Radiation Effects and Nuclear Power

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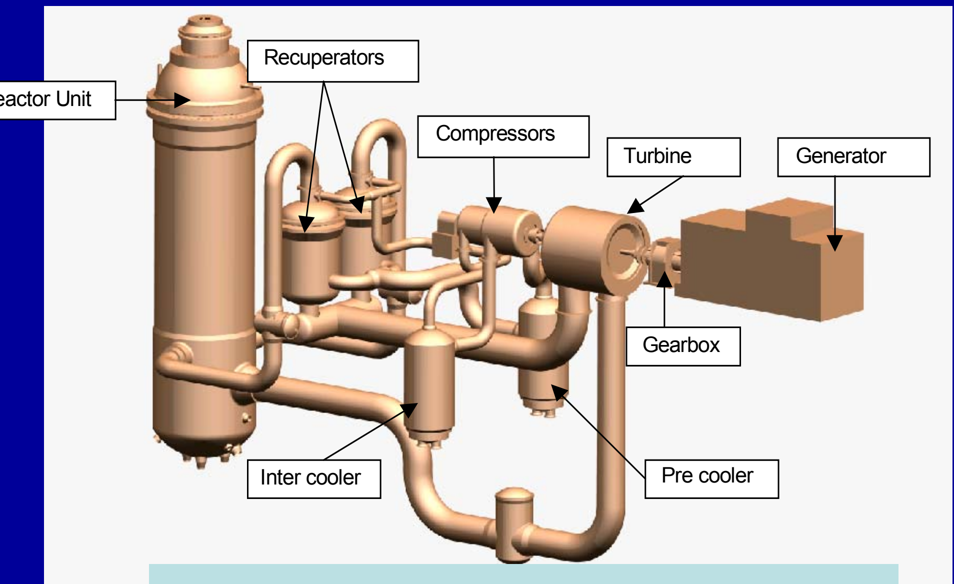
Radiation effects are important in:

- Waste remediation and management
- Spent fuel reprocessing
- Deep geological disposal
- Continued generation
- Naval propulsion
- Next generation new build
- Advanced reactors & fuel cycles

Waste Tanks & Ponds



Next Generation Nuclear Plant

New Fuels

Pu & Spent Fuel Disposition

Fundamental Underpinning Research

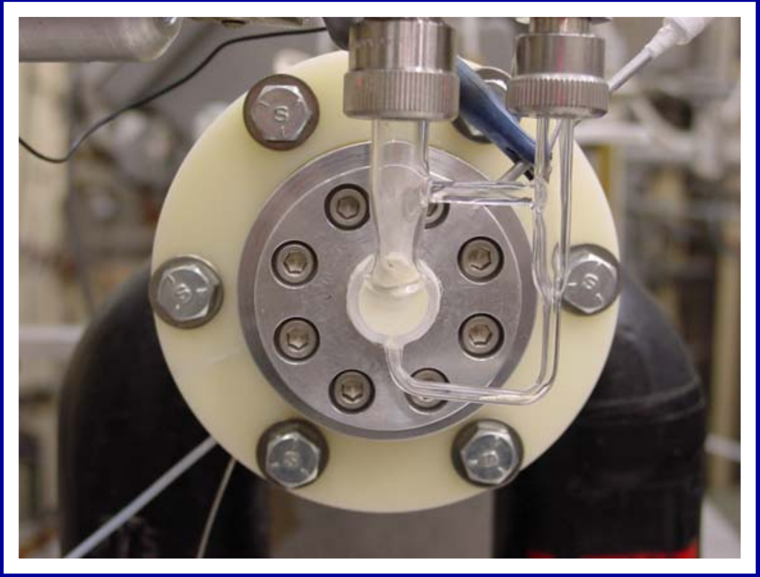
The University of Manchester Dalton Nuclear Institute

Nuclear Decommissioning Authority

Aim:

To develop a mechanistic understanding of performance deterioration and chemical degradation to allow a predictive description of radiation-induced effects and usage lifetime.

- Interfacial water-oxide-metal process
- Heterogeneous systems
- Humid and damp systems
- Hydrocarbons and organic polymers
- Chlorinated polymers & materials



Radiation Effects and Geological Disposal

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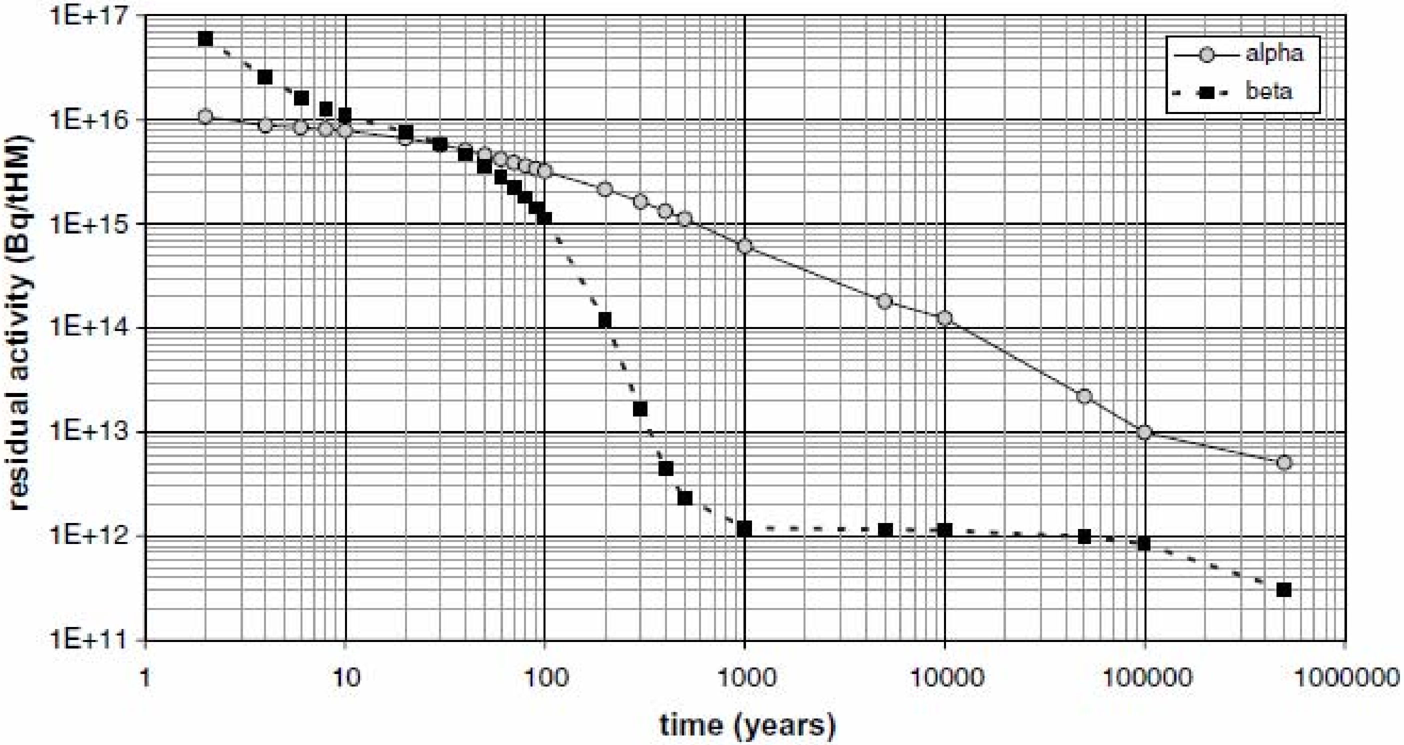
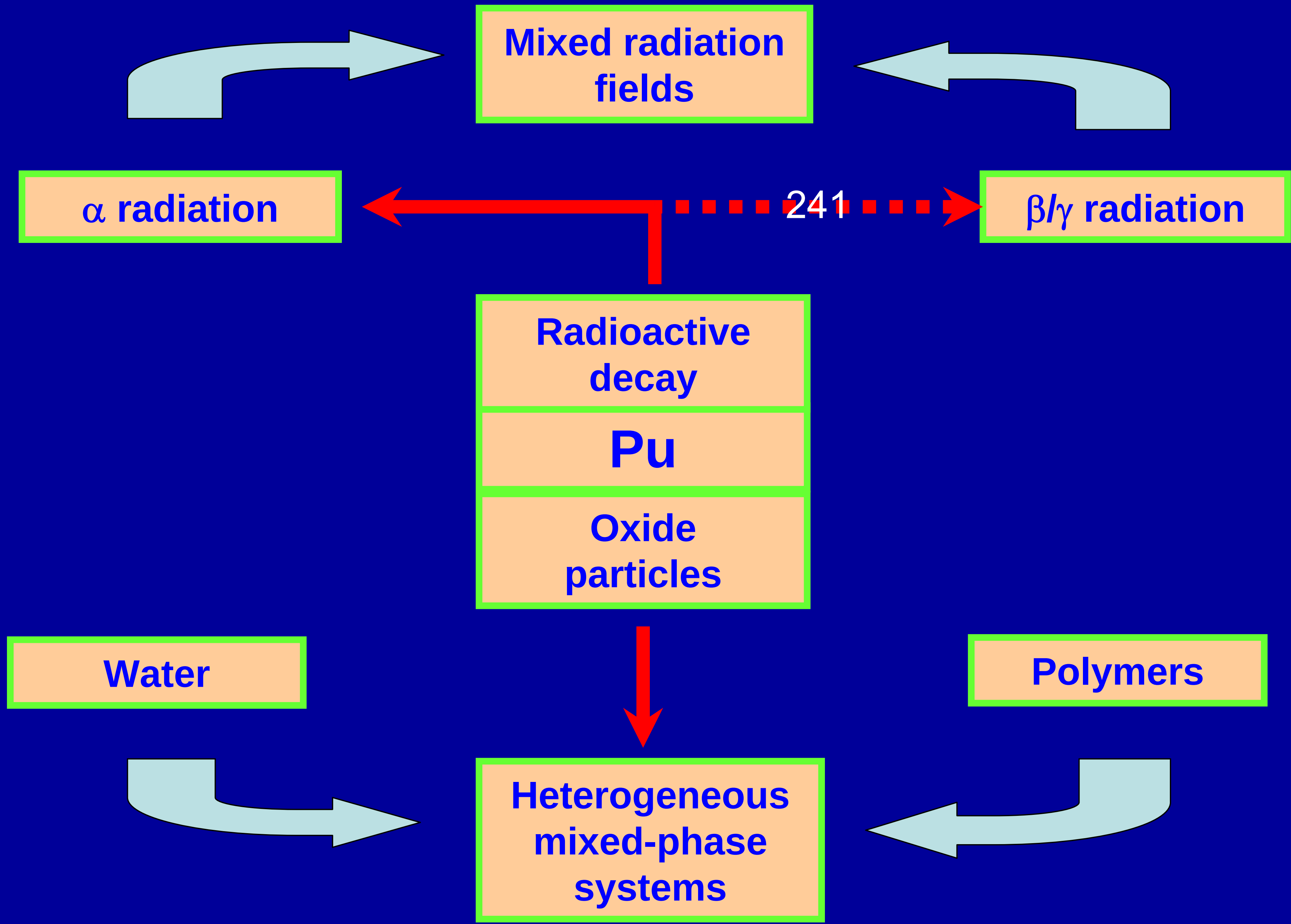
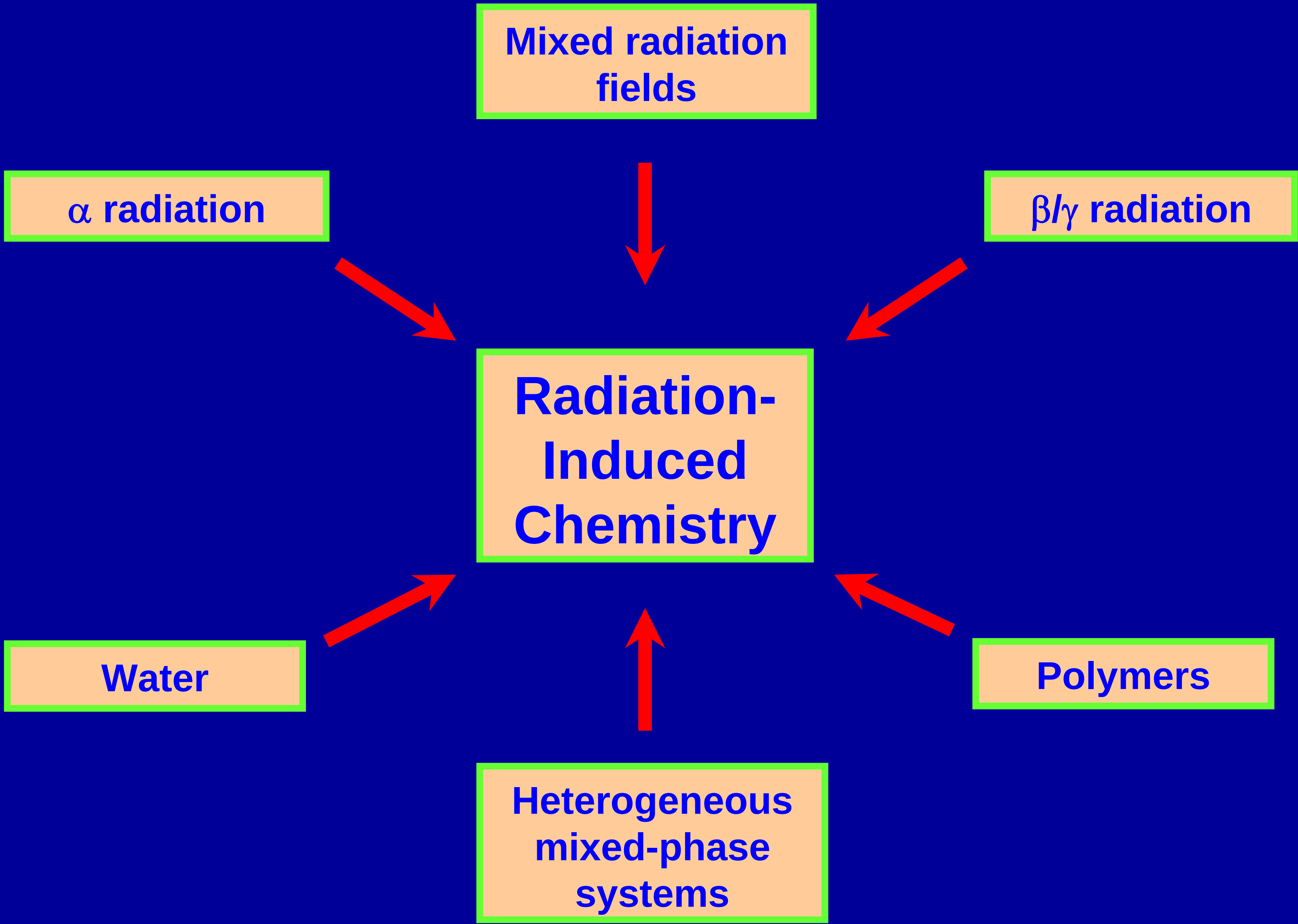
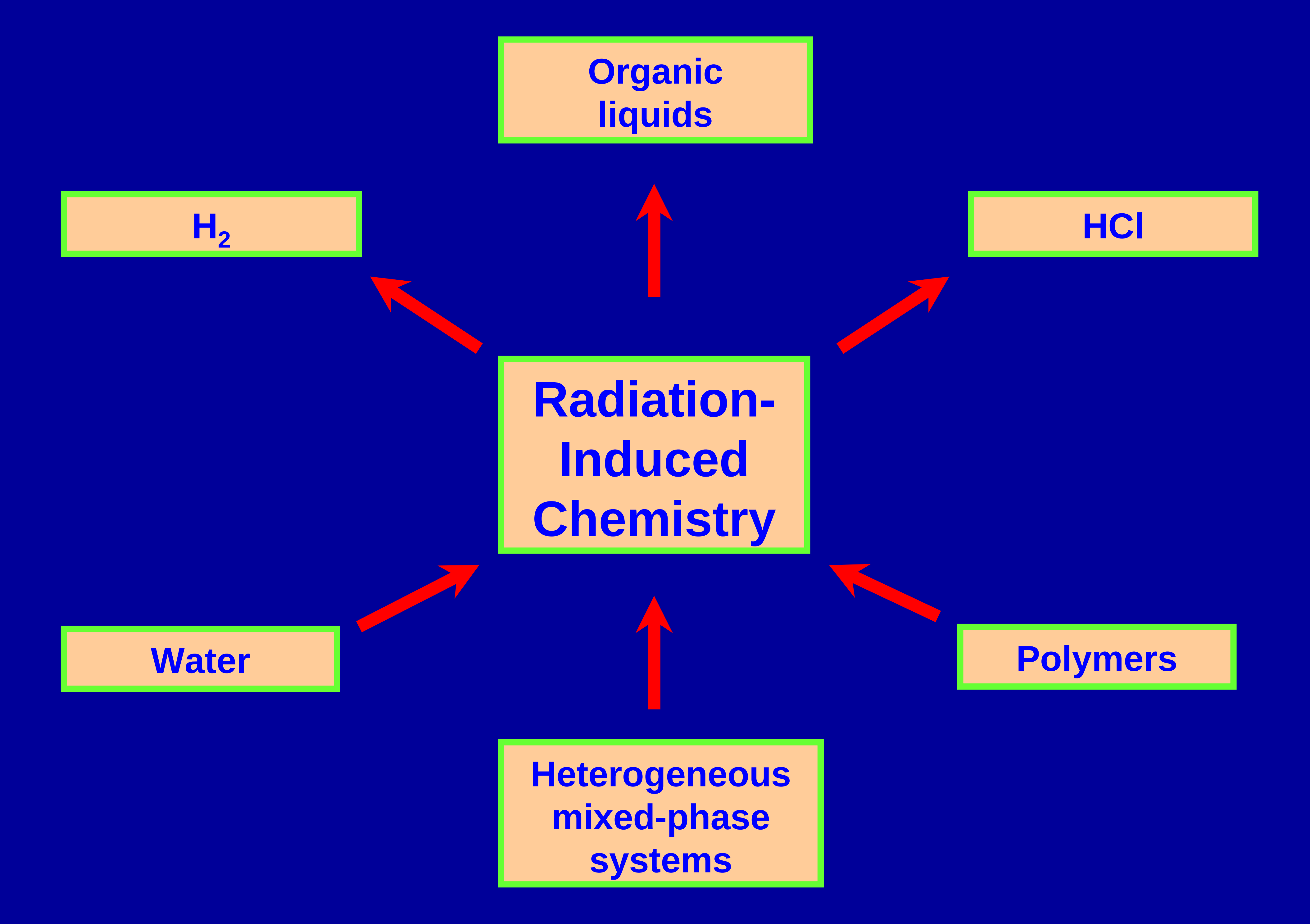


Fig. 1. Evolution of α, β and γ radiations as a function of time for a 55 GWd t^{-1} UOX fuel. Data are calculated from the CESAR isotopic evolution code [35].

Journal of Nuclear Materials 346 (2005) 66–77 Christophe Poinssot et al.


Mixed radiation fields
α radiation
241
β/γ radiation
Radioactive decay
Pu
Oxide particles
Water
Polymers
Heterogeneous mixed-phase systems


Mixed radiation fields
α radiation
β/γ radiation
Radiation-Induced Chemistry
Water
Polymers
Heterogeneous mixed-phase systems


Organic liquids
H$_2$
HCl
Radiation-Induced Chemistry
Water
Polymers
Heterogeneous mixed-phase systems

Research Projects for 2009-2010

Radiolytic off-gassing of organics in aqueous environments.
(NNL, NDRL) ☻ GS

Radiolytic degradation of PVC.
(NNL, NDRL) ☻ GS

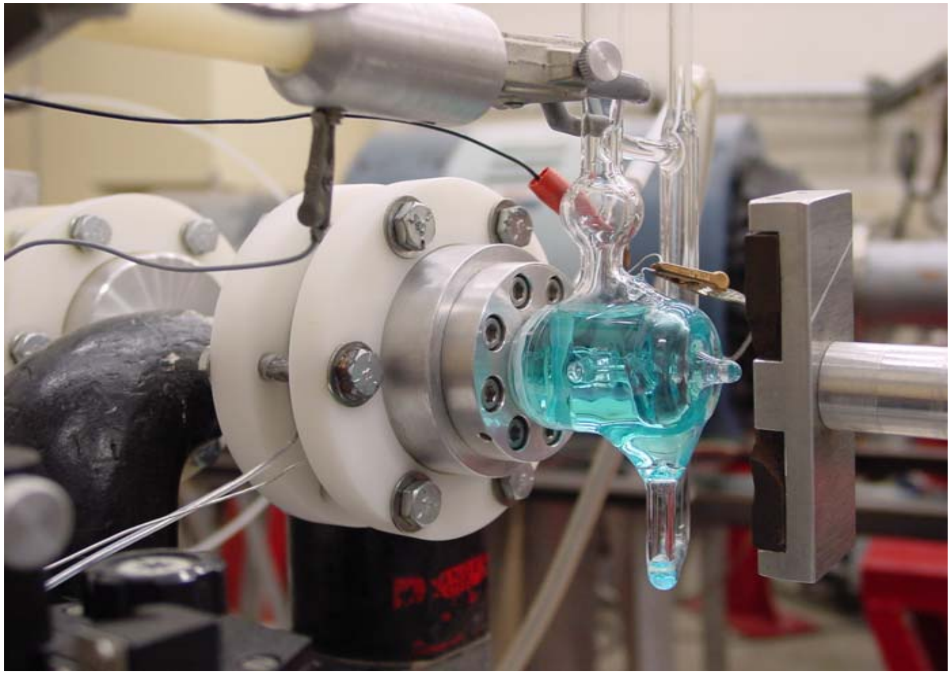
Effects of mixed radiation fields.
(NDRL)

Radiolysis of water in zeolites.
(CEA) ☻ **$EU-Laserlab**

Aqueous radiation chemistry of U(IV).
(CEA, NDRL)

Radiation damage to biopolymers and biosystems.
(PSI, Univ. of Rochester) ☻ PD

H_2 production in the irradiation of water in contact with oxide particles.
(NNL, NDRL) ☻ **GS $EPSRC**



Impact of radiation on microbial cells.
(SEAS) ☻ GS **$BBSRC $NDA**

Radiations chemistry of extremely alkaline systems.
(NNL, NDRL) ☻ GS

Radiolytic degradation of silicones.
(UKAEA, NDRL) **$NDA-DRP**

Polymeric Materials in Nuclear Environments

Aim: To understand and quantify performance deterioration and chemical degradation to allow a predictive description of radiation-induced effects and usage lifetime.

Radiolytic Degradation of PVC

Polymers are found throughout the nuclear portfolio.

- Nuclear waste materials
- Encapsulants
- Nuclear Infrastructure

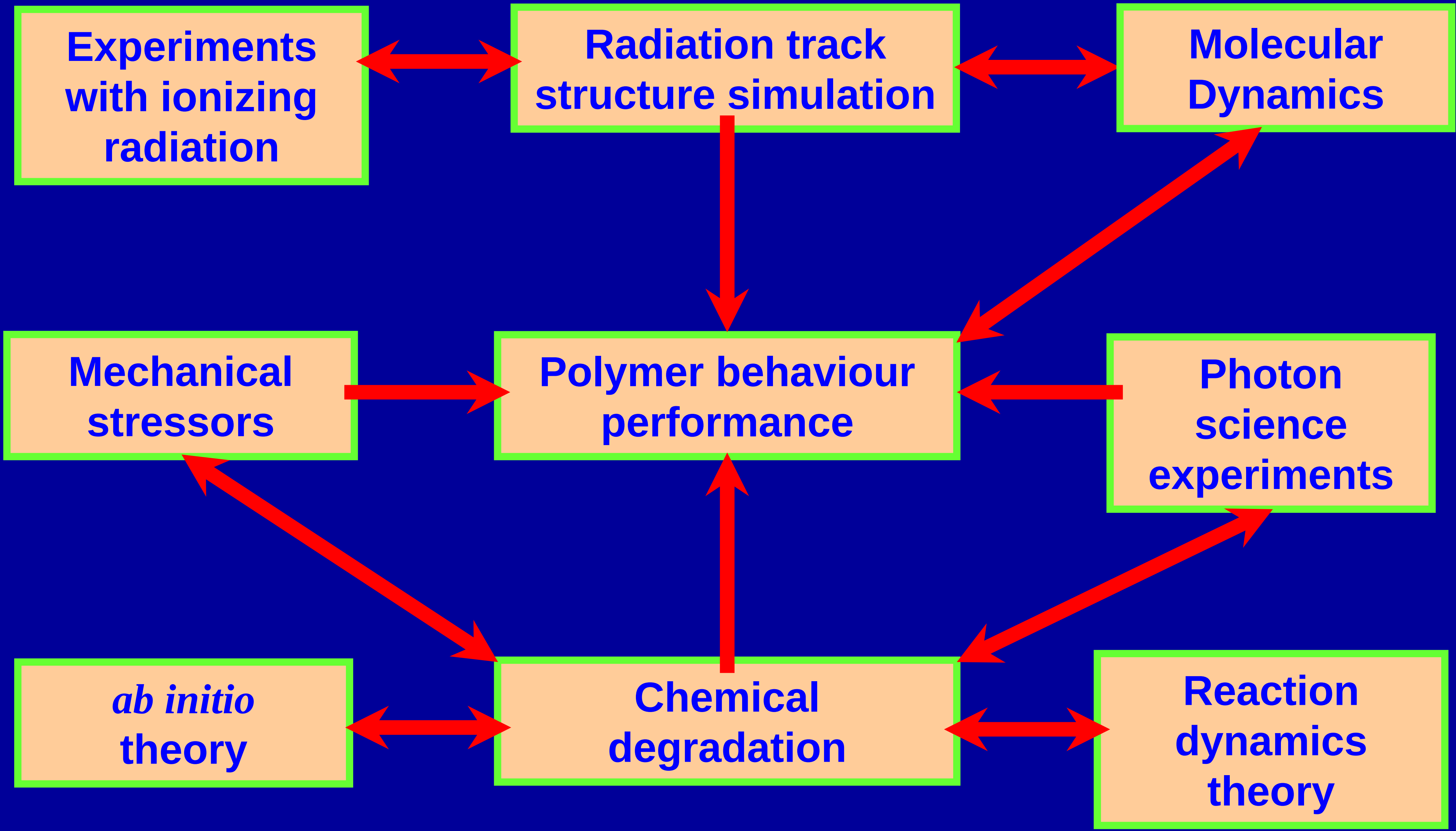
Questions about

- Perfomances
- Degradation
- Off-gasing
- Non-aqueous phase liquid formation

Effects due to

- Aging
- Local environment
- Radiation fields

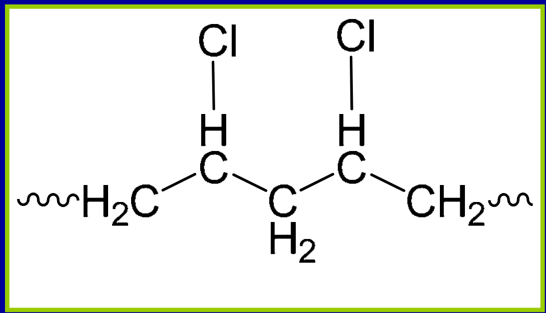
Understanding Performance of Irradiated Polymers: What Does This Involve?

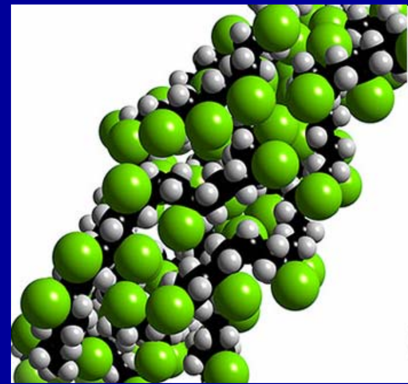


Polyvinylchloride (PVC)

Polychloroethene (IUPAC)

$(—CH_2CHCl—)_n$





www.3dchem.com

Thermoplastic polymer, rigid material

Important physical properties: flexibility, softness, transparency

Additives (plasticisers and stabilisers)

Common applications

Applications in Nuclear industry

- PVC insulation and jacketing materials
- radioactive waste packaging material

Concerns: hazardous compounds released !

Effects of ionizing radiation on PVC

Current Status

- Significant componenet of Nuclear waste management portfolio.
- Post-irradiation degradation of PVC → physical and chemical changes.
- Main products – defined, but
- Mechanisms – poorly understood and inadequately characterised.

Experiment-with-modelling approach to understand and elucidate the effects of radiation (alpha, beta, gamma or n) on PVC in different environments (i. e. the presence of over-gases, humidity, hydrocarbons, ceramic particles etc.).

Experimental work at Univ of Notre Dame (USA) with complementary work at the Central Laboratory of NNL involving plutonium contaminated PVC.

Experiments

PVC Samples

PVC powder, no additives

UPVC film

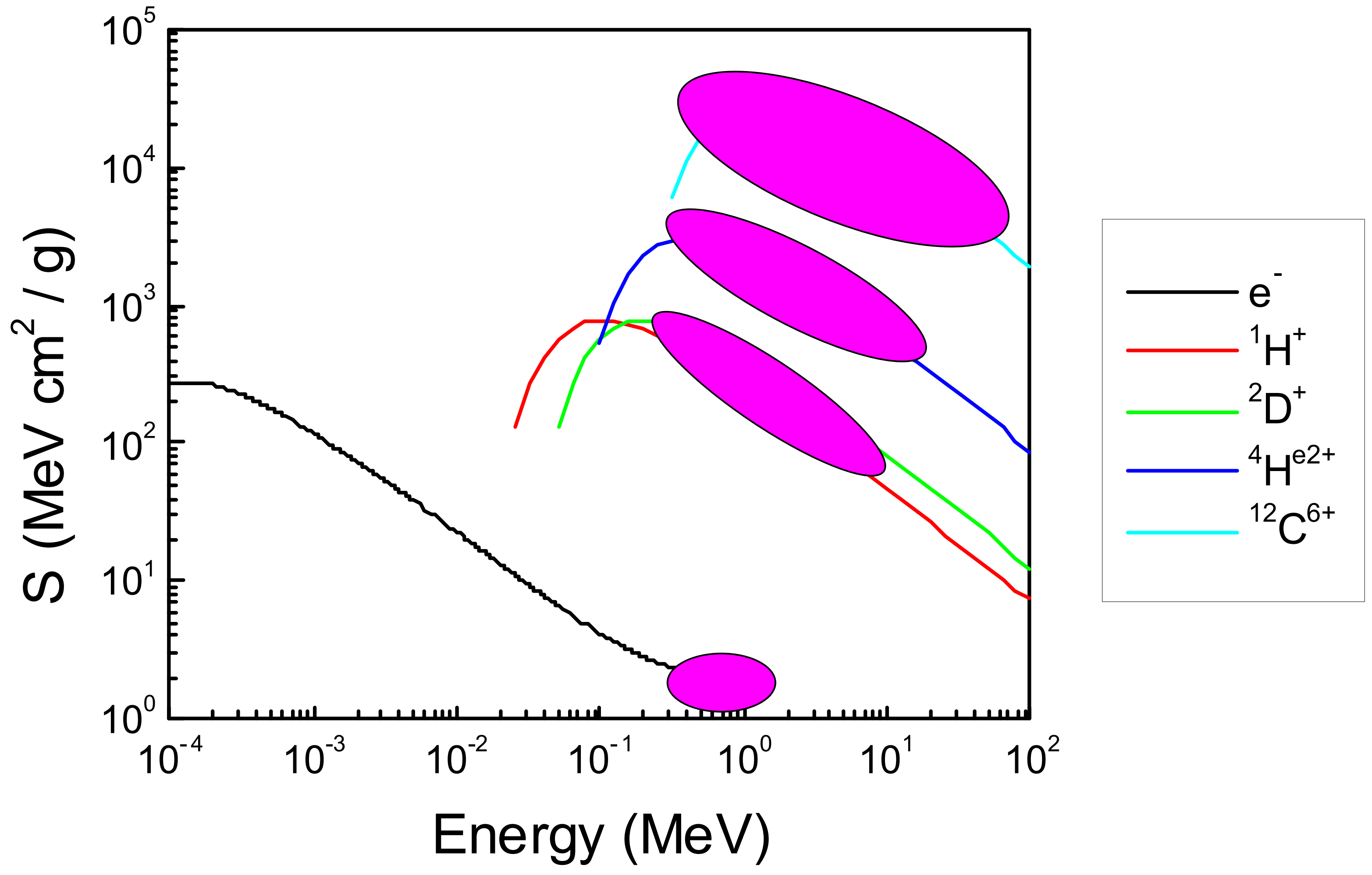
γ-Radiolysis

- Shepherd 109-68 ^{60}Co source, self-contained dose rate of ~8.3 kRads min^{-1} (83 Gy min^{-1}).
- Irradiation: room temperature, 2.5 h (10 kGy) and 12 h (50 kGy).

^{4}He-Radiolysis

- FN Tandem Van de Graaff facility of the University of Notre Dame Nuclear Structure Laboratory.
- Irradiation: with completely stripped ions, charge beam current ~1.5nA, room temperature.

Radiation Quality



Experimental techniques

Chromatography

⇨ Gas chromatography (GC)

⇨ Ion chromatography (IC)

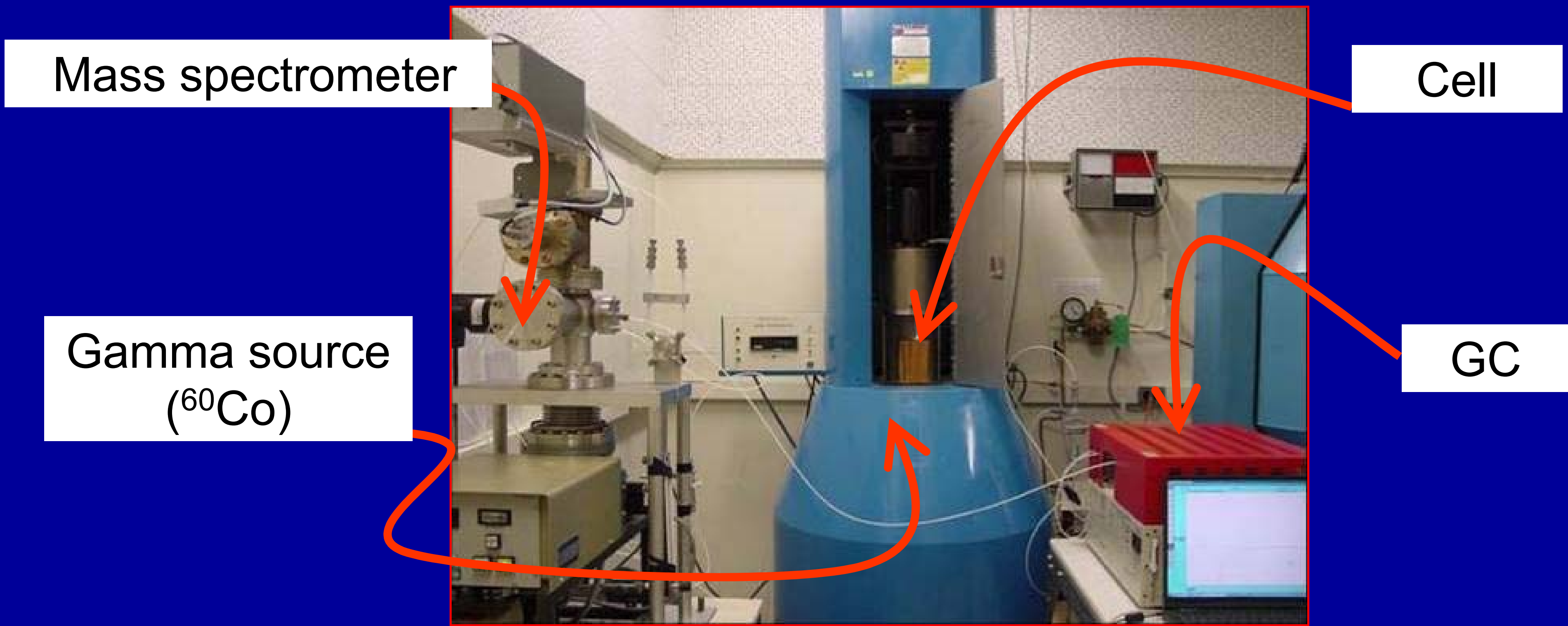
Spectroscopy

⇨ UV/VIS absorbance

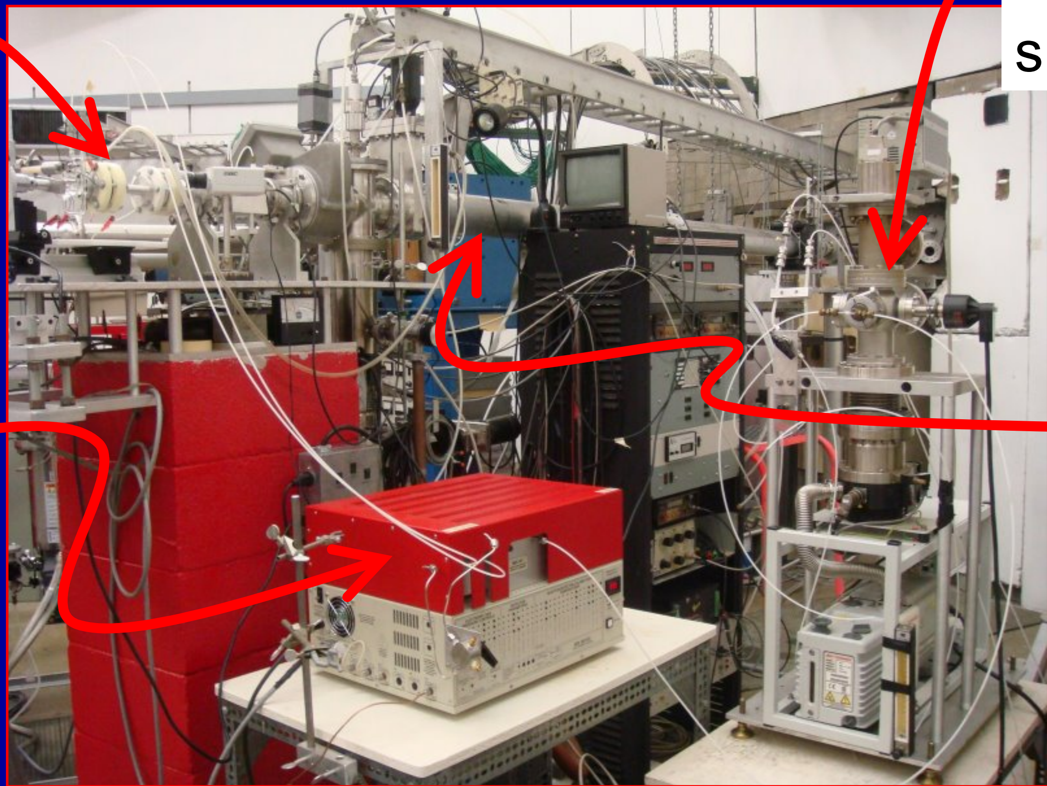
⇨ FT-IR transmission

⇨ EPR

Experimental Setup: Gamma Radiolysis



Experimental Setup: Ion Beam Radiolysis



Radiation induced degradation of chlorinated polymers

Off-gasing of corrosive HCl and H_2 from PVC

- **Yields and post-irradiation behaviour**

Structural degradation of irradiated PVC

- Change in molecular weight and distribution of polymer chain lengths
- Formation of conjugated C=C systems
- Oxidation and production of C=O chromophores

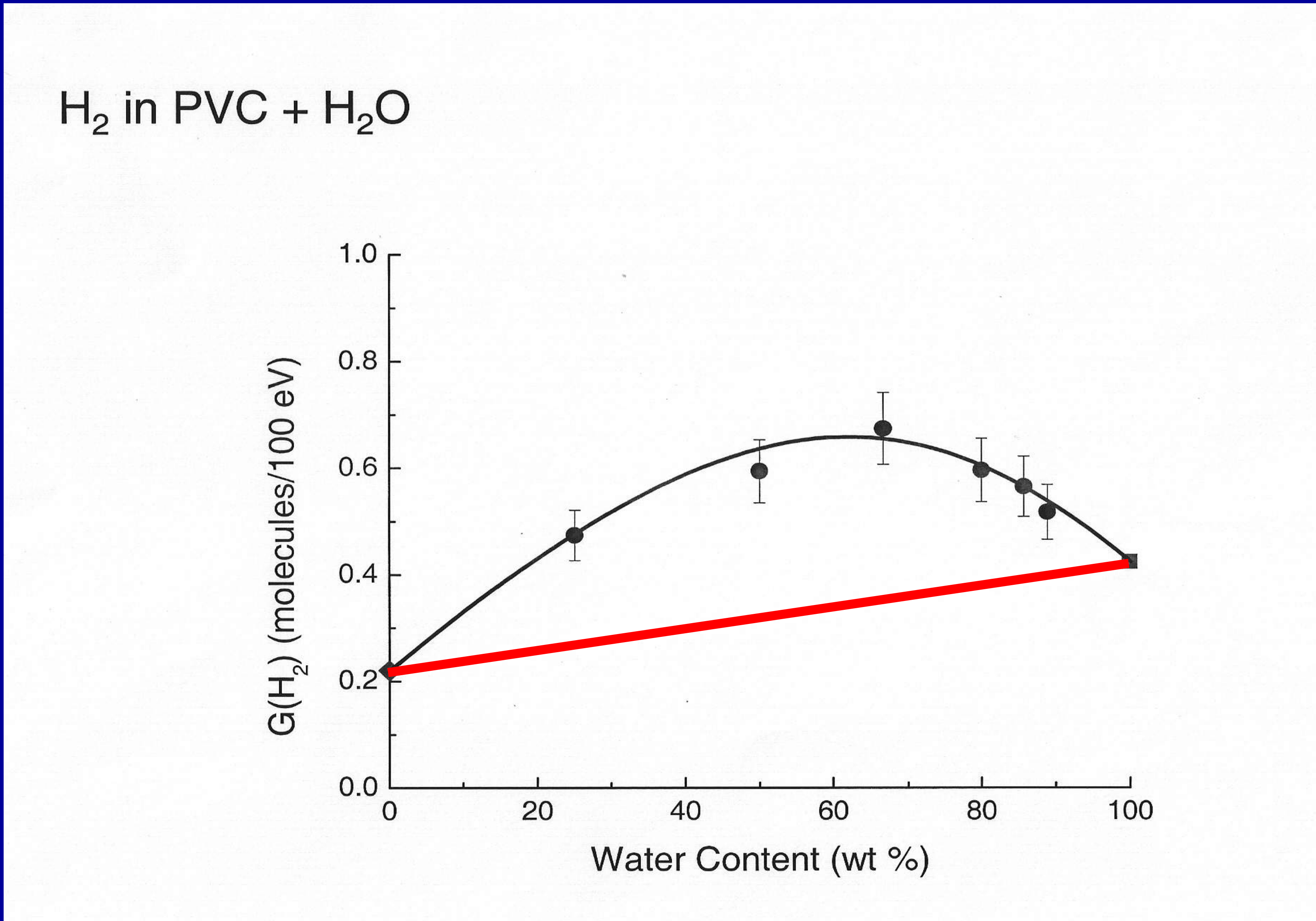
Chemical evolution of irradiated polymer

- Long term survival of radicals

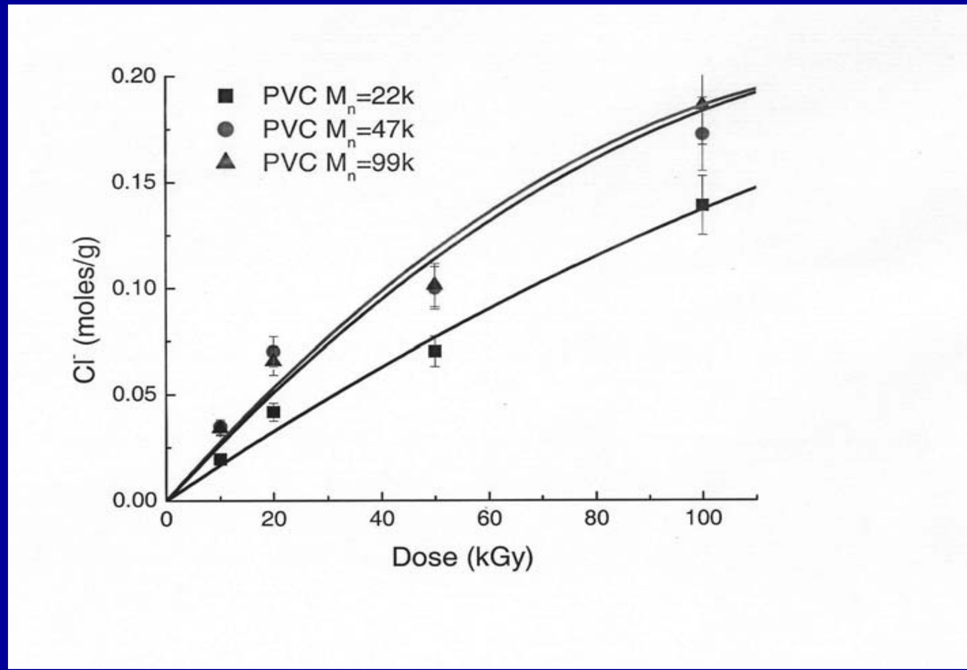
Radiation-induced H_2 Production

	M_n (Dalton)	γ (molec./100eV)	α (molec./100eV)
De-aerated	22 k	0.23	0.45
De-aerated	47 k	0.27	0.41
De-aerated	99 k	0.25	0.39
Aerated	22 k	0.22	
Wet & Aerated	22 k	0.22 - 0.67	

H_2 Production from PVC-H_2O Systems

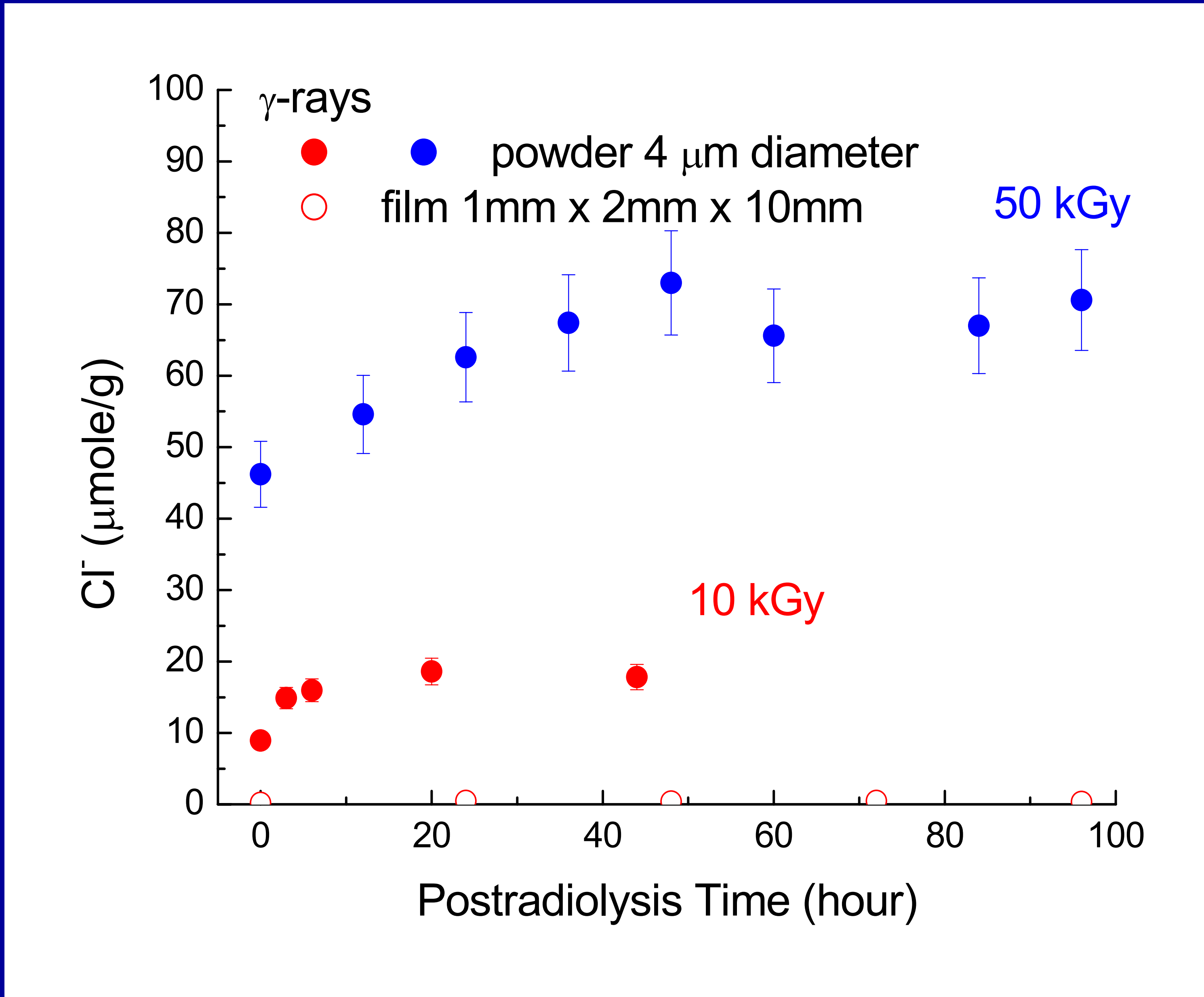


Radiation-induced HCl Production



	M_n (Dalton)	γ (molec./100eV)	α (molec./100eV)
Wet & aerated	22 k	**19.6**	1.18
Wet & aerated	47 k	**33.8**	
Wet & aerated	99 k	**32.5**	

Post Irradiation Release of HCl



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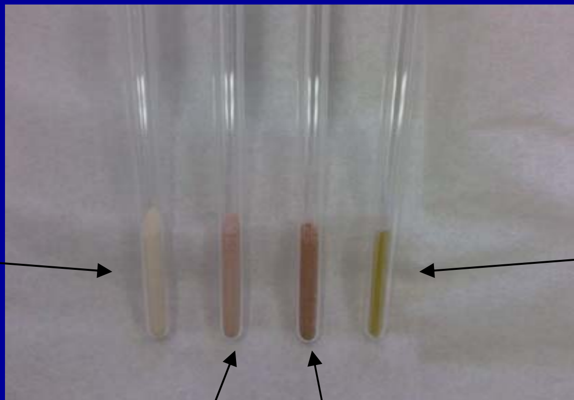
- Long term survival of radicals

Colour changes

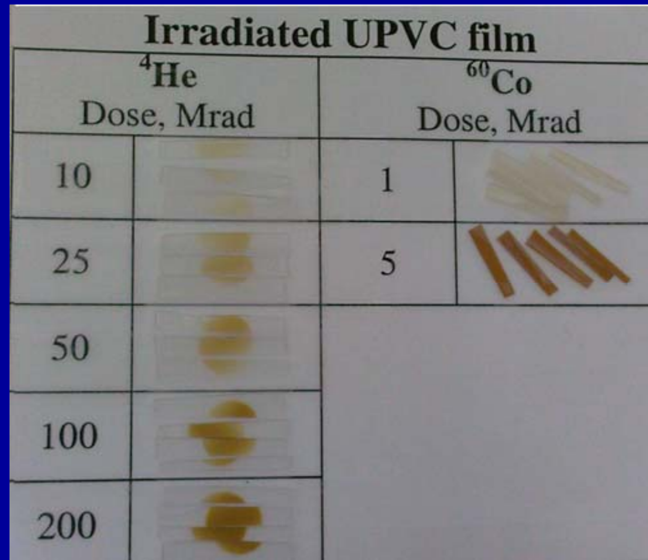
blank 10 kGy 20 kGy 50 kGy 100 kGy

PVC powder,
10 kGy (γ)



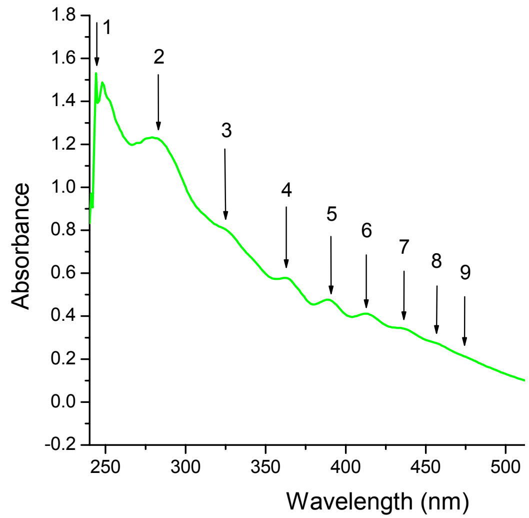
UPVC film
10 kGy (γ)

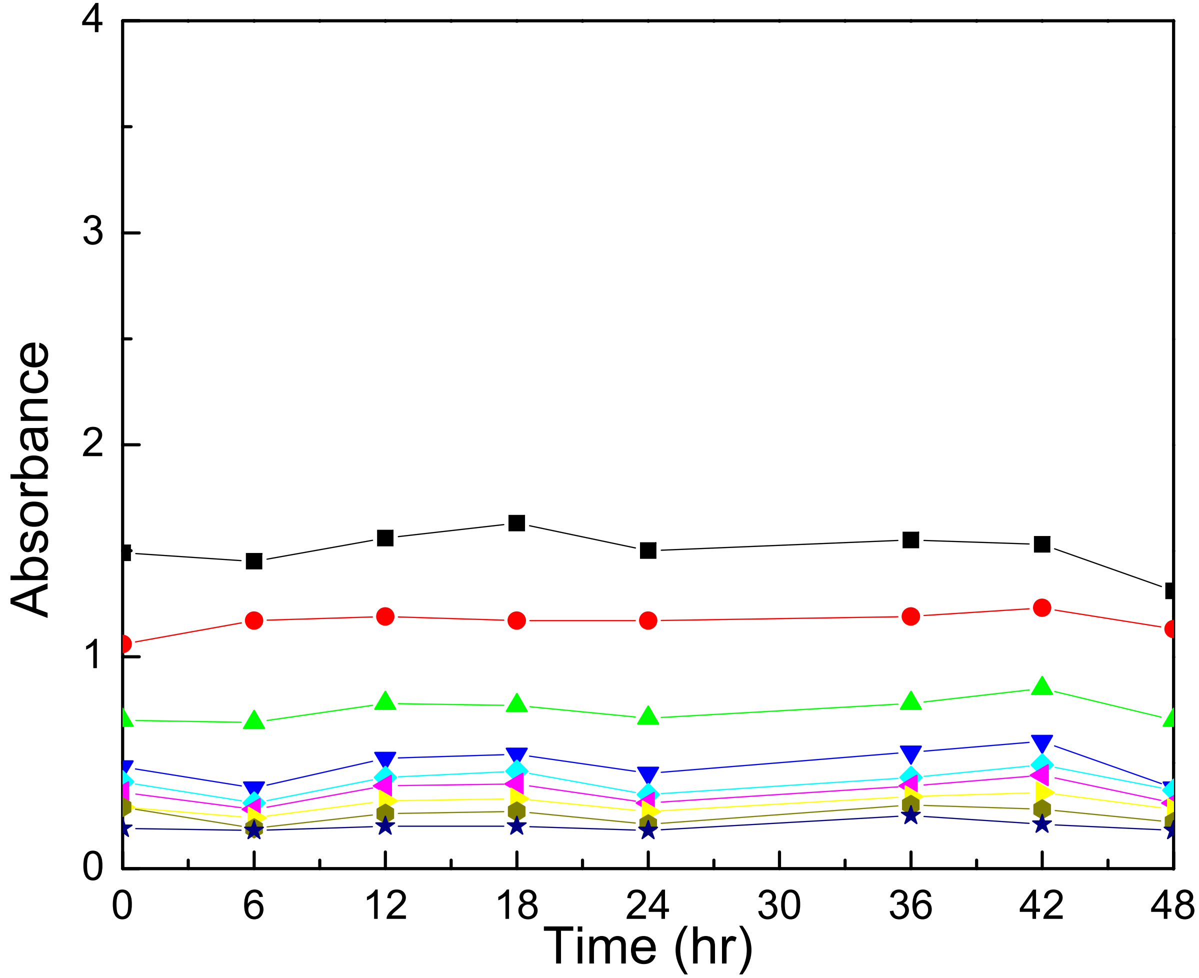
22k PVC powder,
10 kGy (γ, vacuo)



- PVC degrades with formation of observable chromophores – free radicals, conjugated double bonds, carbonyl groups, etc.
- Extent of discolouration depends on applied dose, irradiation environment and post-irradiation time.

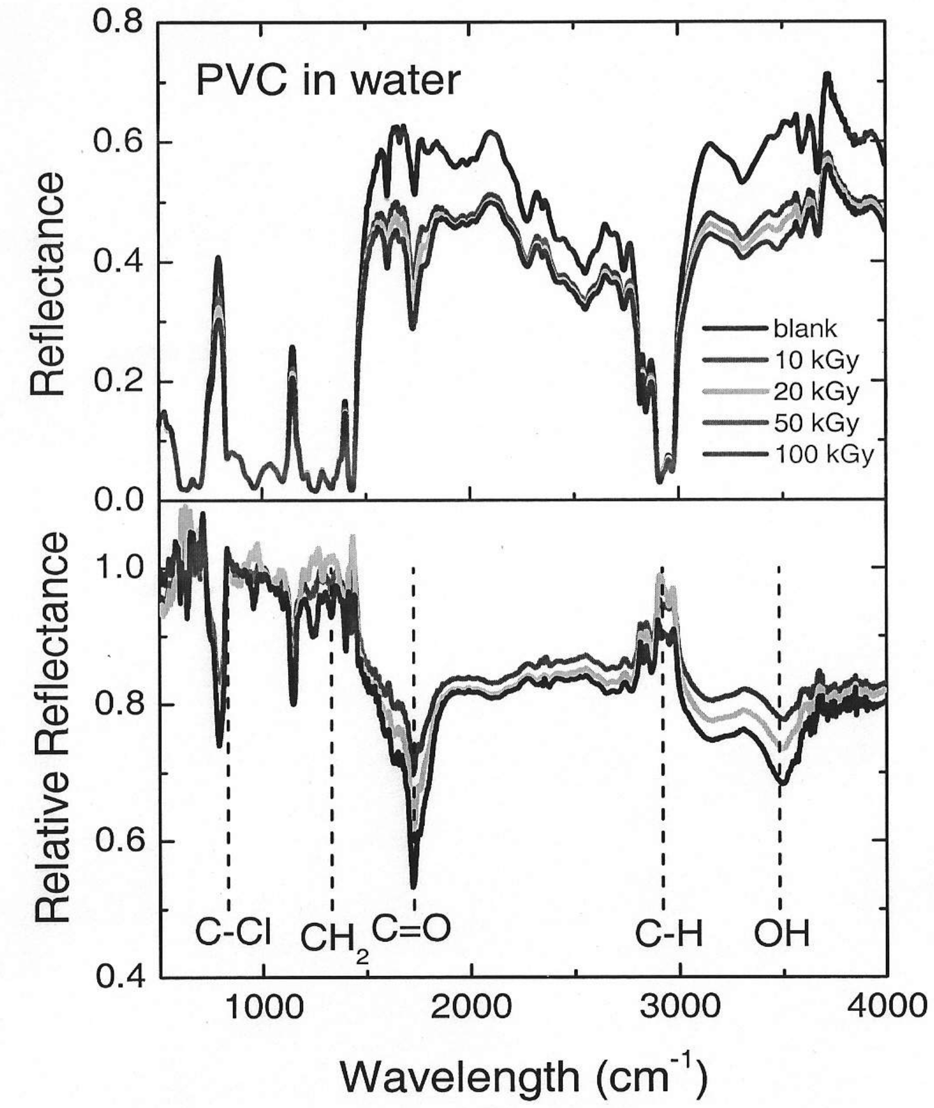
Uv-vis Spectroscopy of Radiation-induced Degradation of PVC
Post Irradiation Evolution



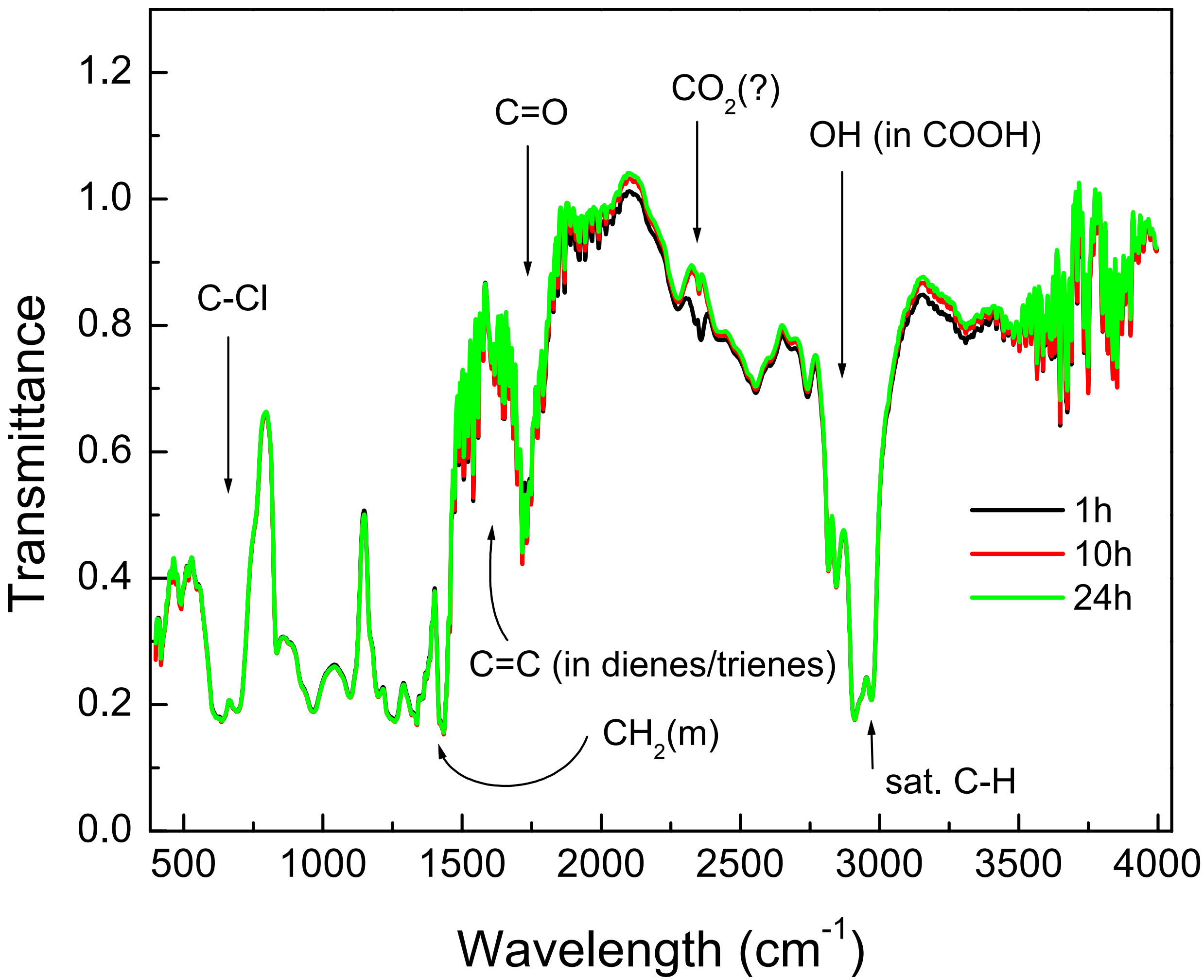


IR Spectroscopy of
Radiation-induced
Degradation
of PVC

Effect of Dose



IR Spectroscopy of Radiation-induced Degradation of PVC
Post Irradiation Evolution



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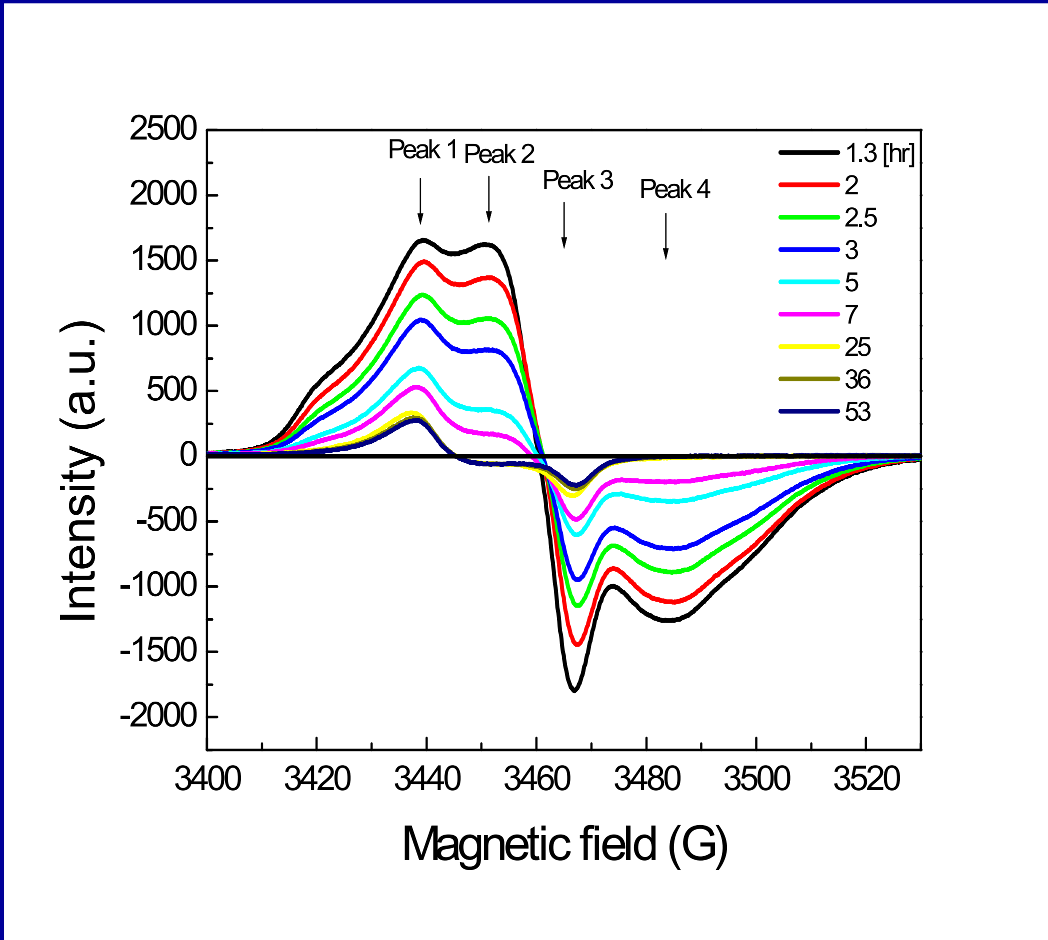
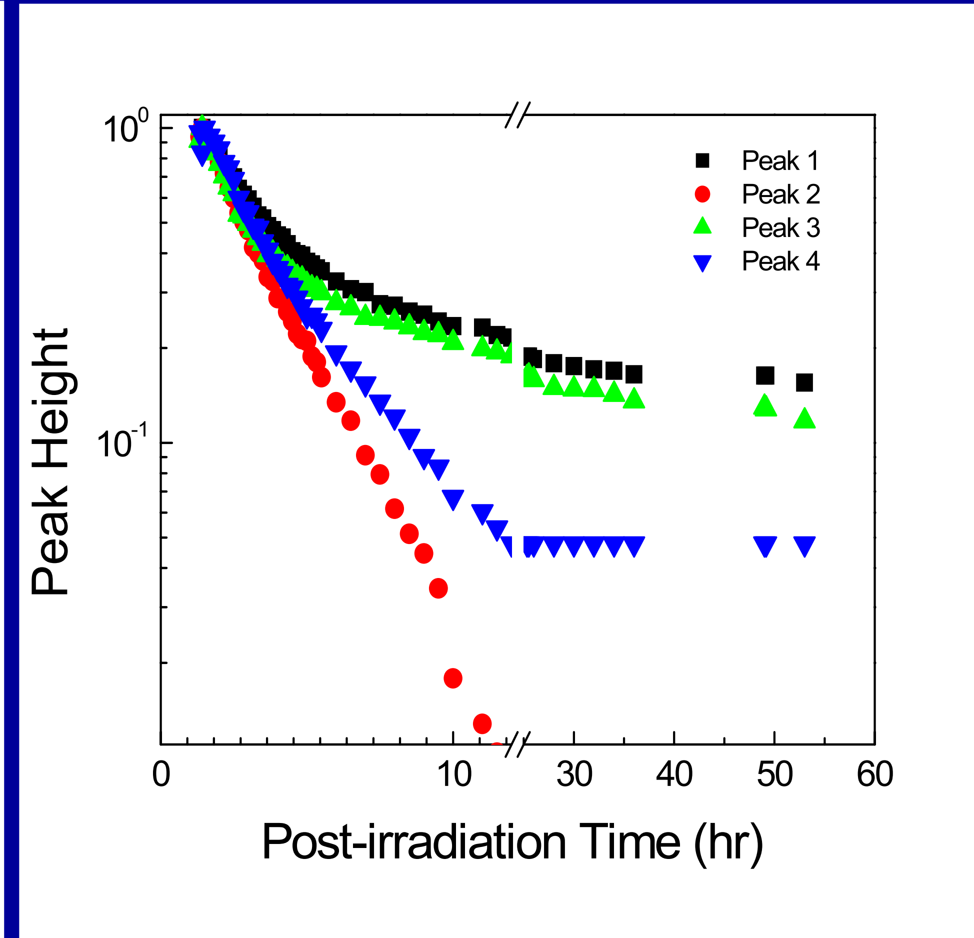
Chemical evolution of irradiated polymer

- **Long term survival of radicals**

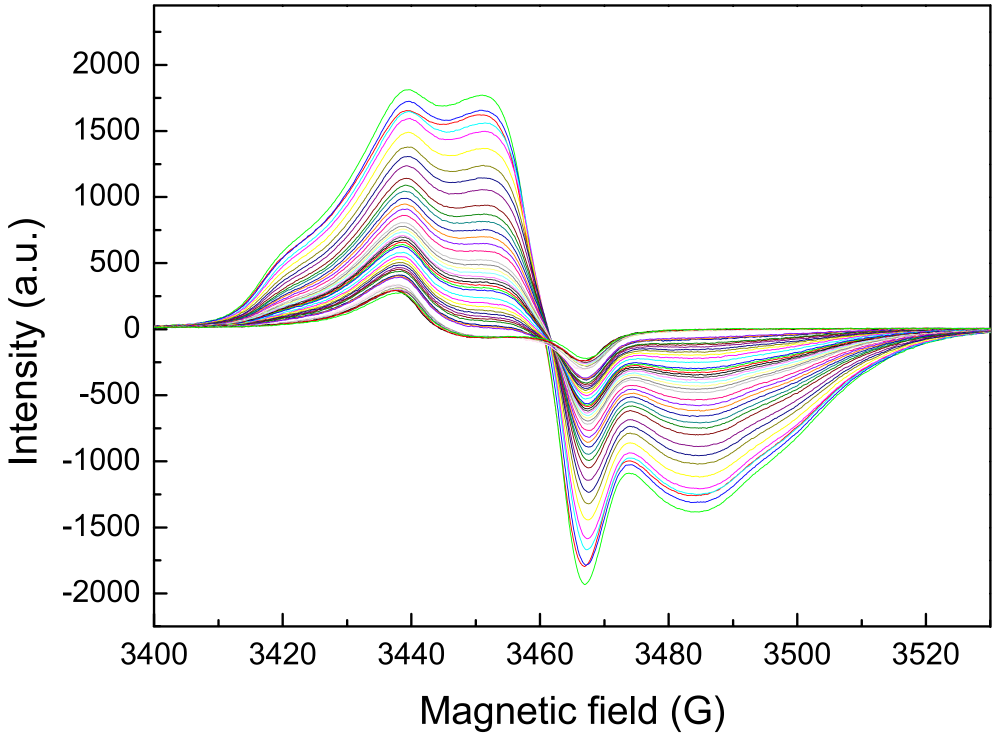
EPR spectroscopy

Variations with time (1.3-53 hr) of the EPR spectrum of γ-irradiated in air 22k PVC powder (50 kGy).

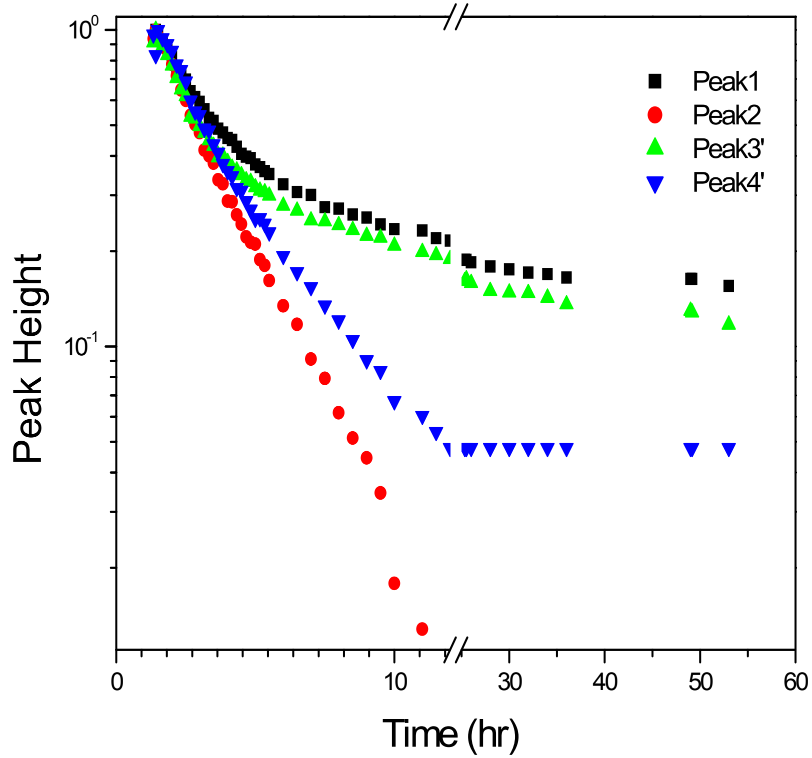




Spectrum of multiple overlapping signals with two observable components: fast decay of primary radicals and slow decay of long-lived peroxyl radical.



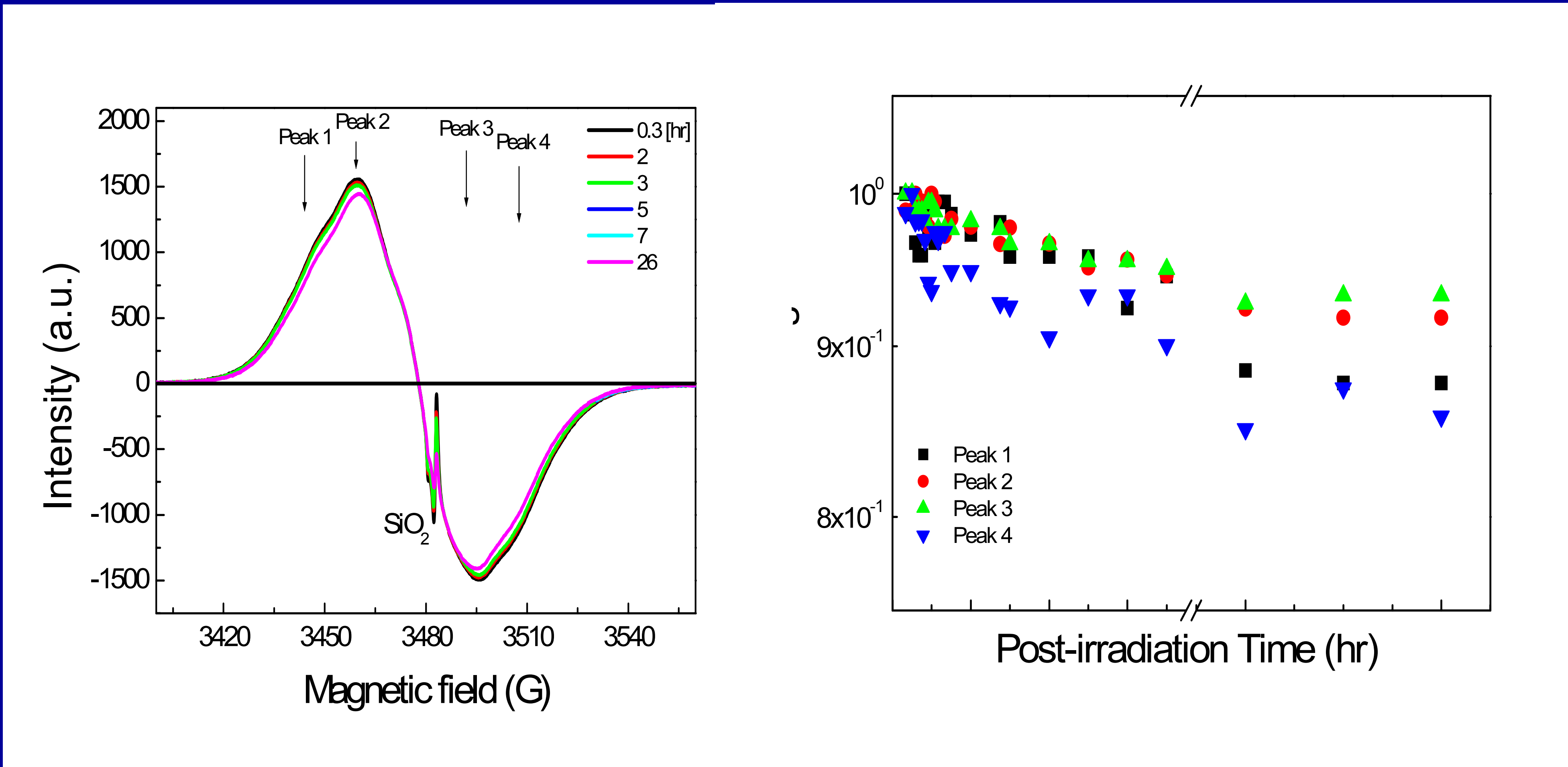
Intensity (a.u.)
2000
1500
1000
500
0
-500
-1000
-1500
-2000
3400
3420
3440
3460
3480
3500
3520
Magnetic field (G)



Peak Height
10^0
10^{-1}
Peak1
Peak2
Peak3'
Peak4'
0
10
30
40
50
60
Time (hr)

EPR spectroscopy

Variation with time (0-26 hr) of the EPR spectra of 22k PVC powder, γ-irradiated in vacuo to 10 kGy.



Polyenyl radical(s) can be very stable under vacuo.

Reaction Mechanisms

Initiation reaction: **C-Cl scission.**

Radical reactions (propagation):

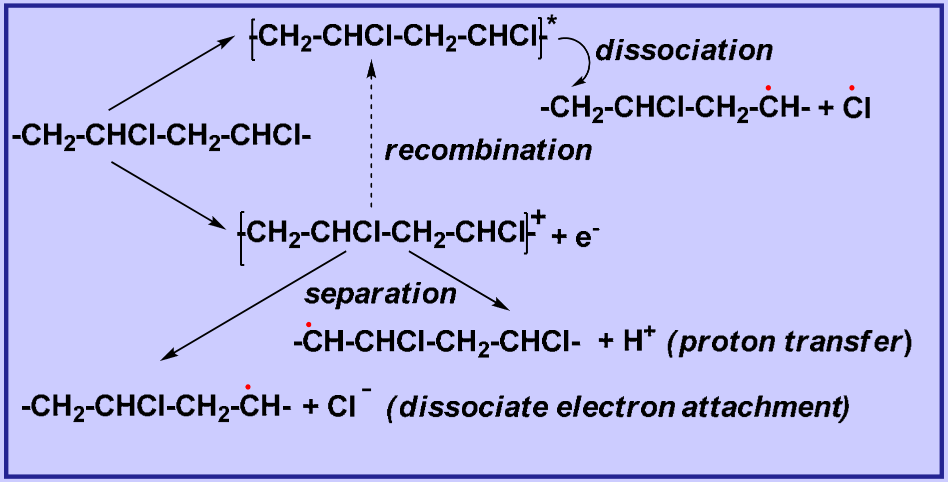
Cl• → R-ĊH-CHCl-R + HCl

R-ĊH-CHCl-R → R-CH=CH-R + Cl•

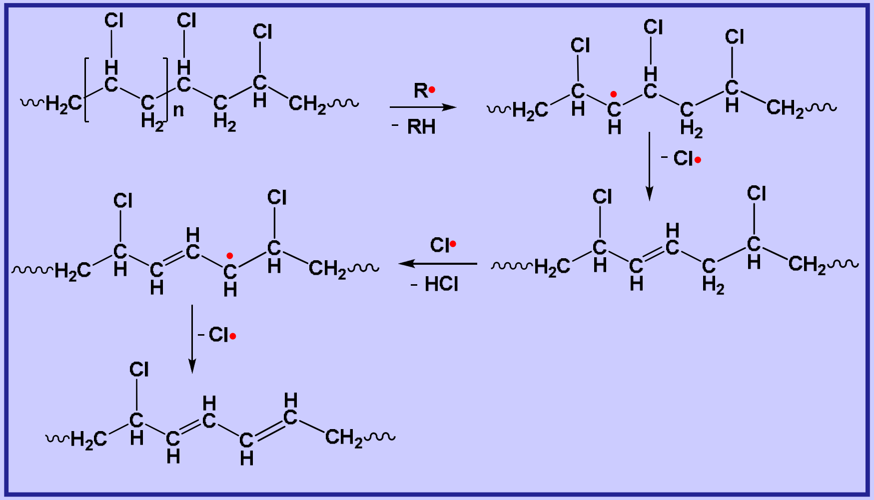
R-CH_2-ĊH-R → R-CH=CH-R + H•

Termination reactions:

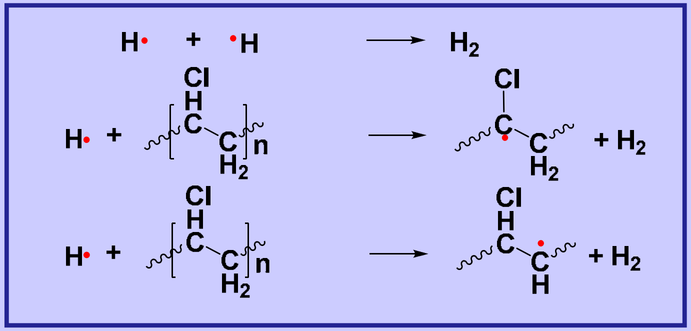
R• + •R → R_2



HCl evolution (free radical mechanism)



Formation of H_2 from H atom precursors



Predictive (Modeling) Capability

Energy transfer from radiation

↓

Radiation-induced ionization

↓

Fragmentation, thermalization and solvation

↓

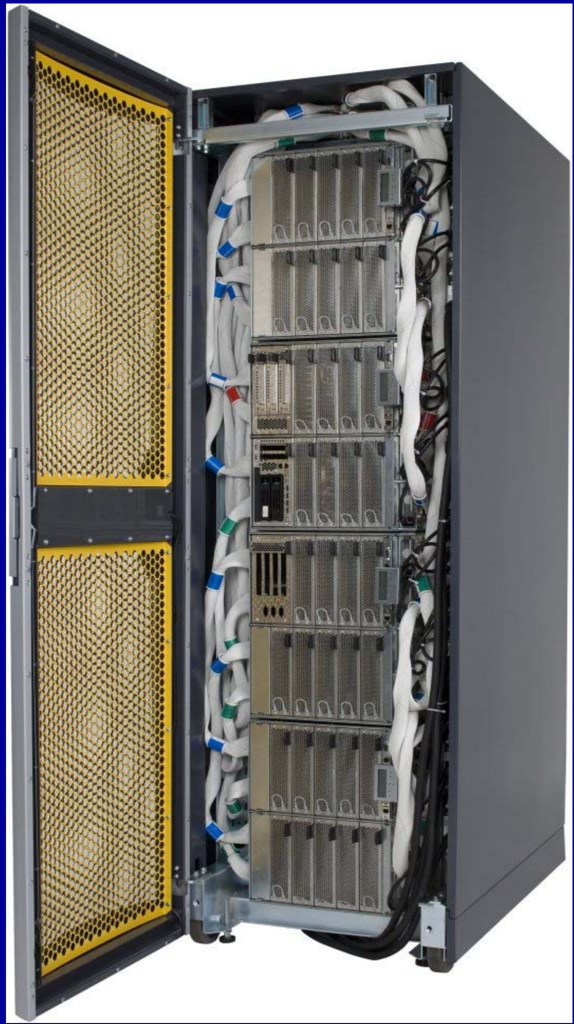
Spatially nonhomogeneous distribution of reactants

↓

Diffusion-limited chemistry

↓

Observed effects



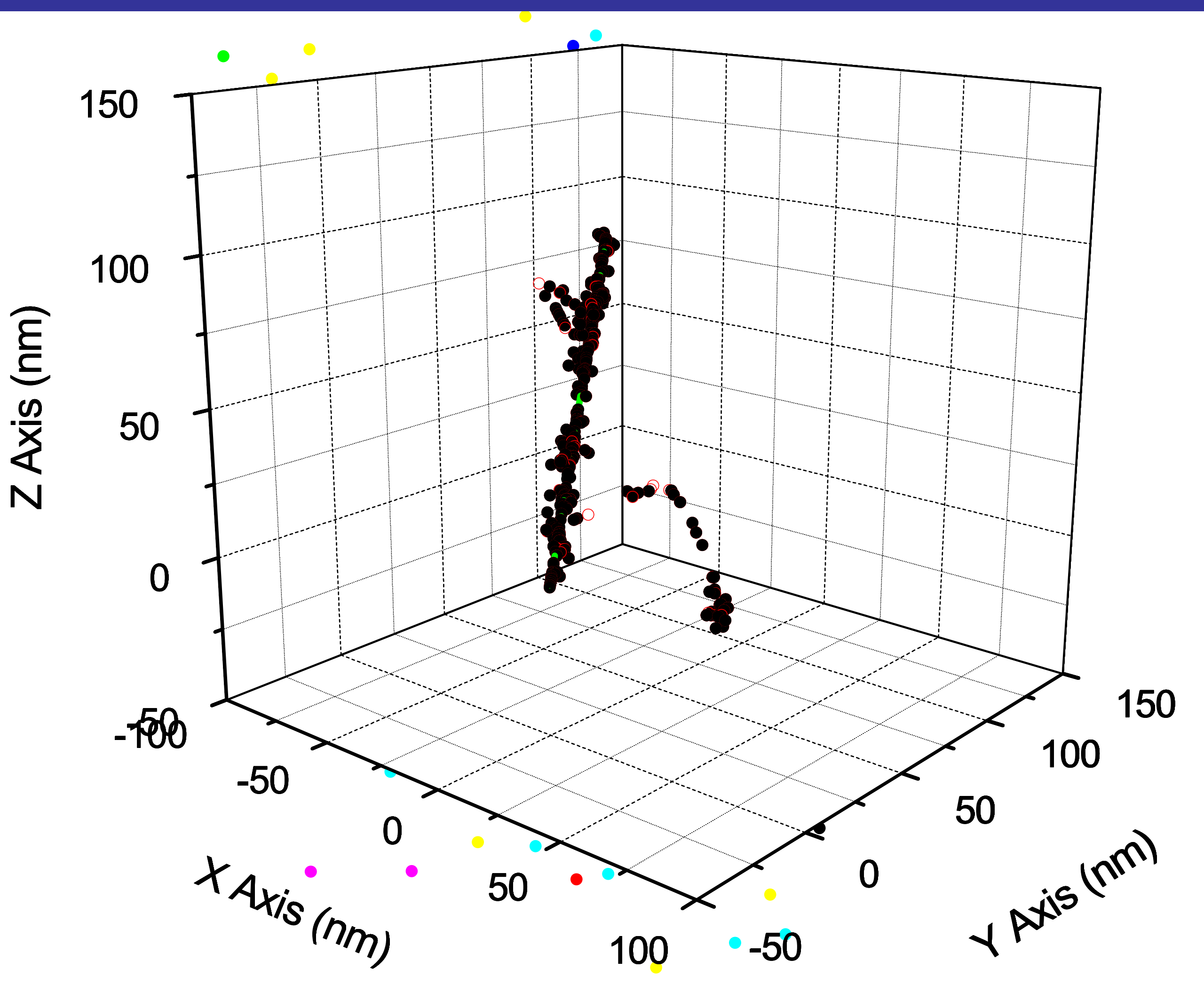
Modelling of polymer degradation

Prediction of

- physical performance
- chemical reactivity

of hydrocarbon and chlorinated hydrocarbon polymers under irradiation.

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



- Complete description of physical and chemical evolution of radiation track

Research Funding

MANCHESTER 1824
The University of Manchester
Dalton Nuclear Institute

NDA
Nuclear Decommissioning Authority

Office of Basic Energy Sciences
Serving the Present, Shaping the Future

Department of Energy
United States of America

EPSRC

The Nuffield Foundation

BBSRC
bioscience for the future

NSF
National Science Foundation
WHERE DISCOVERIES BEGIN

Acknowledgements

School of Chemistry
University of Manchester

Ashley Brown
Rafal Feliga
Matthew Hancock
Monica Huerta
Laura Nunns
Paul Kaufman
Pavlina Pavlova
Stephenie Palmer
Ashley Richardson
Mikko Riese

Oxford University

Nick Green

Radiation Laboratory
University of Notre Dame

M. Soledad Araos
Eduardo A. Carrasco-Flores
Maria Davidkova
Rowan Henry
Bratoljub H. Milosavljevica
Tingting Mu
Barbara Pastina
Puspalata Rajesh

NNL

Howard E. Sims

and especially


D214
LA VERNE

"The lack of fundamental data for the most important chemical species is the single largest factor limiting the successful application … to problems of industrial interest"

NAS Report on Database Needs