INL/CON-22-65844-Revision-0

The Role of Pulse Radiolysis in Advanced Nuclear Fuel Cycles

February 2022

Gregory P Horne

Changing the World's Energy Future

Idaho National Laboratory

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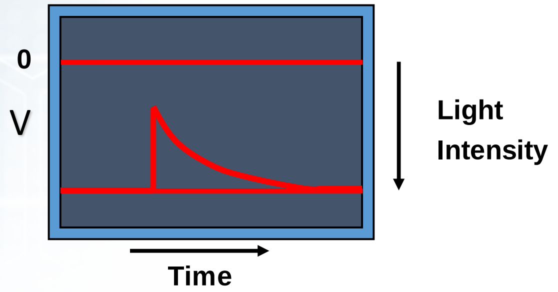
February 10th 2022

Gregory P. Horne
Center for Radiation Chemistry Research

The Miller Trust FOR RADIATION CHEMISTRY

The Role of Pulse Radiolysis in Advanced Nuclear Fuel Cycles

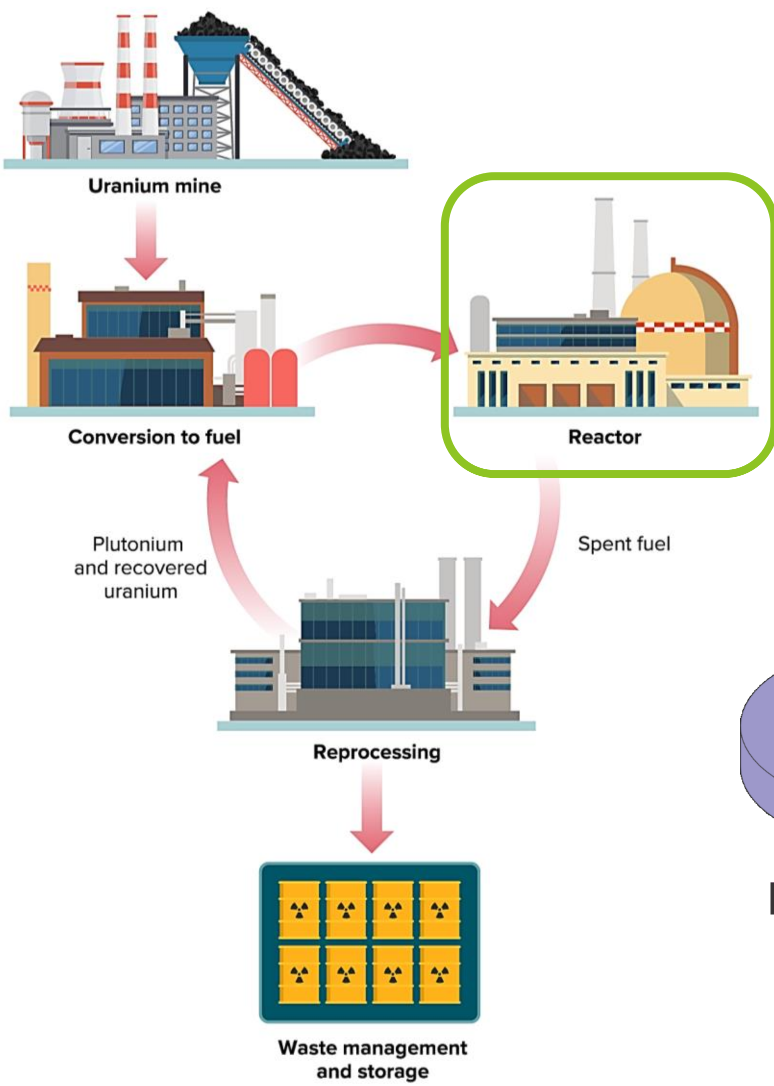
INL/CON-22-01965

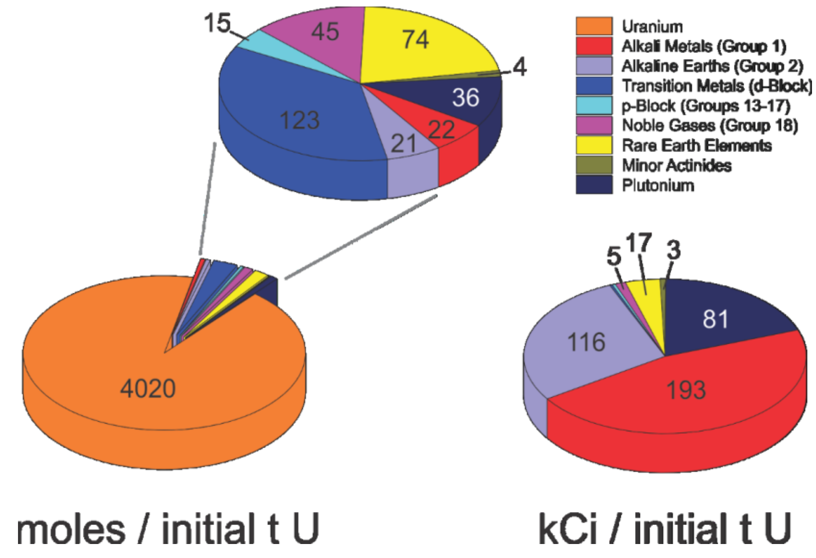


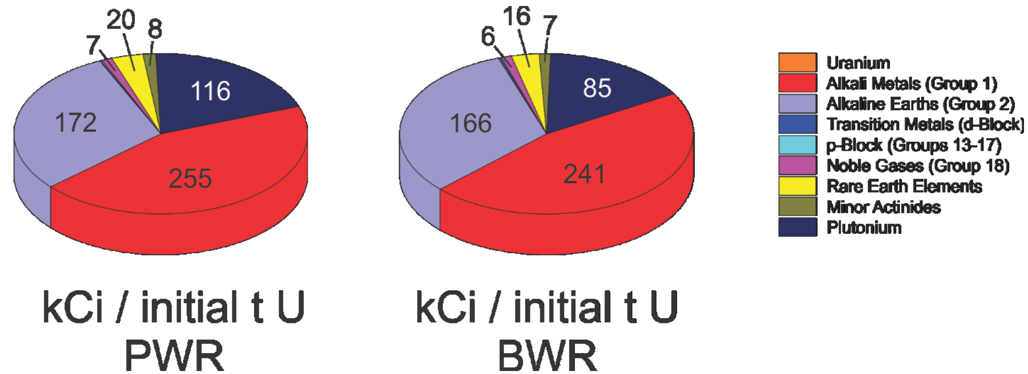
The Miller Online Workshop on Radiation Chemistry
10-12 February 2022

Idaho National Laboratory

Used Nuclear Fuel

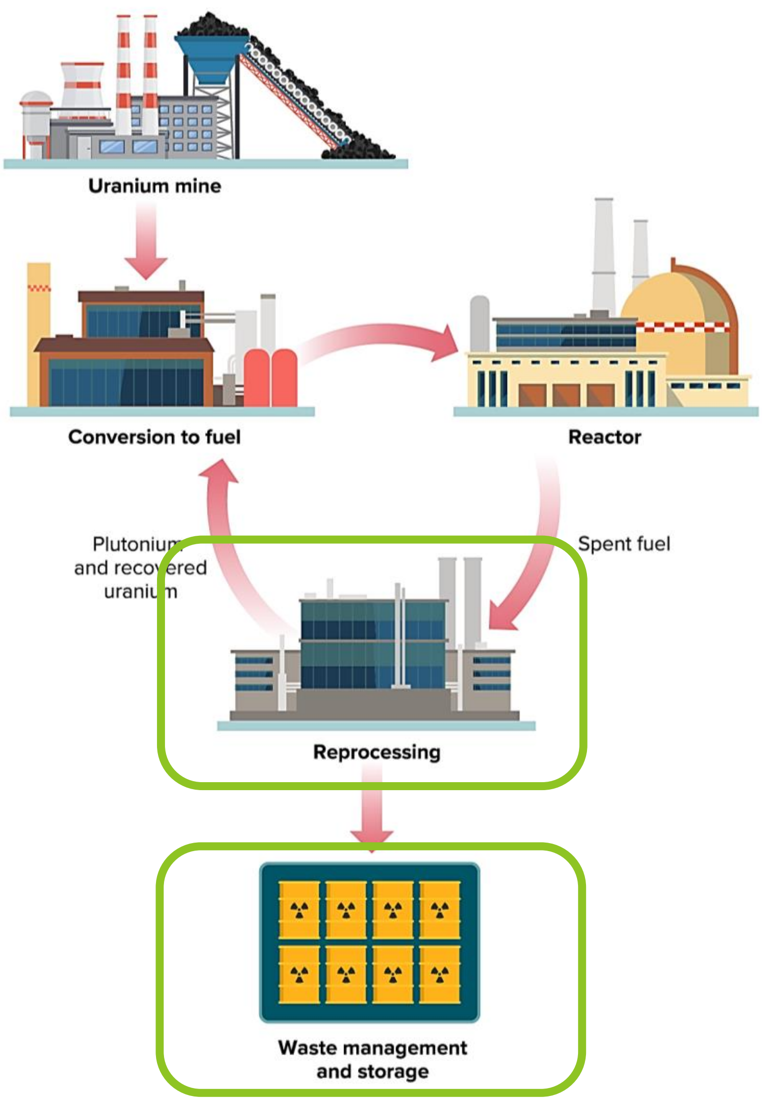


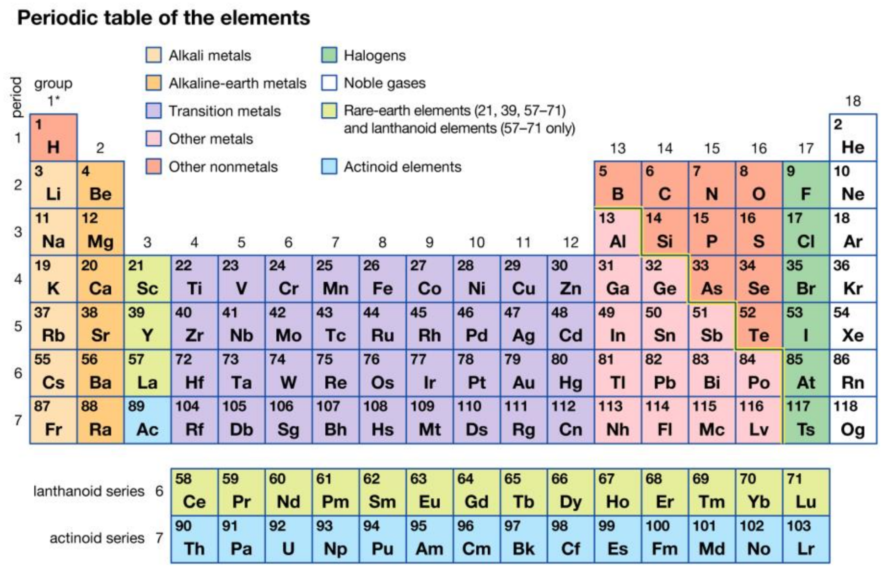




- Choppin, Liljenzin and Rydberg, Radiochemistry and Nuclear Chemistry. Woburn, Massachusetts, Butterworth-Heinemann, **2002**.
- NRC, Characteristics for the Representative Commercial Spent Fuel Assembly for Preclosure Normal Operations. Washington, DC, US Nuclear Regulatory Commission, **2007**.

Used Nuclear Fuel





Periodic table of the elements

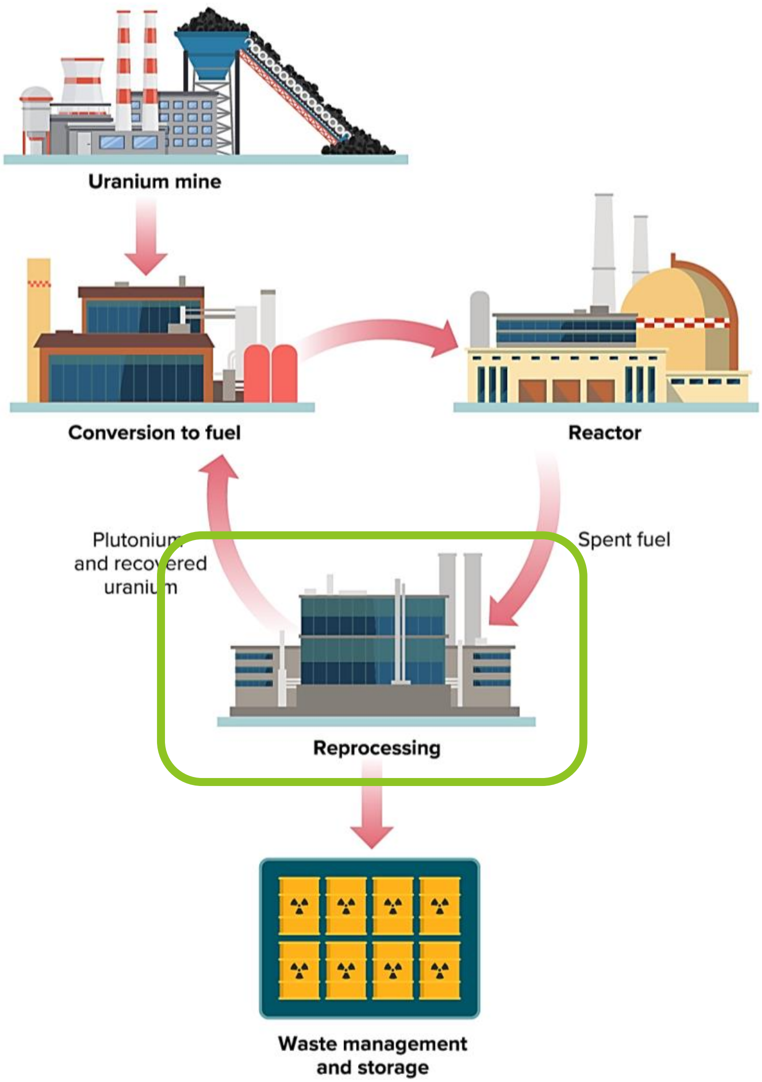
- Alkali metals
- Alkaline-earth metals
- Transition metals
- Other metals
- Other nonmetals
- Halogens
- Noble gases
- Rare-earth elements (21, 39, 57–71) and lanthanoid elements (57–71 only)
- Actinoid elements

period \ group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- https://today.tamu.edu/wp-content/uploads/2020/05/NESC_NuclearWaste_04May2020.jpg
- https://cdn.britannica.com/45/7445-050-BB332C27/version-periodic-table-elements.jpg

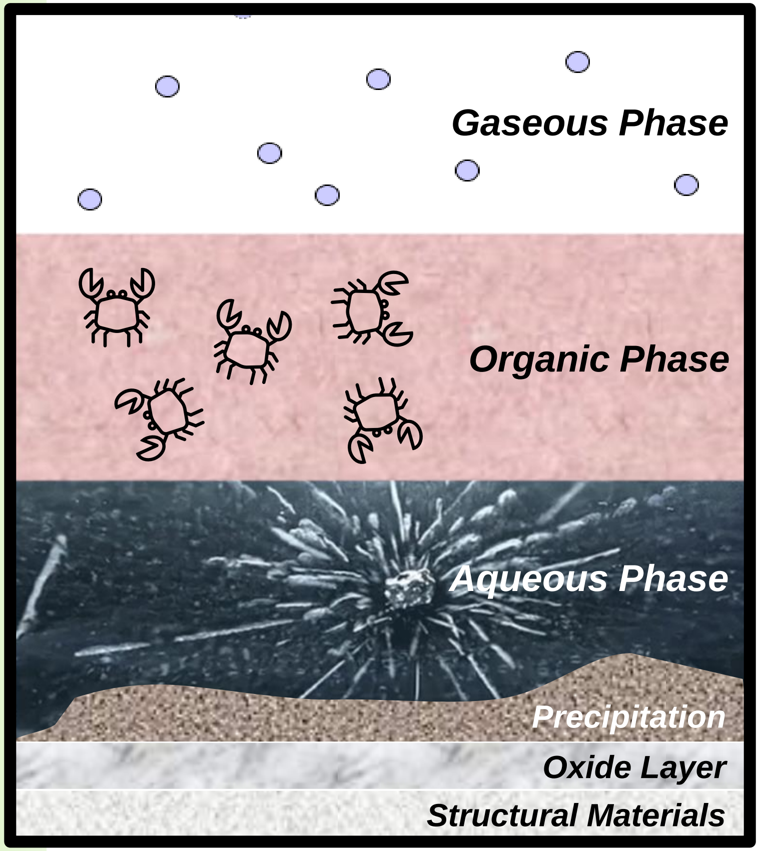
Reprocessing Used Nuclear Fuel



Solvent Extraction Reprocessing

Ligands/organic diluent:HNO_3/H_2O

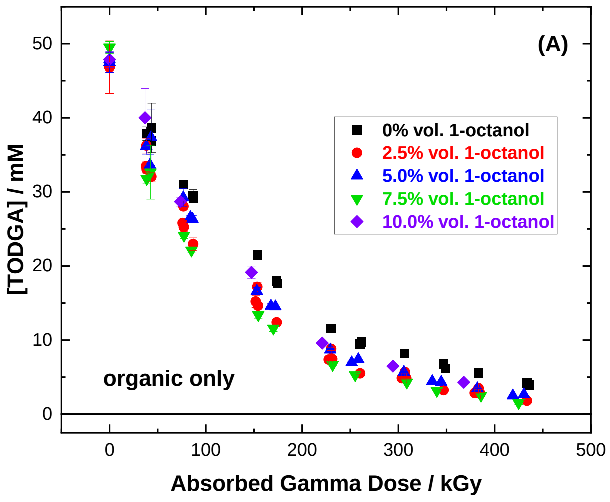
(± additives)

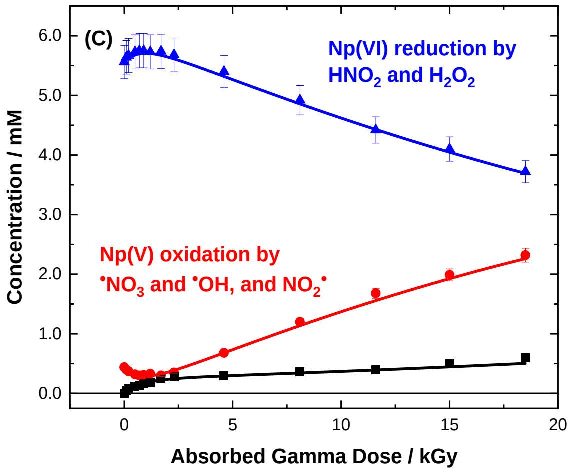


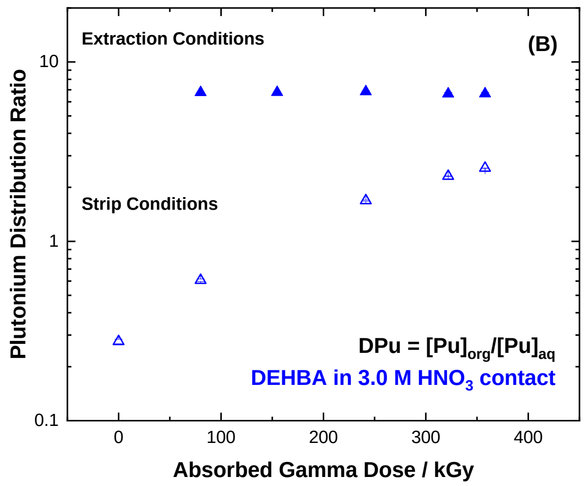
- Strategies and Considerations for the Back End of the Fuel Cycle, Nuclear Technology Development and Economics, NEA No. 7469, **2021**.
- Bruffey *et al.*, Innovative Separations R&D Needs for Advanced Fuel Cycles Workshop, August 30-September 1, 2021. Report for the US Department of Energy, Office of Nuclear Energy Workshop on Innovative Separations R&D Needs for Advanced Fuel Cycles, **2022**, under review.

Reprocessing Radiation Challenges

- **Destruction of active molecules**
- **Degradation product formation**
- **Metal ion redox chemistry**







- Horne, Zarzana, Rae, Cook, Mezyk *et al.*, *PCCP*, **2020**, *22*, 24978.
- Horne, Zarzana, Grimes, Rae, Ceder *et al.*, *Dalton Trans.*, **2019**, *48*, 14450.
- Horne, Grimes, Mincher, and Mezyk, *J. Phys. Chem. B*, **2016**, *120 (49)*, 12643.

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

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

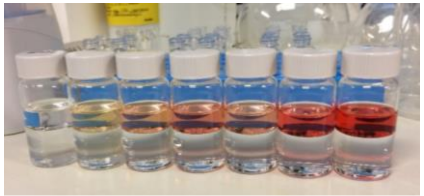
$HNO_3 \rightsquigarrow HNO_3^* \rightarrow HNO_2 + O$

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

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

Alkane Radiolysis

$R\text{-}CH_3 \rightsquigarrow e^-, R\text{-}CH_3^{\bullet +}, R\text{-}CH_2^{\bullet}, {}^{\bullet}CH_3, H^{\bullet}, H_2$



- 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

Radiolysis Products of Concern in Reprocessing

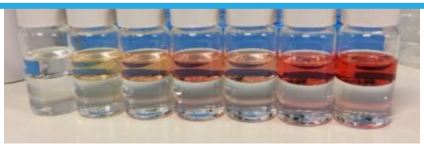
$H^\bullet$, $^\bullet OH$, and H_2O_2 from H_2O

$^\bullet NO_3$ and HNO_2 from HNO_3

e^-, $R\text{-}CH_3^{\bullet+}$, $R\text{-}CH_2^\bullet$, and $H^\bullet$ from **organic diluent**

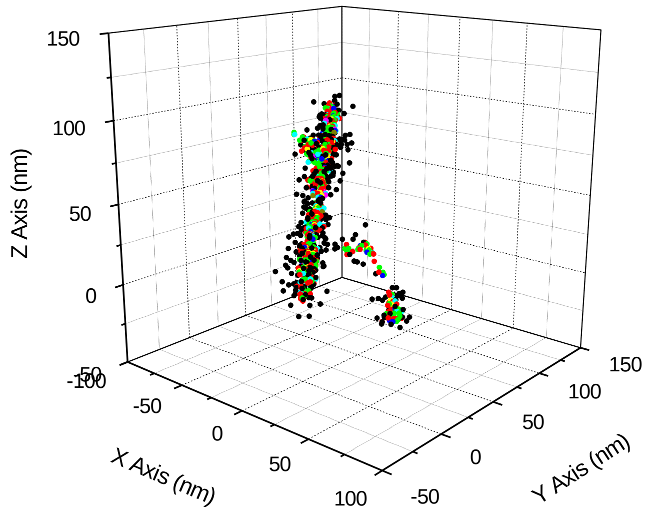
$_3$, $H^\bullet$, H_2

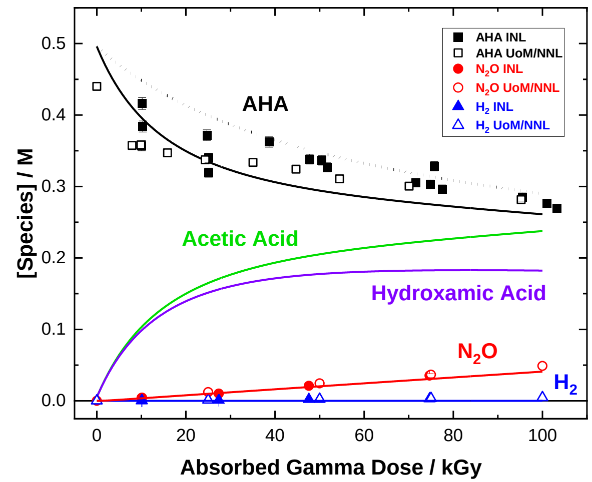
$N_2O_4 \rightarrow HNO_2 + HNO_3$



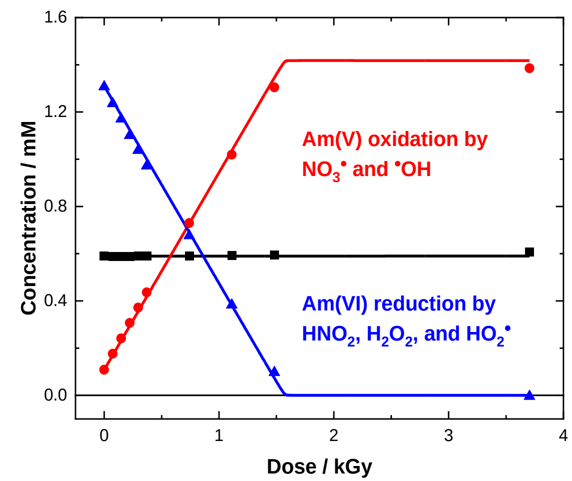
- Buxton, Greenstock, Helman, and Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.
- Katsumura, The Chemistry of Free Radicals: N-Centered Radicals, John Wiley & Sons, Chichester, **1998**.

The Dream – A Complete Multiscale Model



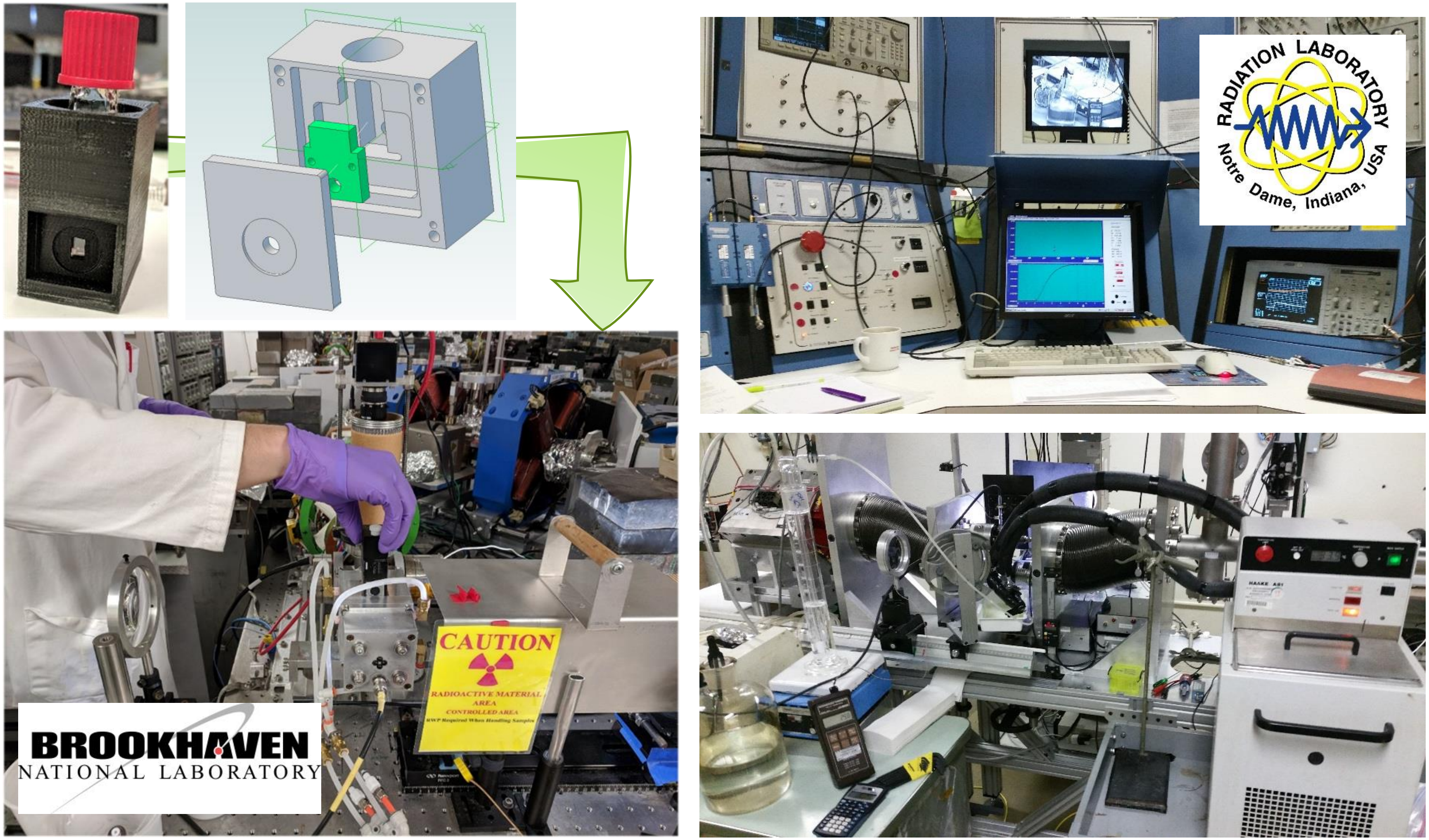


Multi-scale Modelling Approach	Processes	Timescale
1. Track Structure Simulation	Energy Transfer and Track Structure	<1 femtosecond
2. Physicochemical Processes	Ultra-fast Chemistry	<1 picosecond
3. Nonhomogeneous Diffusion-Reaction Kinetics	Intra-track Chemistry	< 1 microsecond
4. Homogeneous Bulk Chemistry	Reaction of Long-lived Radiolysis Species	>1 microsecond

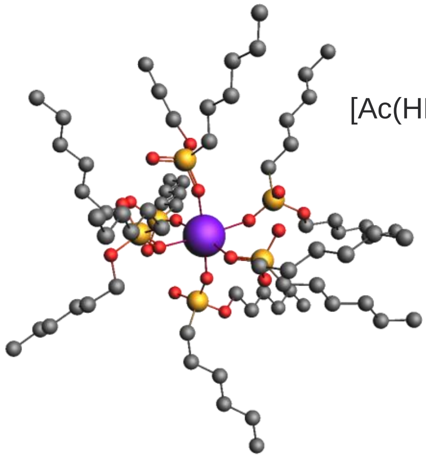


- Clifford, Green, Oldfield, Pilling, and Pimblott, *J. Chem. Soc., Faraday Trans.*, **1986**, *82*, 2673.
- Pimblott, LaVerne, and Mozumder, *J. Phys. Chem.*, **1996**, *100*, 8595.
- Horne, Donoclift, Sims, Orr, and Pimblott, *J. Phys. Chem. B.*, **2016**, *120*, 11781.

How do we get here?...Pulse Radiolysis

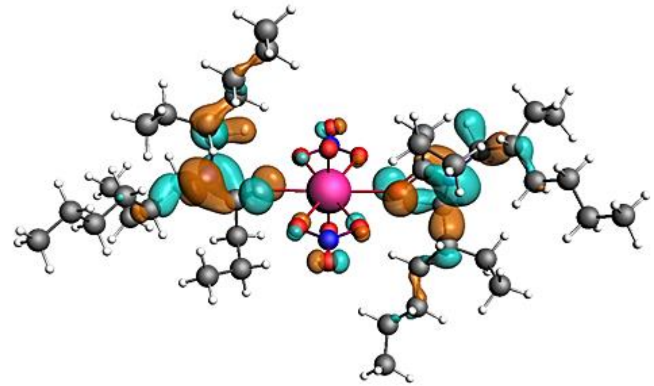


- Wishart, Cook, and Miller, *Rev. Sci. Instrum.* **2004**, *75 (11)*, 4359.
- Hug, Wang, Schoneich, Jiang, Fessenden, *Rad. Phys. Chem.*, 1999, 54, 559.
- Whitman, Lyons, Miller, Nett, Treas *et al.*, Texas, USA, 1996.



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

[$UO_2(NO_3)_2(DEHBA)_2$]$^{\cdot+}$



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. Eruo. Biochem. Soc.*, **1983**, *158 (1)*, 143.
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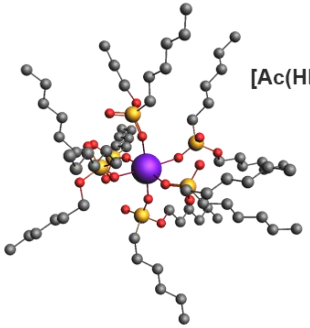
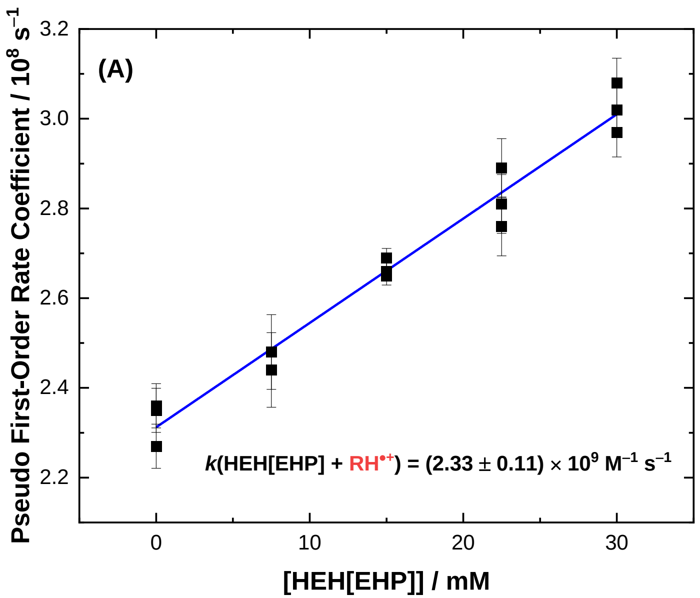
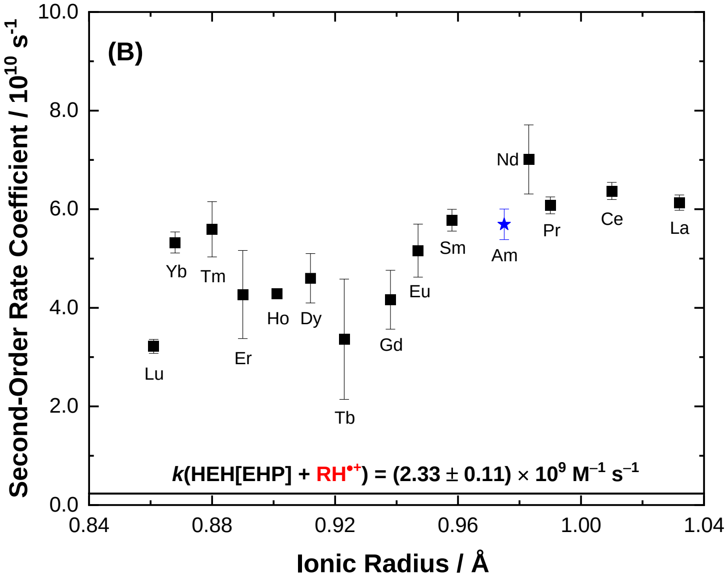
The HEH[EHP] saga…



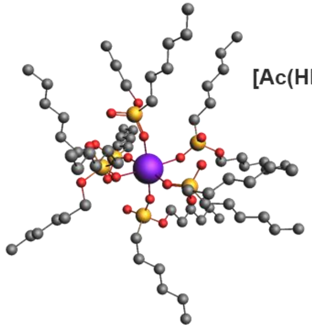


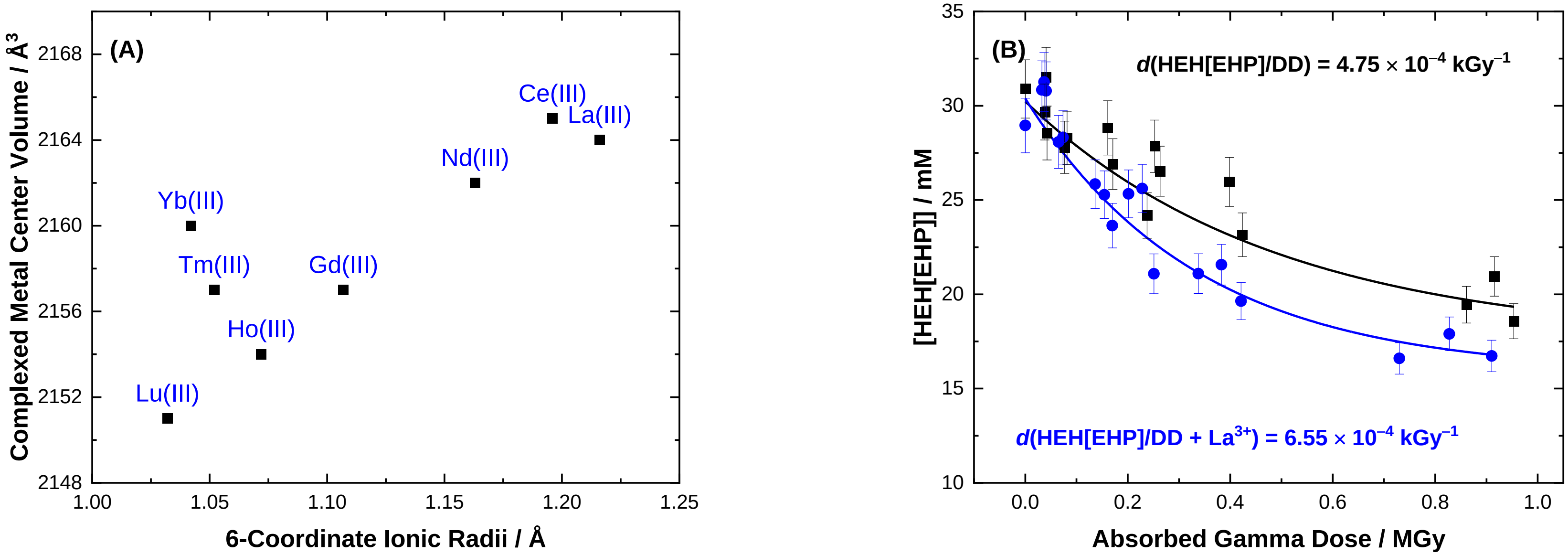


- **Methodology:** Δ[HEH[EHP]]/[M{(HEH[EHP])$_2$}$_3$] in 0.5 M DCM/*n*-dodecane; RH•$^+$ decay measured at 800 nm over 200 ns using the *Brookhaven National Laboratory* (BNL) *Laser Electron Accelerator Facility* (LEAF).

- 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.

…continues…





- **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.

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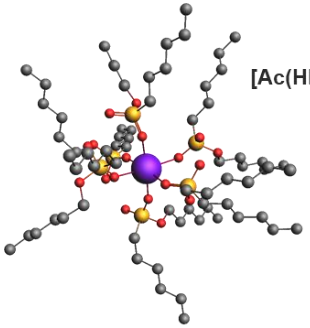
- Baxter, Cellis-Baros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *Dalton Trans.*, **2022**, *in review*.

…continues…



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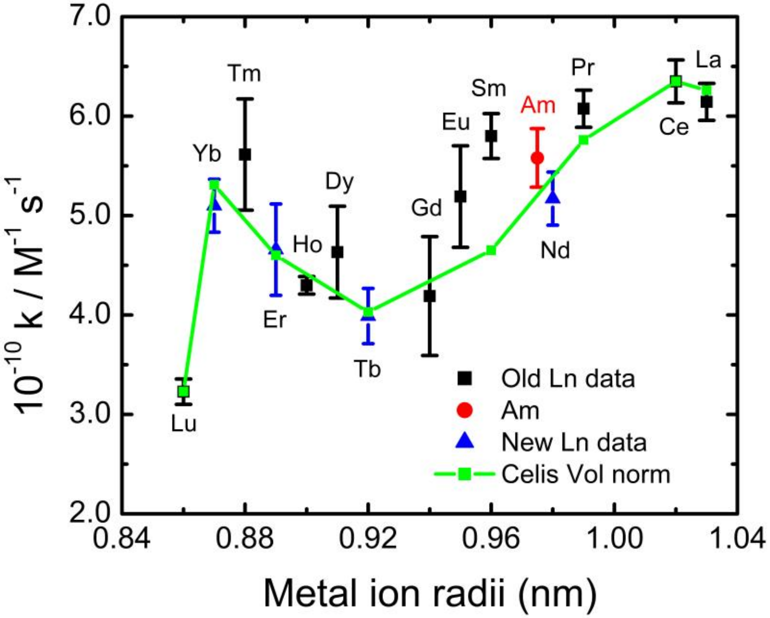

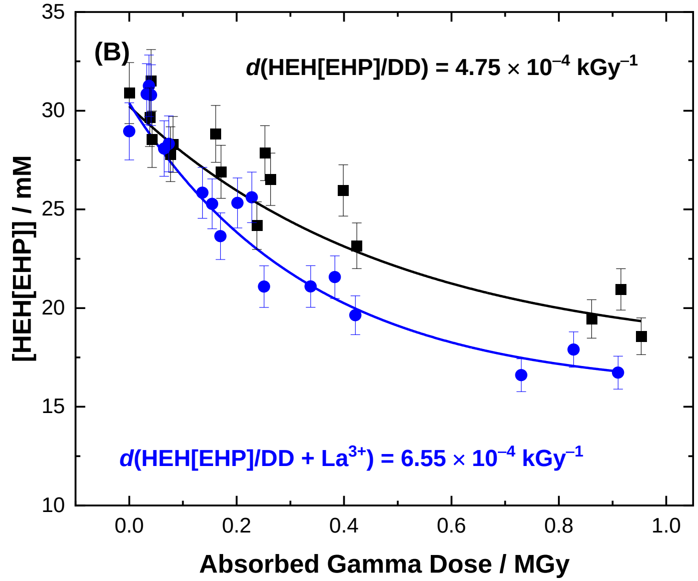

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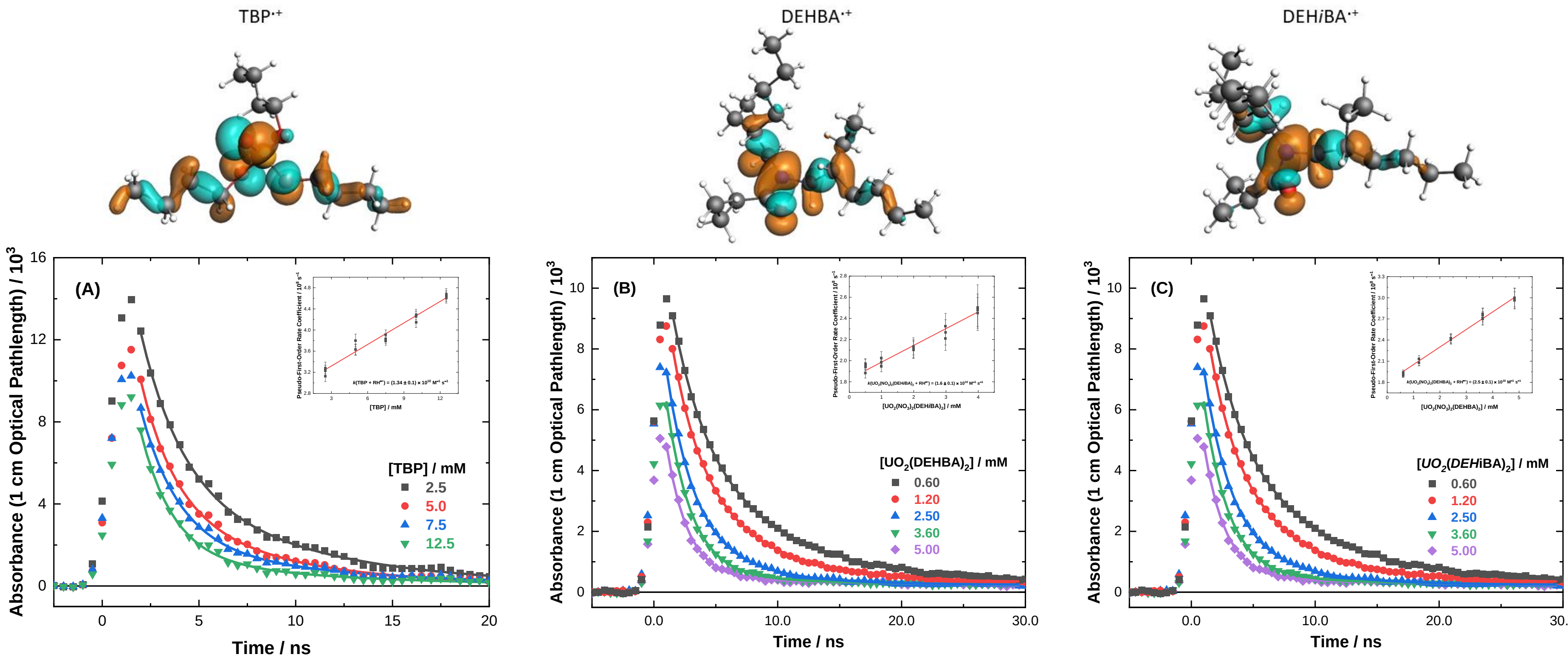
- Baxter, Cellis-Baros, Pilgrim, Cook, Grimes, Zalupski, Meeker, Rae, Zarzana, Mezyk, and Horne, *Dalton Trans.*, **2022**, *in review*.

…and then there’s ligand 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.

- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.
- 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.

…and some answers.

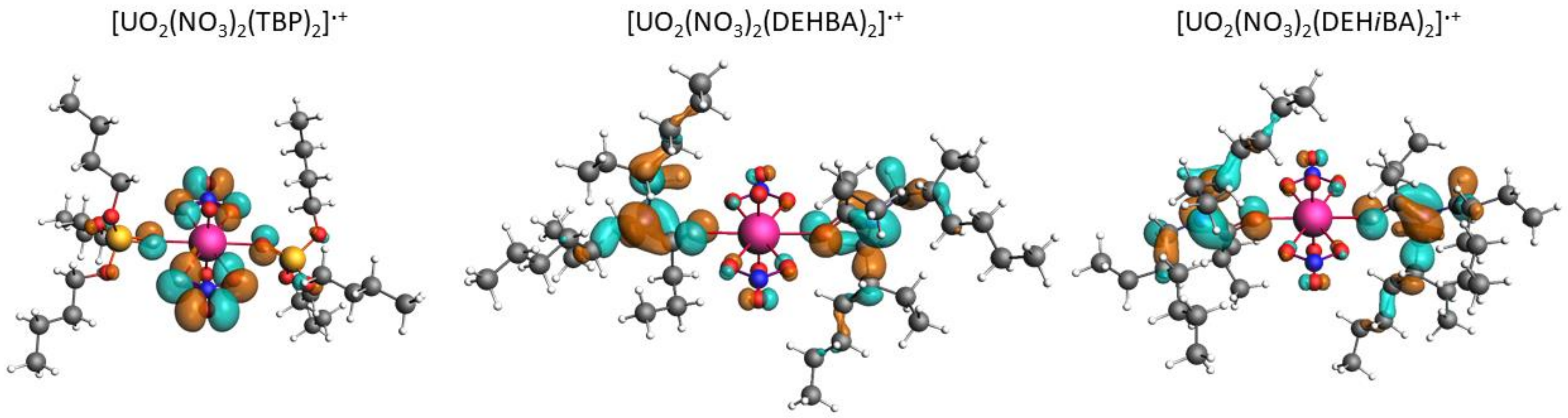


Table 1 Electronic structure calculation free energy (ΔG) values for the reaction of $RH^{\bullet+}$ with TBP, DEHBA, and DEHiBA for electron/hole transfer and proton transfer scenarios

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

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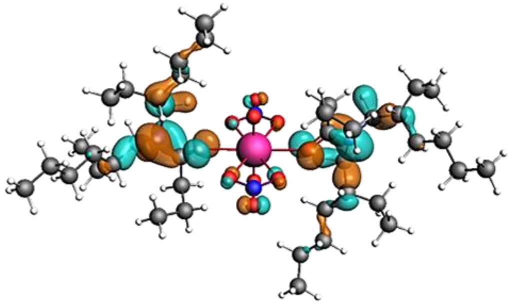
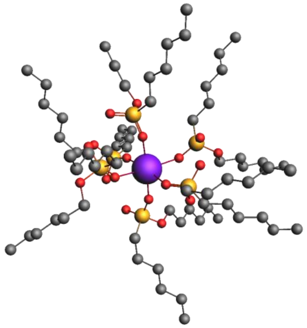
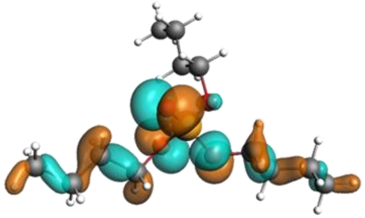
- Celis-Barros, Pilgrim, Cook, Grimes, Mezyk, and Horne, *PCCP*, **2021**, *23*, 24589.
- Frisch, Trucks, Schlegel, Scuseria, Robb, *et al.*, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, **2016**.
- ADF 2021.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.

Summary



- Understanding fundamental radiation chemistry is essential for innovating nuclear technology.
- Predictive models need mechanistic data and reaction kinetics…**and thus pulse radiolysis**!
- Metal ions have a profound effect on reaction kinetics, that varies from changes in electron distribution to generally increasing the size.





Acknowledgements

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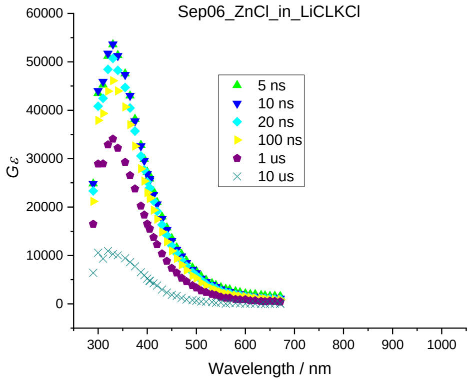
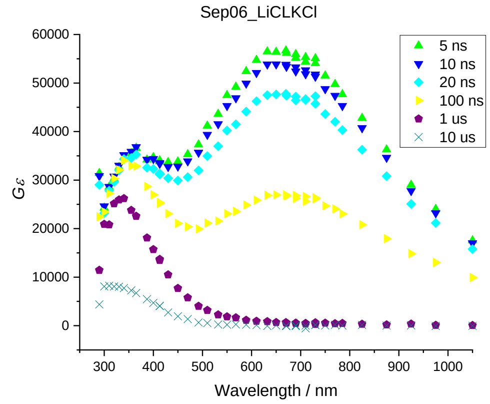
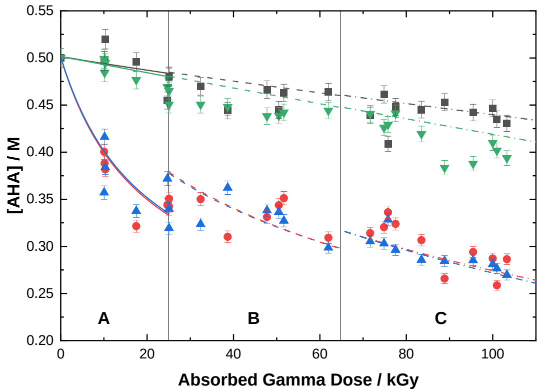
Related Nuclear Fuel Cycle Presentations

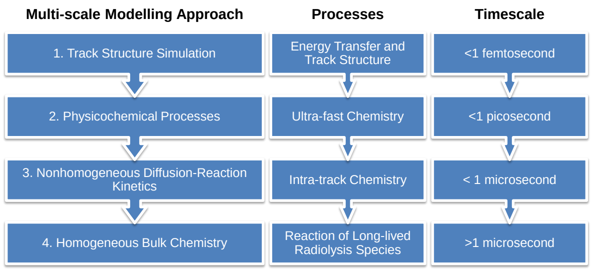
15:00 – 15:20	**O6: Kazuhiro Iwamatsu** (USA) *Pulse Radiolysis Study of Metal Additives in Molten LiCl-KCl Salt*

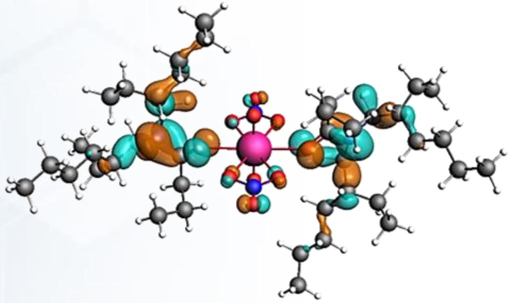




16:10 – 16:15	**F2: Jacy K. Conrad** (USA) *Multiscale Modeling of the Radical-Induced Chemistry of Acetohydroxamic Acid in Aqueous Solution*







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