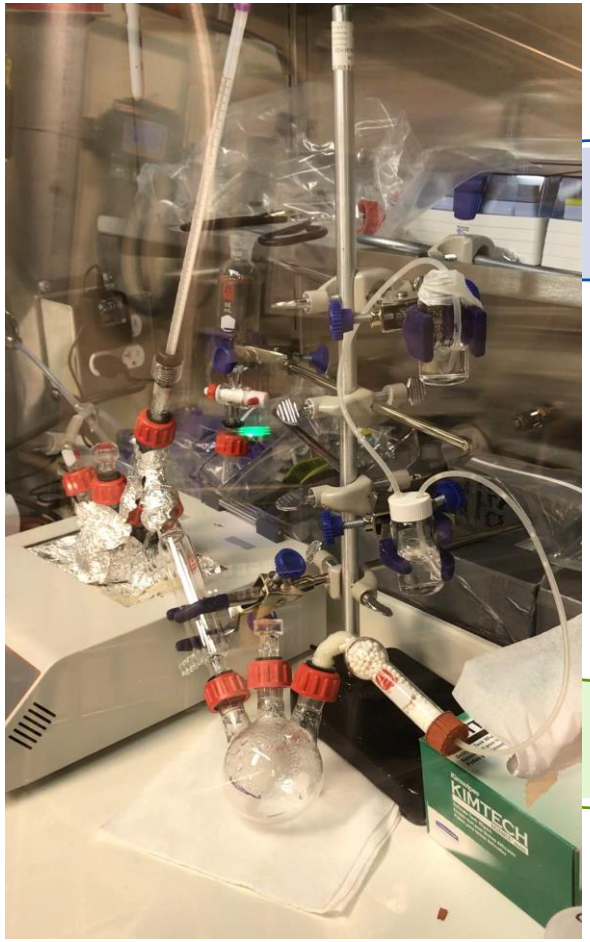
Key Transient Species

Oxidizing = $^\bullet OH$ and $^\bullet NO_3$

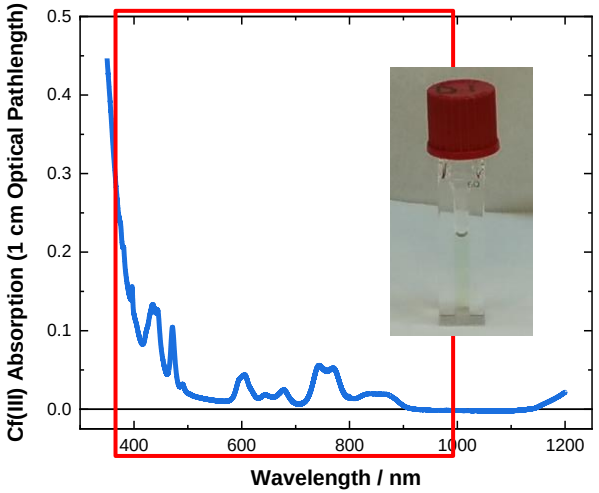
Reducing = e_{aq}^- and $H^\bullet$

- G.V. Buxton, C.L. Greenstock, W.P. Helman, and A.B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Y. Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

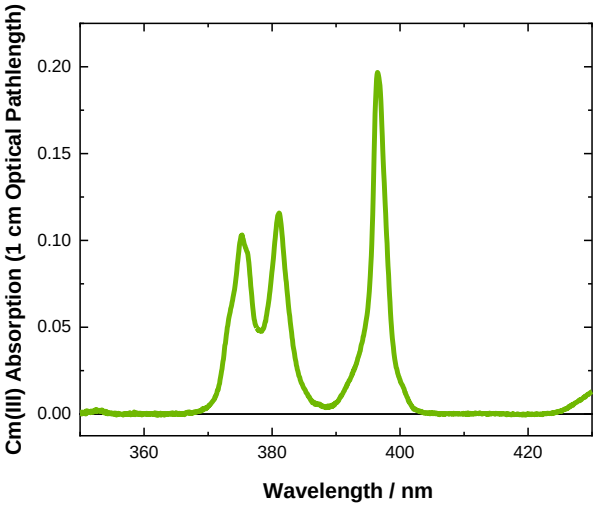
^{248}Cm and ^{249}Cf Sample Preparation

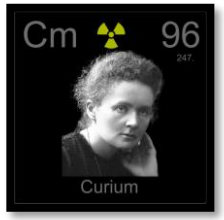


^{249}Cf(III)



^{248}Cm(III)





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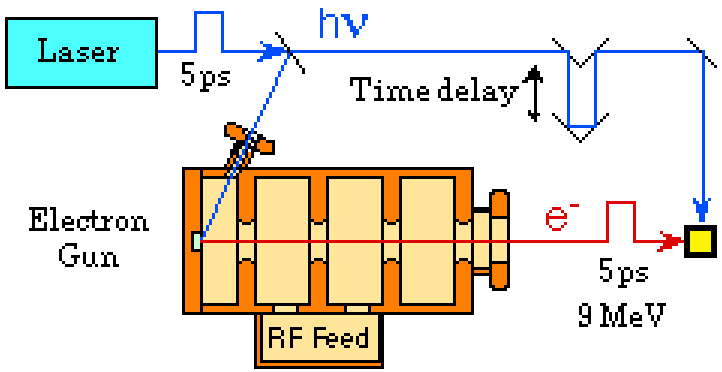
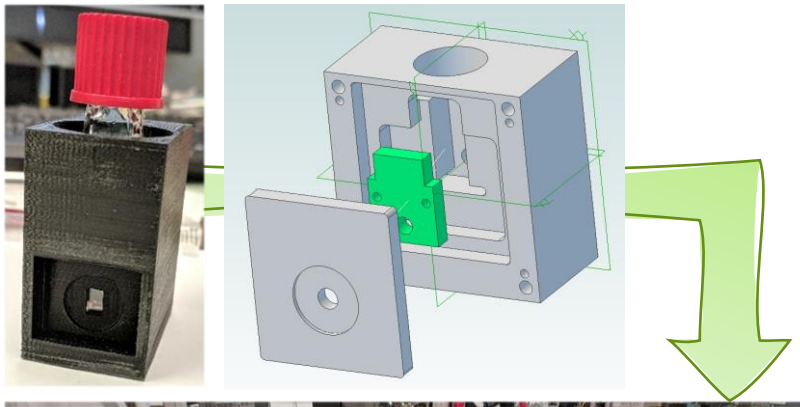
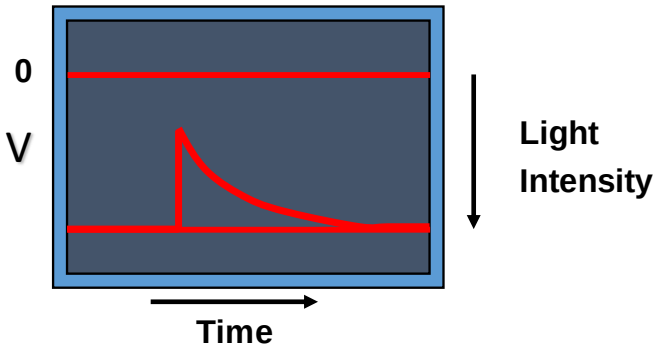
Pulsed Electron Radiolysis





Transients are detected by optical absorption changes.



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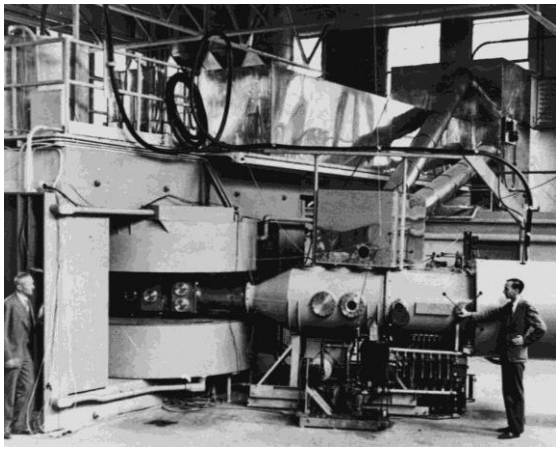
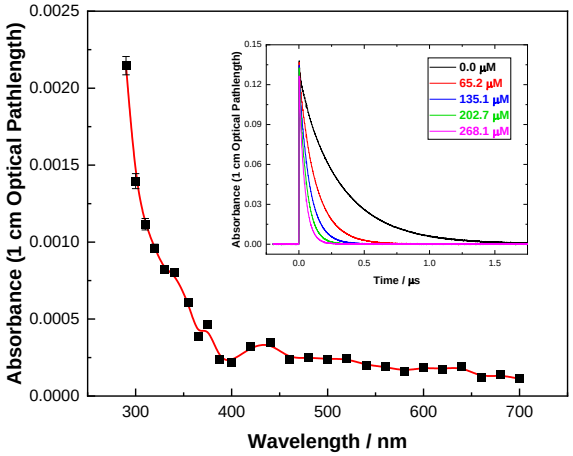
Cm(III) Radiation Chemistry

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.

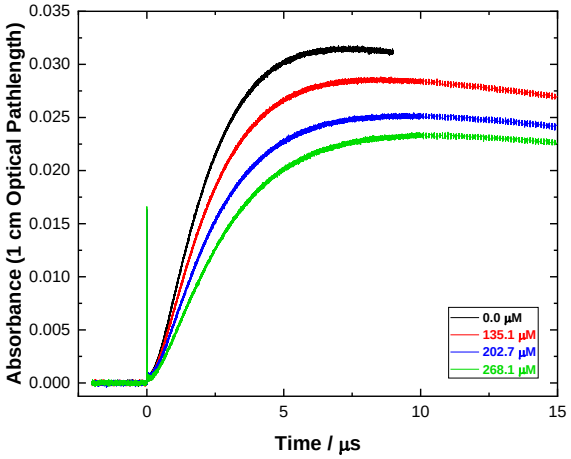
An	λ_{max}(nm)	$t_{1/2}$(sec)
Cm(II)[d]	240	∿12 x 10^{-6}
Cm(IV)	260	∿20 x 10^{-6}



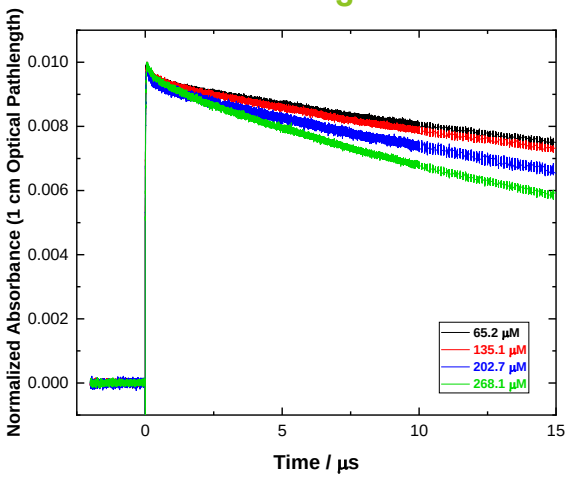
e_{aq}^-



$^{\bullet}OH$



$^{\bullet}NO_3$

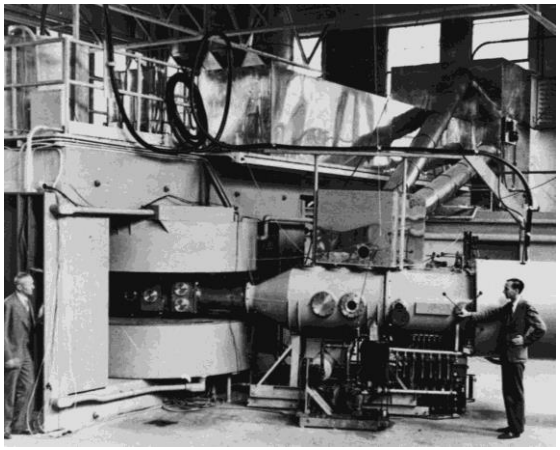


- J.C. Sullivan, S. Gordon, W.A. Mulac, K.H. Schmidt, D. Cohen, and R. Sjoblom, *Inorg. Nucl. Chem. Let.* **1976**, *12*, 599.
- G.P. Horne, T.S. Grimes, P.R. Zalupski, D.S. Meeker, T.E. Albrecht-Schönzart, A.R. Cook, and S.P. Mezyk, *Dalton Trans.* **2021**, *50*, 10853.

Cm(III) Radiation Chemistry

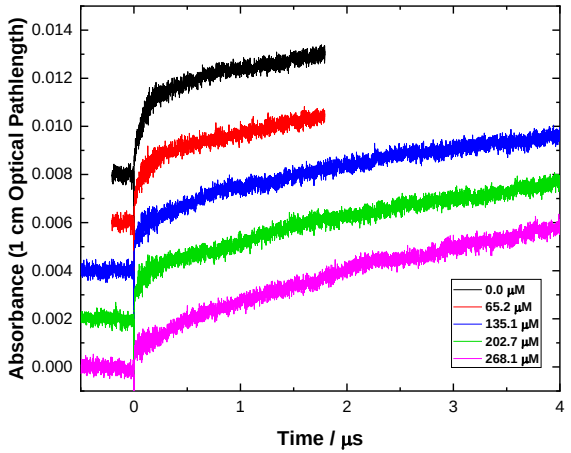
The results obtained with Cm(III) are of importance in the evaluation of redox potentials estimated from spectra. The values for the potentials of OH (-1.90V)(9) and e^-_{aq} (2.86V)(6) are not consistent with the estimates of -3.25V (10) for the Cm(IV)/(III) couple and +5.0V (11) for the Cm(III)/(II)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

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



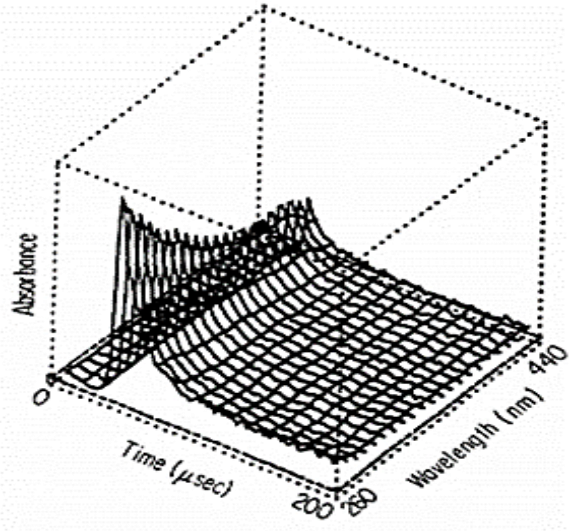
Radical Species	k (M^{-1} s^{-1})
e_{aq}^-	(1.25 ± 0.03) × 10^{10}
$H^\bullet$	(5.16 ± 0.37) × 10^{8}
$^\bullet OH$	(1.69 ± 0.24) × 10^{9}
$NO_3^\bullet$	(4.83 ± 0.09) × 10^{7}

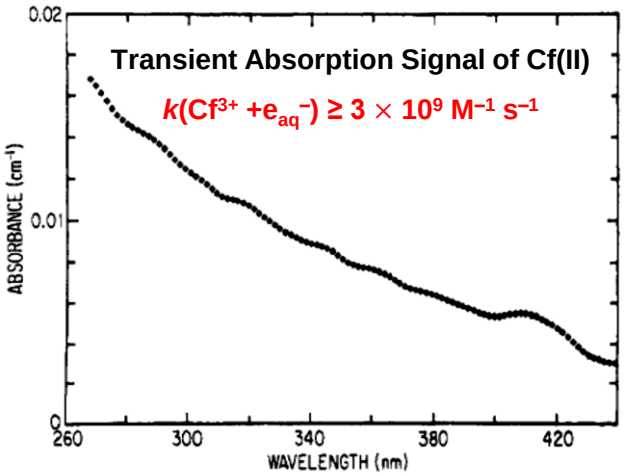
$H^\bullet$



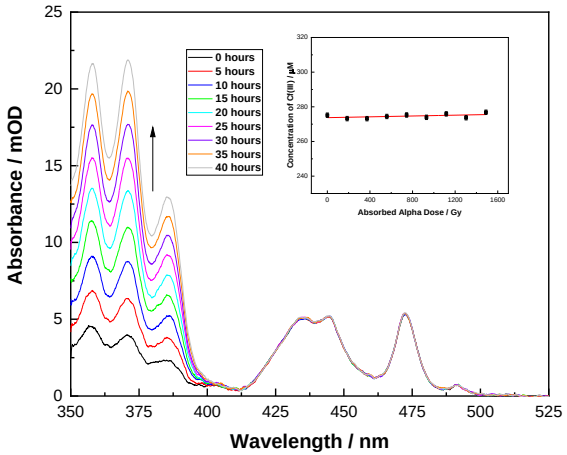
- J.C. Sullivan, S. Gordon, W.A. Mulac, K.H. Schmidt, D. Cohen, and R. Sjoblom, *Inorg. Nucl. Chem. Let.* **1976**, *12*, 599.
- G.P. Horne, T.S. Grimes, P.R. Zalupski, D.S. Meeker, T.E. Albrecht-Schönzart, A.R. Cook, and S.P. Mezyk, *Dalton Trans.* **2021**, *50*, 10853.

Cf(III) Radiation Chemistry





Radical Species	k ($M^{-1}\ s^{-1}$)
e_{aq}^-	$(7.11 \pm 0.18) \times 10^{10}$
$H^\bullet$	$(2.61 \pm 0.54) \times 10^8$
$^\bullet OH$	$(7.2 \pm 0.56) \times 10^8$
$NO_3^\bullet$	$(2.0 \pm 0.5) \times 10^8$



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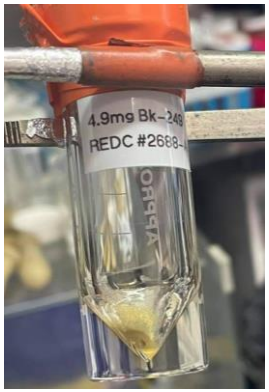
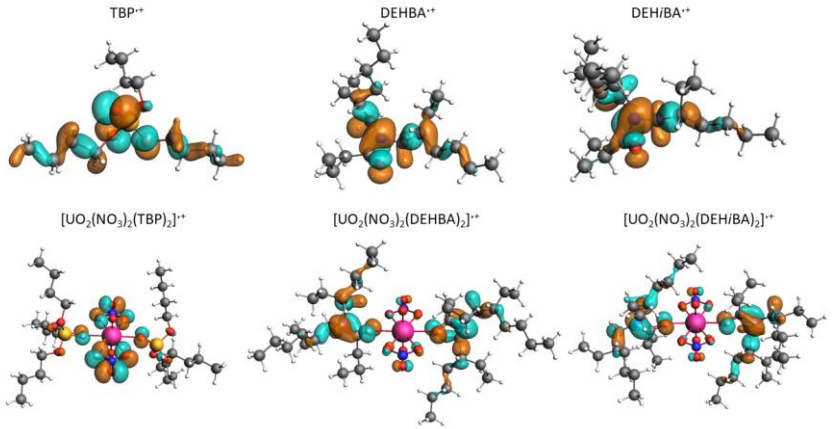
Conclusions and Future Research

- Rate coefficients were measured for **Cm(III)**/**Cf(III)** radiation-induced redox processes for of with key transients from the radiolysis of HNO_3 solutions.
- Reaction kinetics will be employed in multi-scale models for the prediction of steady-state **Cm(III)**/**Cf(III)** radiolytic behavior.



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



Canonical Kohn-Sham molecular orbitals of the electron holes in the geometry-optimized radical cation species for TBP, DEHBA, and DEH*i*BA.

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Acknowledgements

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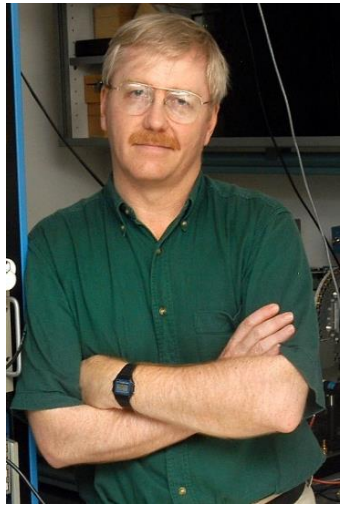

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