



Radiation-induced transients on solid and molten Li and K iodides

June 2024

Changing the World's Energy Future

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Michael Ellis Woods, Jacy Kathleen Conrad



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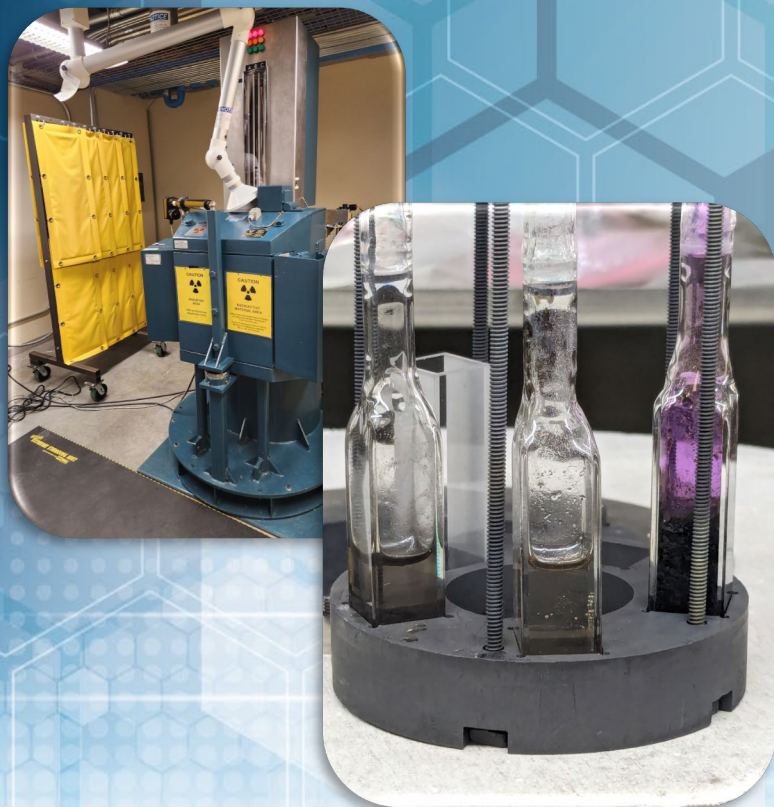
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ACS Northwest Regional Meeting (NORM)
June 23-26, 2024. Washington State
University. Pullman, Washington.

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Exploring the Chemistry of Next-Generation Coolants and
Solvents: Radiation-Induced Chemistry



AToMS

Advanced Technologies on Molten
Salts

 Idaho National Laboratory

Infrastructure and funding



- ⌘ Pyrochemistry and Molten Salt Systems
- ⌘ Center for Radiation Chemistry Research
- ⌘ Advanced Technologies on Molten Salts

- ⌘ Nuclear Science and Technology Department
- ⌘ Chemistry Department



U.S. DEPARTMENT OF
ENERGY

Office of
Science

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How to do it?

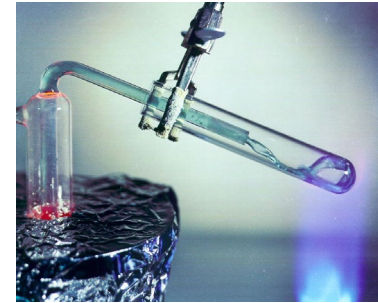
Speciation in conditions of

High Temperature

Ionizing radiation fields

Approach

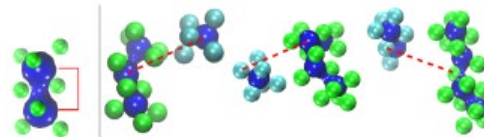
- Solid-state
- Pulse-radiolysis
- Steady state



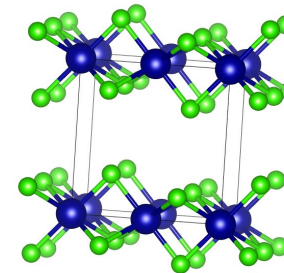
Molten FLiBe . ORNL, 2021

	Liquid	Solid
Density	↓	↑
Coordination	↓ (temperature)	↑ (fixed)
Order	Short-range	Long-range
Diffusion	↑	↓

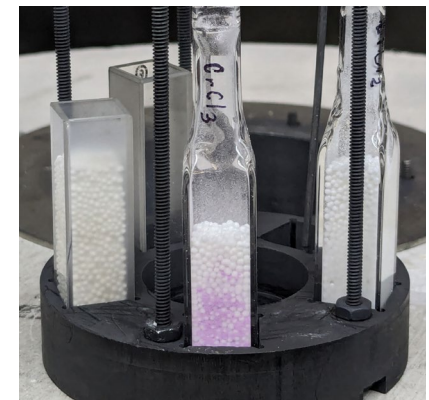
Liquid ²



Solid



Radiolytically speaking, primary transients induced by gamma radiation are essentially the same in both states, with expected spectroscopical differences.

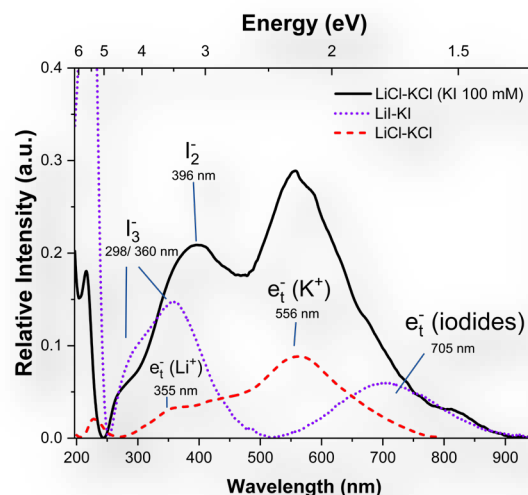
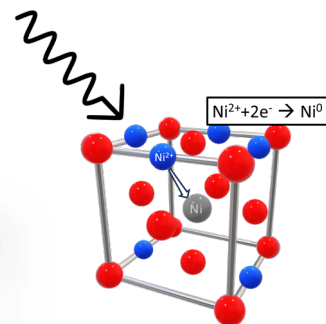


Radiation chemistry of molten salts

Phenomena and kinetic properties are better approximated if treated as an extension of the theory of formation of defects in the solid-state

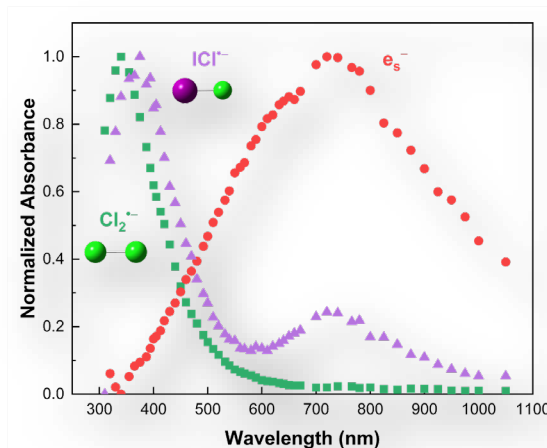
Solid

Solid-state radiolysis

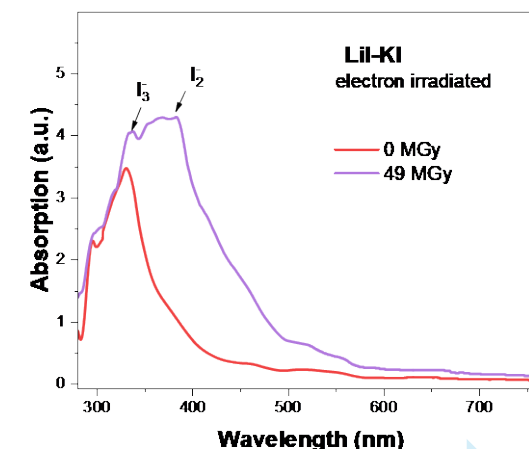


Liquid

Pulse radiolysis



Steady-state irradiation



Time scale

- Discrete energies (narrower peaks)
- Analysis under milder condition
- Identification of aggregates or secondary intermediates

Monitor the production and decay of primary (short-lived) transients like solvated electrons (e_s^-) and K_4 (ns and μ s).

Monitor the concentration of radiation-induced steady-state transients
 $I_2 + I^- \rightleftharpoons I_3^-$

- Conrad et al., Phys. Chem. Chem. Phys. 2023, 25, 16009.

Experimental methods: Diffuse Reflectance

How do we investigate radiation-induced transients trapped in the crystal lattice with minimum perturbation to the system?

- **Diffuse Reflectance**
(defects absorbing in the UV-Vis)
- **Electron Paramagnetic Resonance**
(radical species)



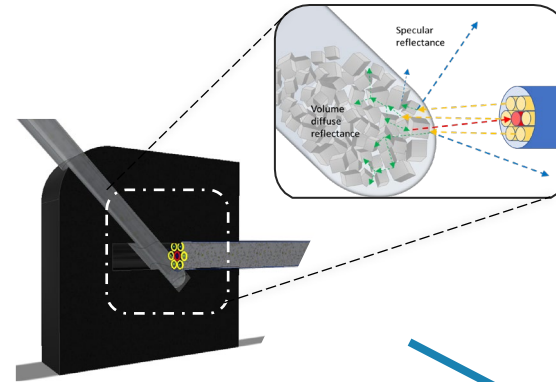
Bruker EPR spectrometer



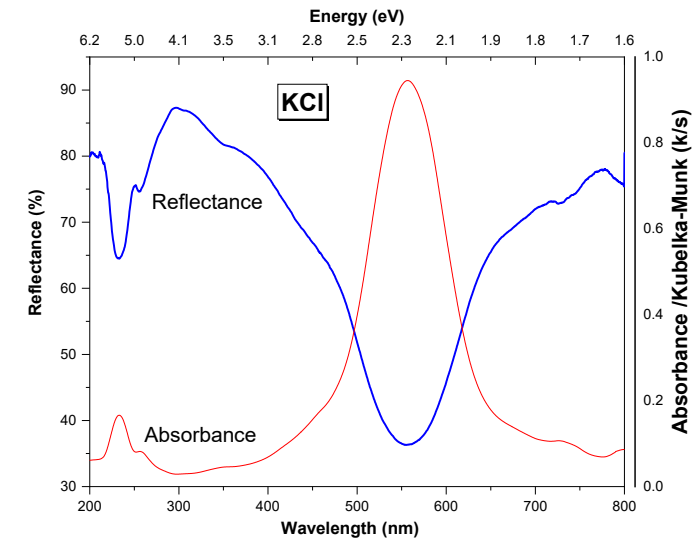
FTS 817 gamma irradiator



High-temperature spectroscopy

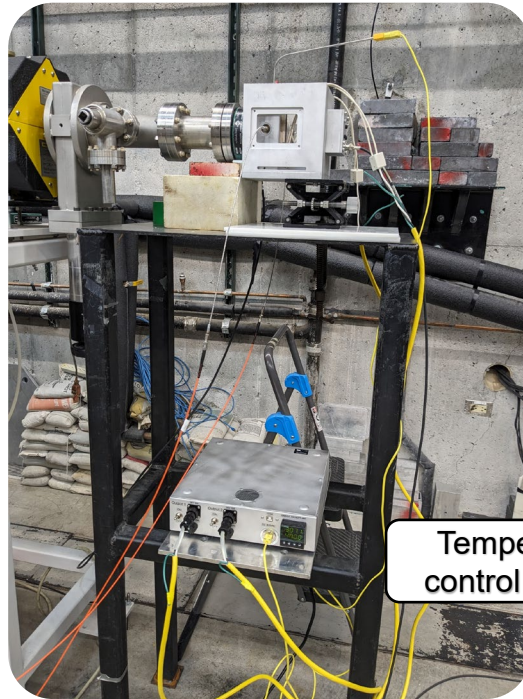
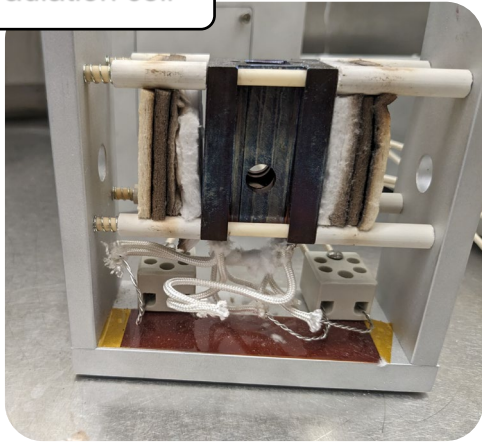


3D Printed sample holder
135° diffuse angle
Probe 6 illumination fibers
1 detection fiber

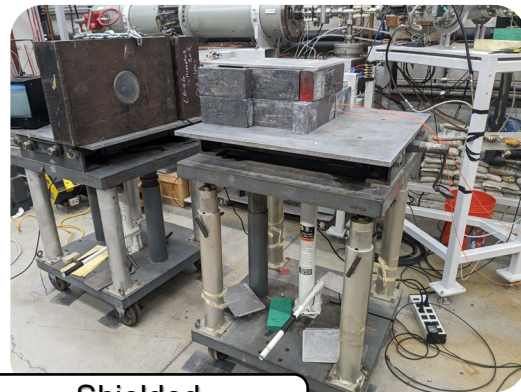


High-temperature experimental setup for Electron/ion irradiation

Irradiation cell



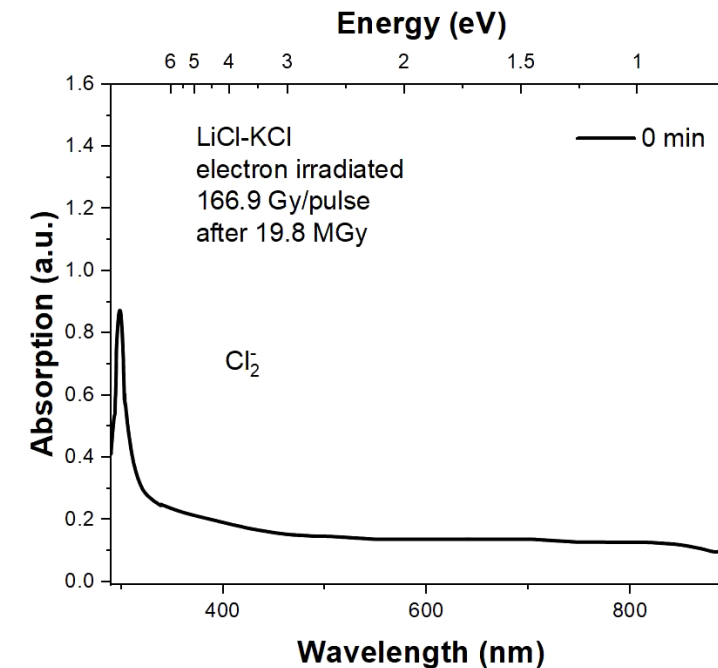
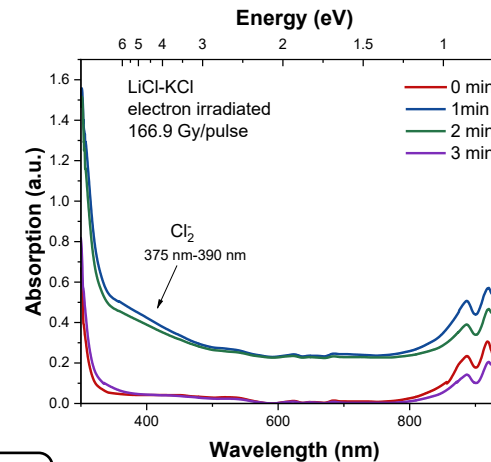
Temperature control system



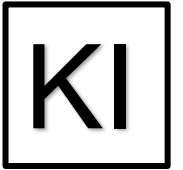
Shielded spectroscopy setup

Real-time monitoring of absorption spectroscopy is possible through our custom-made high temperature irradiation cell (up to 700 C).

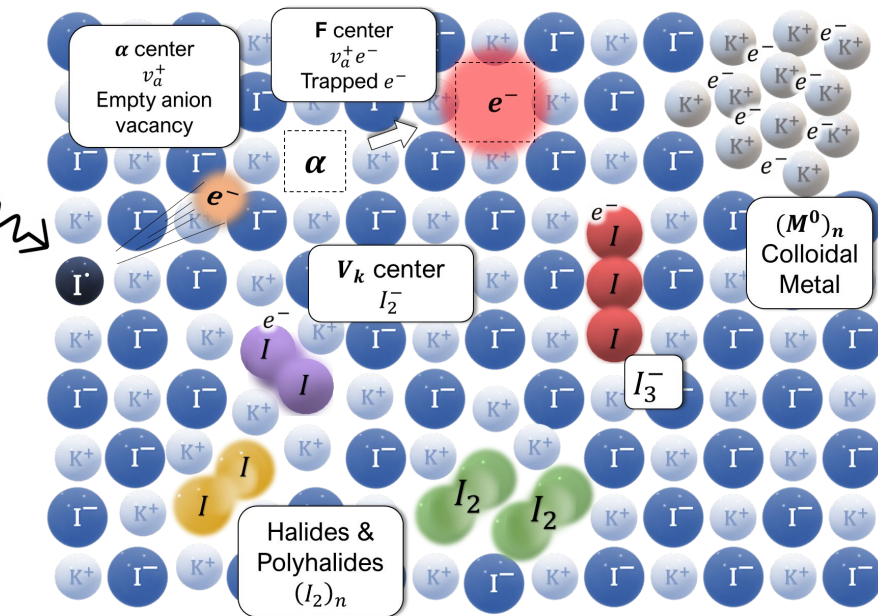
Elucidate their reaction kinetics, mechanisms, and chemical transport as a function of temperature, dose, impurities, and base salt composition



Gamma-irradiation Monovalent (Solid) Iodides

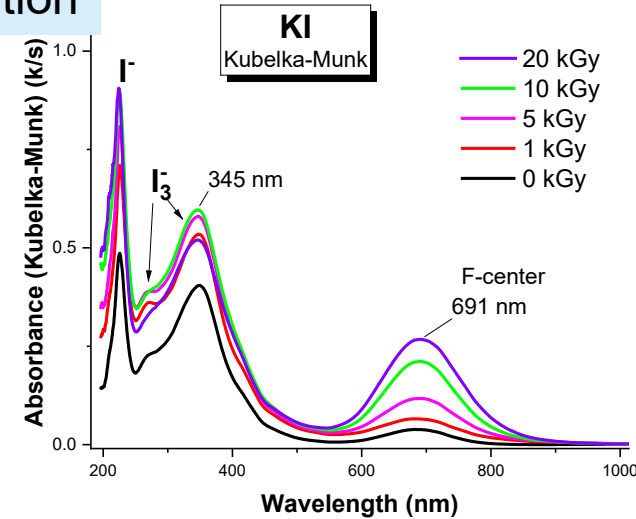


Diffuse Reflectance-Absorption

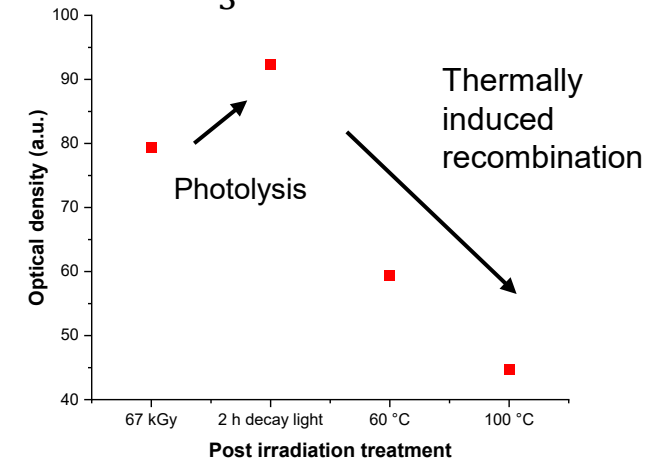
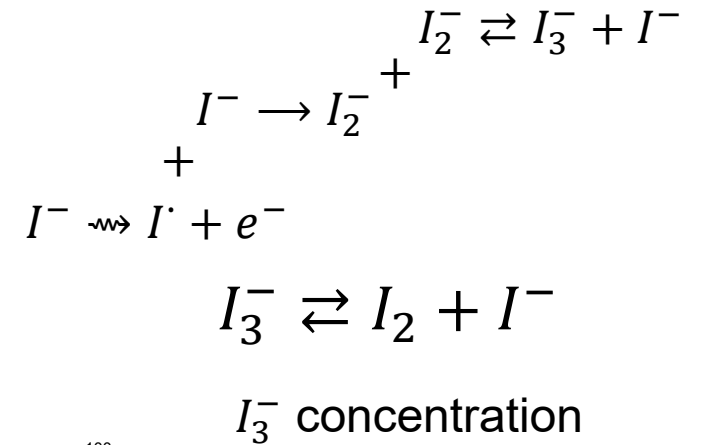
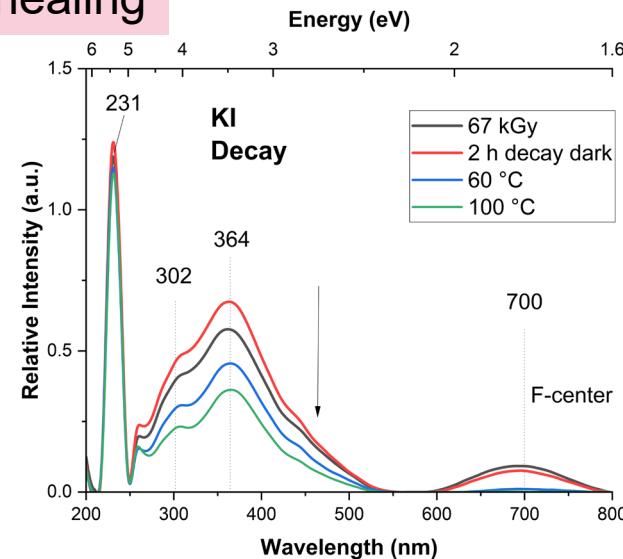


Trapped electrons and IR absorption of I_2^- overlapped, but different decay.

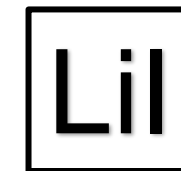
Irradiation



Annealing

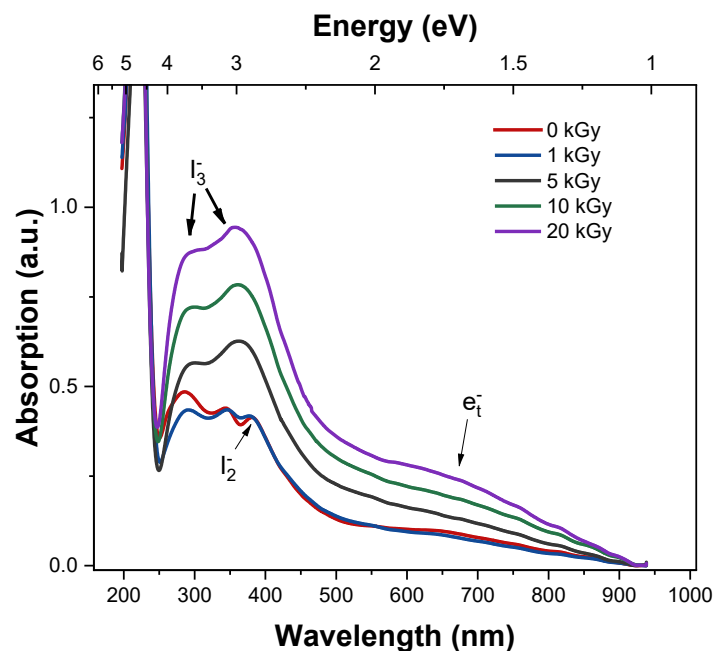


Gamma-irradiation Monovalent (Solid) Iodides

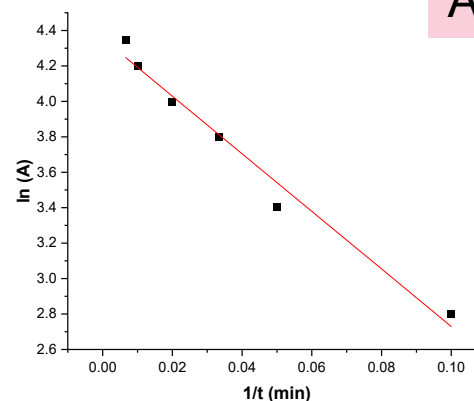


LiI

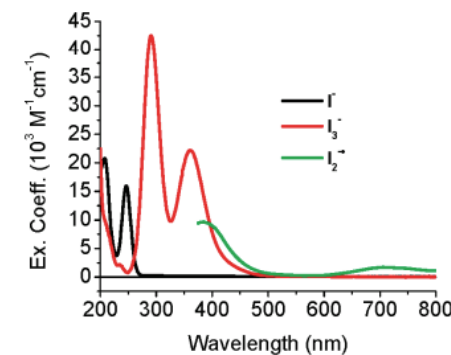
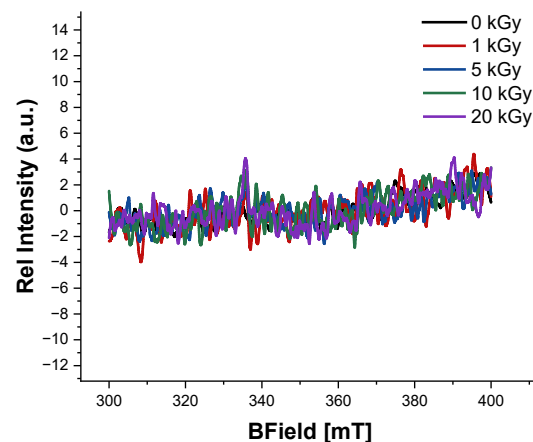
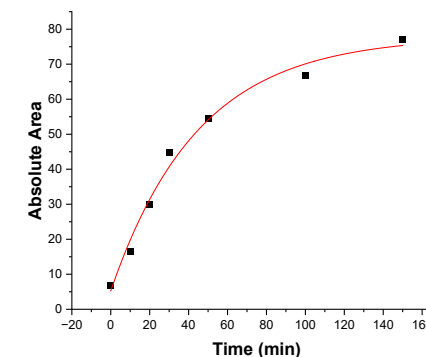
Irradiation



- Higher I_3^- concentration than KI.
- Less stability of trapped electrons



Annealing



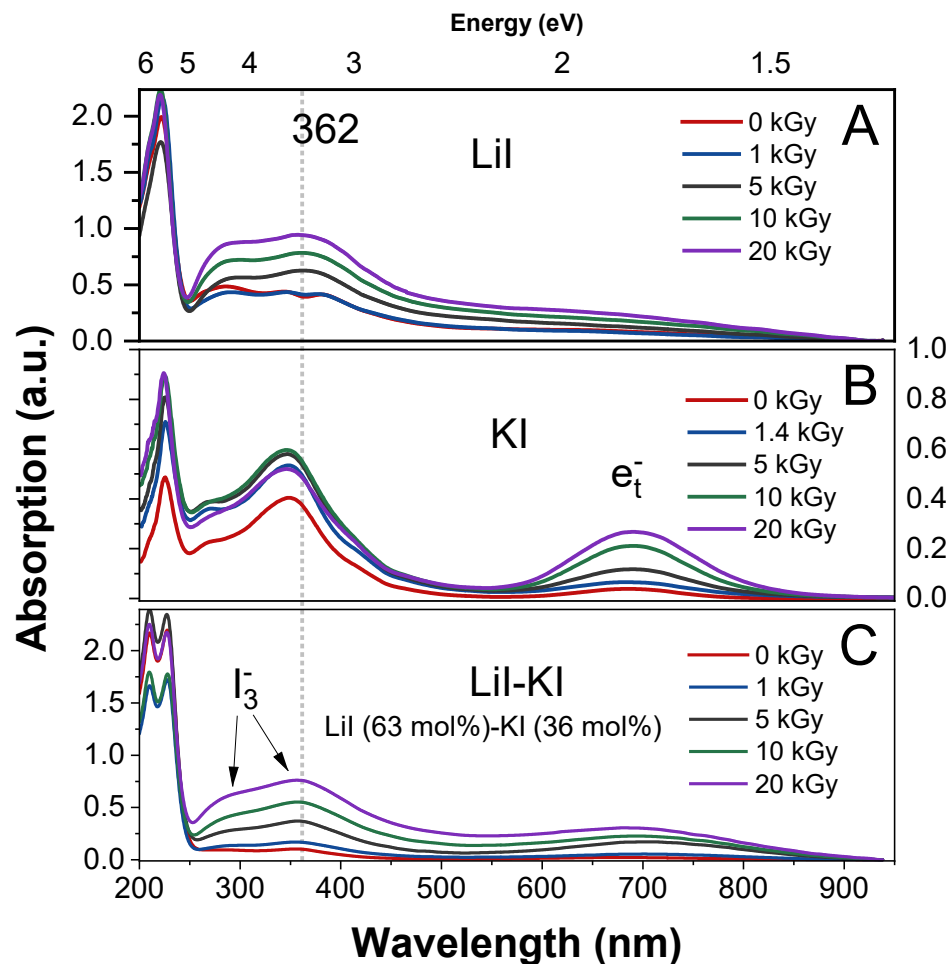
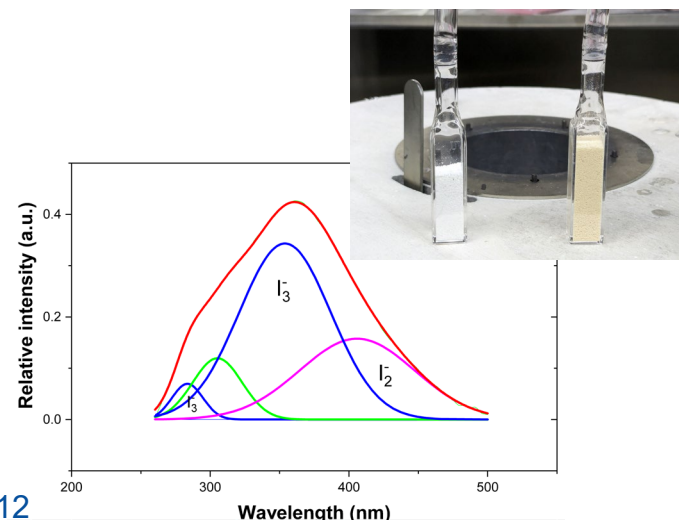
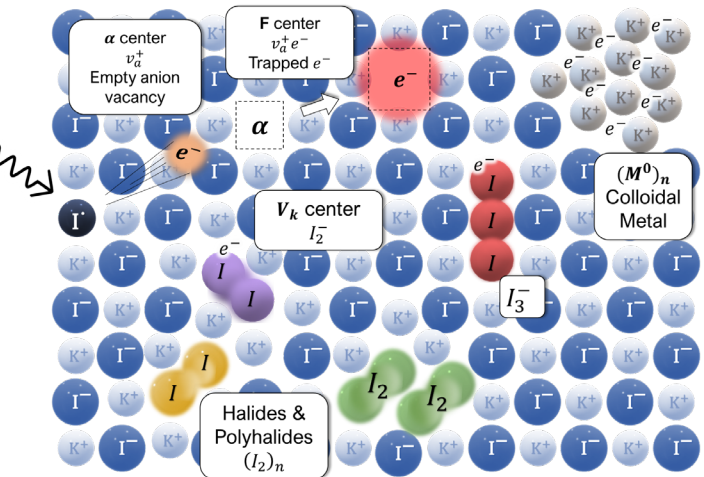
Absorption of iodine in acetonitrile (Gardner et al, 2019)

- Oxidation decreases with heating up to 200 °C $I_2 \rightarrow$
- Crystals at 200 °C for longer times increases I_3^-

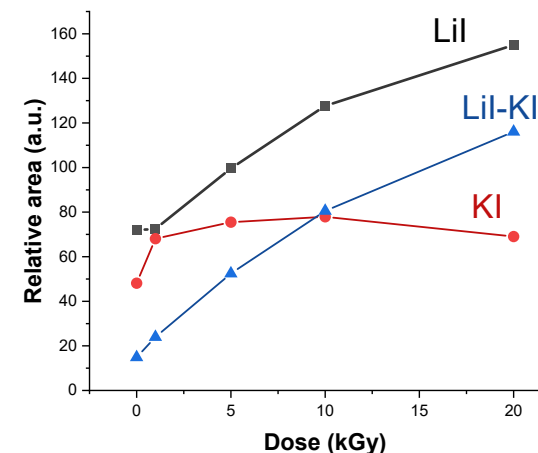
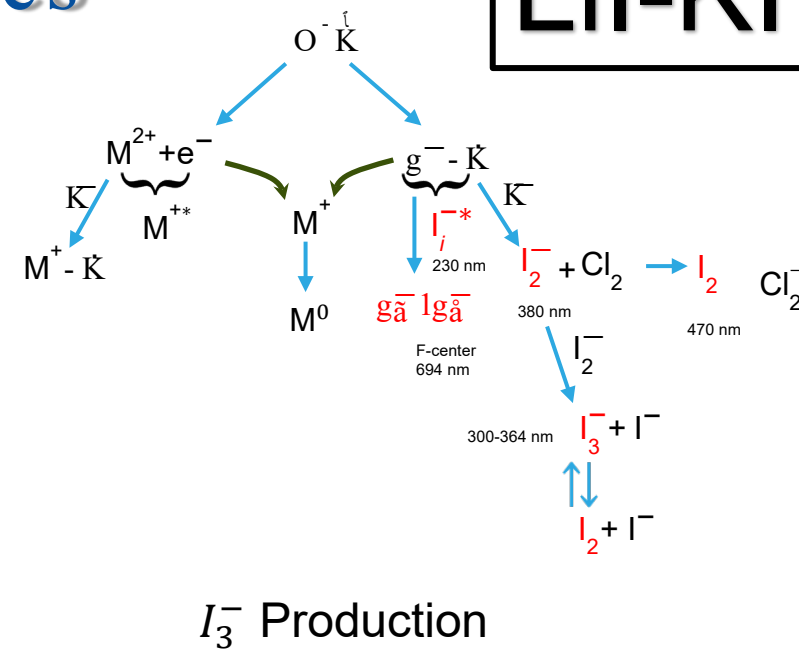
Gardner, J. M., et al. (2009)." Journal of the American Chemical Society 131(44): 16206-16214.

Gamma-irradiation Eutectic (Solid) Iodides

LiI-KI

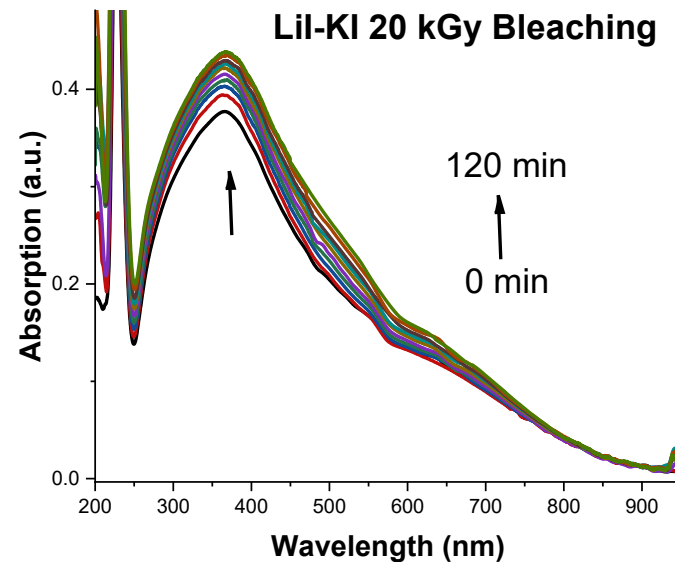
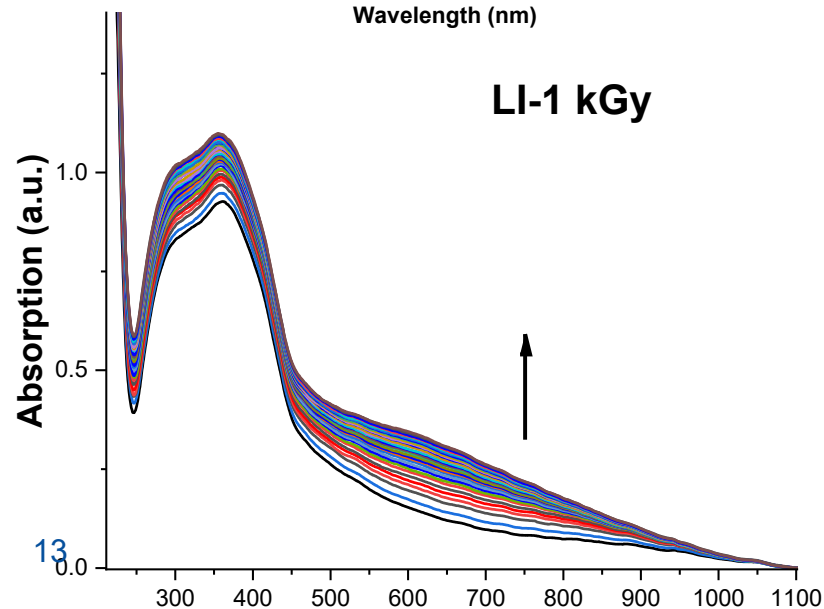
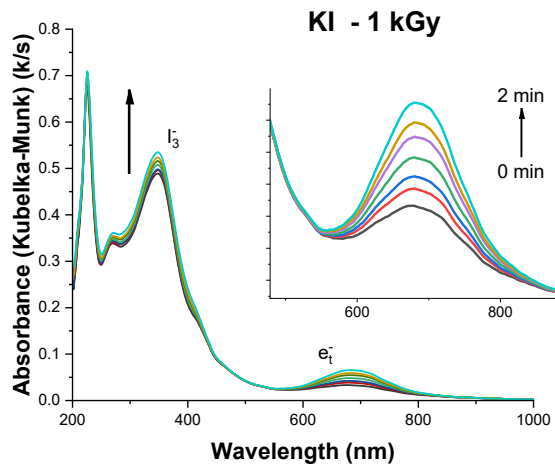
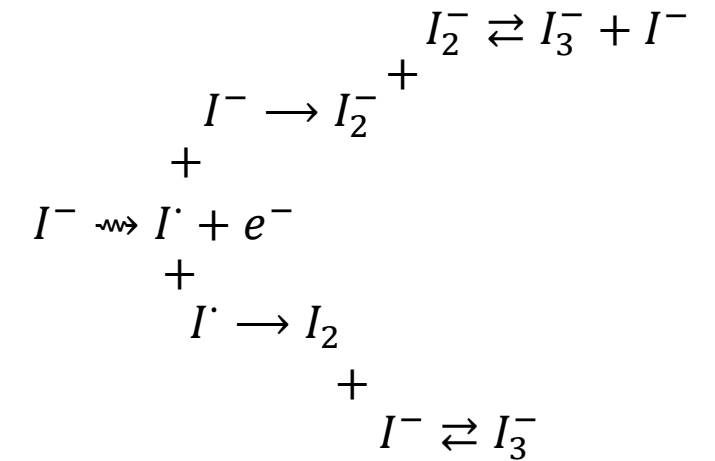


- Faster production/saturation on KI

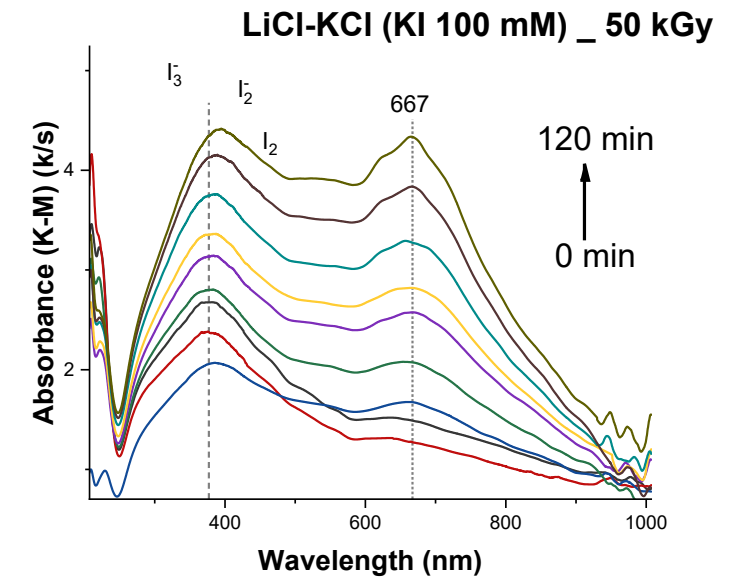


Iodine photolysis

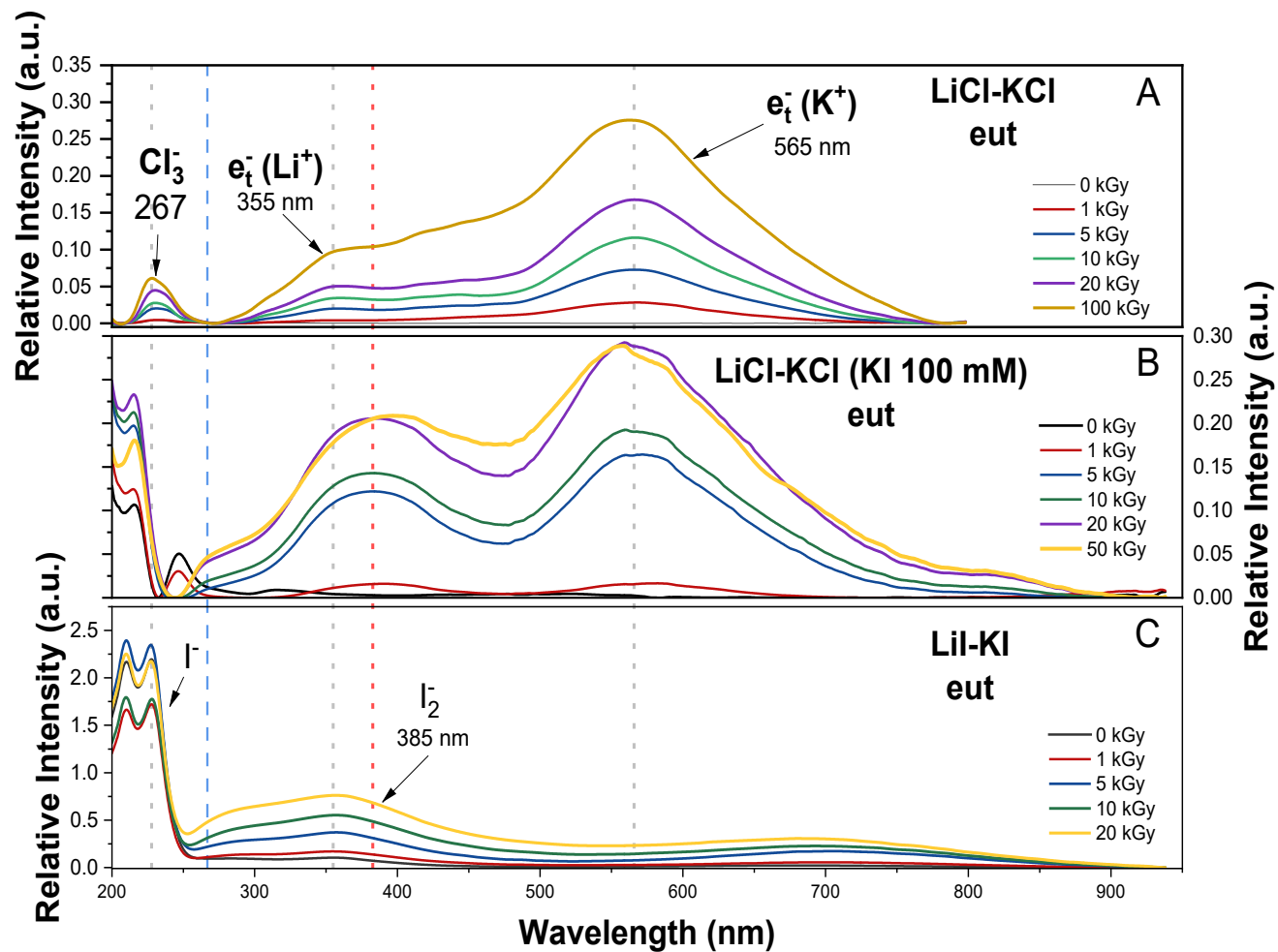
- UV light delivers enough energy to ionize I^- .
- Ionized electrons get trapped in anion vacancies (F-centers)
- Formation of I_3^- .



- LiI $\rightarrow$ more F-centers and I_3^-
- KI $\rightarrow$ Less photolytic effect
- LiI-KI-Unstable trapped electrons

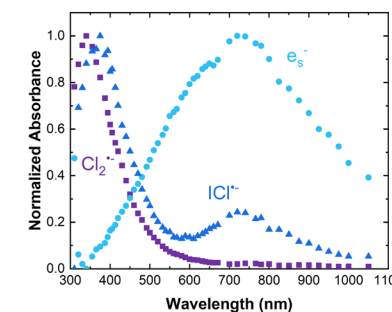
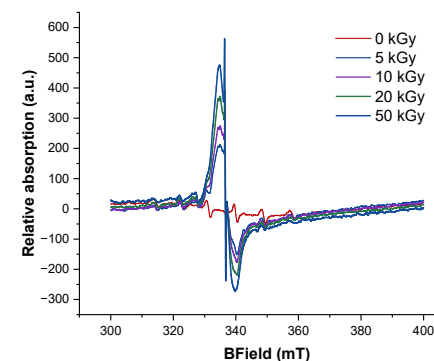
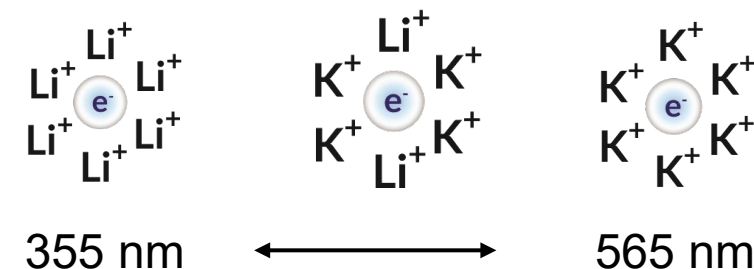


Halide mixtures- Iodide in Chloride media Solid radiolysis



- In chloride media, enhanced production of I_3^- .
- Suppression of Cl_3^- up to 50 kGy.

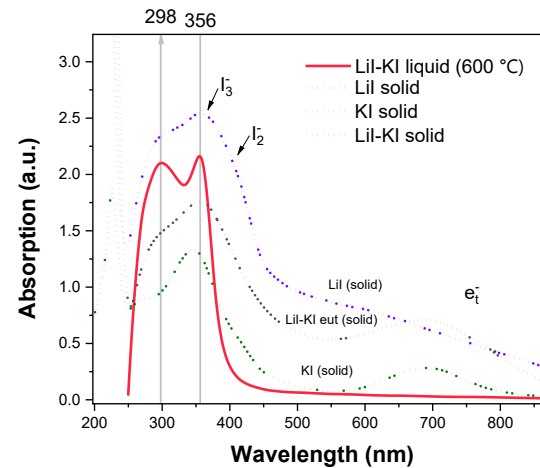
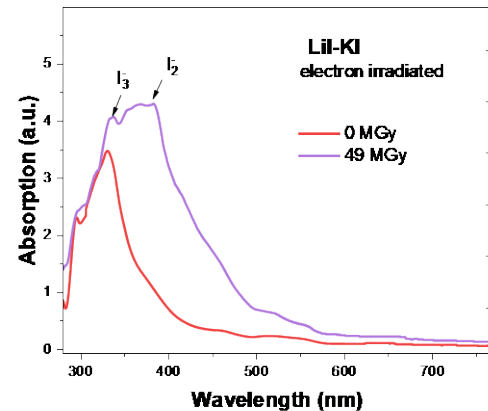
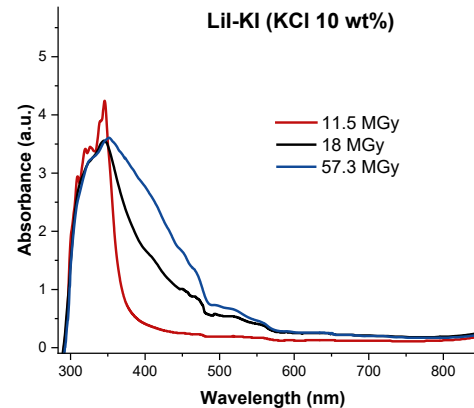
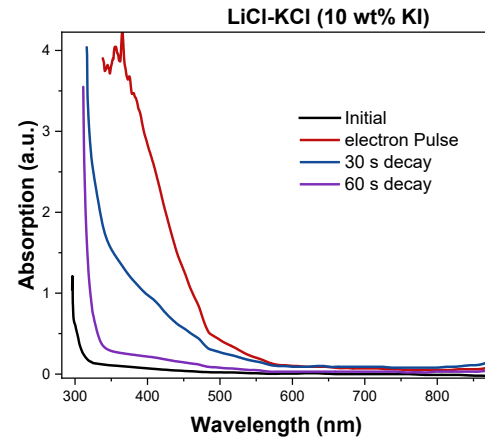
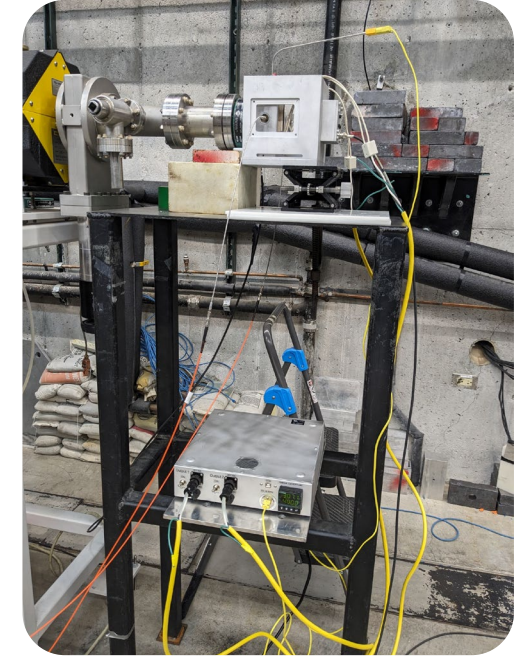
F-centers



Normalized spectra and kinetics after the electron pulse irradiation of 10 wt.% KI in LiCl-KCl eutectic at 400 °C

- Conrad et al., Phys. Chem. Chem. Phys. 2023, 25, 16009.

Electron irradiation of Molten iodides Steady-State

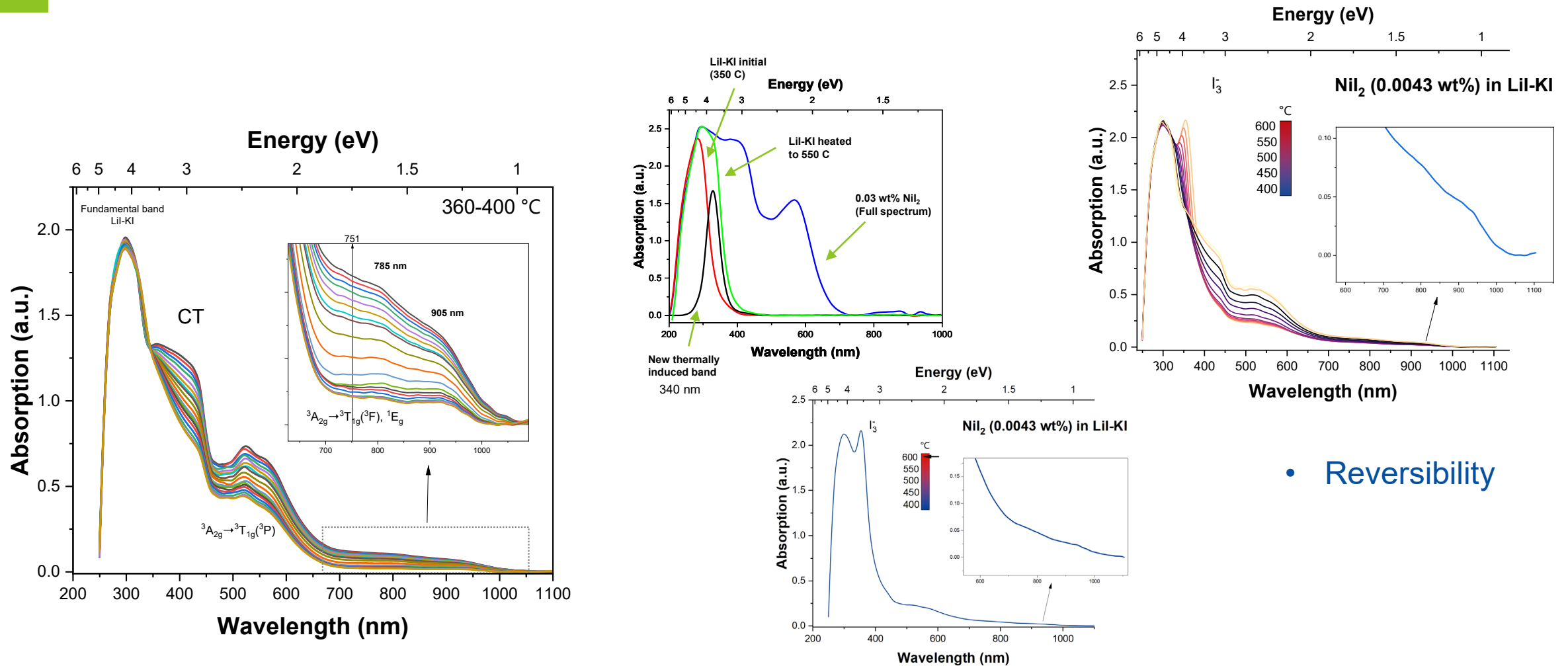


I_3^- Formation
Dissolution in absence of
radiation.

- Formation of colloidal phase.
- Slow dissolution after irradiation.



Temperature and dopant effect ion iodide speciation



- Structural heterogeneity observed for Ni^{2+} in iodide.
 - Ni-I charge transfer. Temperature dependent

• Reversibility

Summary

Objectives:

- Impact of composition, absorbed dose and temperature on Iodine speciation, specifically I_3^- .
- Identification of characteristic absorption features.

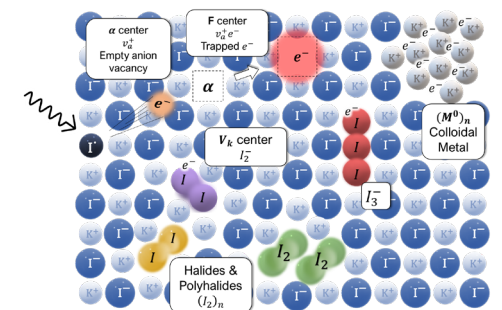
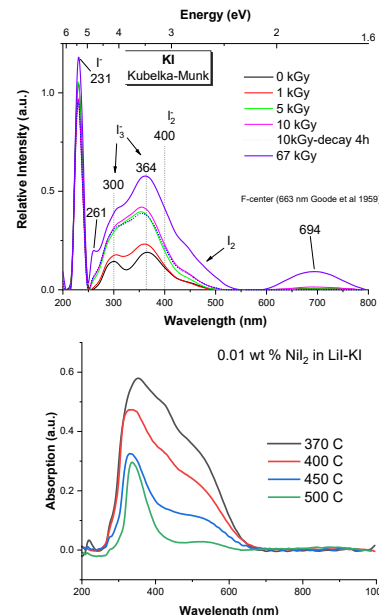


Outcome:

- Establish a technical capabilities for high temp UV-Vis for molten iodides.
- Triiodide (I_3^-) identification in molten salts (chlorides and iodides).
- Temperature and radiation increase triiodide concentration.
- Insoluble phase after irradiation, possible polyiodides
- Nil_2 complexes dependent on temperature and concentration.

Approach:

- **Solid-state radiolysis for**
 - Speciation
- **Steady-state irradiation of Iodides**
 - Changes on $I_3^- \rightleftharpoons I_2^- \rightleftharpoons I_2$
- **High-temperature spectroscopy**





Idaho National Laboratory