INL/CON-24-81793-Revision-0

The Radiation-Induced Fate of Fission Product Iodine in Molten Salts

November 2024

Gregory Peter Holmbeck

Changing the World's Energy Future

Idaho National Laboratory

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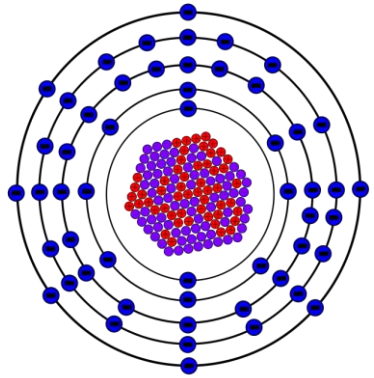

The Radiation-Induced Fate of Fission Product Iodine in Molten Salts

INL/CON-24-81793 Rev:000

Condensed Phase and Interfacial Molecular Science (CPIMS)
Principal Investigators' Research Meeting
November 13–15, 2024 | Washington DC, USA

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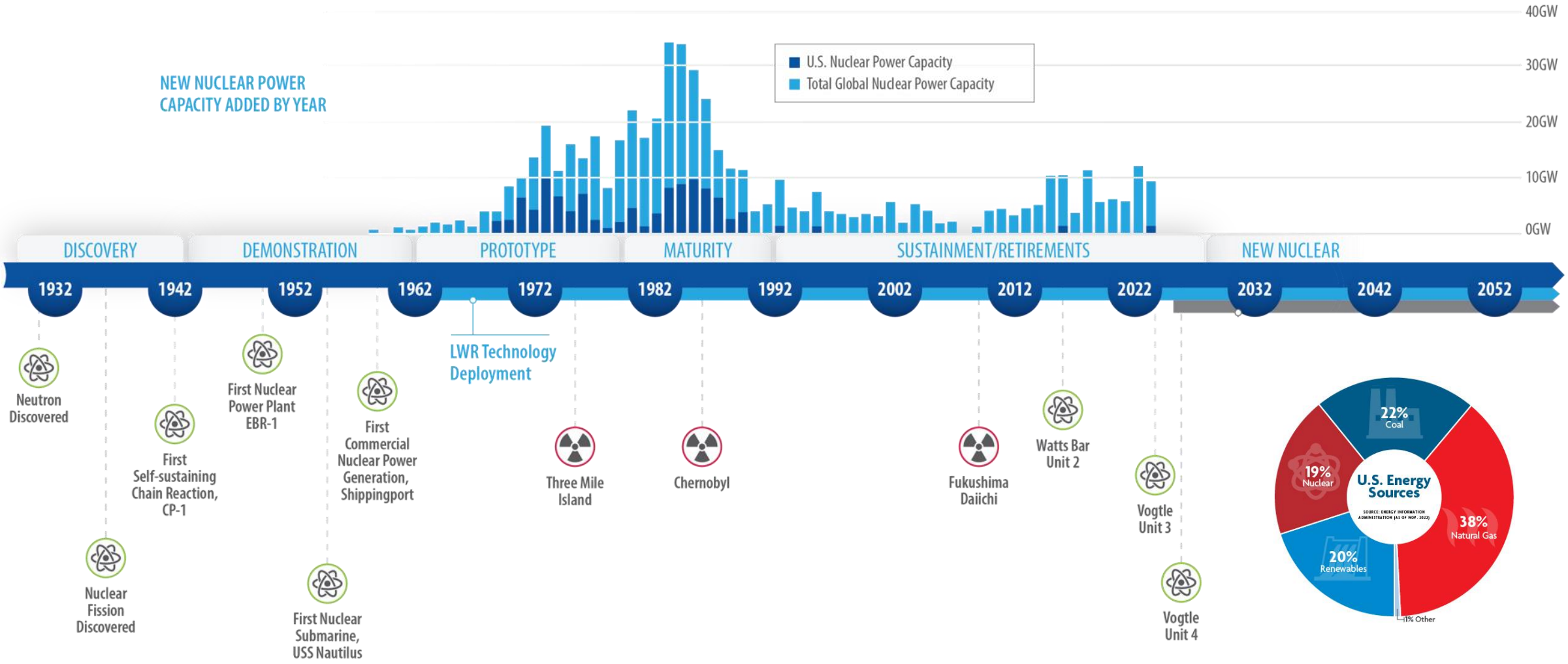
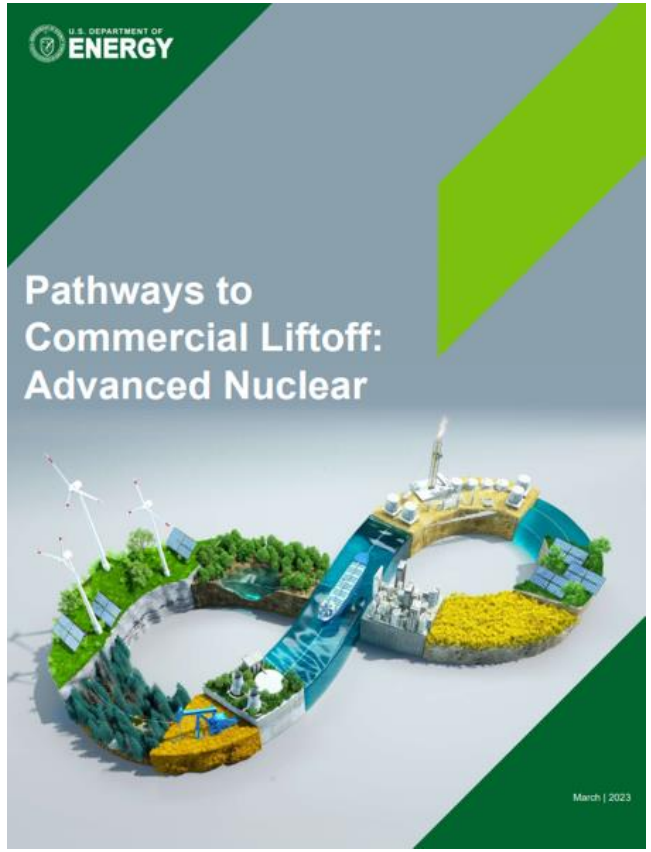
A brief history of nuclear power



https://kclonline.com/wp-content/uploads/2023/03/US-Energy-Sources-Mix.jpg

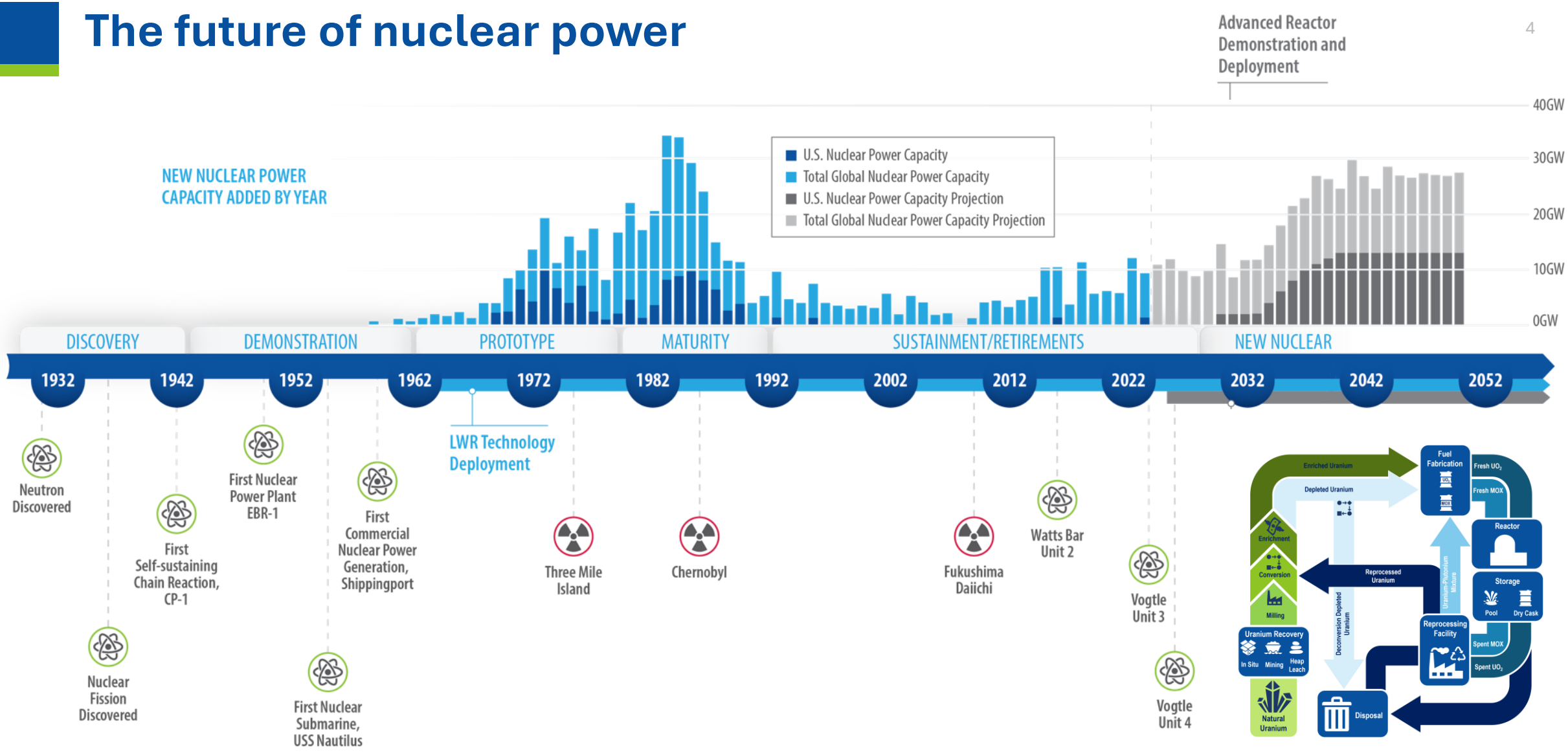
A nuclear renaissance…

- Countries participating in the international climate summit, the *28th Conference of the Parties* (**COP28**), commit to working together to triple nuclear capacity by 2050:
  - For the United States, this would mean going from **100 GWe to 300 GWe**
  - World-wide, this would mean going from **400 GWe to 1200 GWe**
- "*Power system decarbonization modeling, regardless of level of renewables deployment, suggests that the U.S. will need ~550–770 GW of additional clean, firm capacity to reach net-zero.*"



- COP28 declaration language: https://www.energy.gov/articles/cop28-countries-launch-declaration-triple-nuclear-energy-capacity-2050-recognizing-key .
- U.S. Department of Energy Pathways to Commercial Liftoff: Advanced Nuclear report, March **2023**, 1–62.

The future of nuclear power



Brookhaven National Laboratory

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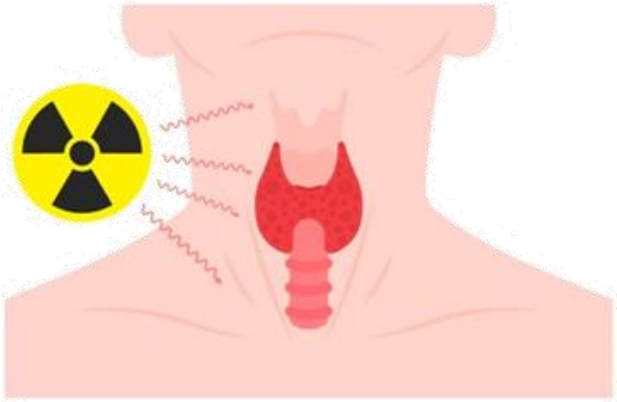
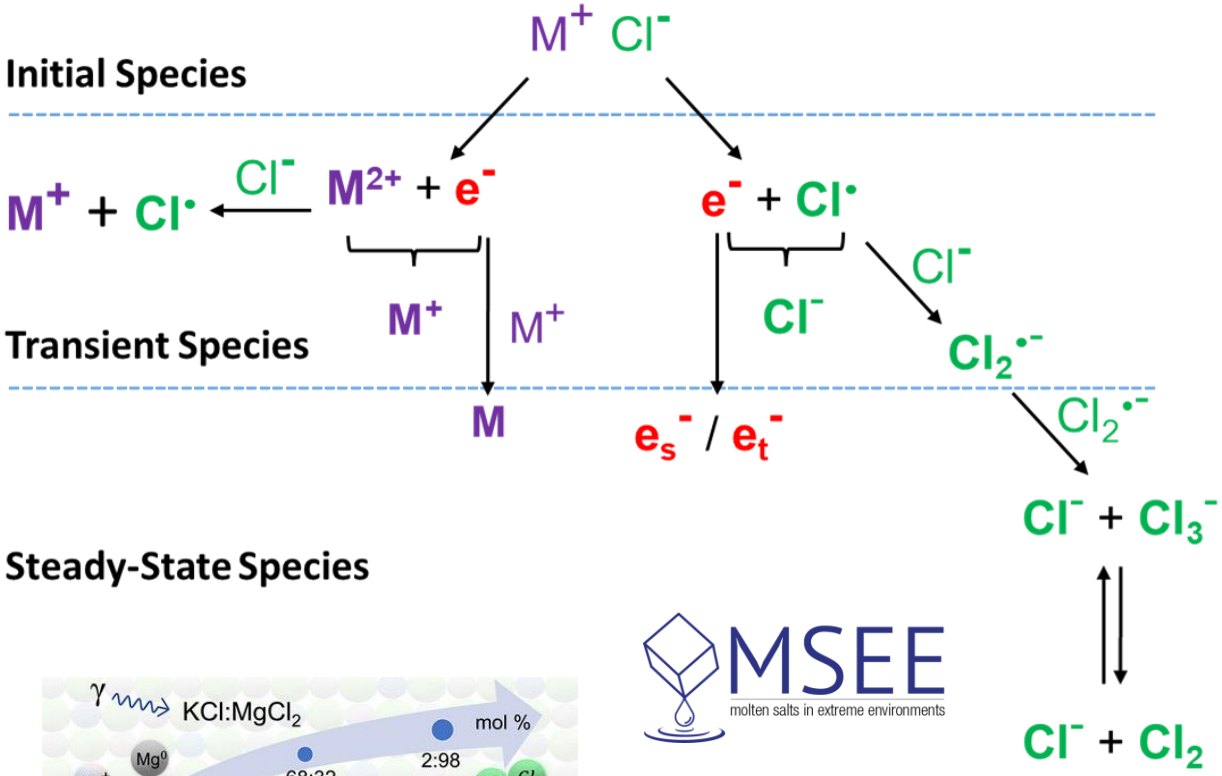
Molten halide salts and fission product iodine

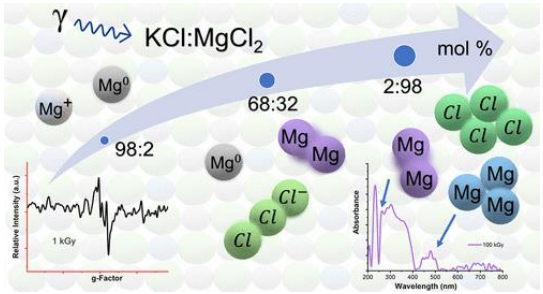
- Advanced nuclear reactor technologies are an integral part of the nation's future clean energy strategy.
- Molten halide salts are expected to play an important role as either *coolant*, *fuel matrix*, or *pyrochemical separations media*.
- **Iodine** is a **high-yield** fission product of concern for environmental release due to uptake in the human thyroid gland, and a precursor to ^{135}Xe.
- Up to **70%** of the **iodine** generated in the 1975 *Molten Salt Reactor Experiment* (MSRE) could not be accounted for in the salt matrix.



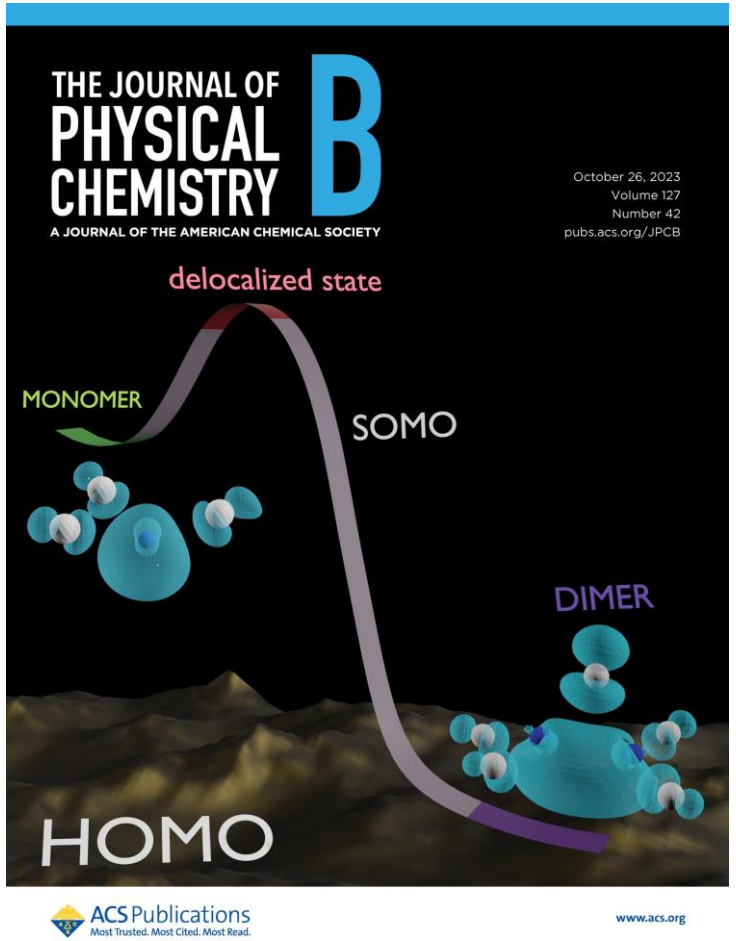
- Compere *et al.* Fission product behavior in the Molten Salt Reactor Experiment. ORNL-4865, **1975**.
- https://www.britannica.com/story/30th-anniversary-of-chernobyl

Molten chloride salt radiation chemistry



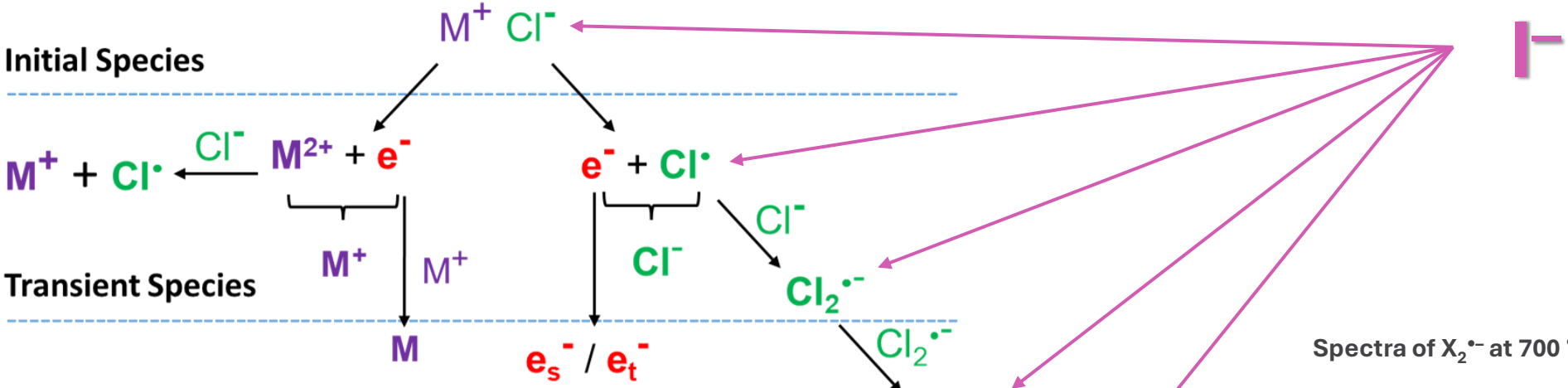


MSEE
molten salts in extreme environments



- Dias, Gill, Liu , Halstenberg, Dai. Huang. Mausz, Gakhar, Phillips, Mahurin, Pimblott, Wishart, and Frenkel, *J. Phys. Chem. Lett.* **2021**, *12*, 157.
- Ramos-Ballesteros, Gakhar, Horne, Iwamatsu, Wishart, Pimblott, and LaVerne, *Phys. Chem. Chem. Phys.* **2021**, *23*, 10384.
- Ramos-Ballesteros, Gakhar, Woods, Horne, Iwamatsu, Wishart, Pimblott, and LaVerne, *J. Phys. Chem. C* **2022**, *126 (23)*, 9820.
- Iwamatsu, Horne, Gakhar, Halstenberg, Layne, Pimblott, and Wishart, *PCCP* **2022**, *24*, 25088.
- Nguyen, Bryantsev, and Margulis, *J. Phys. Chem. B* **2023**, *127*, 9155.

Molten iodine salt radiation chemistry



Halide Radical Reactions

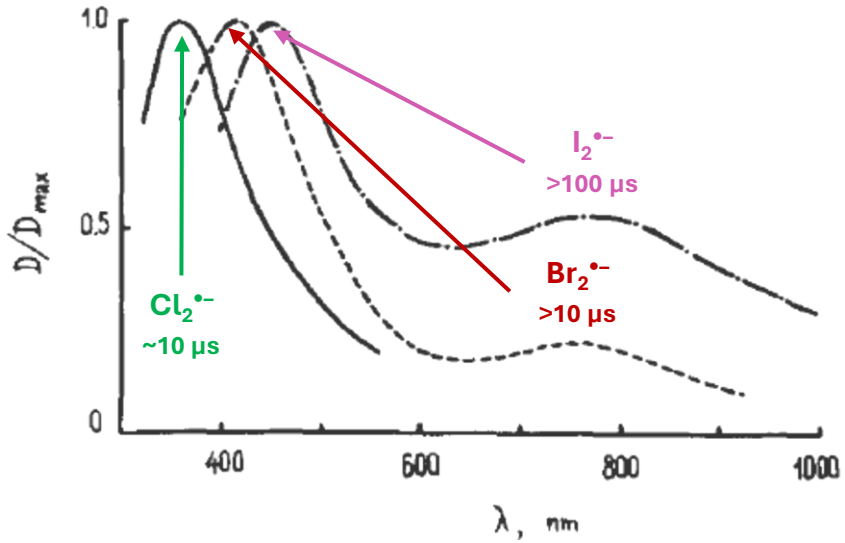
$X^{\bullet} + X^{-} \rightarrow X_2^{\bullet-}$

$X_2^{\bullet-} + M^{(n-1)+} \rightarrow M^{n+} + 2X^{-}$

$X_2^{\bullet-} + X_2^{\bullet-} \rightarrow X_3^{-} + X^{-}$

$X_3^{-} \rightleftharpoons X_2 + X^{-}$

Spectra of $X_2^{\bullet-}$ at 700 °C in molten KX, X = Cl, Br, I



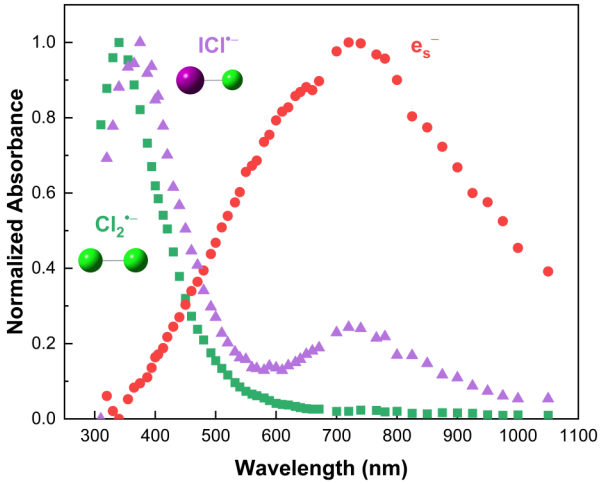
- Pikaev, Makarov, Zhukova, *Radiat. Phys. Chem.* **1982**, *19(5)*, 377.
- Conrad, Iwamatsu, Woods, Gakhar, Layne, Cook, and Horne, *Phys. Chem. Chem. Phys.* **2023**, *25*, 16009.

Research goal

"To quantitatively understand and predict radiation-induced iodine speciation, chemistry, and transport in high-temperature molten salt environments"

Question: How does the absorption of ionizing radiation (**α**, **β**, and **γ**) change the chemical and physical properties of **iodine**-bearing molten salt systems?

Central Hypothesis: The radiation-induced conversion of **iodide** will yield an extensive suite of **iodine** radiolysis products that will alter the bulk chemical and physical properties of the irradiated molten salt system—the *speciation*, *distribution*, and *chemical transport* of which will be dictated by the composition and the availability of multivalent metal cations and metal alloy interfaces.



- Conrad, Iwamatsu, Woods, Gakhar, Layne, Cook, and Horne, *Phys. Chem. Chem. Phys.* **2023**, *25*, 16009.
- Rodríguez-Laguna, M. R.; Garcia, R. H. L.; Yoo, T. -S.; Anderson, S. T.; Horne, G. P.; Gakhar, R. J. Mol. Liq. **2024**, *Accepted*.

Formation of $ICl^{\bullet-}$ in molten chloride eutectic salt mixtures

- Neat molten **chloride** salt radical reactions:

$$Cl^{\bullet} + Cl^{-} \rightarrow Cl_2^{\bullet-}$$

$$Cl_2^{\bullet-} + Cl_2^{\bullet-} \rightarrow Cl_3^{-} + Cl^{-}$$

$$Cl_3^{-} \rightleftharpoons Cl_2 + Cl^{-}$$

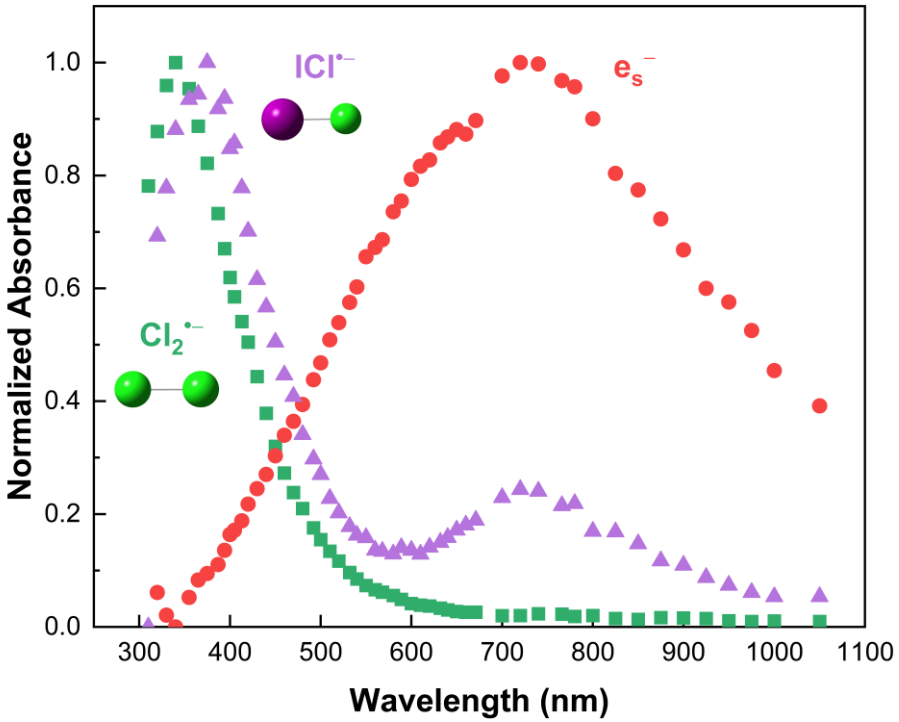
- In the presence of **iodide**:

$$Cl^{\bullet} + I^{-} \rightarrow ICl^{\bullet-}$$

$$ICl^{\bullet-} + ICl^{\bullet-} / Cl_2^{\bullet-} \rightarrow I_2Cl^{-} \text{ or } ICl_2^{-} + Cl^{-}$$

$$I_2Cl^{-} \text{ or } ICl_2^{-} \rightleftharpoons ICl + I^{-} \text{ or } Cl^{-}$$

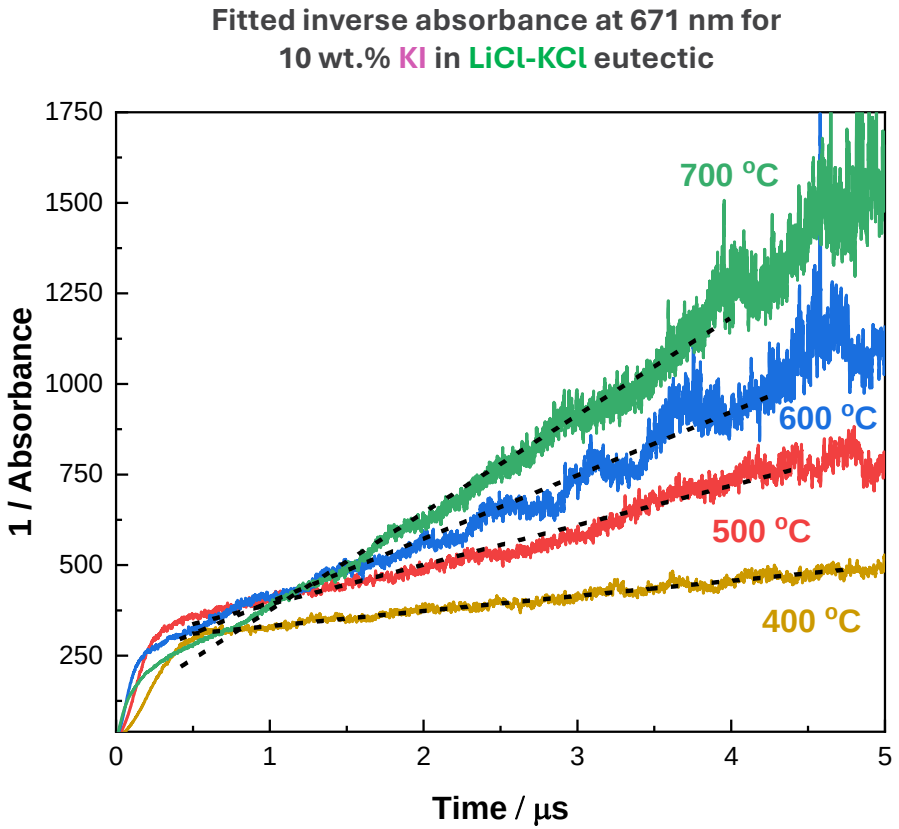
Normalized spectra from *SK-Ana* deconvolution of 10 wt% KI in LiCl–KCl eutectic at 400 °C up to 1 µs.



• Conrad, Iwamatsu, Woods, Gakhar, Layne, Cook, and Horne, *Phys. Chem. Chem. Phys.* **2023**, *25*, 16009.

Formation of $ICl^{\bullet-}$ in aqueous solution?

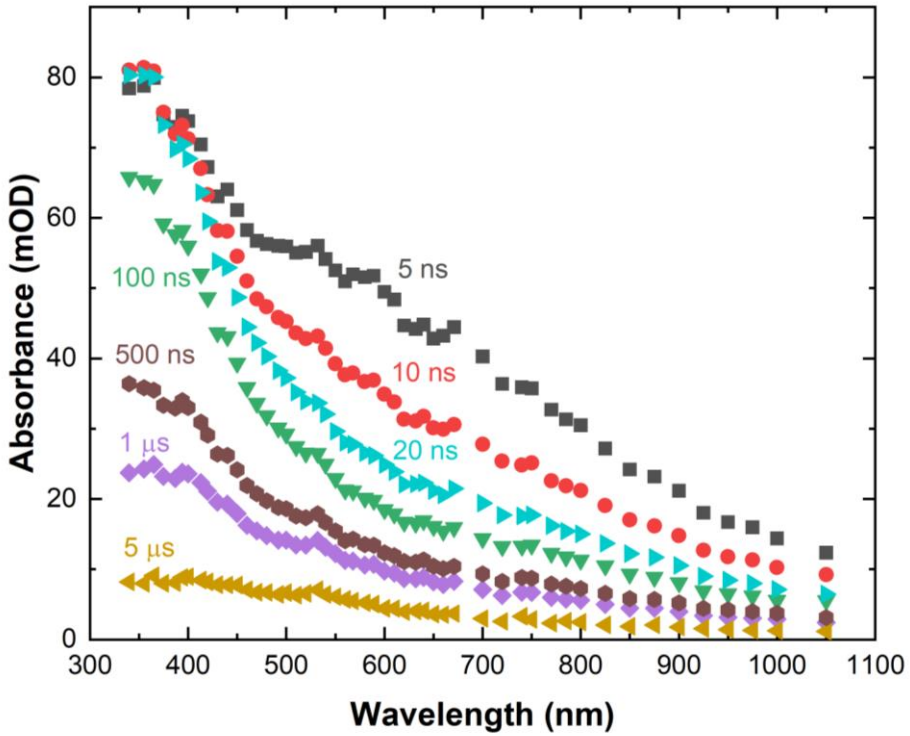
- Ershov *et al*. released a series of articles claiming:
  - the formation of $ClBr^{\bullet-}$ and $BrI^{\bullet-}$ in aqueous solution
  - that $ICl^{\bullet-}$ could not formed due to various reduction potentials
  - $ClBr^{\bullet-} + Cl^{-} \rightleftharpoons Cl_2^{\bullet-} + Br^{-}$
- Janik *et al*. recently reported using Raman:
  - no $ICl^{\bullet-}$ formation in aqueous solution, only $Cl_2^{\bullet-}$ and $I_2^{\bullet-}$
  - however, $ICl^{\bullet-}$ is energetically feasible and must form initially ($ICl^{\bullet-} + I^{-} \rightleftharpoons I_2^{\bullet-} + Cl^{-}$)



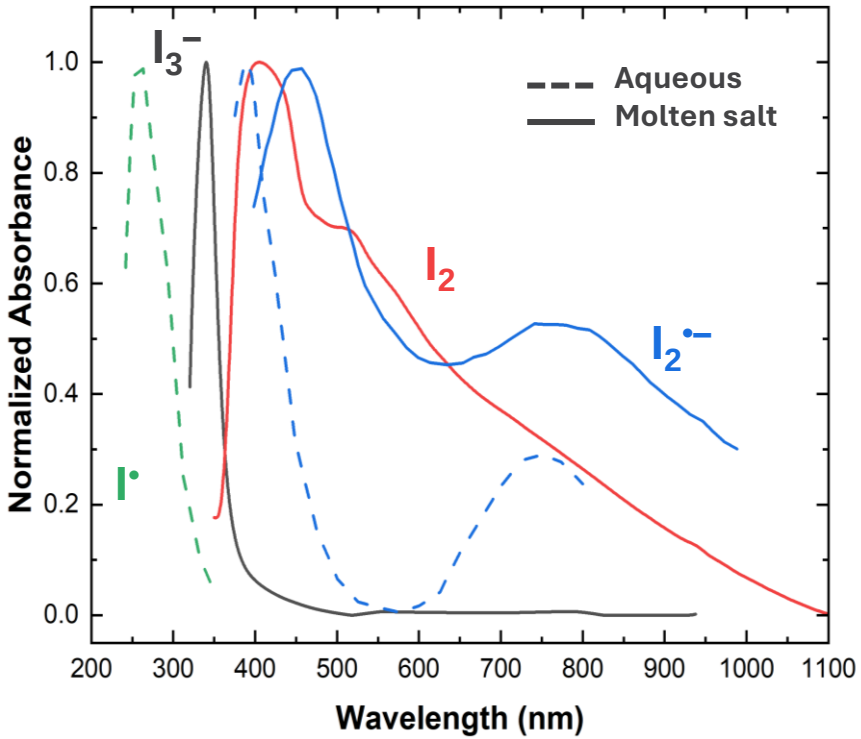
- Ershov, Janata, Kelm, Gordeev, Mendeleev Communications **2002**, *12(2)*, 55.
- Ershov, Kelm, Gordeev, and Janata, *Physical Chemistry Chemical Physics* **2002**, *4*, 1872.
- Ershov, Janata, and Gordeev, *Russian Chemical Bulletin International Edition* **2005**, *54(6)*, 1378.
- Janik, Batharachaya, and Tripathi, *4th International Conference of Ionizing Processes,* Notre Dame, Indiana, USA, August **2024**.

Deconvolution of irradiated neat molten iodide salt mixtures

Pulse irradiation of LiI-KI eutectic (63.3 mol% LiI, and 36.7 mol% KI) at 400 °C



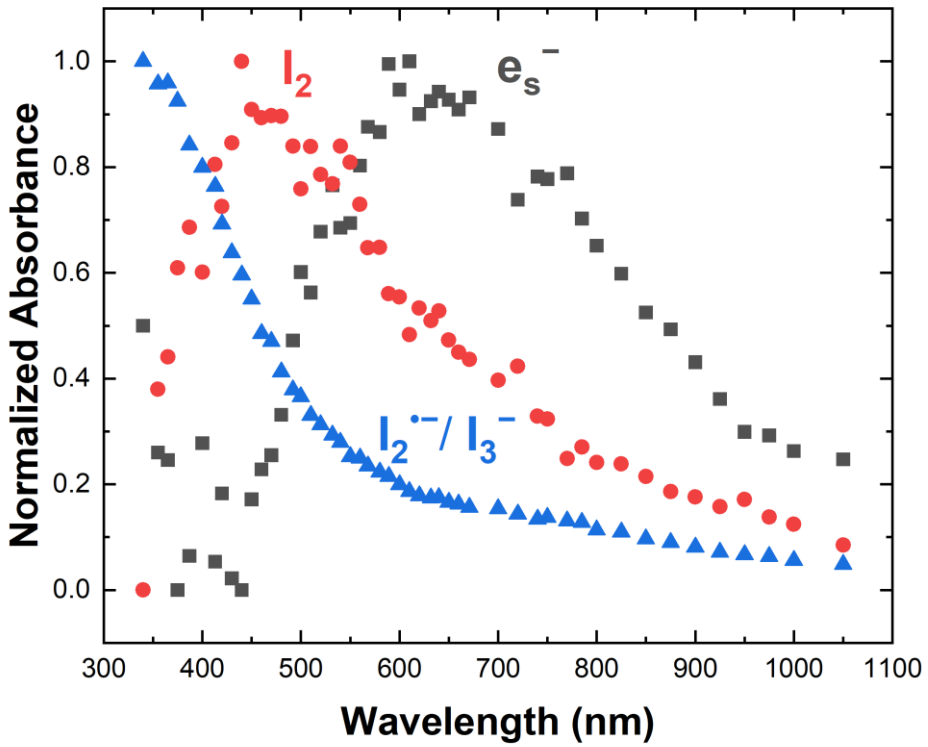
Iodine/iodide literature spectra



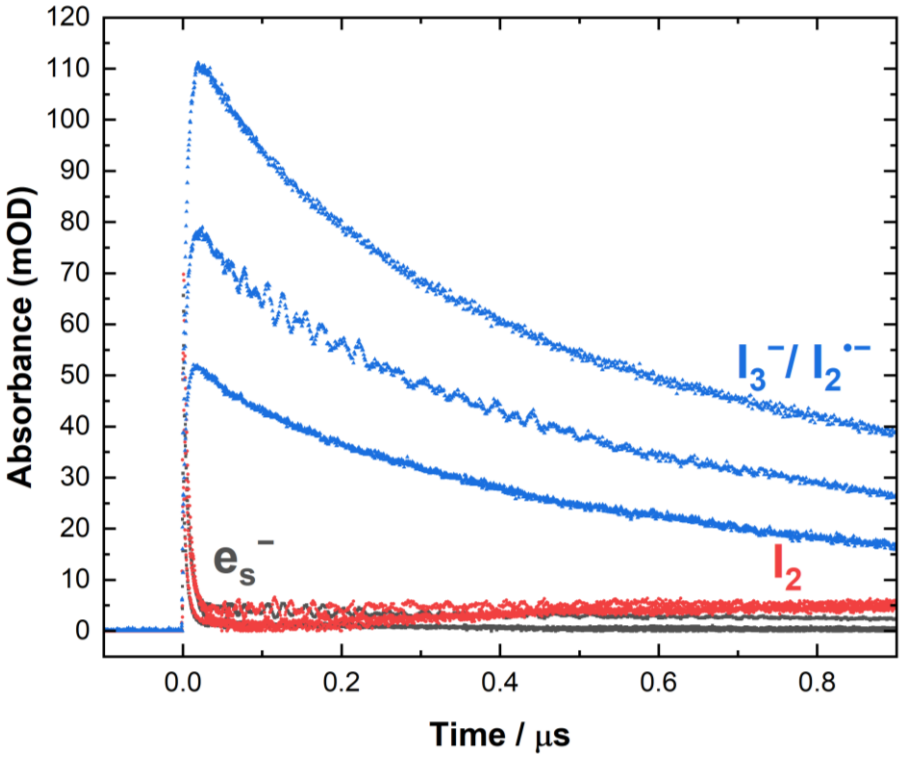
- Hug, Optical Spectra of Nonmetallic Inorganic Transient Species in Aqueous Solution, National Bureau of Standards, Washington, **1981**.
- Pikaev, Makarov, and Zhukova, *Radiat. Phys. Chem.* **1982**, *19(5)*, 377.
- Conrad, Iwamatsu, Rodriguez Laguna, Ramos-Ballesteros, Gakhar, Layne, Cook, and Horne, Time-resolved radiolytic transient spectra and kinetics in iodide molten salts. *In Preparation*.

Deconvolution of irradiated neat molten iodide salt mixtures

3 species *SK-Ana* deconvolution of LiI-KI at 400 °C



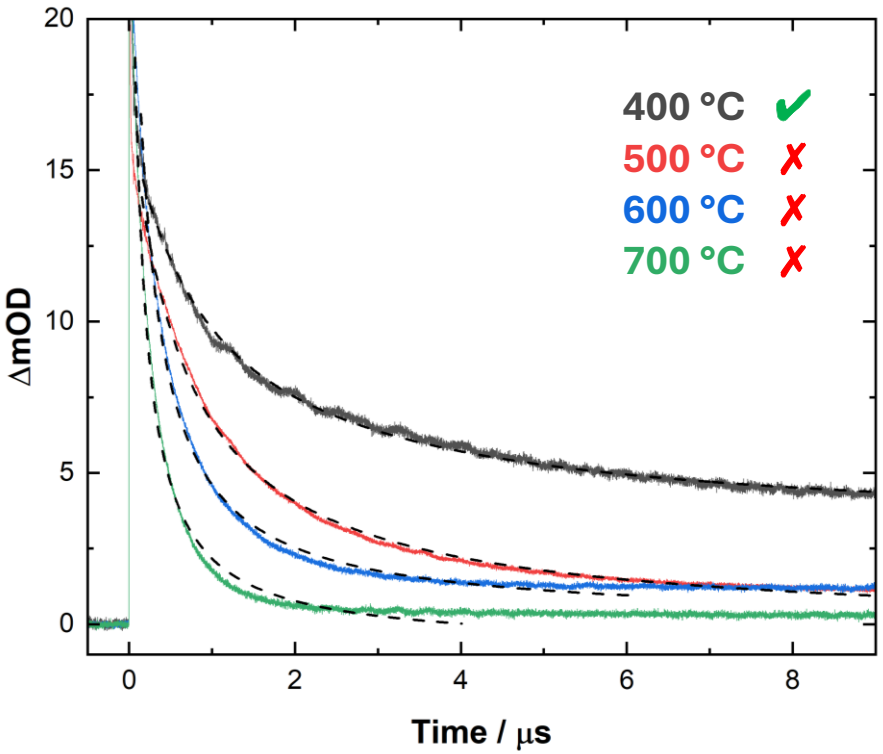
Deconvoluted kinetic contributions at each peak wavelength for LiI-KI at 400 °C.



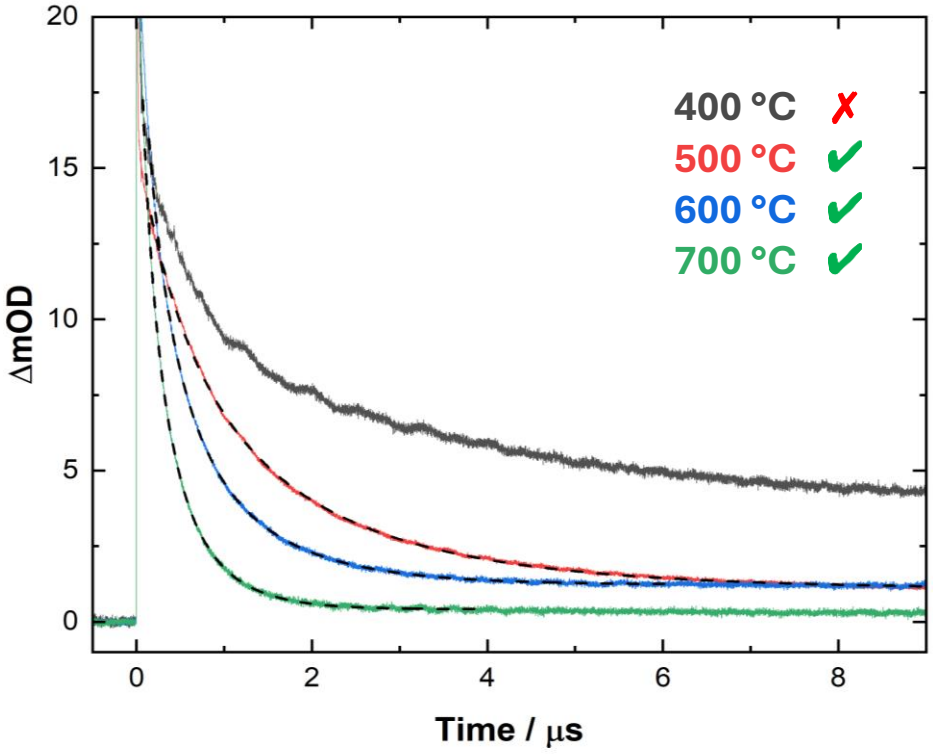
- Pernot, P. SK-Ana: Analysis of Spectro-Kinetic Data, 3.4; **2018**.
- Conrad, Iwamatsu, Rodriguez Laguna, Ramos-Ballesteros, Gakhar, Layne, Cook, and Horne, Time-resolved radiolytic transient spectra and kinetics in iodide molten salts. *In Preparation*.

Deconvolution of irradiated neat molten iodide salt mixtures

Second-order decay fits in molten LiI-KI at 580 nm



Mixed-order (1st + 2nd) decay fits in molten LiI-KI at 580 nm



- Conrad, Iwamatsu, Rodriguez Laguna, Ramos-Ballesteros, Gakhar, Layne, Cook, and Horne, Time-resolved radiolytic transient spectra and kinetics in iodide molten salts. *In Preparation*.

Deconvolution of irradiated neat molten iodide salt mixtures

- Neat molten **iodide** salt radical reactions:

$I^{\bullet} + I^{-} \rightarrow I_2^{\bullet-}$

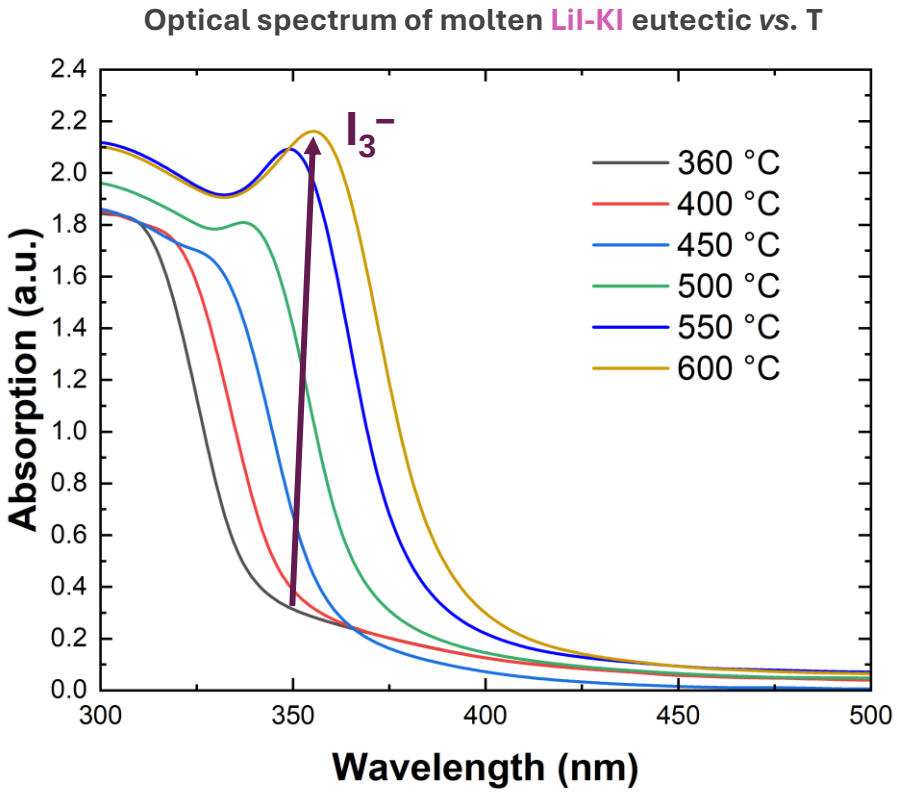
$I_2^{\bullet-} + I_2^{\bullet-} \rightarrow I_3^{-} + I^{-}$ *(second-order process at 400 °C)*

$I_3^{-} \rightleftharpoons I_2 + I^{-}$

- Possible higher E_a first-order processes:

$M^0 + M^{n+} \rightarrow M_2^{n+}\ldots$

$I_2^{\bullet-} + M_2^{n+} \rightarrow 2M^{n+} + I^{-}$



- Pikaev, Makarov, Zhukova, *Radiat. Phys. Chem.* **1982**, *19(5)*, 377.
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- Ramos-Ballesteros, Castro-Baldivieso, Horne, Conrad, and Gakhar, Iodide speciation in molten halide salts. *In preparation*.

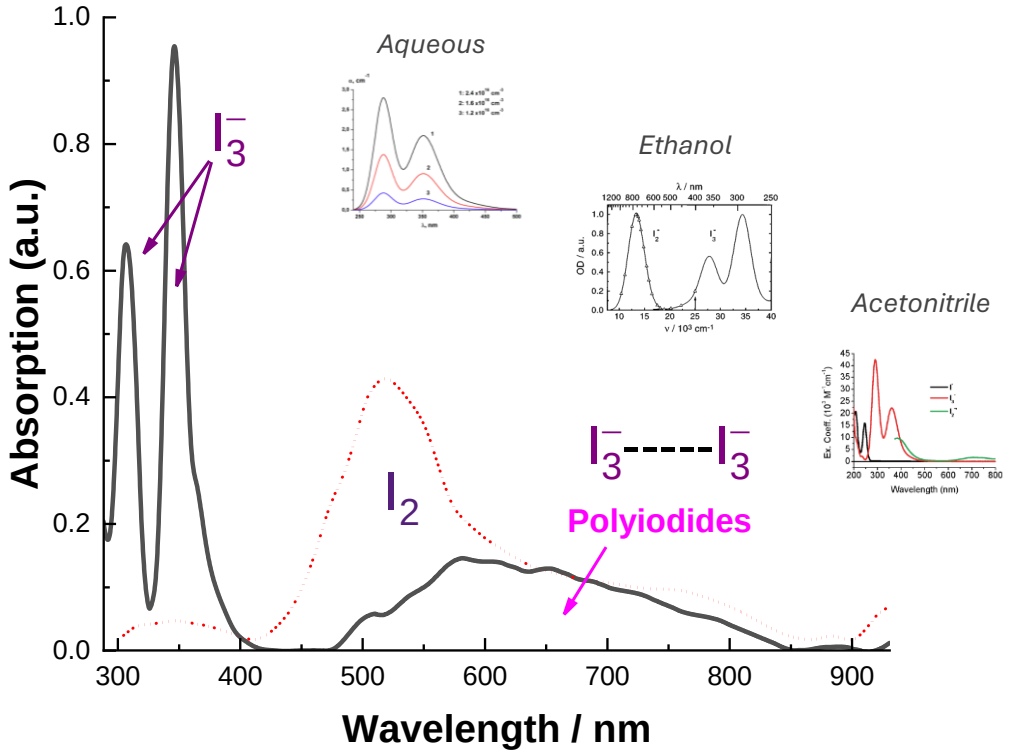
Deconvolution of neat molten iodide salt mixtures

$$I_2 + I^- \rightleftharpoons I_3^-$$

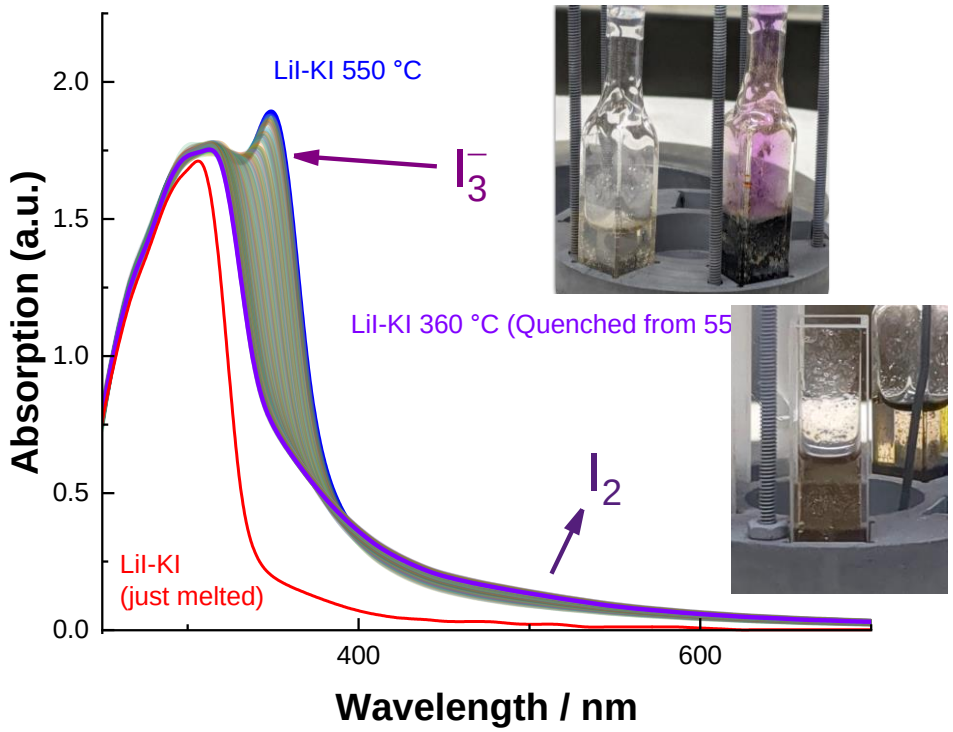
$$I_3^- + h\nu \rightleftharpoons I_2 + I^-$$

$$I_3^- + I^- + h\nu \rightleftharpoons I_2^- + I_2^-$$

- Although reported in aqueous and organic solutions, I_3^- has not been report in molten salts.



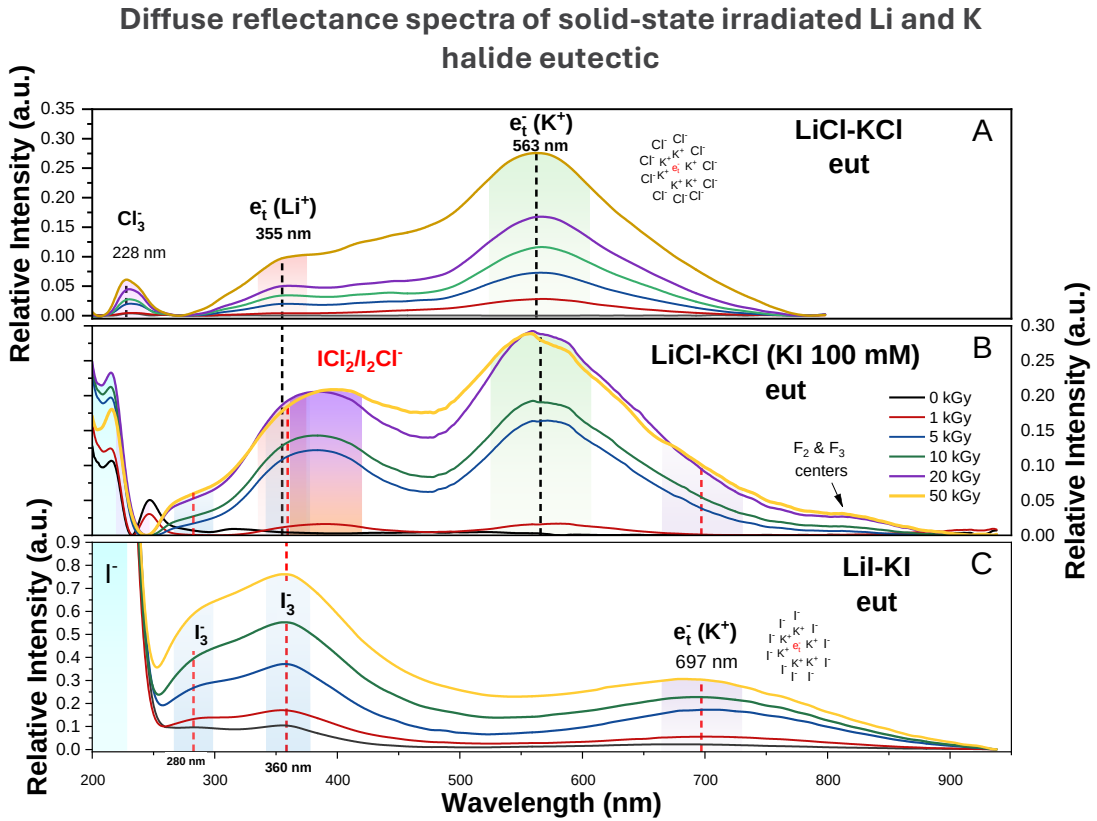
Process is reversible upon cooling in LiI-KI eutectic



- Gardner, Abrahamsson, Farnum, and Meyer, *Journal of the American Chemical Society* **2009**, *131(44)*, 16206.
- Kireev and Shnyrev, *Laser Physics* **2015**, *25(7)*, 075602.
- Ramos-Ballesteros, Castro-Baldivieso, Horne, Conrad, and Gakhar, Iodide speciation in molten halide salts. *In preparation*.

Conclusions and future directions

- The labile nature of **iodine**'s electrons allow for multiple **iodine**/**iodide** species to form in high temperature molten salt radiation environments.
- Further deconvolution of neat **iodine** species and their role in solid/molten **chloride** salt mixtures.
- Interaction of metal ions (Ni^{2+}, Zn^{2+},Cr^{2+}, and Cr^{3+}) with non-equilibrium **iodine** species.



- Ramos-Ballesteros, Gakhar, Conrad, and Holmbeck, Solid-state radiolysis of Interhalogen iodide transients. *In preparation*.
- Castro-Baldivieso, Ramos-Ballesteros, Horne, Conrad, and Gakhar, Impact of multivalent dopant metal ions on odide speciation in molten halide salts. *In preparation*.

Acknowledgements

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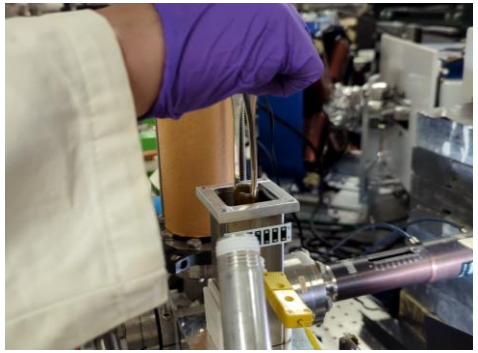

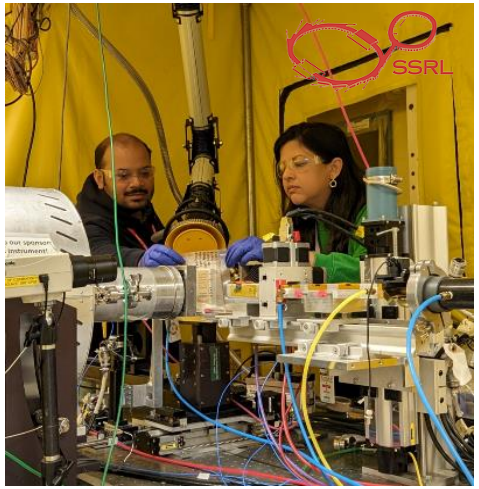

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Questions?