INL/CON-23-71014-Revision-0

Experiment with simulation studies of heavy ion radiolysis of aqueous systems

October 2022

Simon M Pimblott, Marisa E Smith, Jay A. LaVerne

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Idaho National Laboratory

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Idaho National Laboratory

Plan

1. Who did the work?
2. Why am I here?
3. What is our goal?
4. What do we do?
5. What have we discovered?
6. Who paid for the work?

Marisa E. Smith

Why am I here?
Why are we here?

Understanding Radiation Effects

Fundamental physical and chemical information.

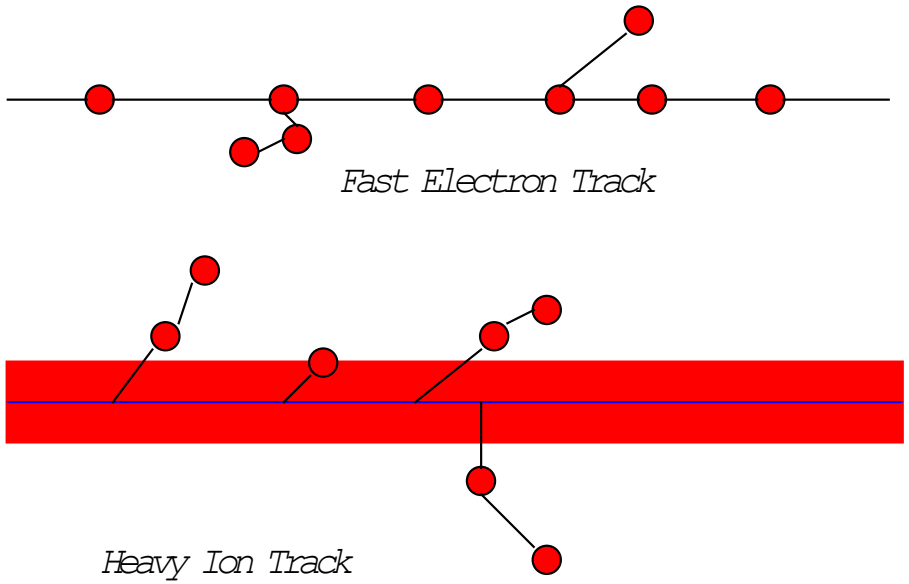
- Cross-sections for collision processes
- Track structures
- Radical chemistry

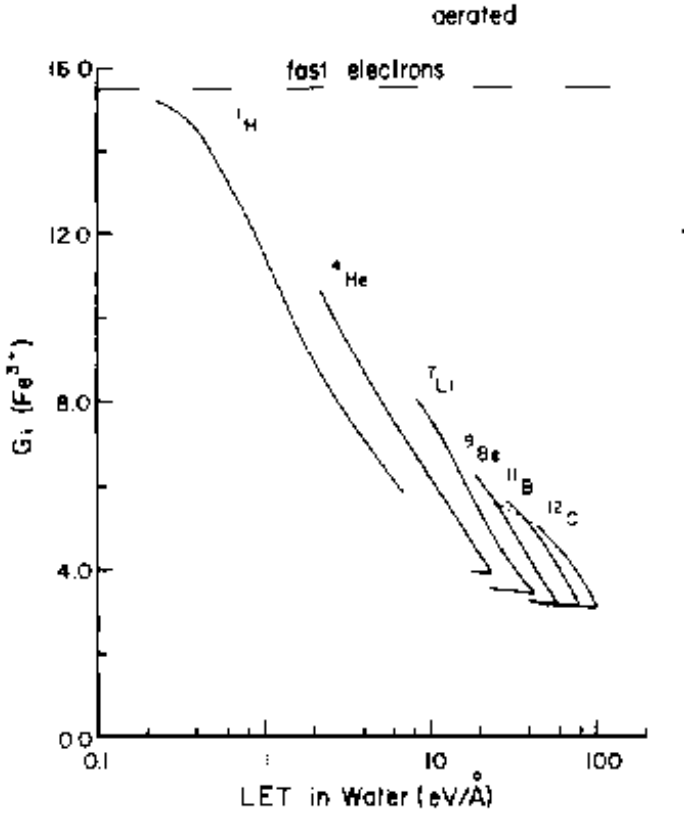
Application in science, medicine and technology.

- **Data of relevance in nuclear power plant design and operation**
- **Radioactive waste management, cleanup disposal and storage**
  - concentrated aqueous systems and polymers
- Cancer therapy - water, aqueous solutions and DNA
- Health physics – predictive models
- Space exploration – solids
- Nanotechnology

Central to the portfolio of DOE ($$$$$), etc …

Radiation Effects for Ions of Different Energies





Radiation Chemical Studies with Heavy Ions: Oxidation of Ferrous Ion in the Fricke Dosimeter[1]

Jay A. LaVerne* and Robert H. Schuler

Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556
(Received: March 30, 1987)

The Journal of Physical Chemistry, Vol. 91, No. 22, 1987

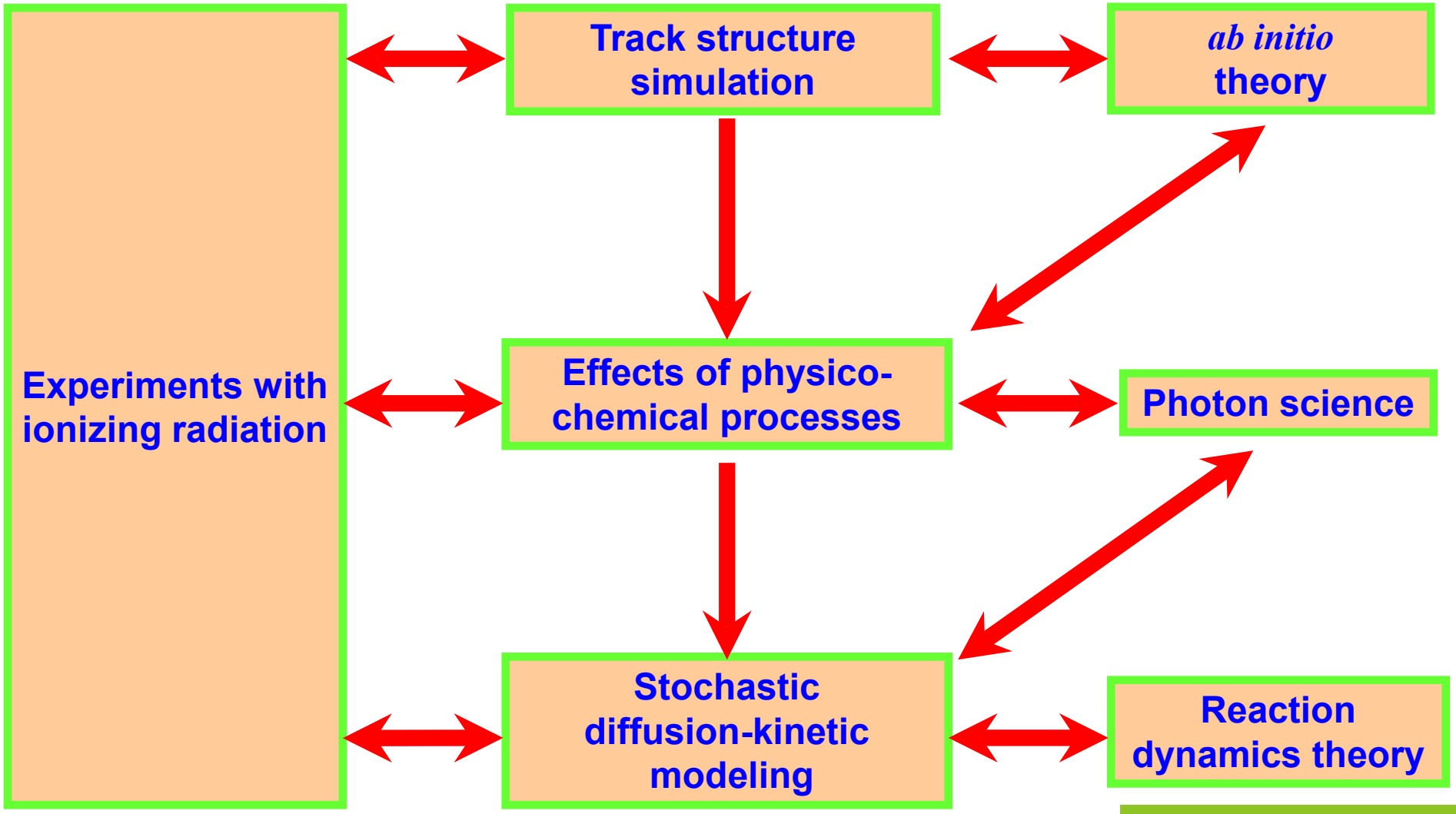
- Observed chemistry relate directly to energy loss properties of radiation.

What is our goal?

Objective

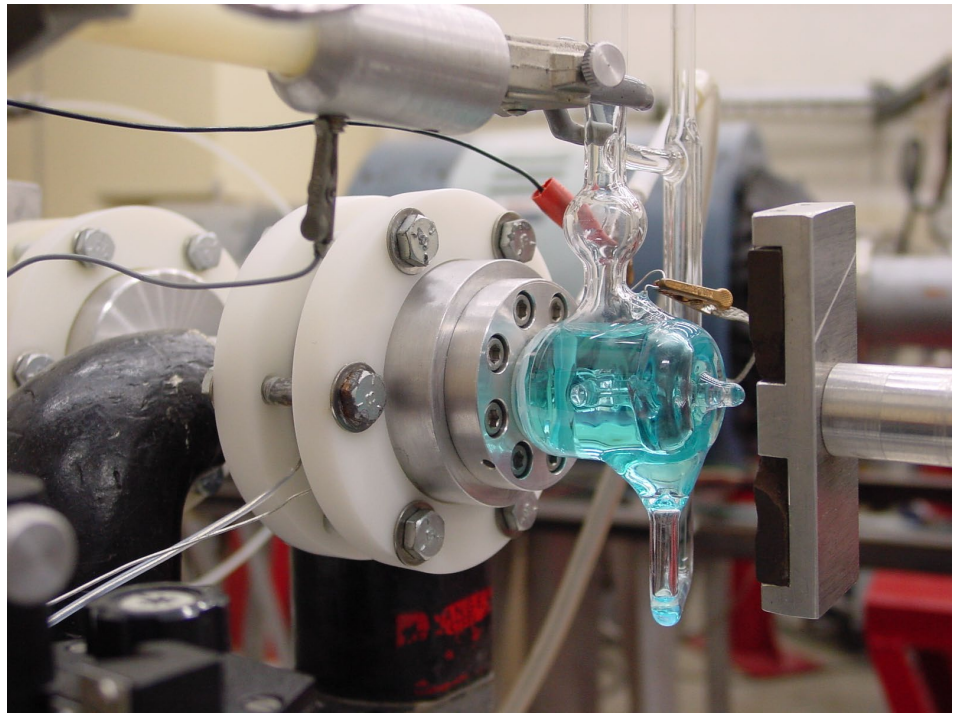
To develop a mechanistic understanding of radiation processes to allow a predictive description of radiation-induced effects

Mechanistic Treatment of Radiation Effects



What do we do?

Radiolysis of Water and Aqueous Solutions



$H_2O \rightarrow e_{aq}^-, H_3O^+, OH, H, H_2, H_2O_2$

e_{aq}^- : dissolution, H_2 formation

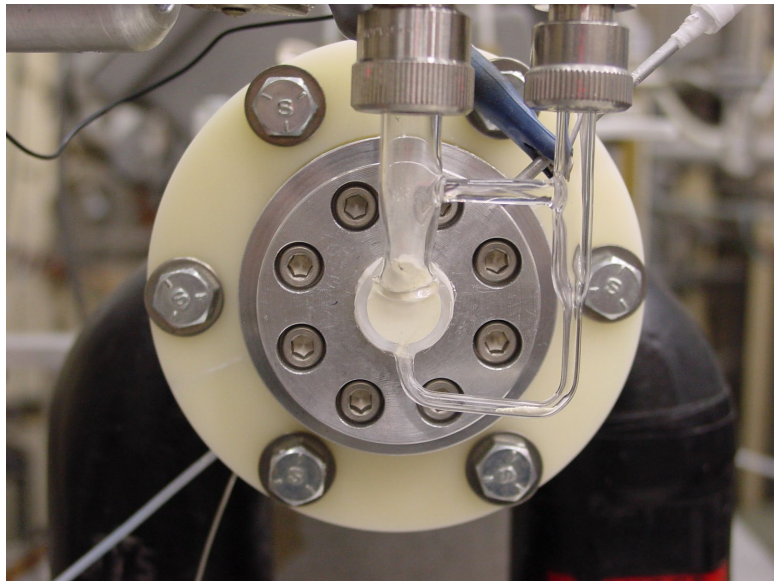
H_2 : explosive, flammable

OH : biological

H_2O_2 : corrosive

fundamental multidisciplinary science → application

Radiolysis of Ceramic Oxide – Water Systems



$H_2O + SiO_2$, ZrO_2, CeO_2, TiO_2, UO_2

- H_2 initiative
- Waste transport / storage
- Fuel rod integrity
- Reactor engineering

fundamental multidisciplinary science → application

Modeling

Energy transfer from radiation

↓

Radiation-induced ionization

↓

Fragmentation, thermalization and solvation

↓

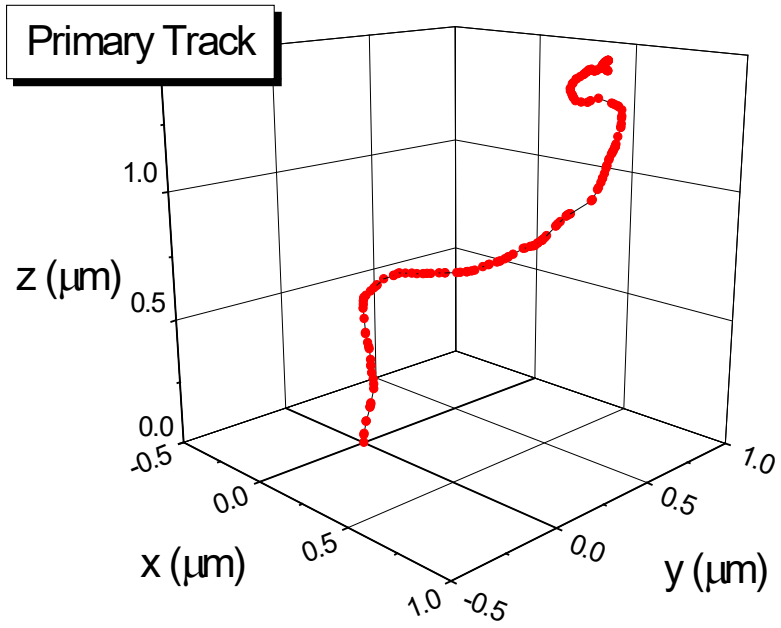
Spatially nonhomogeneous distribution of reactants

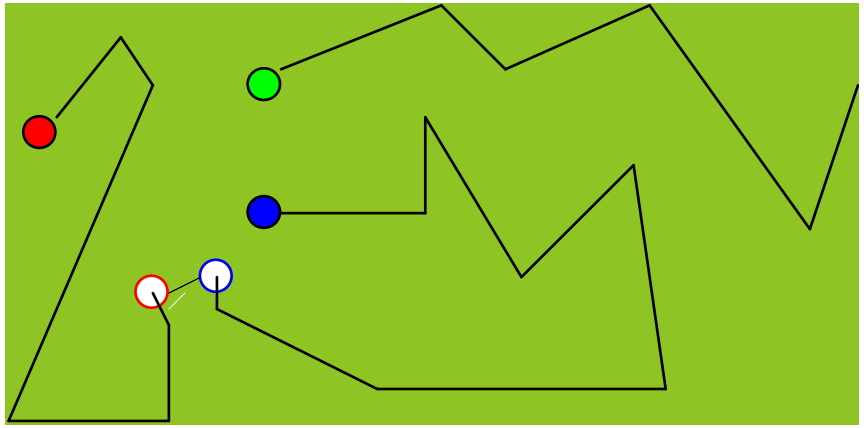
↓

Diffusion-limited chemistry

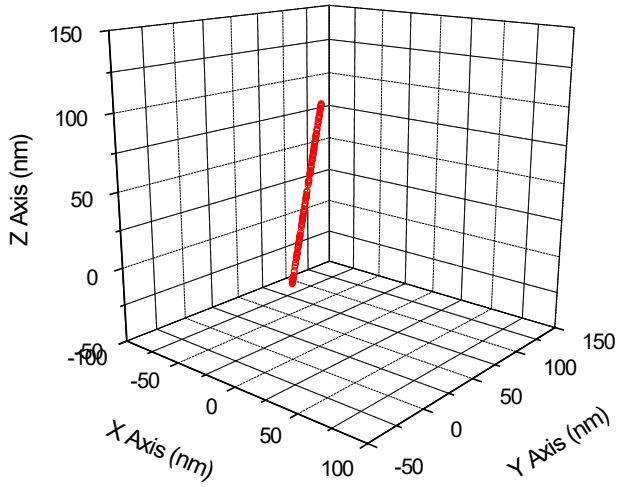
↓

Observed effects

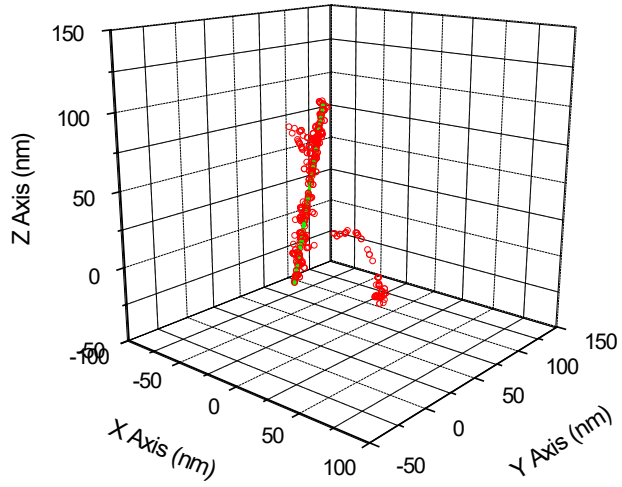




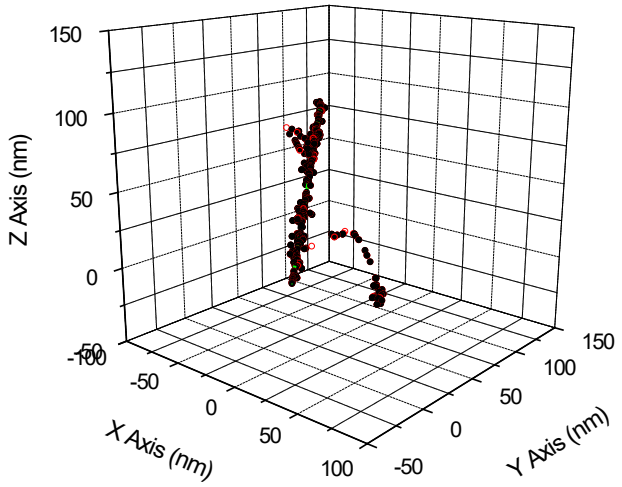
Development of a 10 keV section of a 5 MeV $^{4}He^{2+}$ ion track in water



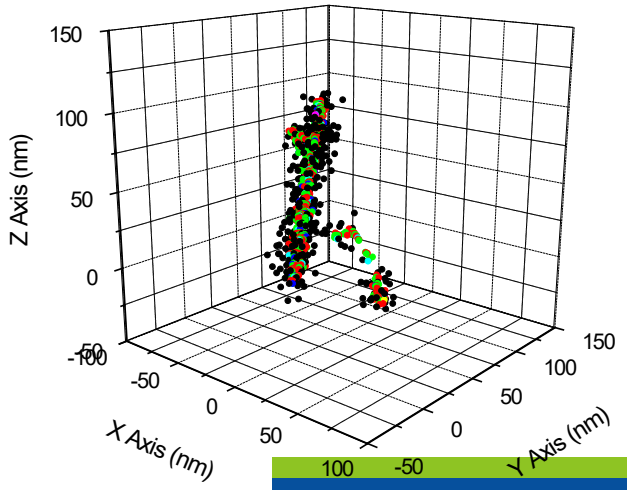
Primary track



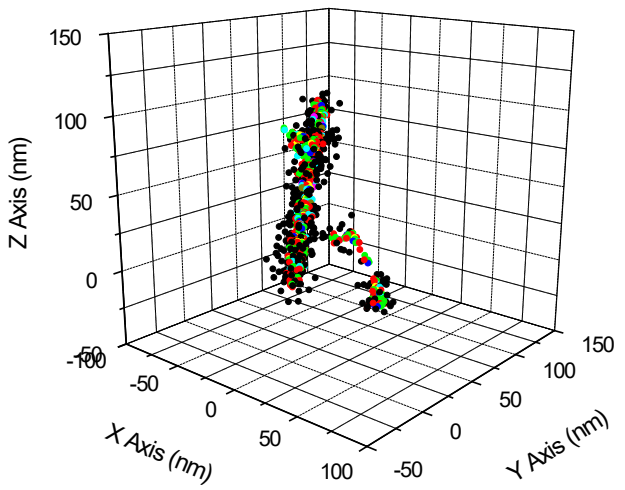
Secondary tracks



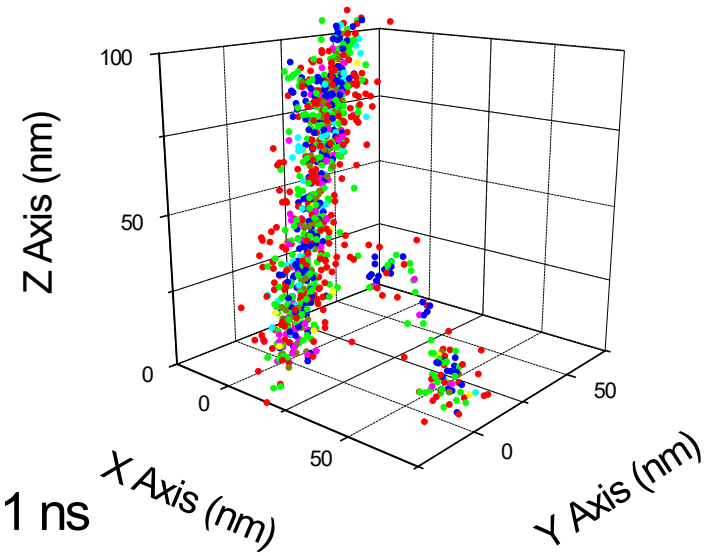
Low energy electrons



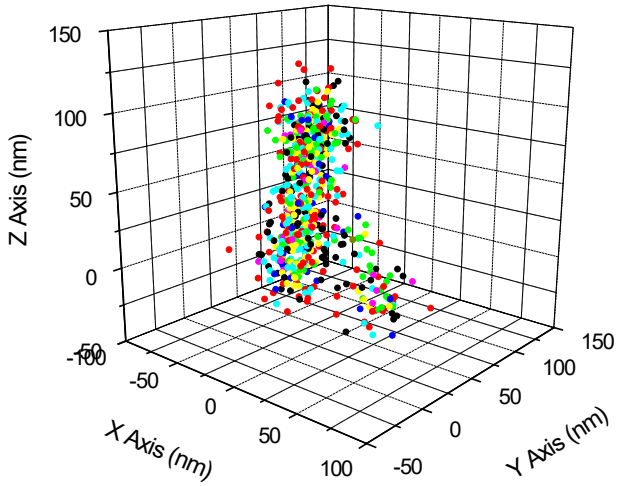
1 ps



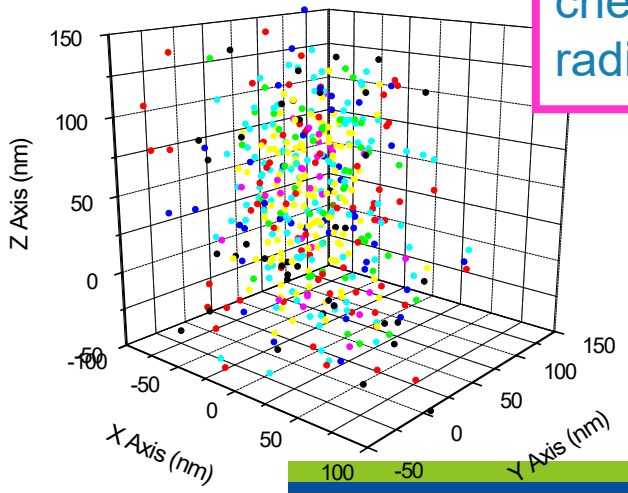
100 ps



1 ns



10 ns



100 ns

Complete description of physical and chemical evolution of radiation track

Effect of Track Structure on Radiation Damage

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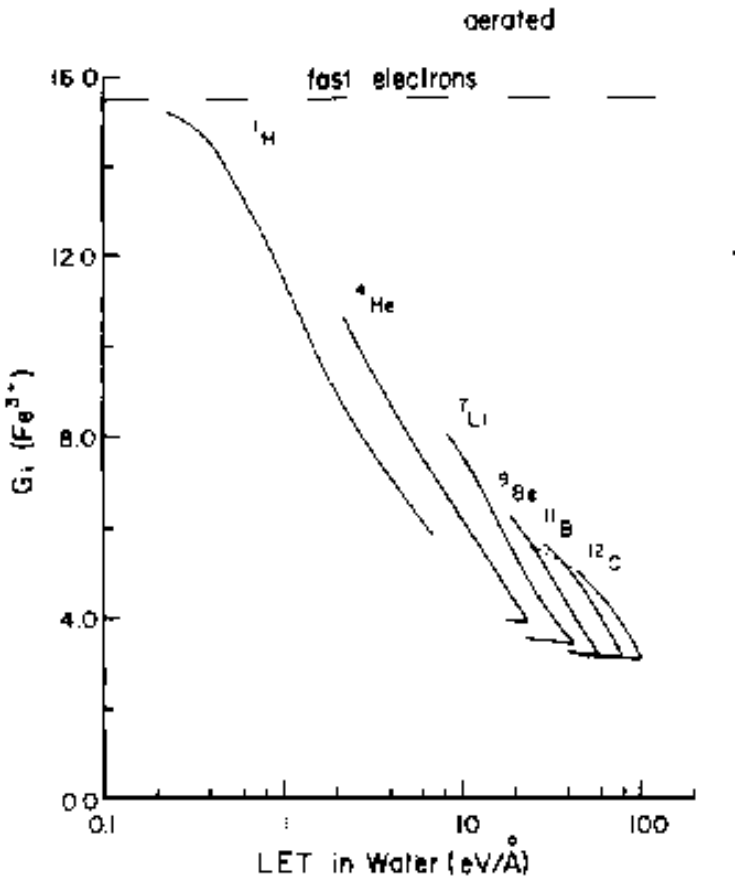
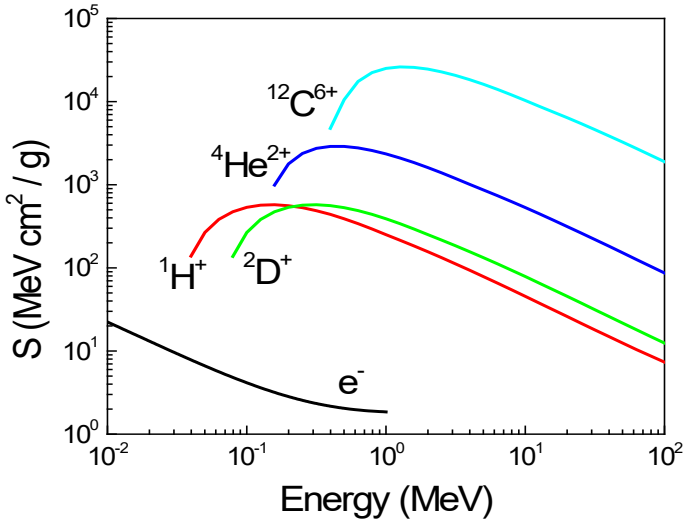


Particle type and energy determine:

- Rate of energy loss
- Track structure
- Spatial distribution of reactants
- Radiation chemistry



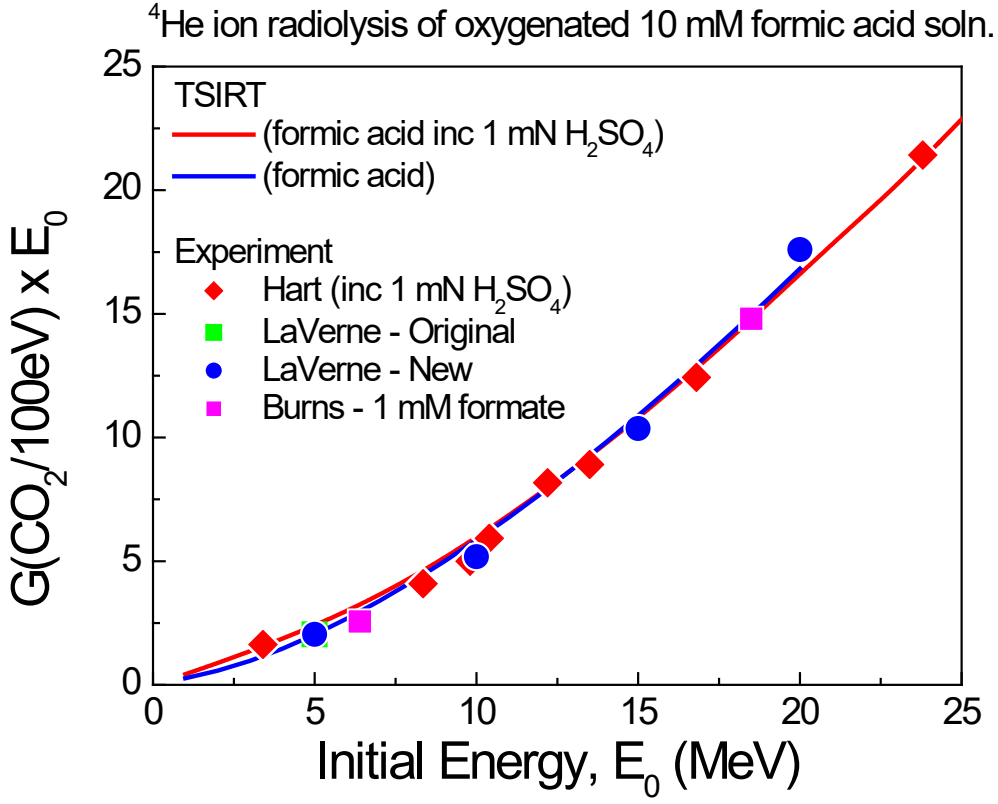
$S(^{W}M^{Z+};E) \sim Z^2\, S(H^+;E/W)$

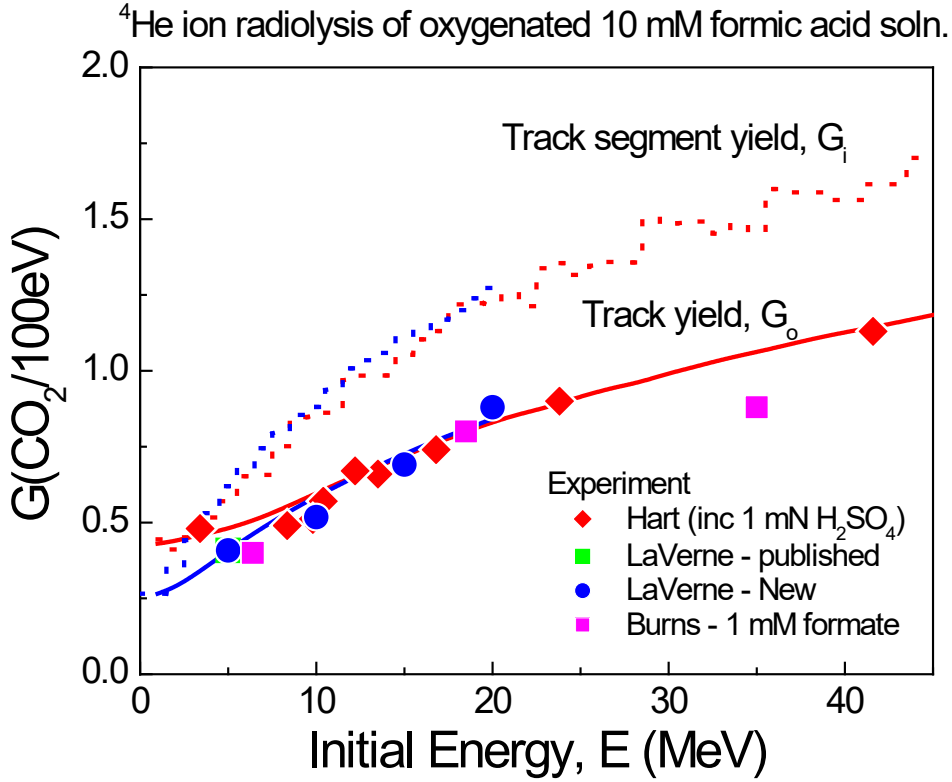
What have we discovered?

Radiolysis of Formic Acid Solution
H-CO-OH

$$\bullet OH + HCO_2H \rightarrow H_2O + \bullet CO_2H$$
$$\bullet H + HCO_2H \rightarrow H_2 + \bullet CO_2H$$
$$\bullet CO_2H + O_2 \rightarrow CO_2 + H_{aq}^{+} + O_2^{-}\bullet$$

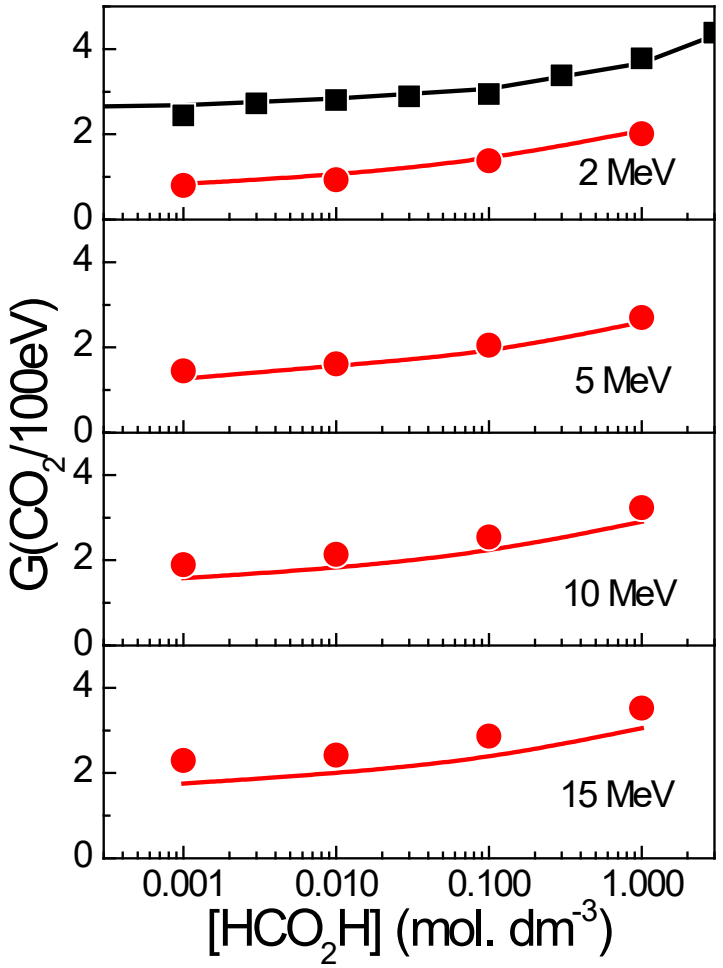
Heavy Ion Energy Dependence of Yields



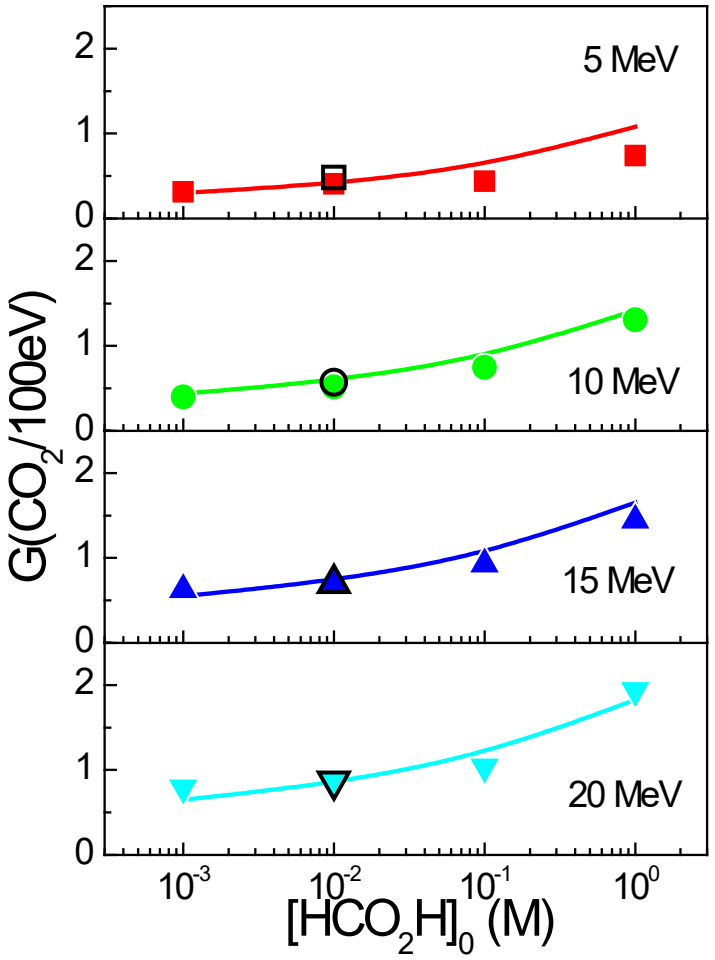


Effects of γ, p^+ and α Radiations

$^1H^+$ radiolysis of oxygenated formic acid solutions



^4He ion radiolysis of oxygenated formic acid soln.

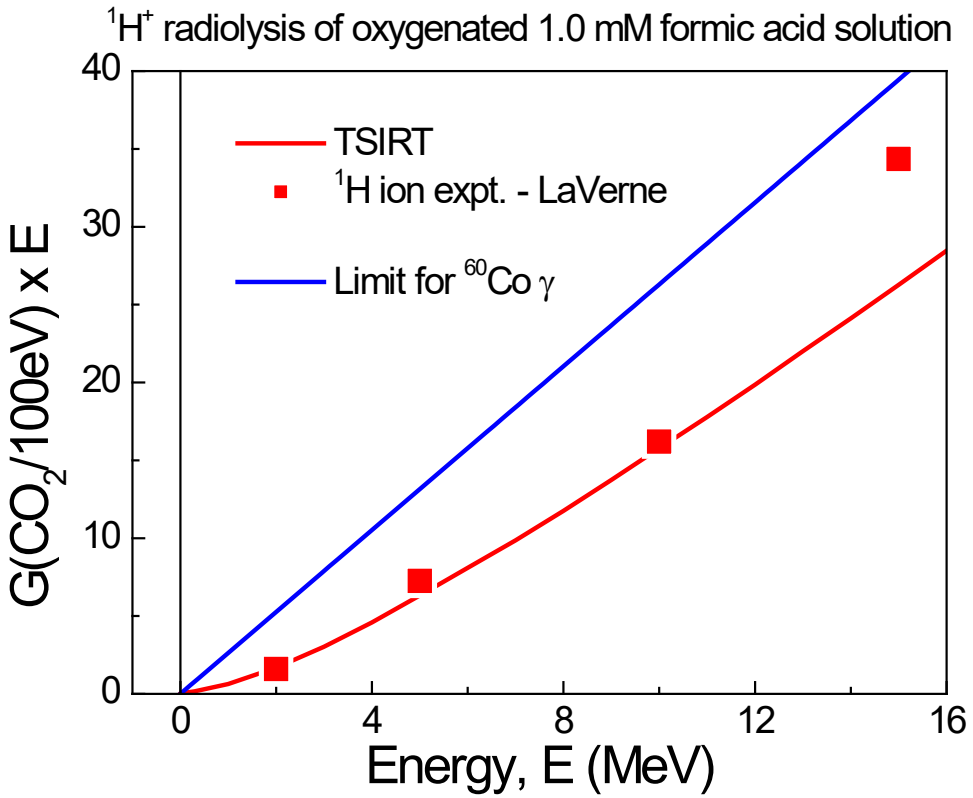


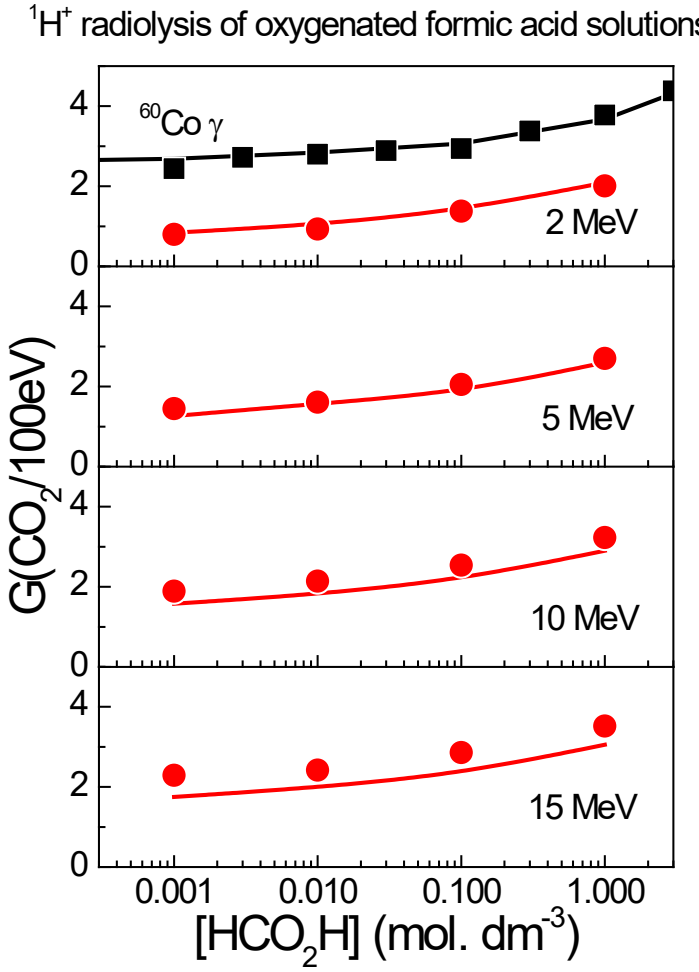
Hydrated electron yield

$$e_{aq}^- + {}^+NH_3CH_2CONHCH_2CO_2^- \rightarrow {}^{\bullet}NH_3CH_2CONHCH_2CO_2^-$$

$$NH_3CH_2CONHCH_2CO_2^- + H_2O \rightarrow NH_4^+ + \ldots$$

Effect of Scavenger Concentration





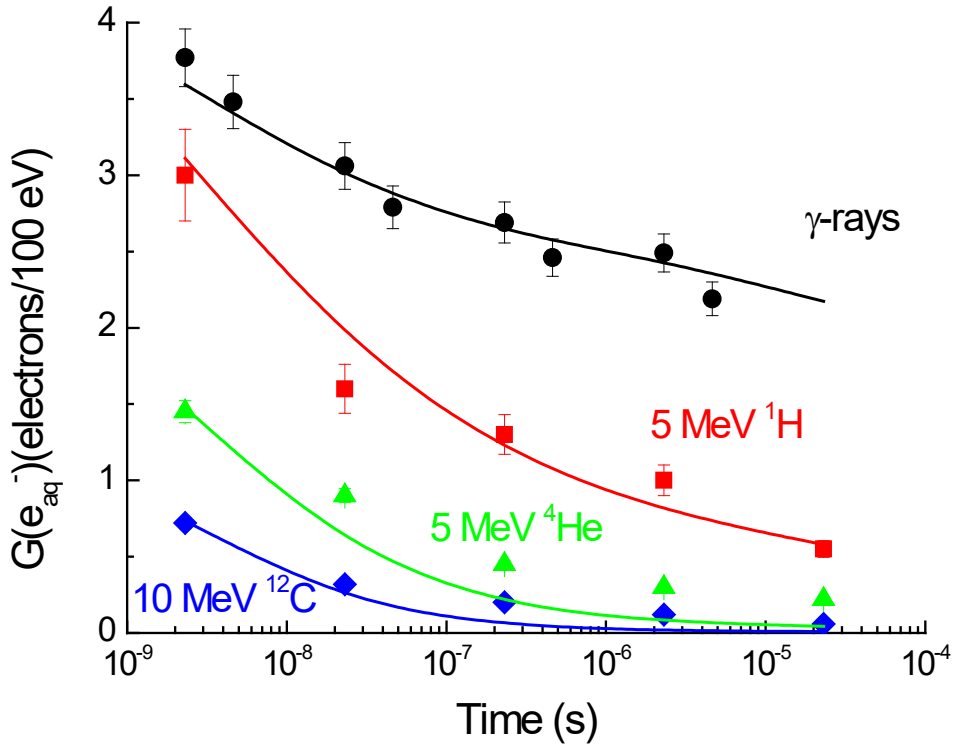
- Yield of OH increases with additive concentration
- Yield of OH decreases with increasing LET

Time Dependent Kinetics

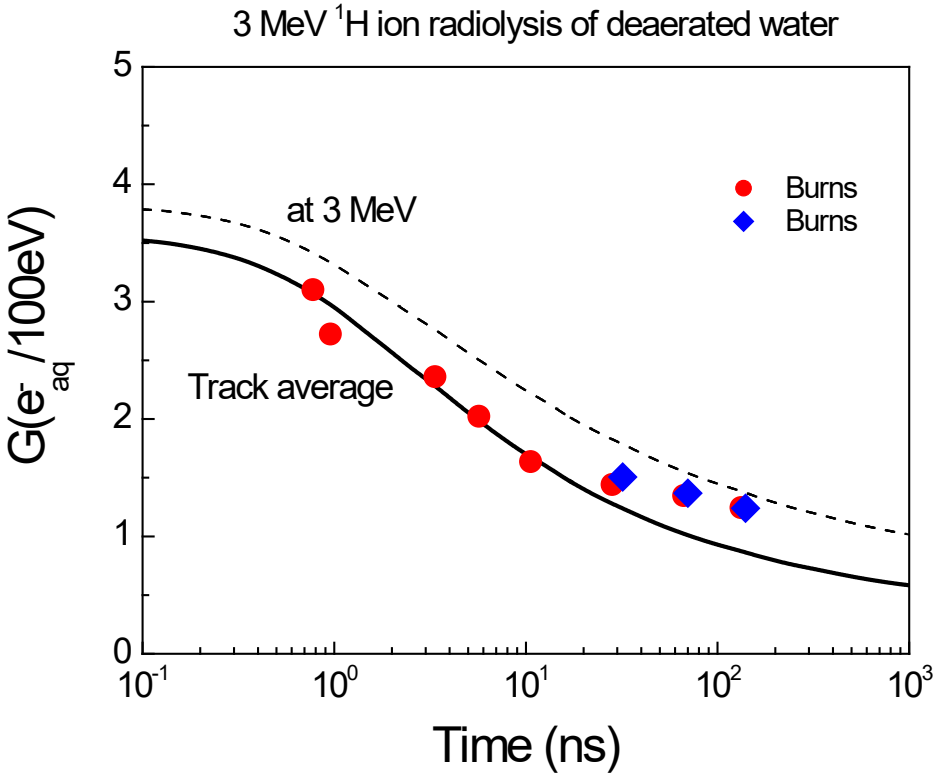
Direct observation of primary transients is desirable but limited.

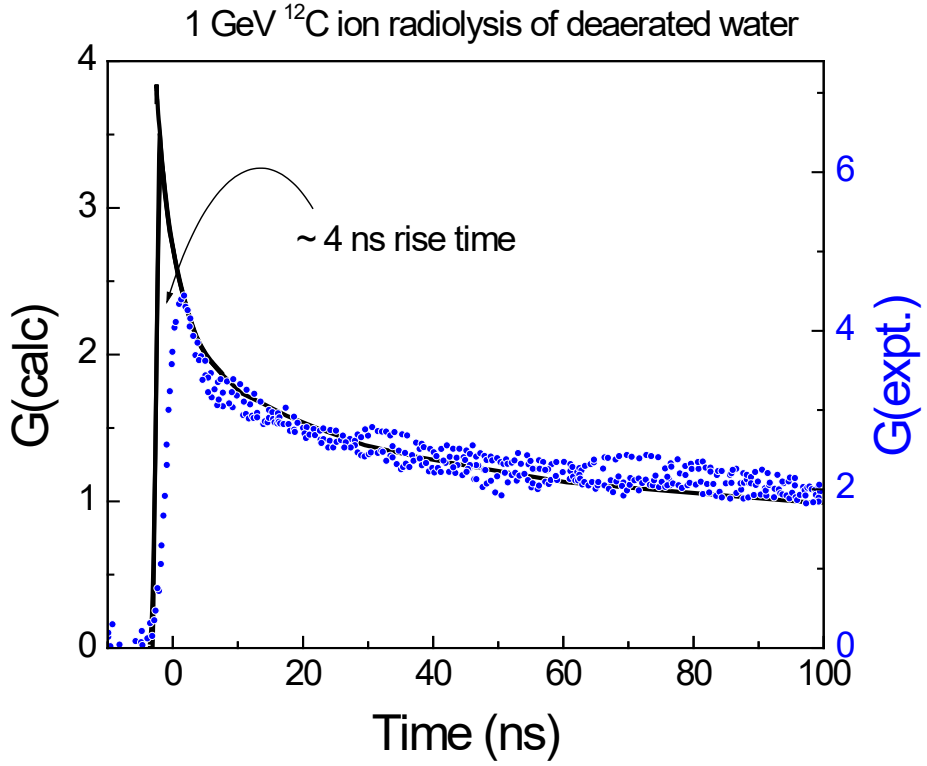
Kinetic studies
- employ added solutes to "scavenge" transient
- monitor effects of scavenger concentration on an observable as

$$k\,[S] \sim t^{-1}.$$



Decay Kinetics of e_{aq}^-

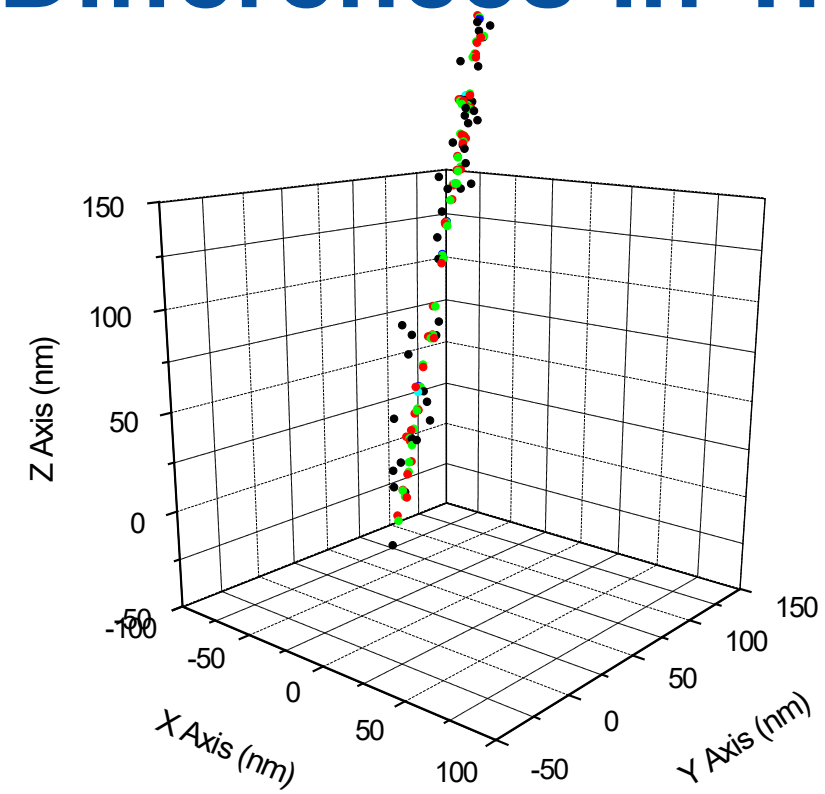




- Limited experimental data
- Yield of e_{aq}^- decreases with increasing LET

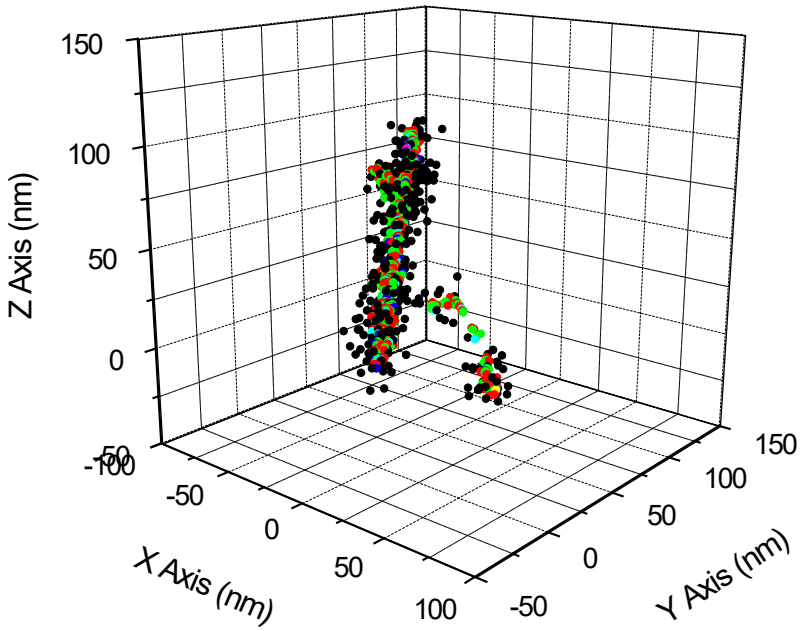
Origin of Track Effects on Radiation Chemistry

Differences in Track Structure



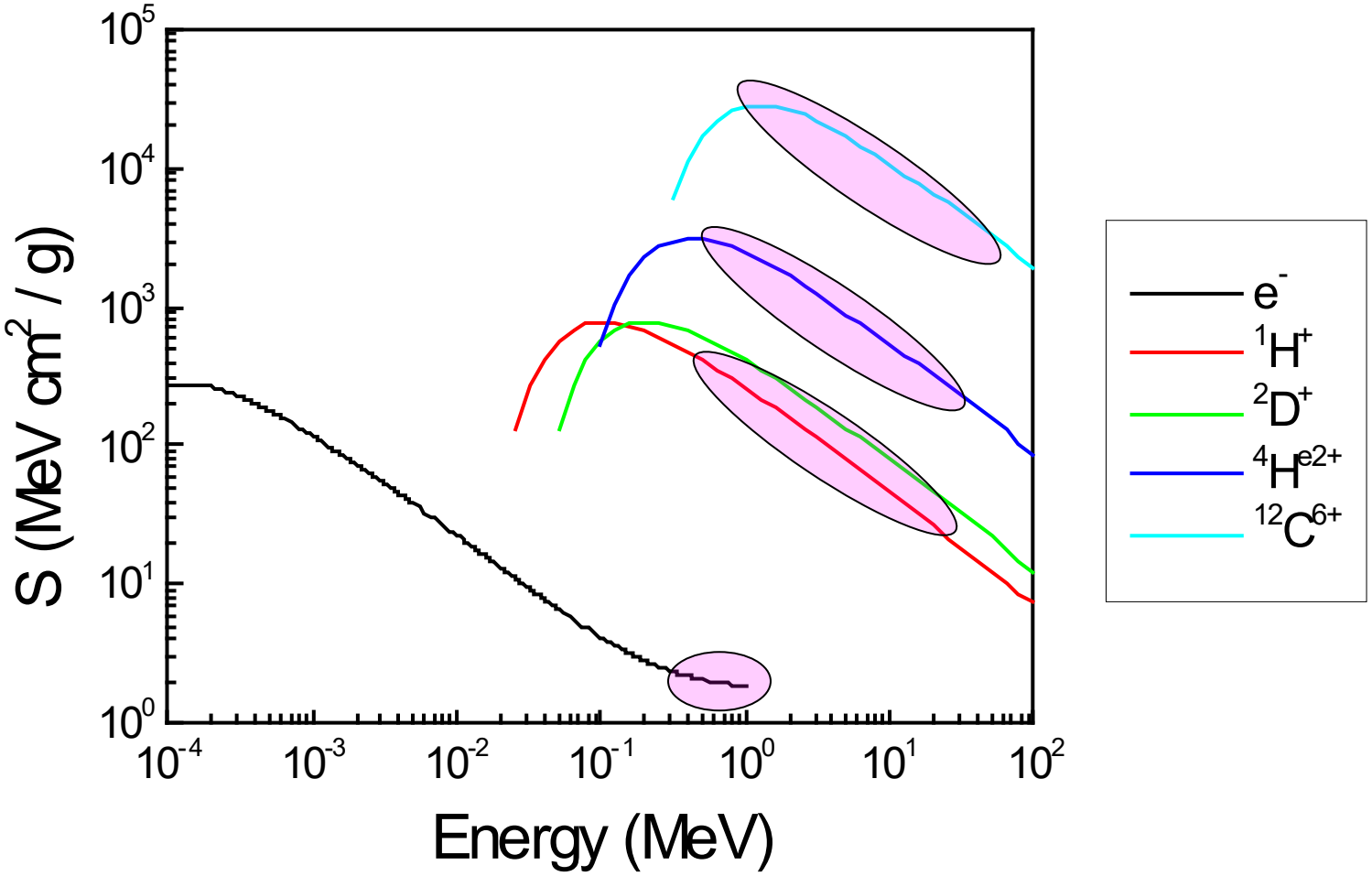
First 10 keV of 10 MeV $^{1}H^{+}$ track at 1 ps

Black : e^-_{aq}
Red : H_3O^+
Green : OH
Blue : H
Cyan : H_2
Magenta : OH^-
Yellow : H_2O_2
Dark yellow : $O(^3P)$



First 10 keV of 5 MeV $^{4}He^{2+}$ track at 1 ps

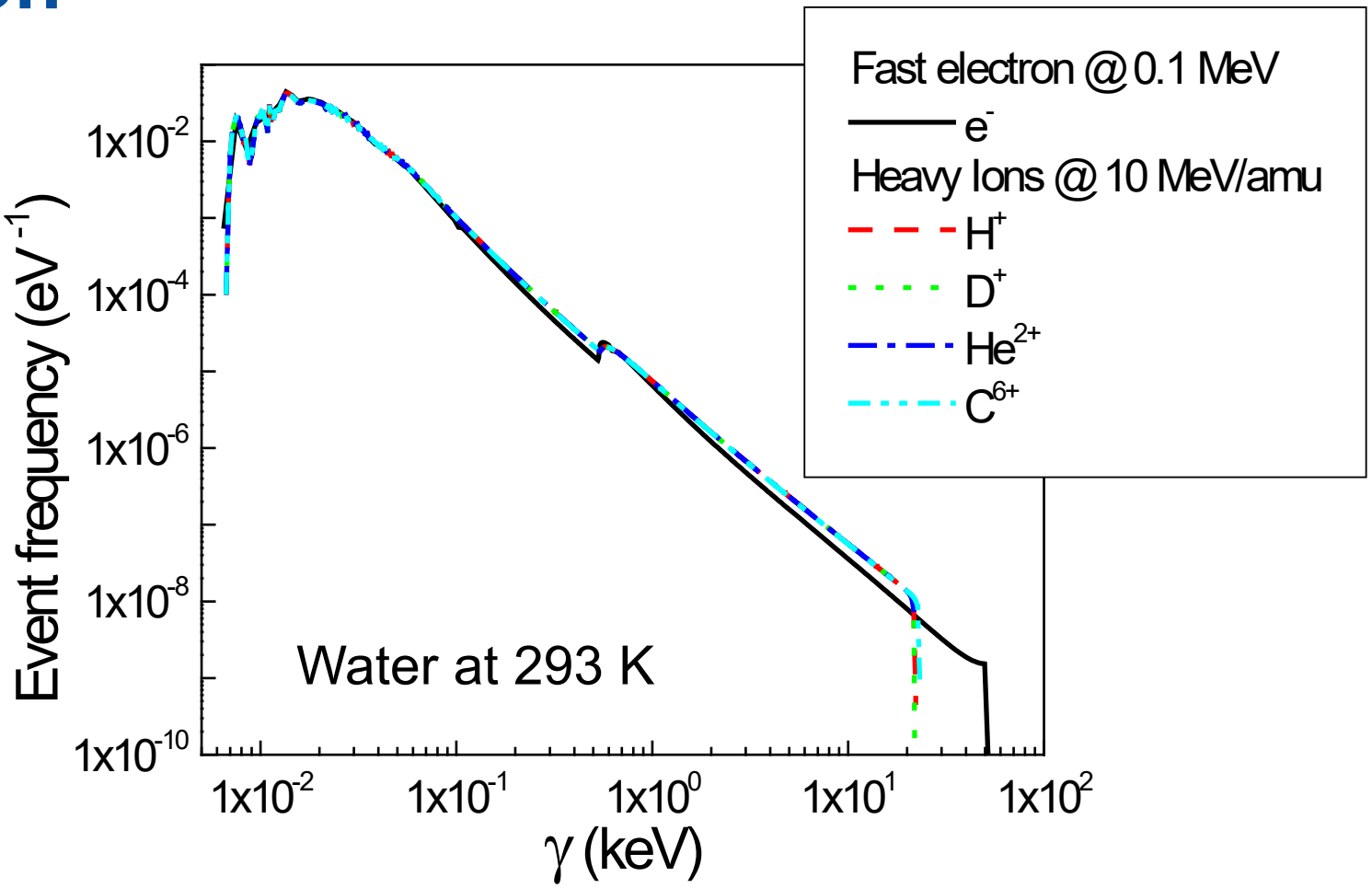
Heavy Ion Radiolysis



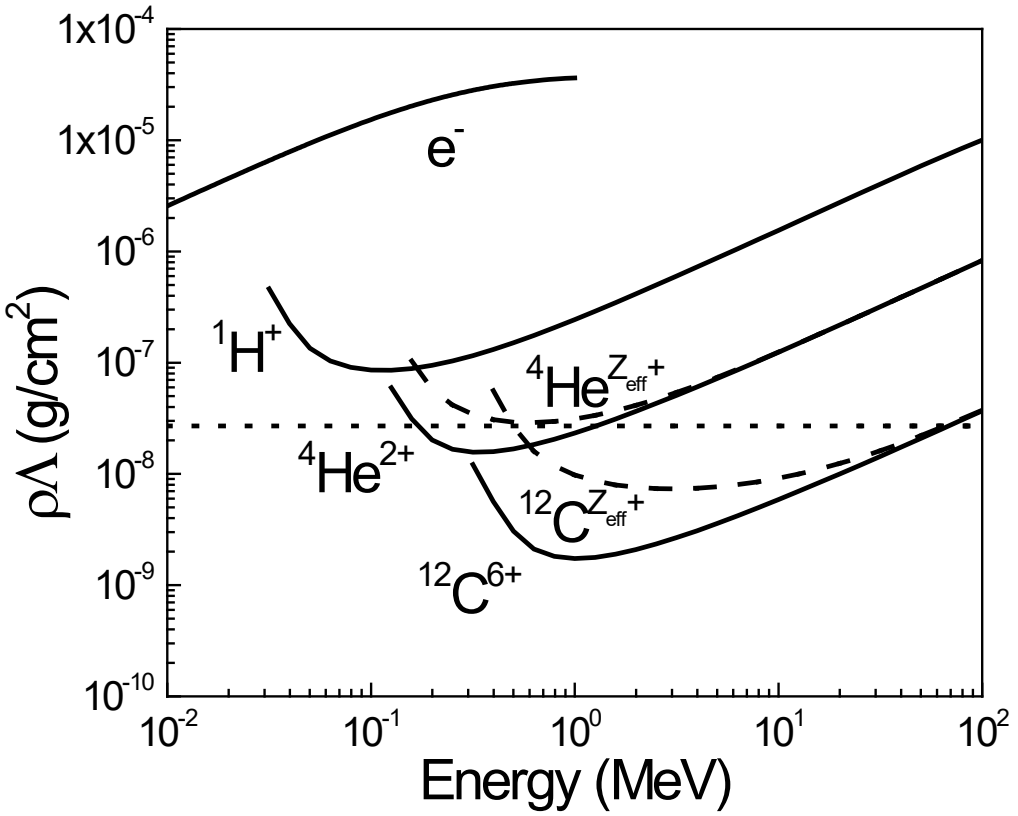
- Stopping power changes by orders of magnitude
- Significant increase in local damage & radical concentration

Effect of Radiation Type on Primary Event Energy Distribution

- Depends on velocity of ion, E/m
- Does not depend upon the charge of the ion, Z



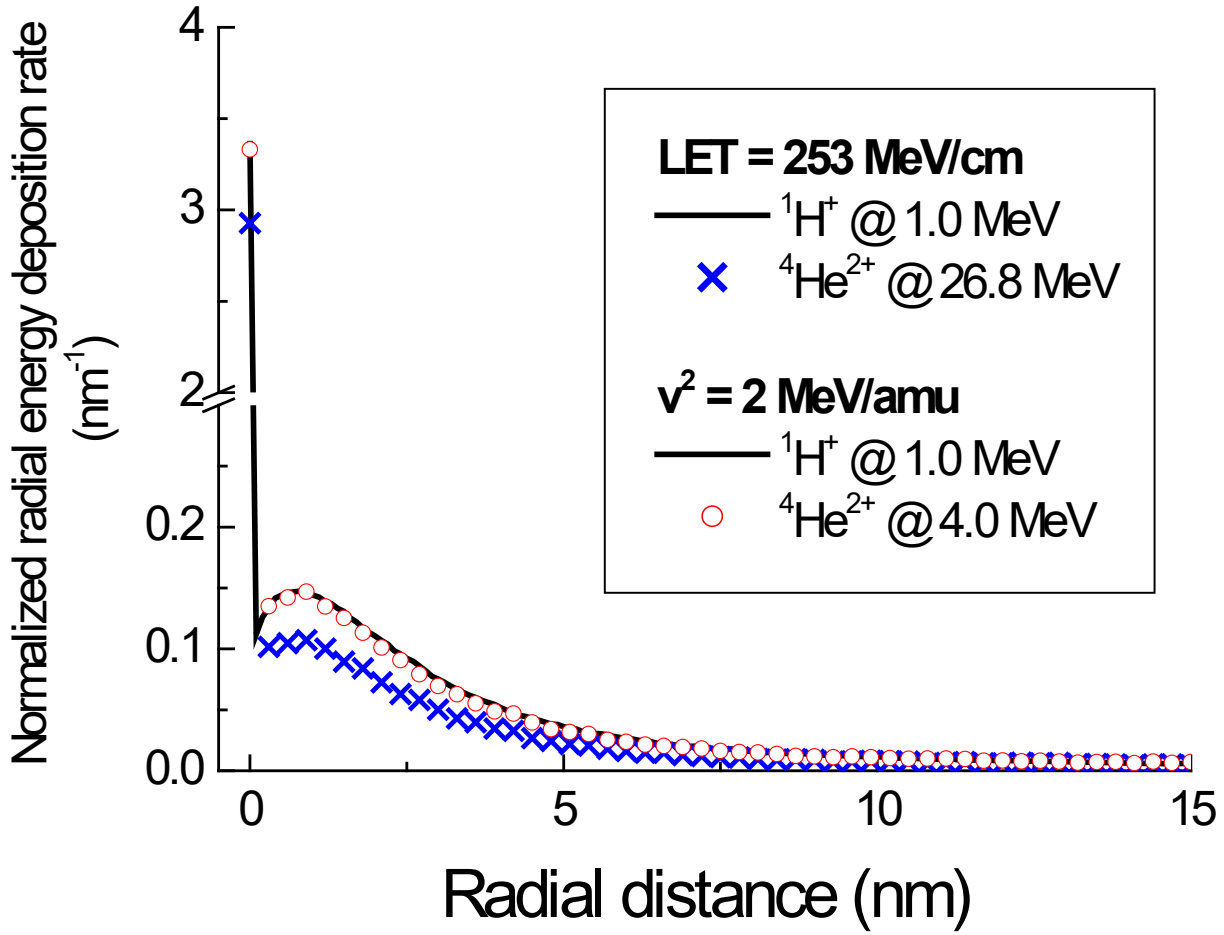
Mean Free Path



Average distance between energy losses depends on

- the velocity, E/M, and
- the charge of the ion, Z.

LEE and The Structure of Heavy-ion Tracks



Two factors determine the structure of a heavy ion track:

- axially, the mean free path of the primary particle.
- radially, the energy loss and physico-chemical processes of the ejected LEE.

Who pays?

NDA
Nuclear
Decommissioning
Authority

National Science Foundation
WHERE DISCOVERIES BEGIN

MANCHESTER
1824
The University of Manchester
Dalton Nuclear Institute

EPSRC

Summary

1. Who did the work?
   Lots of people, but especially Marisa
2. Why am I here?
   Radiation effects depend on ion type and energy and cannot be described or predicted accurately using a deterministic formalism.
3. What is our goal?
   Detailed mechanistic model for physical and chemical processes underlying the observable effects of radiation.
4. What do we do?
   Measurement and Modeling & Simulation and of the radiation damage kinetics in radiolysis of condensed and solid materials.
5. What are the results?
   Accurate prediction of OH and e^-_{aq} chemistry following ion irradiation and a description of the underlying physical, physico-chemical and chemical processes.
6. Who pays?
   US DOE & US NSF, plus NDA & EPSRC

Take Home Message

Effects of ionizing radiation are chemically significant.

Radiation chemistry depend on ion type and energy.

Knowledge about the effects of radiation is important basic science, medicine and technology.

Empirical description of the effects of radiation is unsatisfactory.

Prediction of the effects of radiation needs a mechanistic basis.

Central to the portfolio of DOE ($$$$$), NDA (£££££), CEA (€ € € €)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